AN ISOTOPIC INVESTIGATION OF EARLY PLANETESIMAL DIFFERENTIATION PROCESSES

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Abstract

The differentiation and early evolution of planetesimals is relatively poorly understood. The Main-Group pallasites (PMGs) and IIIAB irons are differentiated meteorite groups from deep planetesimal interiors. They provide a window into the early evolution of rocky planets because of the abundance of samples from these groups and because a common planetary provenance has been proposed. Oxygen isotope analyses are crucial in understanding these relationships. The mineralogy of the PMGs and IIIABs, which seemingly record the magmatic evolution of their parent body, offers a unique opportunity to study early planetary differentiation processes. High-precision oxygen isotope analyses are used in conjunction with petrological characteristics and Cr and W isotope analyses to subdivide these groups and investigate formation processes. Two subgroups are identified in PMGs: PMG-low and PMG-high. The former exhibits an oxygen isotopic disequilibrium between olivine and chromite that is unexplainable through known mass-dependent processes. These minerals therefore either sample multiple isotopic reservoirs mixed during an impact or, less likely, are affected by complex anharmonic or nuclear field shift effects. Further investigation on these effects must be executed to completely discount these latter possibilities. The PMG-high chromite isotope ratios probably record equilibration between these two reservoirs. Chromium and W isotope analyses on PMG samples show no disequilibrium but provide an excellent chronology.

High-precision oxygen isotope analyses of IIIABs has identified three previously unknown subgroups with serious implications for the interpretation of the IIIAB suite of samples. These likely originate from different planetesimals and not from complex core evolution. Finally, chromite in PMGs and IIIABs is shown to be resolvable in $\Delta^{17}$O which precludes a common parent planetesimal. The findings of this study suggest that there may have been many more differentiated planetesimals in the early Solar System than previously thought and necessitate care in future studies linking meteorite groups by parent body.
“Space is big. You just won’t believe how vastly, hugely, mind-bogglingly big it is. I mean, you may think it’s a long way down the road to the chemist’s but that’s just peanuts to space”

- Douglas Adams, The Hitchhiker’s Guide to the Galaxy
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As I write this, it has been over four years since I attended my PhD interview at The Open University. It is difficult to for me to believe it was that long ago, which I suppose lends support to the old adage *time flies when you’re having fun*. I have, over the course of this project, had a tremendous amount of fun developing my understanding of key principles of isotope fractionation, developing as a scientist, and generally thinking about space. I am therefore indebted to the Science and Technology Facilities Council and Space SRA for funding this project as well as to the staff at The Open University who afforded me the incredible opportunity to pursue research in planetary science surrounded by such inspiring academics. My supervisory team has been excellent for the duration and has provided me with any support I needed whenever I needed it. I would like to thank Dr. Ian Franchi, my lead supervisor, for the help and insight he has provided over the duration of this project, as well as for the opportunities to attend conferences and workshops that he created. I could not have asked for a better lead supervisor and I hope that this thesis does justice to the support he has provided. My other supervisors, Professor Mahesh Anand and Dr. Richard Greenwood, have likewise been excellent and were always prepared to give up some of their time to listen to my ideas and provide helpful suggestions. To them, I am also immensely grateful. Other staff and former staff at the Open University to whom I owe thanks include: Dr. Guilia Degli-Alessandrini and Dr Diane Johnson, who provided training and support on the SEM when necessary, Dr. Sam Hammond who, together with Giulia, provided training and support on the EPMA when needed, and James Malley, who is in charge of the oxygen isotope lab. Above all, I owe James’ predecessor, Jenny Gibson, my thanks. Jenny trained me on the laser-assisted fluorination setup as she has dozens of PhD students before, and during her days in the lab sat listening to my ramblings several times a week for two years whilst I collected data. I am immensely grateful to her for her patience and I hope she enjoys her well-deserved retirement. I would also like the acknowledge my fellow PhD (and former
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List of Symbols

γ – Greek letter gamma, used as shorthand for taenite

α – Greek letter alpha, used as shorthand for kamacite

α₂ – Used as shorthand for martensite

σ – Greek letter sigma, used as shorthand for standard deviation

σₘ – Used as shorthand for standard error of the mean when referencing Clayton & Mayeda (1996)

α – Greek letter alpha, used as shorthand for fractionation factor in the context of oxygen isotopes

λ – Greek letter lambda, used to denote the fractionation exponent

‰ – parts per thousand, used in oxygen isotope results

%₀₀₀ – parts per ten thousand, used in context of Cr and W isotope results
List of Abbreviations

AR – Aqua regia. Mixture of nitric and hydrochloric acid

AU – Astronomical Unit.

BIC – Bushveld Igneous Complex

BSE – Back scattered electron

CAI – Calcium-Aluminium-rich inclusions found in some chondritic meteorites

Chropal – Chromite pallasite texture in some PMGs

CRE – Cosmic ray exposure

EDX – Energy dispersive X-Ray

EPMA – Electron probe microanalyser (electron microprobe)

GCR – Galactic cosmic ray

HSE – Highly siderophile elements

ICPMS – Inductively coupled plasma mass spectrometry

IfP – Institut für Planetologie, WWU Münster, Germany

IRMS – Isotope ratio mass spectrometer

IW – Iron Wüstite, mineral redox buffer

Ma – Mega annum, unit of 1 million years – specifically used in context of time before present

MDF – Mass-dependent fractionation

MIF – Mass-independent fractionation

MQ – Milli-Q water

Myr – Mega year, unit of 1 million years – used in any context other than before present
NFSE – Nuclear Field Shift Effect
PMG – Main-Group pallasite
REE – Rare-earth element
SEM – Scanning electron microscopy
SHO – Simple harmonic oscillator
SIMS – Secondary ion mass spectrometry
SL – Significance level
SMOW – Standard Mean Ocean Water, oxygen isotope standard
TFL – Terrestrial fractionation line
UTP – Unnamed Tibetan pallasite
UV – Ultra-violet
ZPE – Zero-point energy
1 INTRODUCTION AND BACKGROUND

1.1 Introduction

This thesis seeks the further understanding of the formation and evolution of early-formed planetary bodies by investigating the nature of metal-silicate differentiation that is potentially recorded in pallasite stony-iron meteorites. This work also evaluates the possible parent-body relationships between the largest pallasite group, Main-Group pallasites, and the largest core-derived magmatic iron group, the IIIAB irons. This chapter provides a literature review of the current understanding of IIIAB iron and Main-Group pallasites. At the end of the chapter, key research questions that have been addressed over the course of this work are discussed.

1.1.1 Planetary formation and the early Solar System

Calcium-aluminium-rich inclusions (CAIs) found in chondritic meteorites are thought to be the oldest solid materials in the Solar System. They likely condensed from a disk of gas and dust surrounding the proto-Sun 4568 million years ago (Ma) (Bouvier & Wadhwa, 2010). Fewer than 1 Myr later, and perhaps as early as 0.3 Myr after CAI formation (Kruijer et al., 2014), sizable planetesimals had accreted and differentiated, as evidenced by Hf-W dating measurements on core-derived iron meteorites (Kleine et al., 2009). These planetesimals were numerous. Up to 60 distinct bodies are thought to be recorded in just the iron meteorite collection (Chabot & Haack, 2006), with the total number of differentiated and undifferentiated bodies perhaps numbering as many as 148 (Greenwood et al., 2020). In addition, planetary accretion from a disk is known to be ongoing in extra-solar systems. Stars both at the beginning of their lives (e.g. David et al., 2016), as well as stellar remnants such as white dwarfs (Gänsicke et al., 2012; Vanderburg et al., 2015) and pulsars (Konacki & Wolszczan, 2003), have been observed with accompanying planetary systems. Circumstellar disks with ring gaps, carved out by the accretion of planets, have also been discovered in abundance around young stars (e.g. Yen et al., 2016; Fang et al., 2012). Taken together, these lines of evidence imply that the formation of planetary bodies occurs early in the history of star systems and is ubiquitous in our universe.
Planets form from the rapid accretion of gas and dust in circumstellar disks (Li et al., 2014) and differentiate following heating caused either by the decay of short-lived radioactive isotopes such as $^{26}$Al (Larsen et al., 2016) or through impact-heating, perhaps both (e.g. Bhatia & Sahijpal, 2017). Core separation during differentiation is thought to require at least 50% partial melting of silicates (Taylor, 1992) and therefore differentiated bodies must have undergone a high degree of partial melting, if not global melting. Despite the observed abundance of planets, the timescales and body-sizes of early-formed planetesimals, as well as their heliocentric distances, the extent to which these bodies melted and the duration of processes such as differentiation are still poorly understood.

Whilst it is abundantly clear that Earth has undergone extensive differentiation, the insights it provides into the earliest stages of planetary differentiation are very limited. Earth is the largest rocky planet in the Solar System but it is also geologically and hydrologically active, therefore a pristine record of processes active early in Earth’s history is extremely difficult to obtain. Furthermore, an understanding of the mechanics of differentiation would require the acquisition of deep-mantle and core material which appears technologically impossible at the present time. Fortunately, material sampling analogous environments is available in the meteorite record. Iron and stony-iron meteorites are fragments of the deep interior of disrupted differentiated planetesimals and record the processes active during differentiation and subsequent evolution of their respective parent bodies. In order to put analyses of these samples into context and to facilitate a wider understanding of planetary evolution, meteorite groups originating from different environments must be grouped by parent planetesimal in order to provide linked information on processes at different depths (see section 1.3.2). Differentiated meteorites are currently classified on the basis of chemical, isotopic, and petrological similarities. Recent studies have shown that all meteorites may belong to two isotopically distinct domains, the “carbonaceous” and “non-carbonaceous” reservoirs which may correspond to inside and outside of the orbit of Jupiter, respectively (Warren, 2011; Kruijer et al., 2017).

### 1.1.2 Meteorite Classification

Meteorites are divided at first order into three categories: chondrites, primitive achondrites, and achondrites (Weisberg et al., 2006). Chondrites are composed of relatively pristine material and
primitive achondrites are thought to comprise chondritic components subjected to partial melting or recrystallization (Weisberg et al., 2006). This thesis is not concerned with these categories, but will focus on groups of the achondrite category; meteorites that sample differentiated parent bodies (see Figure 1.1). Two types of achondrite, the pallasites and magmatic irons, are of particular interest in seeking to understand planetesimal evolution. Pallasites are mixtures of silicate and metal, likely representing material from a planetary mantle and core, respectively (see section 1.2.2) and therefore have the potential to tell us about deep planetary processes of which we would otherwise remain ignorant. Magmatic iron meteorites are largely core-derived (Goldstein et al., 2009) and therefore offer unique insights into core formation and evolution in rocky planets. The most abundant sub-groups of these two meteorite types are the Main-Group pallasites (hereafter Pallasite Main Group or PMG after Wasson & Choi, 2003) and the IIIAB irons. As well as their relative abundance – and therefore comparative ease of acquisition and sampling – these groups have important similarities that have led to the inference of a common planetary provenance (e.g. Scott, 1977; Clayton & Mayeda, 1996; Wasson & Choi., 2003; Dottin et al., 2018) and consequently have the potential to provide an unrivalled view into the differentiation and core formation processes.

The current iron meteorite chemical classification scheme is based on the measured Ge, Ga, and Ni content (Scott & Wasson, 1975; Weisberg et al., 2006). This method has been used since the 1950s (Goldberg et al., 1951, as cited in Weisberg et al., 2006) prior to which classification was based on the morphology of Widmanstätten bands (see section 1.2.1.2). Today this latter method for classifying irons is purely descriptive and has limited or no use for linking individual meteorites. The pallasite classification scheme is based on the mineralogy, the composition of silicates and metal, and the oxygen isotope signature.

This thesis is directed towards understanding the formation of the PMGs and IIIAB irons, as well as the evolution of their parent planetesimal(s) in order to better understand the processes and conditions present during early planetary formation and differentiation. This chapter provides a detailed overview of previous research into PMGs and IIIAB irons.
Figure 1.1 – The meteorite classification tree. This diagram shows the division of meteorites into the three broad groups and further subdivisions. Ungrouped irons and pallasites are not shown on this chart. The positions of the PMGs and IIIAB irons are form the focus of this thesis are highlighted with red arrows. After Weisberg et al. (2006)
1.2 Differentiated Achondrites

1.2.1 IIIAB irons

1.2.1.1 Chemical composition and trends

The IIIAB irons are the most abundant group of magmatic irons (see Table 1.1), a type of meteorite with chemical and compositional trends consistent with fractional crystallisation from a single molten reservoir, probably a core (Goldstein et al., 2009).

Table 1.1 – Table of iron meteorites. The magmatic and non-magmatic iron meteorite groups with the number of meteorites in that group shown in brackets (as of 23/05/2020). The “carbonaceous” groups are thought to have accreted and differentiated outside of the orbit of Jupiter (Kruijer et al., 2017). Not included in this table are 121 ungrouped irons, of which 86 are magmatic (Wasson & Kallemeyn, 2002). Modified from Goldstein et al. (2009) and updated using the Meteoritical Bulletin Database (https://www.lpi.usra.edu/meteor/metbull.php).

<table>
<thead>
<tr>
<th>Magmatic</th>
<th>Magmatic “carbonaceous”</th>
<th>Non-magmatic (non-carbonaceous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC (13)</td>
<td>IIC (8)</td>
<td>IAB</td>
</tr>
<tr>
<td>IIAB (141)</td>
<td>IID (29)</td>
<td>IIICD</td>
</tr>
<tr>
<td>IIE (24)</td>
<td>IIF (6)</td>
<td></td>
</tr>
<tr>
<td>IIG (6)</td>
<td>IIIF (9)</td>
<td></td>
</tr>
<tr>
<td>IIIAB (325)</td>
<td>IVB (17)</td>
<td></td>
</tr>
<tr>
<td>IIIIE (16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVA (86)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The current number of planetesimals thought to be represented by grouped magmatic iron meteorites is 12 (see Table 1.1). With the inclusion of ungrouped irons, this number may be as high as 60 (Chabot & Haack, 2006), or as low as 26 (Wasson, 2013). In either case the number of planetary bodies large enough to differentiate and undergo core-formation in the early Solar System ran to several dozens, some of which may have been larger than 1000 km in size (Goldstein et al., 2009).

Of great importance when studying iron meteorites are siderophile trace element concentrations. A good example of this is Ir, which is used as a proxy for fractional crystallisation due to the highly-siderophile partitioning behaviour it exhibits in crystallising metal which generates variations in Ir content that span three orders of magnitude in IIIAB irons (Wasson, 1999; Mullane et al., 2004). Samples with high-Ir concentrations are thus more primitive than those with low-Ir concentrations.
from the same chemical reservoir. Contrastingly, the elements Ni and Au are both incompatible in crystallising metal (Wasson, 1999) and display the opposite behaviour, albeit with less sensitivity. Accordingly, they can also be used as proxies for fractional crystallisation and should show an inverse correlation with Ir content as crystallisation of a metal melt progresses. The application of these principles allows for an understanding of the partitioning behaviour of other elements during core crystallisation. A key consideration in this regard is the amount of the non-metals S, P, and C, and other fluxing elements such as Co that are present in the crystallising metal. These elements can have considerable impact on the partitioning behaviour of other elements as crystallisation progresses (Goldstein et al., 2009), an effect particularly noticeable in the IIIAB irons, which the highly siderophile elements indicate sample a wide range of fractional crystallisation stages (Wasson, 1999). Furthermore, the incompatibility of S, P, Co, and C in crystallising metal (Chabot, 2004) means that with increasing crystallisation, the relative concentration of these elements increases in the residual liquid. This further increases the effect they have on the partition coefficients of other elements in the later stages of crystallisation. The presence of schreibersite (Fe,Ni₃P), and troilite (FeS) as trapped melt inclusions (Wasson et al., 1999) in iron meteorites is strong evidence for the incompatibility of these non-metals. An example of the effect that these elements can have is well illustrated by the increase in partition coefficient of Ir by a factor of almost 10³ as S content increases from 0 to 30 wt% in liquid metal (Jones & Drake, 1983) as shown in Figure 1.2.

The non-metal content of iron meteorites is therefore an important consideration when examining crystallisation histories. The IIIAB iron parent melt is thought to have had an initial S content of 12.5 ± 1.5 wt% (Chabot, 2004), consistent with the Ge vs. Au relationship observed in the group (Goldstein et al., 2009). It is worth noting, however, that the Ge partition coefficient at 12.5 wt% S would be > 1 (see Figure 1.2) and therefore the cause of the initial incompatibility of Ge in IIIAB irons (see Figure 5c in Goldstein et al., 2009) is not explainable by simple fractional crystallisation if this initial S content is correct. The complex partitioning behaviour described in this section means that it is desirable to use isotope systems in conjunction with chemical groupings when seeking to sort meteorite groups by parent body.
Figure 1.2 – Partition coefficient of Au, Ge, Ir, and Ni vs. wt% of non-metals S, P, and C in crystallising liquid metal. Note that the partition coefficients for Ir and Ni, both of which are used as proxies for fractional crystallisation, vary with differing non-metal contents. For Ir this is not a big problem as it is always compatible, Ni becomes compatible with increasing S content, as do Au and Ge, but has a partition coefficient little affected by P and C. Figure from Goldstein et al. (2009).

1.2.1.2 Texture in magmatic irons

The characteristic texture of magmatic iron meteorites is the Widmanstätten pattern (see Figure 1.3), most visible following etching with acid of polished surfaces of an iron meteorite (Goldstein et al., 2009). This texture forms when the body centred cubic form of FeNi, known as kamacite which shares properties with α-iron, nucleates and grows from γ-taenite (face centred cubic) during slow sub-solidus cooling (Goldstein et al., 2009). The size of the kamacite bands are linked to the cooling rate and have been used in cooling rate determinations for iron meteorites and pallasites, the metal of which also exhibits Widmanstätten bands (Yang & Goldstein, 2005; Yang et al., 2008; Goldstein et al., 2009b; Yang et al., 2010). This has been done in conjunction with cloudy zone particle size and Ni profiles across taenite bands. Like the partition coefficient for certain elements, the Widmanstätten pattern is strongly affected by P content (Yang & Goldstein, 2005). Meteorites with high P undergo cooling from the γ + Ph (phosphide [(Fe,Ni)3P]) field to the α + γ + Ph field which results in kamacite exsolution from taenite (Yang & Goldstein, 2005). Where iron meteorites contain low P, the pattern is thought to form via γ → α2 + γ → α + γ where martensite (α2) decomposes to α + γ during cooling (Yang & Goldstein, 2005). In order to understand the cooling rate, it is important
to know which of these reactions has occurred (Yang & Goldstein, 2005). Therefore, as with interpreting partition coefficients with progressive fractional crystallisation, it is crucial to constrain the non-metal contents of the parent melt in order to fully understand its subsequent evolution (Goldstein & Doan, 1972).

The P content of IIIAB irons and PMGs is relatively low (Yang & Goldstein, 2005; Boesenberg et al., 2012), and therefore the reaction $\gamma \rightarrow \alpha_2 + \gamma \rightarrow \alpha + \gamma$ is followed. Plessite, a texture comprising a fine-grained mixture of $\alpha$, $\gamma$, and sometimes tetrataenite, forms by the same reaction (Goldstein & Michael, 2006).

![Figure 1.3 – Widmanstätten pattern on IIICD iron meteorite Carlton. The Widmanstätten pattern is shown clearly in this image. Kamacite is blue in this image, taenite is yellow. Image from Goldstein et al. (2009).](image-url)

1.2.1.3 The evolution of the IIIAB core

The Earth’s core is crystallising radially outward from the centre as the liquid outer core gradually cools and solidifies. It was believed that cores of smaller planetesimals must crystallise in a similar manner (e.g. Ebensen et al., 1982) until careful interpretation of meteorite chemical data led to the discovery that asteroid cores may crystallise inwards in a dendritic manner (e.g. Haack & Scott, 1993). There is reasonably strong evidence that the IIIAB core crystallised inwards (Yang &
The metallographic cooling rate of IIIAB irons decreases with increasing Ni content (Yang & Goldstein, 2006). This means that at higher degrees of melt evolution, the cooling rate was lower. The more evolved melt was therefore closer to the centre of the core, suggesting that it likely crystallised inward. Discrepancies in Ir, Re, and W compositions vs. Ni content between members of the IIIAB iron group, specifically between Cape York and other IIIAB irons, have led to the suggestion that the IIIAB core experienced dendritic inward crystallisation (Haack & Scott, 1993), however there may be an alternative reason for these discrepancies (see Chapter 6). As the name suggests, this model posits heterogeneous inward crystallisation of branch-like dendrites, caused by insufficient mixing of the liquid (Chabot & Haack, 2006) which then results in the isolation of pools of melt and gives the observed compositional variation (Haack & Scott, 1993). The inward formation of huge dendrite structures from the core-mantle boundary that act as a barrier to effective large-scale mixing is thought to be a consequence of the lack of a sufficient pressure differential in asteroid cores to increase the liquidus temperature with depth (Haack & Scott, 1993). This effect concentrates elements such as S and P, which depress the liquidus temperature in the outer parts of the core and enable the formation of dendrite structures (Haack & Scott, 1993). Variability in IIIAB Ir vs. Au values (Figure 1.4d) are interpreted by other authors as being the result of varying amounts of trapped melt sampled in different meteorites (Wasson, 1999), and as representative of liquid immiscibility (Ulff-Møller, 1998). Observations across individual masses of Cape York (e.g. Agpalilik), confirm that chemical zoning was present on a small scale in the IIIAB core (Chabot & Haack, 2006). The Ir vs. Au composition of Cape York can be matched by mixing solid and melt at around 30% fractional crystallisation of the IIIAB core (Wasson, 1999). The presence of elongate troilite nodules in some Cape York samples, with phosphate and chromite at antipodal edges has been interpreted as evidence of original gravitational settling, chromite sinking and phosphate being buoyant in a trapped melt pocket (Buchwald, 1971; 1975; Chabot & Haack, 2006). The fact that the chemical gradient and this gravitational gradient are perpendicular in the sample analysed led Chabot & Haack (2006) to suggest that the IIIAB core did not experience concentric growth in a similar way to Earth’s core. This is consistent with the idea of a dendritic inward crystallisation mechanism as compositional variations over relatively small distances, as observed in Agpalilik, would be expected in such an environment. Due to its apparent utility in understanding the crystallisation of
the IIIAB core, Cape York is a sample of high importance. It is possible that a process such as dendritic inward crystallisation would inhibit mixing and may result in measurable isotopic and chemical heterogeneity between different isolated pools of melt, especially if this crystallisation was cotemporaneous with later stages of core growth. This is testable with high-precision oxygen isotopes (see Chapter 6).

1.2.1.4 Chromium in IIIAB irons

In the context of this study, Cr is of particular interest in both IIIAB iron meteorites and PMGs as chromite is a relatively abundant oxygen bearing phase. The behaviour of Cr in fractionally crystallising magmatic iron meteorites, as well as its behaviour in PMG metal, is enigmatic and the observed trend contrasts with what would be expected given experimentally derived partition coefficients (Wasson et al., 1999).

Figure 1.4 – A series of cross-plots of Cr and Ir vs. Ni and Au. Note the negative correlations between melt evolution and Cr/Ir in IIIAB irons. As melt evolution increases, Cr content in IIIABs decreases. This is contrary to experimentally derived partition coefficients which suggest that the opposite trend should be observed. Figure from Wasson et al. (1999). The labelled samples are Bagdad (Bag), Agpalilik (Agp – Cape York), and Bear Creek (BC).
Figure 1.4 shows the observed behaviour of Cr at different stages of melt evolution, as recorded by the progressive evolution of Ni and Ir concentration. Iridium, also plotted against Au and Ni on the bottom two diagrams, has a partition coefficient of around 5 (see Figure 1.2) at the IIIAB S-content of 12.5 ± 1.5 wt% (Chabot, 2004). Accordingly, Ir is strongly partitioning out of the melt, into the crystallising solid metal phase. By contrast, Cr has a partition coefficient of around 0.2 at 12 wt% S (Jones & Drake, 1983) and 0.5 at moderate S-contents (Ulff-Møller, 1998), yet is also partitioning out of the liquid phase (Figure 1.4). This relationship cannot be explained by simple fractional crystallisation (Chabot et al., 2009). Experimental studies show that Cr behaviour is largely unaffected by pressure (Fischer et al., 2015), suggesting that depth within the parent body is not responsible for this effect. As Cr has such a low partition coefficient, it is unlikely to be partitioning into the crystallising metal and is therefore probably moving into another mineral phase, most likely chromite. This would mean that chromite and metal may be co-crystallising in the IIIAB core (Ulff-Møller, 1998). This idea could perhaps be supported if V shows the same partitioning behaviour as Cr (Chabot et al., 2009); both elements are sensitive to metallic melt composition (Fischer et al., 2015). In silicate melts, V partitions strongly into chromite and so may be a good indicator of chromite co-crystallisation with the metal (Chabot et al., 2009). It is not known whether V exhibits the same behaviour in metallic systems, although experiments do show that it is incompatible in crystallising metal (Chabot et al., 2009) and previous work suggests that V is enriched in PMG chromite relative to coexisting phases (Bunch & Keil, 1971). It may be that apparent removal of Cr from the IIIAB core with crystallisation is a sampling artefact created by the preferential selection of chromite-free samples by researchers seeking to chemically analyse pure IIIAB metal (Wasson et al., 1999), although this is unverified.

A potential implication for the co-crystallisation of chromite in asteroid cores on planetary differentiation is that it would be buoyant in the metallic melt, as evidenced by the lack of FeNi metal in the large chromite-rich “chropal” regions (regions where chromite replaces metal in pallasite textures) of Brenham (PMG) (Wasson et al., 1999). Resultantly, co-crystallising chromite would buoyantly rise in an inwardly crystallising core (as is the case for IIIAB irons) and could conceivably affect dynamo activity or perhaps even create sufficient compositional convection to generate one. Phosphates would also be buoyant (Chabot & Haack, 2006), although the fact that phosphates
represent residual melt means that, despite their buoyancy, they would be contained near the centre of an inward-crystallising core or perhaps in pockets of trapped melt in a core evolving by dendritic crystallisation.

1.2.1.5 Cooling rates in IIIAB irons

Studies quantifying cooling rates for meteorites (e.g. Buseck & Goldstein, 1969; Pellis et al., 1983; Ito & Ganguly, 2006; Yang & Goldstein, 2006; Yang et al., 2008; Goldstein et al., 2009b; Yang et al., 2010; Goldstein et al., 2014) have been important in seeking to understand their formation. The cooling rates of IIIAB irons have been studied extensively and are important in understanding any potential relationship with PMGs (Yang et al., 2010). Recent studies, using improved cooling rate determination models (e.g. Yang & Goldstein, 2006; Yang et al., 2008), have further constrained our understanding of the thermal histories of asteroid cores.

There is a large variation in sub-solidus cooling rates for IIIAB irons, from 56–338 K Myr$^{-1}$ (Yang & Goldstein, 2006). This has been interpreted as evidence for partial exposure of the IIIAB core at ~873–993 K, during the nucleation of kamacite and the formation of the Widmanstätten pattern from which the cooling rates are derived (Yang & Goldstein, 2006). In a more extreme case, the IVA magmatic iron group sample suite exhibits enormous variations in cooling rate, from 100 to 6600 K Myr$^{-1}$ (Yang et al., 2008). IVA irons show an inverse correlation, although not a linear one, of cooling rate with Ni content; this means the IVA core, like the IIIAB core, probably crystallised inwards (Yang et al., 2008; McCoy et al., 2011). The very high cooling rates (~6600 K Myr$^{-1}$), coupled with the low Ni-content of these samples, have been used to conclude that the IVA core was not insulated during cooling (Yang et al., 2008). Given this interpretation, and the order of magnitude difference in maximum cooling rates between IVAs and IIIABs, it is likely that the IIIAB samples were in a core that was at least thinly insulated, or were a deeper part of a much larger core. The proposed loss of insulation of the IVA core is interpreted as being due to a grazing impact with another planetary body (e.g. Asphaug et al., 2006), stripping the core of its insulating mantle (Yang et al., 2008). The techniques used to obtain these metallographic cooling rates were recently placed under scrutiny (Wasson & Hoppe, 2012) but were subsequently shown to be robust (Goldstein et al., 2014).
1.2.1.6 Oxygen isotopes in iron meteorites

Oxygen isotope studies of iron meteorites rely on the presence of O-bearing phases in samples. Principally those used are silicates, chromite, and phosphates. In IIIAB irons, silicates are very rare (Clayton & Mayeda, 1996) and neither any silicates nor phosphates could be obtained for this study (see section 2.2). As a result of this, only chromite is analysed for oxygen isotopes in IIIABs.

Nine IIIAB irons were analysed for O-isotopes by Clayton & Mayeda (1996) by direct fluorination of samples in a Ni-bomb and found to have a mean $\Delta^{17}O$ of -0.21‰ (± 0.12 ‰ 2σ) (for a description of O-isotope terminology, see section 2.1.1). These results have a standard deviation that is comparable with other differentiated groups measured by the Ni-bomb technique (see Clayton & Mayeda, 1996) such as angrites ($\Delta^{17}O = -0.15 \pm 0.12 ‰ 2\sigma$), PMGs ($\Delta^{17}O = -0.28 \pm 0.12 ‰ 2\sigma$), and aubrites ($\Delta^{17}O = 0.02 \pm 0.08 ‰ 2\sigma$). Laser fluorination analysis (see section 2.5) and accompanying developments in mass spectrometry have subsequently provided significant improvements in precision over the Ni-bomb technique and the precision of these early measurements has since been greatly surpassed (e.g. Greenwood et al., 2006; 2015; 2017; 2018; Ali et al., 2018; Pack & Herwartz, 2014; Young et al., 2016). A direct comparison between the precision afforded by the two techniques is clearly demonstrated by published average $\Delta^{17}O$ results for PMG olivines. Using the Ni-bomb technique, the average $\Delta^{17}O$ of 25 PMG olivines was measured at -0.28 ± 0.12 (2σ) (Clayton & Mayeda, 1996), by contrast the laser fluorination technique yields the considerably more precise -0.187 ± 0.016 (2σ) on 24 PMG olivines. Consequently, the new analyses of O-bearing phases in IIIAB irons performed in this study are timely and should help better constrain the origins of these samples.

1.2.2 Main-Group Pallasites

1.2.2.1 Background

Owing to their unusual and striking appearance (see example in Figure 1.5), pallasites were the first objects identified as extra-terrestrial (Chladni, 1794, cited by Buseck, 1977). Pallasites are stony-iron meteorites and are typically around 65% olivine and 30% FeNi metal by volume (Yang et al., 2010; Solferino & Golabek., 2018), often with low amounts of troilite, schreibersite, chromite, phosphates, and in rare cases low-Ca orthopyroxene and phosphoran olivine (Buseck, 1977;
Boesenberg et al., 2012). The metal in pallasites is texturally similar to a matrix or solidified intercumulus liquid (Buseck, 1977) that is roughly one-third of the volume and accounts for over half of pallasite mass; in about half of pallasites, this metal is highly fractionated with low Ir contents (Boesenberg et al., 2012) (see Figure 1.4), although in some cases Ir content is high (Wasson & Choi, 2003) suggesting a lower degree of metal fractionation. Initially, pallasites were divided into two groups: PMG and the Eagle Station trio (ES), although recently the probable number of parent bodies has increased from two to between five and eight (Scott, 2007; Boesenberg et al., 2012; Boesenberg et al., 2017). Each pallasite group has a distinct oxygen isotope signature (Mullane et al., 2004, see Figure 1.6).

Figure 1.5 – A polished and etched slice of Seymchan, a PMG. Note the clusters of olivines and the variation in metal:silicate ratio across even this small sample. Figure from Yang et al. (2010).

These groups include the Pyroxene pallasites, as well as Milton, Zinder and Northwest Africa 1911 (NWA 1911). Vermillion and Yamato 8451 (ungrouped) contain up to 2% orthopyroxene of differing Ca composition and display different O-isotopic compositions to PMGs or Eagle Station
pallasites (ES) (Boesenberg et al., 2012). The pallasites Zinder and NWA 1911 contain even more orthopyroxene, 28% and 35% by volume respectively (Bunch et al., 2005). NWA 1911, and NWA 10019 are potentially linked to PMGs and IIIAB irons, although this relationship requires further verification.

Figure 1.6 – The distribution of different pallasite groups in oxygen 3-isotope space. Note that PMG are close to the terrestrial fractionation line (TFL) whilst the pyroxene pallasites, Milton, and the Eagle Station grouplet are offset. The Y&R and CCAM lines are the Young and Russell and Carbonaceous Chondrite Anhydrous Minerals lines, respectively. Figure from Greenwood et al. (2017).

1.2.2.2 Main-Group pallasite metal

The metal in PMG is comprised of α-kamacite and γ-taenite and forms a matrix-like texture that encloses the silicate minerals (Buseck, 1977) – see Figure 1.5. Some pallasites were initially mistaken for irons (e.g. Seymchan) on the basis of high metal to silicate ratios, likely because the specimens sampled a metal vein, some of which are tens of cm in diameter (van Nickerk et al., 2007). Similar metal-dominated regions are also recorded in the PMG Glorieta Mountain and Brenham (van Nickerk et al., 2007) and may be evidence for an impact formation mechanism or perhaps ferrovolcanism (see section 1.3.1). In one PMG, Glorieta Mountain, most samples are olivine-free (Wasson & Choi, 2003).
Pallasite metal is formed in the same manner to that in magmatic iron meteorites and often displays the same textural characteristics (Buseck, 1977). In PMGs, Ge and Ga exhibit a negative correlation with Au and Ni (Scott, 1977), suggesting that Ge and Ga are compatible in the crystallising metal. This is the case in IIIAB irons at higher degrees of melt evolution, although not in less evolved samples because of the effects of S on the Ge partition coefficient. It has also been predicted that the Fo content of olivine is inversely correlated with Ni (Scott, 1977), meaning that early crystallising olivine (Fo-rich) would be found in pallasites that also contain more primitive metal compositions (low-Ni). This similarity in Ge, Ga, and Ni behaviour is a key reason that PMG and IIIAB irons have been interpreted as genetically linked (Scott, 1977b).

Six PMGs have anomalous metal compositions on element vs. Au diagrams (Wasson & Choi, 2003). These meteorites all show distinct differences from other PMGs in some of the following elements: Ir, Au, Co, As, Sb, Ga, Ni, Cu, W, Ge, Pt (Wasson & Choi, 2003). The anomalous metal PMG do not exhibit a corresponding olivine Fo-Fa compositional difference (Wasson & Choi, 2003). This confounds the earlier prediction by Scott (1977) that Ni and Fa content would have a positive correlation. The lack of a relationship between increasing Ni, a proxy for metallic melt evolution, and increasing Fa content, which is often associated with more evolved melt than Fo-rich olivine (Goodrich & Delaney, 2000), is perhaps evidence that the pallasite metal and silicates are not in equilibrium. This may lend support to formation models invoking separate evolution models for the metal and silicate, such as the impact origin proposed by Tarduno et al. (2012) (see section 1.3.1).

As in IIIAB iron formation, there are two key components controlling the distribution of highly siderophile elements (HSEs) in PMGs: fractional crystallisation and kamacite-taenite exsolution (Mullane et al., 2004). The PMG metal is often cited as being consistent with an ~80% fractionally crystallised melt of IIIAB-like composition (Wasson et al., 1999; Wasson & Choi, 2003; Scott, 2007); however, Boesenberg et al. (2012) argue that in many siderophile trace elements (Ir, Ni, W, Co, Pt, Ga, Ge, Cu, and Sb) this is not the case.

Measured Cr content in PMGs agrees with the predictions from experimental data and is incompatible in the metal (see Figure 1.4) (Jones & Drake, 1983; Wasson et al., 1999), despite the fact that chromite may be co-crystallising based on the chropal texture in Brenham (Wasson et al.,
This suggests that the cause of the Cr depletion with evolving metal in IIIABs (see section 1.2.1.4) may be due to sampling artefacts as has been discussed previously (Wasson et al., 1999) and above (see section 1.2.1.4).

### 1.2.2.3 Main-Group Pallasite cooling rates

Yang et al. (2010) examined the absolute metallographic cooling rates for eight PMGs using Ni profiles across taenite lamellae, and the relative cooling rate of 28 PMG from cloudy zone particle size. The results of these analyses show that PMG cooling rates below 975 K range from 2.5–18 K Myr\(^{-1}\), consistent with the lower limit of cooling rates from Pu fission track analysis (Pellas et al., 1983). Such a wide range of cooling rates is inconsistent with the view that PMG formed in a band at the core-mantle boundary of an asteroid where consistent cooling rates would be expected across PMG samples (Yang et al., 2010). Manganese-Cr systematics in pallasite metal (Ito & Ganguly, 2006) are also roughly consistent with cooling rate values calculated from taenite edge compositions (Buseck & Goldstein, 1968; 1969).

The high temperature cooling rates of PMG have been calculated at 100–300 K Myr\(^{-1}\) from olivine zoning in some samples (McKibbin et al., 2016; Donohue et al., 2018). Despite being two orders of magnitude greater than the cooling rates recorded in the metal, this rate is consistent with the low temperature metallographic cooling rates discussed above assuming that the cooling rate decreased asymptotically over time (Donohue et al., 2018). The peak temperature of pallasites is thought to have been no more than 1973 K on the basis of the Fo composition of PMG olivine and the preservation of Cr-Al zoning in PMG chromite (Boesenberg et al., 2012). Combined with the fact that Mn compositions in some PMG olivines suggest equilibration with PMG metal at ~1573–1773 K (Donohue et al., 2018), this places constraints on the temperature at which the phases were mixed. Based on experiments on metal alloys of similar composition to PMG metal, the liquidus temperature for PMG metal was likely 1753–1798 K (Donohue et al., 2018 and references therein). Given that this is similar to the temperature of Mn equilibration (~1573–1773 K) it can be concluded that the metal temperature during mixing was probably somewhere between 1798 and 1973 K and probably nearer the upper limit in order to allow time for Mn equilibration during cooling from 1973 K to
~1573 – 1773 K at a cooling rate of 100 – 300 K Myr\(^1\). Such equilibration could not be achieved in all elements (see section 3.5).

### 1.2.2.4 Olivine in Main-Group Pallasites

Pallasite olivines often exhibit textural and compositional differences both between meteorites and sometimes between different grains within meteorites. Texturally, olivines within pallasites are divided into three groups: fragmental, rounded, and angular (Figure 1.7) (Buseck, 1977; Scott, 1977; Buseck & Clark, 1984; Mittlefehldt et al., 1998; Wasson & Choi, 2003; Boesenberg et al., 2012; Solferino et al., 2015). It seems likely that the presence of angular olivine implies that the PMG silicates were solid and the metal liquid during mixing (Wasson & Choi, 2003). Crystal size is variable; crystals in Mount Vernon and Esquel have been found measuring ≥ 30 cm and ≥ 20 cm, respectively (Scott, 1977; Ulff-Møller et al., 1998; Wasson & Choi, 2003) which may suggest very slow growth. The formation of rounded olivine in PMGs is thought to occur by alteration of pre-existing angular olivine in the presence of FeS melt (e.g. Solferino et al., 2015; McKibbin et al., 2019). Fragmental olivine is probably formed by mechanical break-up of the other two types, perhaps induced by impact shockwaves during large impact bombardment (Boesenberg et al., 2012).

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**Figure 1.7** – Olivine textures in Seymchan. This sample of Seymchan exhibits angular olivine clusters surrounded by fragmental olivine. Rounded olivine can be seen in the Brenham sample in Figure 1.8. Figure from Boesenberg et al. (2012).
The olivine in PMGs ranges compositionally from Fo$_{82}$ to Fo$_{88}$ and is generally relatively uniform within individual meteorites (Boesenberg et al., 2012; McKibbin et al., 2019). According to Buseck & Goldstein (1969), > 80% of measured olivines fall in the range Fo$_{86.5}$ to Fo$_{88.4}$, although a subgroup identified as “anomalous silicate” have typically lower Fo values, ranging between ~81.5 and ~84.5 (Wasson & Choi, 2003). As of 2003, four PMGs were known to possess anomalously low Fo compositions: Rawlinna, Phillips County, Zaisho, and Springwater (Wasson & Choi, 2003), perhaps representing less primitive mantle material.

PMGs have been sub-divided according to olivine texture and composition into the following subgroups (McKibbin et al., 2019):

- **Common PMG** – ~Fo$_{87-88}$, ~0.30 wt% MnO, predominantly angular olivine, some rounded and fragmental

- **Low-MnO PMG** – MnO lower than 0.25 wt%, usually rounded olivine, some angular, some fragmental

- **High FeO PMG** – Fo$_{82-84}$, usually rounded olivine, higher Ni content in coexisting metal

- **Transitional** – transitional between low-MnO and common PMG subgroups

In addition to these groups, one anomalous PMG was identified, Pavlodar. In interpreting the findings of this PhD project, new subgroups are defined on the basis of these prior subgroups and new isotopic data (Chapter 3, Table 3.1).

Phosphoran olivine is a rare phase that is also found in some pallasites (Buseck, 1977; Boesenberg & Hewins, 2010; Fowler-Gerace & Tait, 2015). It is metastable and typically present as overgrowths on earlier-formed olivine crystals that are often P-free (Fowler-Gerace & Tait, 2015). In pallasites these olivine overgrowths have 4 – 7.4 wt% P$_2$O$_5$ (Boesenberg et al., 2012). Only five pallasites (all PMG) are known to contain phosphoran olivine: Brenham, Brahin, Zaisho, Springwater, and Rawlinna (Boesenberg et al., 2012; Fowler-Gerace & Tait, 2015). The presence of FeO-rich olivine (see above) and phosphoran olivine in Zaisho, Rawlinna, and Springwater could be due to O-rich magmatic gas oxidising Fe and P during the formation of these meteorites (Wasson & Choi, 2003). Experimental work by Boesenberg & Hewins (2010) has shown that the silicate melt from which the
phosphoran olivine crystallises is required to be P-bearing. This phosphorus probably diffused into
the silicate melt from the metal (Boesenberg et al., 2012). The temperature of formation was
approximately 1523 K (Boesenberg et al., 2012); experimental studies suggest that, after formation,
phosphoran olivine can only remain in silicate melts for a few weeks (Boesenberg & Hewins, 2010)
which indicates that the temperature cannot have exceeded ~1523 K after the phosphoran olivine had
formed (Boesenberg et al., 2012). It seems difficult to reconcile this apparent need for rapid cooling
(e.g. Fowler-Gerace & Tait, 2015) with the slow cooling rates measured at both high (McKibbin et
al., 2016; Donohue et al., 2018) and low (Yang et al., 2010) temperatures in PMGs. Phosphoran
olivine was not identified in the samples analysed for this study, however its existence does provide
some constraints on temperatures and the presence of silicate melts during PMG formation (see
Chapter 4).

Olivine clusters (see Figure 1.5, Figure 1.7), large areas of almost metal-free olivine that can be up
to 30 cm across, have so far been identified in eight PMGs: Esquel, Admire, Albin, Huckitta, Imilac,
Mount Vernon, Fukang, and Seymchan (Boesenberg et al., 2012). None of these pallasites except
Seymchan have rounded olivine grains and olivine clusters are absent from almost all specimens
with rounded grains examined so far (Boesenberg et al., 2012). Fragmental olivine appears to be
more abundant in pallasites with primitive metal compositions than those with more evolved metal
compositions (Boesenberg et al., 2012). The reasons for this are currently unclear but some
possibilities are explored later in this thesis (see Chapter 4).

1.2.2.5 Chromite

Chromite can be abundant in pallasites and typically is euhedral, more rounded, or forms large (up
to 10s of cm) polycrystalline masses where it appears to have replaced, or displaced, the metal
(Wasson et al., 1999; Wasson & Choi, 2003). The chromite grain size in these regions is up to 15
mm (Wasson et al., 1999). There is symplectic chromite in some samples (Boesenberg et al., 2012).
Pallasite chromite composition is related to oxygen fugacity ($f_{O_2}$) (Bunch & Keil, 1971);
FeO/FeO+MgO ratios in co-existing olivine and chromite in pallasites are low compared with
meteorite groups forming in higher $f_{O_2}$ conditions (Bunch & Keil, 1971). Chromite compositions
are known to vary between pallasites and to a lesser extent within individual pallasites (Wasson et
with Cr and Al being the most variable between samples (Bunch & Keil, 1971). Variability in Al/(Al+Cr) can be significant, and the Fe/Mn and Fe/Mg ratios are greater than in co-existing olivine (Boesenberg et al., 2012). There is also often variability from core to rim: Fe/(Fe+Mg) increases, Al/(Al+Cr) and TiO\textsubscript{2} decrease (Boesenberg et al., 2012). Compositionally, the PMG chromite can be very different from that seen in IIIAB irons. In IIIAB irons the chromites have near end-member compositions with high Cr\textsubscript{2}O\textsubscript{3} and FeO as well as low Al\textsubscript{2}O\textsubscript{3}. Such chromites are thought to be derived from an environment where no silicate melt was present (Boesenberg et al., 2012). The scale of the difference between analysed PMG chromite and endmember composition is important in understanding the formation environments for these pallasites (see section 3.2.2.2). Chromite with elevated levels of Al is generally found with olivine of the common subgroup, whilst the low-MnO PMG subgroup, high-FeO subgroup, and transitional pallasite Seymchan typically exhibit near-endmember chromite compositions (McKibbin et al., 2019). Some implications of this in the context of results from this study are discussed in Chapter 3.

Textural differences are evident in chromite from different pallasites. Chromite grains are often angular to rounded (Wasson & Choi, 2003; Boesenberg et al., 2012) and this is the case for chromite studied in Mount Vernon and Fukang for this study (see section 3.2.2.1). In other PMGs, however, there are large areas where the metal matrix is replaced by chromite and FeNi metal is totally absent (Wasson et al., 1999) – see Figure 1.8. These areas are probably the result of late-stage chromite crystallisation from evolved liquid metal or the formation of a buoyant chromite phase during co-crystallisation of metal and chromite. Main-Group pallasites Seymchan and Brenham both display notable examples, with the latter exhibiting this texture on a scale of tens of cm (e.g. Wasson et al., 1999). Phosphoran olivine and phosphate contents are higher in these regions (Wasson et al., 1999).
1.2.2.6 Phosphates

Main Group pallasites contain varying amounts of five different phosphates, in descending order of abundance these are: merrillite \([\text{Ca}_{18}\text{Na}_2\text{Mg}_2(\text{PO}_4)_2]\), stanfieldite \([\text{Ca}_3\text{Mg}_3(\text{PO}_4)_4]\), farringtonite \([\text{Mg}_3(\text{PO}_4)_2]\), a silico-rich phosphate, and an Fe-rich phosphate (Boesenberg et al., 2012). Whilst phosphates are a minor phase, they are widespread and occur in nearly all PMGs, although often in low quantities (Buseck & Holdsworth, 1977). This phase is significant as it plays an important role in hosting the elements Na, K, U, and Th, amongst others (Buseck & Holdsworth, 1977). Trace element analyses of phosphates in pallasites have shown that whilst they have relatively low rare earth element (REE) concentrations, heavy REEs are strongly enriched compared to light REEs (Davis & Olsen, 1991). Higher REE concentrations in Ca-phosphates of two pallasites, enrichment in light REEs relative to heavy REEs, and an observed negative Eu anomaly, have led to the
interpretation of phosphate formation from late-stage crystallisation of a Eu-depleted liquid at shallow depth (Davis & Olsen, 1991).

1.2.2.7 Oxygen isotopes in Main-Group Pallasites

Main-Group pallasites, IIIAB irons and howardite-eucrite-diogenite (HED) meteorites were initially believed to be from the same parent body based on oxygen isotope composition (Mittlefehldt et al., 1998; Ziegler & Young, 2007). Early isotopic work on 18 PMGs yielded a $\Delta^{17}O$ value of -0.28 ± 0.02‰ ($2\sigma_m$) (Clayton & Mayeda, 1996). This was not resolvable from the $\Delta^{17}O$ value for HEDs of -0.24 ± 0.08‰ ($2\sigma_m$) (Clayton & Mayeda, 1996). The $\delta^{18}O$ values for PMG olivine of 2.94‰ and the value for diogenite pyroxene of 3.33‰ was interpreted as being further evidence for a link, the difference being consistent with that expected for oxygen isotope fractionation between the two minerals in an igneous environment (Chiba et al., 1989; Clayton & Mayeda, 1996). Recent improvements in the precision of the techniques used to measure oxygen isotopes have, however, allowed $\Delta^{17}O$ values for HEDs to be resolved from the fractionation line thought to be shared by PMGs and IIIAB irons (e.g. Franchi et al., 2013; Greenwood et al., 2006) (see Figure 1.9).

![Oxygen isotopes of PMG and HEDs](image)

Figure 1.9 – Oxygen isotopes of PMG and HEDs. This figure shows a clearly resolvable difference in mean $\Delta^{17}O$ values between the PMG group ($\pm 2\sigma$ shown in blue) and the diogenite group ($\pm 2\sigma$ in green). Sample error bars are $2\sigma$ variation for each sample. Figure from Greenwood et al. (2017).
In a recent study, Ali et al. (2014; 2018) identified two populations in oxygen isotopes across 10 analysed PMGs (see Figure 1.10).

Ali et al. (2014; 2018) identify a low-Δ¹⁷O group, with an average of -0.213 ± 0.011‰ (2σ), containing the pallasites: Brahmin, Esquel, Fukang, Giroux and Seymchan, they also highlight a high-Δ¹⁷O group, with an average of -0.172 ± 0.007‰ (2σ). This latter group consists of the meteorites: Brenham, Huckitta, Imilac, Springwater and Sterley. When interpreting these observed oxygen isotope populations, the authors suggested that it may be recording the isotopic signature of the original parent body and an impacting body – see section 1.3.1 (Ali et al., 2014). Further evidence
for two PMG populations was suggested on the basis of higher MgO content in the low-Δ\(^{17}\)O group, a higher but less dense volume of olivine in the low-Δ\(^{17}\)O group, and higher Ni-content in the high-Δ\(^{17}\)O group (Ali et al., 2014; 2018), these observations all require verification. A recent study by Greenwood et al. (2015) was unable to replicate this bimodality.

A preliminary study by Franchi et al. (2013) identified an anomalous oxygen isotope value for chropal chromite analysed from Brenham, a PMG. Whilst Δ\(^{17}\)O values of the silicates from Brenham plot on the PMG fractionation line on a 3-isotope diagram, the chromite gives values between the PMG and the HED/mesosiderite fractionation lines (Franchi et al., 2013). This difference may suggest that olivine and chromite originate from different isotopic reservoirs during pallasite formation. The present study involved a detailed investigation of this potential olivine-chromite disequilibrium (see Chapter 3).

### 1.3 The origins of PMGs and their relationship to other meteorite groups

#### 1.3.1 Candidate pallasite formation mechanisms

The PMGs are an enigmatic meteorite group, the origins of which have been a subject of debate for decades (e.g. Urey, 1956; Scott, 1977; Mittlefehldt et al., 1998; Wasson et al., 1999; Yang et al., 2010; Tarduno et al., 2012; Solferino & Golabek, 2018; McKibbin et al., 2019). This section summarises the current contending models for the formation of pallasites and discusses the evidence for a shared parent planetesimal with the IIIAB iron meteorites.

As a result of their mineralogy, the canonical environment for pallasite formation has been at or near the core-mantle boundary of a differentiated body, in a zone where molten metal from the core mixed with cumulate or restite dunite of a lower mantle (Buseck, 1977; Mittlefehldt et al., 1998). Some current models for pallasite generation still follow a similar model (e.g. Boesenberg et al., 2012), although recent studies have shown a number of pallasite characteristics that are seemingly incompatible with this view. Whatever the mechanism for pallasite formation, the fact that ES pallasites, Pyroxene pallasites, PMG, and the ungrouped pallasites are from a range of isotopically distinct parent bodies suggests that their environment of formation was not unique and was perhaps more common in the early Solar System than previously thought (Boesenberg et al., 2012). In light
of this, it is important to examine current hypotheses for the formation of pallasites and test them where possible.

The classical interpretation of pallasite formation at a core-mantle boundary (Buseck, 1977; Mittlefehldt et al., 1998) is over 30 years old (Boesenberg et al., 2012). This model requires outward-crystallisation of an asteroidal core in order to form pallasites exhibiting low-Ir highly fractionated metal compositions. Oxygen isotope data have been cited as evidence in favour of the classic pallasite formation model, suggesting that at the core of the PMG parent body were the IIIAB irons (Buseck, 1977; Clayton & Mayeda, 1996) (see section 1.3.2.5). However, given that the IIIAB core likely crystallised inward (Yang & Goldstein, 2006) and hence the fractionated metal would be in the centre of the core and separated from the overlying dunite mantle by the crystallised metal, PMGs are unlikely to have formed at the core-mantle boundary in an asteroid where IIIAB irons were the core.

Urey (1956; 1966) proposed that pallasites formed in separate metal pools within the parent body as they are too abundant to sample a boundary layer. Such a model could explain observed differences in PMG olivine and chromite composition and texture (e.g. McKibbin et al., 2019) as well as the range in cooling rates (e.g. Yang et al., 2010). Another model for pallasite formation requires pallasites to have a near surface origin and be subjected to heating from an external source. Silicate-metal mixing then occurs in a zone just below a dunite layer (Mittelfehldt, 1980). However, this last model has a major challenge explaining the relatively slow cooling rates measured in some of these materials that appear to require significant insulation (Yang et al., 2010). Others have, however, suggested that some pallasites perhaps may have formed as shallow as 25 km from the surface of a parent body with a radius of 200 km (Nichols et al., 2016).

Very recently, active ferrovolcanic processes on metallic asteroids (e.g. Abrahams & Nimmo, 2019) have been proposed to explain pallasite formation (Johnson et al., 2019). In this model, an overpressured pool of isolated S-rich metal melt propagates as a dyke into the overlying mantle. This melt evolves in conjunction with the inward-formation of core dendrites and the residual S-rich melt is lower-density than the surrounding material (Johnson et al., 2019). There are several problems with this model. The first is that the metal cooling rate differences exhibited by different PMGs are
not consistent with the small depth of propagation expected from an over-pressured melt. For the PMG body core estimate of ~5 wt% S, this depth of propagation is around 3 km (see Figure 2 in Johnson et al., 2019). The second issue is the low S content itself. Pallasites contain very low amounts of S (Wasson & Choi, 2003; Boesenberg et al., 2012) with a few notable exceptions, e.g. Hambleton, Glorieta Mountain, and Philips County (Scott, 1977; Buseck, 1977; Johnson et al., 2006; Boesenberg et al., 2012). This seems to preclude the possibility that pallasites are a mixture of dyke-propagated, over-pressured, S-rich metal and host mantle material. Assuming that a ferrovolcanic process requires high-S melt pools to generate the overpressure, it cannot have been the process forming PMGs unless the S-rich pallasites are vastly underrepresented (Johnson et al., 2019). Such a process could, however, provide a mechanism for evolving S-rich liquid metal near the centre of an inwardly crystallising core to be extruded into the overlying mantle. If this mechanism is applied to the IIIAB core, it provides a process by which evolved metal near the centre of an inwardly crystallising core could be extruded into and mixed with silicates at the core-mantle boundary.

The suggestion that pallasites may be formed as a result of impacts has been the focus of several studies in the last few decades (e.g. Scott, 2007; Yang et al., 2010; Tarduno et al., 2012). This idea has gained traction on the basis that observed variation in PMG cooling rates are not consistent with formation in the core-mantle boundary layer of an asteroid and seem to require formation at varying depths (e.g. Yang et al., 2010). In order to explain the cooling rates observed in PMGs, Yang et al. (2010) propose a model in which a differentiated protoplanet is involved in a hit-and-run style collision (e.g. Asphaug et al., 2006). The model requires the separation of the solid core from both the liquid outer core and the mantle during the collision (see Figure 1.11). The initial differentiated planetesimal is interpreted to have crystallised outward; this is required in order for the Ir-depleted fractionated metal observed in PMGs to be free to re-accrete with the silicate mantle. Yang et al. (2010) suggest the cooling rate variations in PMGs result from differing sample depths within the re-accreted pallasite body (see Figure 1.11). Thermal calculations based on this model give an estimate of 400 km for the radius of the newly formed pallasite body assuming no insulation from regolith. The presence of regolith would reduce the radius required to get the lowest observed cooling rates (Yang et al., 2010).
Figure 1.11 – Grazing impact model for PMG formation. This figure illustrates the model used to explain the observed variation in cooling rates in PMGs. This model requires the re-accretion of olivine mantle and the fractionated molten FeNi of the outer core into a “pallasite body”. From Yang et al. (2010).

Figure 1.12 – Impact injection model for PMG formation. This figure illustrates how PMGs may have formed in relatively shallow mantle where mixing of mantle olivine and metal from an impacting body could occur. The discovery that the PMG body had a strong magnetic field is represented on this diagram. B on this figure is a close-up of the metal-silicate mixing zone. From Tarduno et al. (2012).
More recently, it has been proposed that the metal component of PMGs is actually the result of dyke-like intrusions of molten metal into a silicate mantle that is impacted by another body (Tarduno et al., 2012), see Figure 1.12. This scenario is consistent with the fact that some PMGs have very high metal/silicate ratios and exhibit metal veins 10s of cm across (van Niekerk et al., 2007). Analyses of magnetic inclusions identified within pallasite olivine have led to the discovery that the PMG parent body had a strong magnetic field and hence likely had a core dynamo (Tarduno et al., 2012; Nichols et al., 2016). An investigation of magnetic remanence in cloudy zones of two PMGs, Brenham and Marjalahti, combined with cooling rate vs. depth calculations, have shown that their depths of formation would be 24 ± 1.5 km and 22 ± 1.5 km, respectively assuming a 200 km diameter parent body (Nichols et al., 2016). This requires the extent of the intrusion of impactor metal in the Tarduno et al. (2012) model to be at least this deep and probably considerably deeper. Fragmental olivine in PMGs appears to be more prevalent in those meteorites with more primitive metal compositions (Boesenberg et al., 2012). This could be interpreted as evidence supporting the Tarduno et al. (2012) impact model. If the metal of the initial impactor core composition at impact cooled relatively high up in the planetary mantle, together with entrained fragmental olivine from the impact then this relationship could be explained. If the remaining metal fractionated as it sank through the mantle, perhaps in a similar manner to the “iron rain” proposed for 4 Vesta core formation by Kiefer & Mittlefehldt (2017), then it is conceivable that more evolved metal compositions might be associated with a higher proportion of rounded olivine – the increase in depth and slower cooling rates perhaps making rounding more efficient.

The presence of a dynamo requires at least a partially liquid core, which in turn requires temperatures exceeding 1200 K (Ghosh & McSween, 1998). For the magnetism to be recorded in PMGs, there must have been dynamo action present until PMGs cooled to around 630 K (Tarduno et al., 2012) which is difficult to reconcile with PMG formation taking place too close to the core of the parent body. Recent work (Scheinberg et al., 2016) has shown, however, that if the PMG parent body core crystallised inwards, it is possible that that there could have been a temperature gradient sufficient to allow for ongoing dynamo action in the core whilst the core-mantle boundary was cooling past the Curie point (Johnson et al., 2019). Given that many iron meteorite groups show evidence for inward crystallisation (e.g. Yang & Goldstein, 2006), the same process may have been active in the core of
the PMG parent body. Based on pallasite formation depths and the observed cooling rates, the radius of the pallasite parent body has been estimated at around 200 km (Tarduno et al., 2012), half that of Yang et al. (2010) when they assume no regolith. Cooling rate variations in this model can still be attributed to varying depths. Calculated average field values for the Esquel meteorite show a magnetism weaker than is thought to be present at Earth’s core-mantle boundary but stronger than observed on its surface, again consistent with its formation in the middle-upper part of the mantle in a differentiated body (Tarduno et al., 2012).

In contrast to models requiring impact mixing of metal and silicate, Boesenberg et al. (2012) suggest that olivine-metal residue is a natural stage reached after extensive fractional melting with minor phases produced by fractional crystallisation. This formation model suggests that a chondritic precursor asteroid began fractional melting, fuelled by the decay of $^{26}$Al and $^{60}$Fe. During differentiation the sulphide ponds in the core and, due to basaltic and pyroxenitic melts buoyantly migrating, there is a zone where olivine and metal are mixed (Boesenberg et al., 2012). In this model, olivine ripening then occurs as a result of the high olivine content, giving rise to the large clusters of olivine seen in some pallasites (Boesenberg et al., 2012). This occurs over a timescale of around $10^5$ years (Cabane et al., 2005; Boesenberg et al., 2012). Following the formation of olivine clusters that are perhaps up-to kilometers in diameter, Boesenberg et al. (2012) suggest that these masses buoyantly rise, forming a dunitic layer above the pallasite layer. Figure 1.13 shows the interaction posited between metal and smaller olivine clusters where the buoyancy is less than the convection dragging them down (Boesenberg et al., 2012). Figure 1.14 shows a diagrammatic overview of the Boesenberg et al. (2012) model. Fragmental olivines in pallasites are interpreted to be the result of impact shockwaves after crystallisation (Boesenberg et al., 2012).

The Boesenberg et al. (2012) model (see Figure 1.14) suggests that pallasites formed as a layer of gradational olivine and metal above an S-rich core and below a dunite layer. The size of the pallasite layer in this model, with a thickness equal to 34% of the radius, could perhaps explain the variations in cooling rates of pallasite metal highlighted by Yang et al. (2010). This model does not, however, address the fact that magnetic data from some pallasites require their formation in the upper 60% of the mantle (Tarduno et al., 2012). The observed palaeomagnetic evidence (e.g. Tarduno et al., 2012)
could perhaps be explained in a core-mantle boundary context if some PMGs formed in closer proximity to dendrites that enhanced a weak magnetic field (McKibbin et al., 2019). Other factors not considered by models requiring pallasite formation at great depth include that phosphate crystallisation systematics (Davis & Olsen, 1991) as well as cooling rate calculations (e.g. Nichols et al., 2016) indicate their formation at relatively shallow depths.

Figure 1.13 – Olivine – metal mixing zone. This diagram displays the hypothesised interaction between metal and olivine at the base of the dunite layer, where downward metal crystallisation, combined with convection and buoyancy driven olivine clusters, creates a pallasite layer between the dunite and molten metal. From Boesenberg et al. (2012).

Figure 1.14 – Partial melting model for PMG formation. A diagram showing the various stages of evolution of the pallasite parent body according to a partial melting model for pallasite formation (Boesenberg et al., 2012). Time slice I shows the initial chondritic precursor through to time slice V which shows the final differentiation of the pallasite body. From Boesenberg et al. (2012).
1.3.2 The relationship between IIIAB irons and PMGs – linking two differentiated groups

1.3.2.1 Metal chemistry – evidence for a relationship

The trace element composition of PMG metal is broadly consistent with a IIIAB-like parent melt (Buseck, 1977), as is bulk composition, if the PMG metal is ~80% fractionally crystallised (Scott, 1977b; 2007; Wasson & Choi, 2003). On diagrams of incompatible elements vs. Au, PMGs follow the IIIAB trend but at higher Au contents and hence melt evolution (Wasson & Choi, 2003) (see Figure 1.15).

In the case of compatible elements such as Ir, the PMGs are consistent with a continuation of the IIIAB trend to higher Au contents, although the relationship is less well defined (Wasson & Choi, 2003). The deviations from the expected compositions for compatible elements in PMGs are interpreted as due to mixing with early-crystallising metal and/or residual mantle material (Scott, 1977; Wasson & Choi, 2003). This interpretation has been contested. Boesenberg et al. (2012) argue that many siderophile trace elements such as W, Ga, and Ge (Goldstein et al., 2009; Boesenberg et
al., 2012), do not show the same tight linear trends in PMGs as in IIIAB irons; they are too high in the pallasite metal (Goldstein et al., 2009). The existence of some high-Ir pallasites, representing much less fractionated metal, adds difficulty to the interpretation of PMG metal as the product of IIIAB-melt fractionation (Goldstein et al., 2009), as does the difference in Ga and Ge concentrations between the two groups (Wasson & Choi, 2003) Whilst there is an argument for the derivation of PMG metal from IIIAB metal, despite the need to invoke mixing with an early crystallised component, it is also possible that there is no genetic relationship between the two groups, especially in light of, for example, cooling rate evidence (e.g. Yang & Goldstein, 2006; Yang et al., 2010).

1.3.2.2 Inward crystallising IIIAB core and dynamo activity

The discovery of evidence for strong magnetic fields from magnetic inclusions in some PMG olivines (Tarduno et al., 2012; Bryson et al., 2015) means that if IIIAB irons formed the core of the same planetesimal, the magnetic field would be generated there. The core dynamo evidenced in PMGs is thought to have occurred in two stages, separated by a period of no dynamo (Nichols et al., 2016). The first stage of dynamo action was thermally driven, the later stage driven by compositional convection in a crystallising core (Nichols et al., 2016) with incompatible elements (e.g. S – see section 1.2.1.1) moving to create an outer core (Chabot, 2004). This movement of incompatible elements into an outer core would be difficult in a shared PMG-IIIAB parent body if the IIIAB core crystallised inwardly (Yang & Goldstein, 2006; Yang et al., 2008) as the incompatible elements would increase in concentration toward the centre or pool locally where the liquidus temperature is depressed by their presence (e.g. Haack & Scott, 1993). Any such localised pooling of S might serve to aid ferrovolcanism (e.g. Johnson et al., 2019).

1.3.2.3 Non-metals and the behaviour of Cr

For an 80% fractionally crystallised IIIAB iron melt the expected S-contents would be 120 mg g\(^{-1}\) (Wasson & Choi, 2003) based on initial IIIAB S-contents of 24 mg g\(^{-1}\) (Wasson & Richardson, 2001). This value is much larger than the highest S-contents calculated in studies of PMG metal composition, 41 mg g\(^{-1}\) (Wasson & Choi, 2003). If PMG metal did represent a more evolved melt of IIIAB composition, the S content should be higher. The initial IIIAB S-content of 24 mg g\(^{-1}\) (Wasson & Richardson, 2001) is much lower than suggested by other authors (Wasson & Choi,
meaning that, if other estimates of initial IIIAB S-contents were used, the results would be even less in line with those observed in PMGs.

Figure 1.4 shows a change in Cr partitioning behaviour between IIIAB irons and PMGs. In IIIAB irons, Cr appears to be compatible and partitions out of the liquid phase with melt evolution. This is contrary to the expected trend (Wasson et al., 1999). In PMGs, the opposite is true. Chromium acts as an incompatible element and remains in the melt – see Figure 1.4. Given that experimentally derived partition coefficients for Cr show it should be incompatible in crystallising metal (Jones & Drake, 1983), the behaviour of Cr in IIIABs is enigmatic.

1.3.2.4 Cosmic ray exposure ages

The cosmic ray exposure (CRE) ages of IIIAB irons and PMGs are known to be considerably different, with only a slight overlap (Herzog et al., 2015). Main-Group pallasite CRE ages are < 200 Myr. Conversely IIIAB CRE ages, whilst spread out, cluster around 650 – 700 Myr (see Figure 1.16).

Figure 1.16 – CRE ages for IIIABs and PMGs. Measured cosmic ray exposure ages for selected PMGs and IIIAB irons. From Herzog et al. (2015).
Just six of 33 measured IIIAB irons fall in the range of PMGs (Herzog et al., 2015). The overall difference suggests that the two groups did not have the same break-up history, although it does not mean that a genetic relationship for their formation is impossible. A scenario where a IIIAB – PMG parent body was disrupted, creating a smaller core-derived body and a mantle-derived body is conceivable. Were these subsequent bodies then disrupted at different times, the differences in cosmic ray exposure ages between the two groups could plausibly be explained. Additionally, the difference could be accounted for by differing depths of the groups within their respective pre-atmospheric meteoroids.

1.3.2.5 Oxygen isotope evidence

Crucially, PMGs and IIIAB iron meteorites have $\Delta^{17}O$ signatures that have so far been indistinguishable and this is consistent with formation in a common parent body (Clayton & Mayeda, 1996). Average $\Delta^{17}O$ values for IIIAB iron chromite, phosphate, and silicates have been reported as $-0.20 \pm 0.04\%$ (2σ) (Clayton & Mayeda, 1996) and more recently $-0.176 \pm 0.022\%$ (2σ) for chromites (Franchi et al., 2013). These are within error of the most recent average $\Delta^{17}O$ values for PMG olivines obtained by Greenwood et al. (2015). In order to better determine whether IIIABs and PMGs are linked, new analyses of IIIAB irons have been conducted as part of this study (see Chapter 2, Chapter 5). This is particularly important considering that only 3 IIIAB irons have been analysed for O-isotopes at high precision and at optimised analytical conditions (Franchi et al., 2013). Resultantly, it is crucial to understand the O-isotope systematics in more detail, especially considering the possibility of complex formation models involving multiple bodies and the reported existence of isotope heterogeneity in PMG silicates (e.g. Ziegler & Young, 2007; Ali et al., 2013; 2014; 2018).

1.4 Aims of the thesis and research questions

The nature of planetary embryo growth, as well as the relative timing of differentiation and the processes involved in core-mantle separation are still relatively poorly understood. The PMGs and IIIAB irons have the potential to provide a window into these early planetary processes and aid our understanding of the details of planetary differentiation and perhaps planetesimal-scale impacts. Despite the extensive study of PMG meteorites to date, no consensus on formation environments or
processes exists. Similarly, the nature of their relationship to the IIIAB iron meteorite group, if any, is still hotly debated. The following research questions were identified to be addressed through this work:

1) **What is the role of impacts in pallasite formation?**

Recent models (e.g. Yang *et al*., 2010; Tarduno *et al*., 2012) suggest that PMGs may be impact-formed with the metal and silicate portions of PMGs originating from different parent bodies. These hypotheses are testable through the analysis of different PMG components using high-precision oxygen isotopes, Cr isotopes, and W isotopes. These were conducted on PMG olivine, representative of the mantle, and PMG chromite, representative of the metal fraction. Answering this research question would have implications for the understanding of differentiated planetesimals in the early Solar System. If there is no resolvable difference, PMG samples provide information on the processes active at a core-mantle mixing zone (e.g. Boesenberg *et al*., 2012) and isotope fractionation will provide key information into formation temperatures. If a difference is found, it suggests that PMG are perhaps recording the growth of planets by planetesimal impact and mixing. Given that pallasite groups are found in both the non-carbonaceous and carbonaceous Solar System reservoirs (e.g. Warren, 2011), likely representing inner and outer Solar System reservoirs respectively, the process forming these meteorites was spatially widespread and therefore has implications for planetary formation models. Assuming that the metal in PMGs has come from an impacting body (Tarduno *et al*., 2012), its isotopic composition should be distinct from the silicates in the impacted body. Chromite oxygen isotopic variations may reflect this. Chromite crystallising from or as a buoyant phase in the metal would inherit its isotopic signature from dissolved oxygen in the metal that subsequently (or coevally) partitioned into the crystallising chromite. This means that if the metal is not from the same isotopic reservoir as the olivine, oxygen isotope results for the olivine and chromite should be distinct, a prediction that is testable and addressed in this thesis (see Chapters 2 and 3). Verification of such a difference would have significant implications for the current understanding of PMG formation. Another important observation was made by Wasson *et al*. (1999) and concerns a compositional heterogeneity in pallasite chromites based on their Al-content. It has been suggested that an order of magnitude difference in Al-content between chromite in Brenham
and Albin is the result of their formation in the Al-low core and the Al-high mantle cumulate respectively (Wasson et al., 1999). The fact that the Al component in PMG chromite seems related to the olivine composition and texture (McKibbin et al., 2019) suggests that PMG may have formed over a range of environments. The core and rim compositions of chromite analysed in this study were obtained using electron microprobe (EPMA) analyses and scanning electron microscopy (SEM) and have been combined with O-isotope data where possible in order to better understand their origin (see Chapter 3). Should the low-Al, core-derived chromite be in isotopic disequilibrium with coexisting silicates and the high-Al, cumulate-derived chromite not, then the data would also support an impact model for pallasite formation.

2) Are PMG and IIIAB irons from a common parent planetesimal?

The PMG and IIIAB meteorite groups are the largest groups of their respective meteorite types (stony-iron and iron). The evaluation of a potential link between these groups is of critical importance because confirmation would mean that a vast array of samples from different deep geological environments are available for a single disrupted planetesimal. If there is no such link, the compositional similarities between IIIAB and PMG metal must be due to initial similarities in the composition of precursor material. This may have implications for understanding the distribution of oxygen isotopes in the protoplanetary disk and also the use of oxygen isotopes as an indicator of planetary provenance.

3) What can PMG and IIIABs tell us about parent body conditions?

These two groups, whether related or not, sample the deep interiors of their parent body(ies). Such samples are crucial in gaining insight into the formation and evolution of rocky Earth-like planets. As such, isotopic information from these meteorites relating to factors such as temperatures and timescales is important in developing our understanding of the evolution of all rocky planets, including our own.

This study will conduct high-precision oxygen isotope analyses on PMG and IIIAB metal-hosted minerals as well as PMG olivine in order to establish fractionation relationships and planetary provenance. The isotope measurements will be used in conjunction with EPMA and SEM analyses in order to better constrain the formation environments of both PMG and IIIAB, as well as evaluate
the possibility of a common parent planetesimal. Samples of olivine and chromite from PMGs will be analysed using Cr isotopes in order to establish whether any provenance-derived difference is present. Hf-W analyses on PMG metal will provide differentiation timescales and temporal context for the O, Cr, and petrographic analyses. In performing the above, this thesis seeks to advance the current understanding of processes active in early-formed differentiated planets.

1.5 Thesis structure

This thesis is structured in the following way:

Chapter 1 – Introduction and background

A comprehensive overview of the literature concerning IIIAB irons, PMGs, their formation processes and possible links.

Chapter 2 – Samples and analytical method

An introduction to the isotope systems employed in this study is provided, followed by detailed descriptions of the methods used in this study including: sample selection, analytical techniques, data reproducibility over study duration, and development of optimized techniques for laser-assisted fluorination.

Chapter 3 – Main Group pallasite results

Results of petrographic investigations into the texture and composition of minerals in available PMG samples and reporting of the O, Cr, and W results for samples analysed in this study. Also presented are results from Eagle Station and terrestrial Bushveld material for comparison.

Chapter 4 – Main Group pallasite interpretation

This chapter evaluates the results presented in Chapter 3 and compares them with published literature data. The discussion covers formation mechanisms, body sizes, temperatures, and heliocentric distance of formation, amongst other things.

Chapter 5 – IIIAB iron results

Oxygen isotope results of the IIIAB iron chromite samples analysed in this study.
Chapter 6 – IIIAB iron interpretation

A detailed discussion of implications of the results for IIIABs, including the likelihood of a common parent body for the two meteorite groups.

Chapter 7 – Revisiting research questions and implications of this work

A chapter directly answering the key research questions identified in Chapter 1 and discussing the wider implications of the findings of this study.

Chapter 8 – Conclusions and future work

A summary of the key findings of this PhD thesis in the context of wider understanding for cosmochemistry and planetary science as well as a discussion of the identified avenues for continuation of this research and suggestions for future work.
2 SAMPLES AND ANALYTICAL METHOD

The main focus of this study is the oxygen isotope analysis of PMG and IIIAB iron samples by laser-assisted fluorination, however other techniques and isotope systems have been employed for characterisation, further investigation, and consistency of analyses. This chapter introduces these isotopic systems, details the sample selection procedure, analytical techniques used, and the reproducibility of analyses.

2.1 Isotope systems useful in the study of metal-rich meteorites

Prior isotope studies on metal-rich meteorites have included W, Cr, and Mo to investigate differentiation timing and nucleosynthetic parent reservoirs (e.g. Kruijer et al., 2017; Murthy & Sandoval, 1965; McKibbin et al., 2016), Cu to investigate parent body links (e.g. Bishop et al., 2012), and Fe to investigate fractionation during planetary differentiation (e.g. Weyer et al., 2005). Oxygen isotope studies have also been conducted on IIIAB irons and PMGs, albeit at a precision significantly lower than is now achievable (e.g. Clayton & Mayeda, 1996). The present study utilises O, Cr, and W isotope analyses to investigate the petrogenesis and timescales involved in PMG and IIIAB iron formation.

2.1.1 Oxygen

The use of oxygen isotope analysis to understand meteorite relationships and processes on meteorite parent bodies is well established and has become an important tool in planetary science (Clayton et al., 1973; Clayton, 2003; Franchi, 2008). The fact that the protoplanetary disk was isotopically heterogeneous with respect to oxygen means that accreting parent bodies record the isotopic signature of the region in which they formed. This, coupled with the plenitude of oxygen in the Solar System, means that it has been used extensively in studies seeking to understand links between different meteorite groups as well as water-rock interactions and mixing processes (e.g. Clayton et al., 1973; Greenwood et al., 2006; 2012; 2014; 2015 Ziegler & Young., 2007; Franchi, 2008; Lee et al., 2013; McDermott et al., 2016; Krot et al., 2019).

Oxygen has three naturally occurring stable isotopes: $^{16}$O, $^{17}$O, and $^{18}$O. The lightest of these isotopes, $^{16}$O, is also by far the most common (99.762% of Solar System oxygen) and after $^1$H and
$^4$He, is the most abundant nuclide in the universe (Bao et al., 2016). It forms from nuclear fusion processes in stars, specifically helium burning (Bao et al., 2016). The rarest of these isotopes (0.038% of Solar System oxygen) is $^{17}$O. A secondary nuclide, it probably forms by $^{16}$O + $^1$H → $^{17}$F → $^{17}$O, and requires $^{16}$O to be present from earlier stellar bodies (Bao et al., 2016). Recently, planetary nebulae containing extreme enrichments of $^{17}$O have been identified (e.g. planetary nebula K4-47) and are probably the remnants of J-type stars that were likely carbon-rich (Schmidt et al., 2018). Given the scarcity of $^{17}$O in our own Solar System, it is unlikely that the precursor to the Sun was such a star. The heaviest stable oxygen isotope is $^{18}$O. Also a secondary nuclide, it is formed by $^{14}$N + $^4$He → $^{18}$F → $^{18}$O (Bao et al., 2016) and is dependent on pre-existing $^{12}$C or $^{14}$N to facilitate its formation (Bao et al., 2016), $^{18}$O accounts for the remaining 0.200% of Solar System oxygen (Bao et al., 2016). The $^{14}$N required to initiate this reaction is produced from the reactions $^{12}$C + $^1$H → $^{13}$N → $^{13}$C and subsequently $^{13}$C + $^1$H → $^{14}$N (Meyer et al., 2008), in previous generation stars.

The fact that oxygen has three stable isotopes whereas other light elements (e.g. carbon) have only two, means that two distinct isotope ratios can be evaluated for oxygen content in samples. This allows the creation of 3-isotope diagrams (Clayton et al., 1973) which provide an excellent means to evaluate mass-dependent and mass-independent fractionation as well as mixing processes in various environments. Oxygen is very abundant in minerals and ices – it is the most common element in the Earth (Yurimoto et al., 2007) – meaning that an understanding of the behaviour of oxygen isotopes in different environments is an important tool in a wide array of fields including planetary science, cosmochemistry, environmental science, climatology, archaeology, and geology.

Oxygen isotopes are typically reported using δ notation – the per mil (‰) deviation of a sample from a standard, typically standard mean ocean water (VSMOW) in the case of oxygen.

Equation 2.1

$$\delta^x O = 10^3 \left( \frac{R_x^{\text{sample}}}{R_x^{\text{standard}}} - 1 \right)$$

In this equation, $x$ is the isotope of interest and $R_x$ is the ratio of that isotope over $^{16}$O.

The importance of the oxygen 3-isotope system in planetary science was first highlighted with the discovery of a mass-independent relationship between oxygen isotopes in CAIs where it was
expected that a mass-dependent relationship, *i.e.* one where the proportion of the isotopes in a material is related to their mass differences, would exist (Clayton *et al.*, 1973). This mass-independent relationship manifested as a slope ~1 line on a 3-isotope diagram (Figure 2.1). The origin of this slope 1 line remains contentious nearly 50 years after its initial discovery and numerous models have been proposed explaining its existence (*e.g.* Jacobsen *et al.*, 2007; Thiemens & Heidenreich III, 1983; Thiemens 1992; 1996; Young *et al.*, 2008; Clayton, 2002; Yurimoto *et al.*, 2007).

The largest scale model for this mass-independent fractionation (MIF) is the galactic evolution model (*e.g.* Jacobsen *et al.*, 2007). This model suggests that the origin of the MIF line observed in primitive
Solar System materials is tied to the natural evolution of isotope abundances in an evolving galaxy. In this model, the abundance of $^{16}$O is posited to increase linearly over time whilst the abundance of the secondary nuclides $^{17}$O and $^{18}$O increases with the square of time (Young et al., 2008). The result is that $\delta^{17}$O and $\delta^{18}$O vs time are the same in this model and therefore plot as a slope 1 line in 3-isotope space (Young et al., 2008). The “box model” (Jacobsen et al., 2007) for galactic evolution has a key prediction and so can be tested. Assuming that the rate of dust destruction and dust production in the proto-solar nebula are equal, subsequent injections of supernova-derived oxygen would change the absolute isotopic composition of the gas phase over time. In contrast, a dust portion – formed from condensation of the coexisting gas – would preserve a prior oxygen isotope composition. The difference between the isotope compositions of the dust and gas would be dependent on the residence time of the dust prior to destruction and presumably, re-equilibration (see Young et al., 2008). Given that the $\delta^{17}$O and $\delta^{18}$O values increase over time in this model, the gas phase should be enriched in heavier isotopes relative to the dust phase. Assuming that the gas phase is represented by the Sun, and the dust phase by the rocky planets, the Sun should be heavier in $\delta$ ratios relative to inner Solar System bodies (Young et al., 2008). Ireland et al. (2006) estimated the degree of this enrichment in the present-day Sun and concluded that it should be around 50 ‰ heavier than the Earth-derived standards (Young et al., 2008). NASA’s Genesis mission returned samples of solar wind from the L1 Earth-Sun Lagrange point. Subsequent analyses of the samples returned showed a marked enrichment in $^{16}$O relative to inner Solar System rocky bodies (McKeegan et al., 2011) suggesting that the Sun, and therefore also the nebular gas was likely $^{16}$O enriched relative to the dust (Krot et al., 2010; McKeegan et al., 2011). This is not in agreement with the predictions of the galactic evolution model.

Another possible mechanism for producing the MIF slope seen in primitive Solar System materials are symmetry-based MIF effects (Thiemens, 1992; 1996; Thiemens & Heidenreich III, 1983; Young et al., 2008). Any molecule that is triatomic or larger and also capable of forming symmetrical isotopomers could be subject to dust surface reactions that give rise to MIF effects (Young et al., 2008). Consider the following two scenarios adapted from Young et al. (2008).
Scenario 1 (Figure 2.2) shows the adsorption of SiO and O onto the surface of a forming CAI. Both oxygen atoms in this reaction are $^{16}\text{O}$. The dissociated oxygen combines with SiO to form a vibrationally excited SiO$_2$ molecule, as denoted by the * (Young et al., 2008). This molecule is symmetrical and therefore the redistribution of vibrational energy from the initial bonding is efficient throughout the molecule (Young et al., 2008). This redistribution of energy occurs because symmetrical isotopomers have fewer intramolecular dynamical couplings for energy redistribution than is the case in non-symmetrical molecules (Young et al., 2008). The consequences of this include the occupation of less “phase space” and resultantly these excited molecules typically have shorter lifespans before re-dissociation than their asymmetric counterparts (Young et al., 2008). As a result of this shorter lifespan, there is a lower chance for these molecules to be involved in a collision which could reduce their vibrational energy and thus stabilize them by the reaction SiO$_2^* + M \rightarrow \text{SiO}_2$ (Young et al., 2008), where M is any molecule. Consequently, symmetric isotopomers are more likely to re-dissociate and subsequently be incorporated into the forming CAIs by reaction x (shown in scenarios 1 and 2). Scenario 2, by contrast, shows the creation of an asymmetrical isotopomer on the surface of a CAI grain. In this example, the Si$^{16}\text{O}$ and $^{18}\text{O}$ bond to form a vibrationally excited but isotopically asymmetric SiO$_2$ molecule. This molecule lasts longer than its symmetrical
counterpart, increasing the likelihood that it will be involved in a collision ($\text{SiO}_2^* + \text{M} \rightarrow \text{SiO}_2$) to stabilize it by reducing its vibrational energy. If it is stabilized and re-dissociation does not occur, it may evaporate into the gas phase by reaction $y$. The result of this process is that the gas phase becomes enriched in $^{17}\text{O}$ and $^{18}\text{O}$ over time relative to the forming CAI which preferentially incorporates lighter isotopes as symmetrical molecules are more readily dissociated. Given that the $\text{SiO}_2$ in scenario 2 would be asymmetrical regardless of whether the dissociated O molecule is $^{17}\text{O}$ or $^{18}\text{O}$, the result will be the same for both of the heavy isotopes, leading to a mass-independent enrichment of these nuclides in the gas phase. There is no time constraint on either of these processes and they have yet to be fully examined empirically (Young et al., 2008).

Currently, perhaps the most popular explanation for the presence of the primordial mass-independent distribution of oxygen isotopes in Solar System materials is a process called photochemical self-shielding of CO. This idea is not new (e.g. Thiemens & Heidenreich III, 1983; Kitamura & Shimizu, 1983 – as cited by Young et al., 2008) but has seen a revival in popularity after it was suggested that this process could be active at the inner margin of the circumstellar disk, giving rise to the slope 1 line in CAI data (Clayton, 2002). The process has been observed in the interstellar medium and in extra-solar circumstellar disks; the key marker being an overabundance of $^{16}\text{C}^{16}\text{O}$ relative to heavier oxygen isotopologues of that molecule (Young et al., 2008). There are a range of candidate environments where this self-shielding may occur and give rise to slope 1 variation: the inner circumstellar disk (Clayton, 2002), the outer circumstellar disk (Lyons & Young, 2005), and the protosolar molecular cloud (Yurimoto & Kuramoto, 2004; Yurimoto et al., 2007). Critical to the photochemical self-shielding model is the destruction of carbon monoxide by photodissociation as a result of interaction with far-ultraviolet stellar radiation (Yurimoto et al., 2007; Young et al., 2008). The wavelengths that induce this behaviour range from 91.3 nm to 107.6 nm (Yurimoto et al., 2007). Photodissociation occurs predominantly as a result of predissociation, which is isotope-specific and results in destruction of excited molecules (Young et al., 2008). The UV absorption bands of the heavier isotopes in molecules that have been excited are red-shifted by approximately 25 cm$^{-1}$ per amu compared to the light oxygen isotopologue (Young et al., 2008) due to rotational-vibrational energy level differences (Yurimoto et al., 2007). The abundance of CO gas in the nebula means that there is a much greater attenuation of UV radiation at wavelengths absorbed by $^{16}\text{C}^{16}\text{O}$ than is the case
for C\textsuperscript{17}O or C\textsuperscript{18}O which means that CO containing the heavier isotopes can be dissociated even when deep inside a molecular cloud or circumstellar disk (Yurimoto et al., 2007). This process resulted in the enrichment of the environment in dissociated \textsuperscript{17}O and \textsuperscript{18}O relative to \textsuperscript{16}O in a non-mass-dependent manner as the evolution of the protoplanetary disk progressed. The mass-independent signature of this process was recorded in the condensation of e.g. CAIs from this disk.

Whichever (if any) of the current models is responsible for mixing or mass-independent fractionation in the early Solar System, the result is that mass-dependent fractionation lines are offset by a non-mass-dependent component due to the initial heterogeneity in the disk. This mass-independent component is visible in the oxygen isotope compositions of the most primitive Solar System materials (Young & Russell, 1998; Ushikubo et al., 2012). Following accretion and melting, the precursor isotopic signatures are homogenised to a single composition. This is subsequently affected by mass-dependent planetary processes that give rise to small offsets along a single mass-fractionation line in homogenised parent bodies (e.g. Figure 2.3).

Figure 2.3 – A three isotope diagram showing the relationship between different meteorite groups. Note the highly populated area just below the TFL in which angrites, PMGs (MGP), HEDs, brachinites, and winonaites are situated. Mass-dependent fractionation lines for individual meteorite groups are horizontal on this diagram and differences in y-axis between groups indicate differing planetary provenance. Figure from Greenwood et al. (2017b).
Mass-dependent fractionation lines have slopes of approximately 0.5 due to the differences in isotopic mass between $^{18}\text{O}$ and $^{17}\text{O}$ relative to $^{16}\text{O}$, mass-dependent effects have twice the impact on $\delta^{18}\text{O}$ as $\delta^{17}\text{O}$. These signatures enable planetary provenance to be evaluated using oxygen isotope ratios (see Figure 2.3).

In recent years, advances in oxygen isotope analysis have led to the discovery of multiple such fractionation lines (e.g. PMGs, HED/mesosiderites) where initially only one was resolvable (e.g. Clayton & Mayeda, 1996; Greenwood et al., 2006). This crowded area of isotope space is evident on Figure 2.3 and necessitates the use of high-precision techniques in order to resolve small $^{17}\text{O}$ excesses between different differentiated meteorite groups.

2.1.1.1 Mass-dependent fractionation of oxygen isotopes

Whilst the effects of planetary melting result in homogenisation of primordial isotopic variations towards a single value, the mass difference of the isotopes mean that subsequent processes such as crystallisation and diffusion result in the manifestation of small mass-dependent offsets. Mass-dependent fractionation can be broken down into two categories: equilibrium mass-dependent fractionation, and kinetic mass-dependent fractionation (e.g. Criss, 1999; Young et al., 2002; Dauphas & Schauble, 2016). In the high-T magmatic environments relevant to this study, equilibrium mass-dependent fractionation is most important.

2.1.1.2 Equilibrium mass-dependent fractionation

Equilibrium mass-dependent fractionation (EMDF) effects are an important component of isotope fractionation, and occur in systems that are in thermodynamic equilibrium. Given that the electronic structure of all isotopes of an element are identical, the chemical properties of different isotopes of the same element are also nearly identical (White, 2015). However, small differences do arise as a result of translational, rotational, and vibrational energies within a given molecule (White, 2015). Of the energies that affect isotope fractionation, vibrational energy differences are the most substantial and have the largest effect on isotope fractionations. The temperature-dependence of equilibrium fractionations relevant for this thesis is dictated by quantum mechanical effects on vibrational motions in phases between which equilibrium fractionation is taking place (White, 2015). In fact, the application of quantum mechanical theory to these fractionations enabled the calculation of the
equilibrium constant for simplified diatomic systems from the partition function of statistical mechanics (Urey, 1947; Bigeleisen & Mayer, 1947; Young et al., 2002; White, 2015). This method assumes that inter-atomic vibrations are harmonic oscillations. This is a simplification but a reasonable approximation (Urey, 1947). The application of this technique to oxygen isotope fractionation between minerals is considerably more complicated than in the case of diatomic molecules. High-temperature equilibrium mass-fractionation lines are characterised by $\lambda$ values from $\sim$0.525 – 0.529 (Young et al., 2016). The $\lambda$ value is the slope of isotope fractionation on a three-isotope diagram (see section 2.1.1.4).

2.1.1.3 Kinetic mass-dependent fractionation

Kinetic mass-dependent fractionation processes are often unidirectional or fast processes such as diffusion, evaporation or processes involving biological systems (White, 2015). As such, they are expected to have little influence on isotope fractionation in high-T geological environments. Kinetic mass-fractionation lines are typically shallower than equilibrium mass-fractionation lines and $\lambda$ range from $\sim$0.514 – 0.525 (Dauphas & Schauble, 2016; Young et al., 2016).

2.1.1.4 Measurement of oxygen isotopes and the use of fractionation exponents

An important quantity when investigating the differences between distinct planetary bodies is the $\Delta$ value or “capital delta”. This quantity is a measure of the difference in $\delta^{17}$O at constant $\delta^{18}$O between two materials and can be defined as (Clayton & Mayeda, 1988):

Equation 2.2

$$\Delta^{17}O = \delta^{17}O - \lambda \delta^{18}O$$

The term $\lambda$ is the fractionation exponent and the value often used is 0.52, derived from a combination of theoretical work and empirical data from the quartz-water system (Matsuhisa et al., 1978).

Equation 2.2 is sufficient when working with materials that have a large range in $\delta$ values. At the level of precision achievable by laser fluorination and when dealing with the small differences in isotope composition displayed by most differentiated meteorites, a slightly different definition is used after Miller (2002):
Equation 2.3

$$\Delta^{17}O = 10^3 \ln \left(1 + \frac{\delta^{17}O}{10^3}\right) - \lambda 10^3 \ln \left(1 + \frac{\delta^{18}O}{10^3}\right)$$

This linearizes the terms and as such, this fractionation exponent is now equal to the slope between points on a 3-isotope plot where $\delta^{17}O$ is the ordinate and $\delta^{18}O$ the abscissa. Linearizing the terms is important as Equation 2.2 is an approximation of a power law (Miller, 2002; see Equation A 2 in Appendix 1). The $\delta'$ notation refers to the linearized version of $\delta$:

Equation 2.4

$$\delta'\times O = 10^3 \ln \left(1 + \frac{\delta^{X}O}{10^3}\right)$$

Such that:

Equation 2.5

$$\Delta^{17}O = \delta^{17}O - \lambda \delta^{18}O$$

Equation 2.3 and Equation 2.5 are equivalent. In some published literature, the term $\Delta^{17}O$ is used to distinguish the linearized calculation (Equation 2.3) from that shown in Equation 2.2 (e.g. Kohl et al., 2017). Whilst the $\Delta^{17}O$ data presented in this study are calculated using the linearized method shown in Equation 2.3, they are referred to without the prime symbol following the example of Miller (2002). The $\lambda$ values in this study are calculated by taking a regression through oxygen data recalculated to $\delta^{17}O$ and $\delta^{18}O$. Where $\Delta^{18}O$ is referred to in the context of isotope fractionation in this study (e.g. Chapters 4 and 6), it is the difference between $\delta^{18}O$ values for two minerals.

It is critically important when evaluating mass-dependent processes at high precision to use an appropriate value for $\lambda$. Whilst the value 0.52 is a good approximation for the fractionation exponent in systems where precision is less important, when analysing planetary materials, it is imperative to be aware of the behaviour of $\lambda$ in various environments. The $\lambda$ term in Equation 2.3 can affect the $\Delta^{17}O$ by several tenths of per mil, a range greater than the offset between the PMG and HED fractionation lines (e.g. Greenwood et al., 2006). For example, if $\delta^{17}O$ and $\delta^{18}O$ values are assigned to a hypothetical sample the effect of $\lambda$ on $\Delta^{17}O$ is readily observable. In this case, the $\delta^{17}O$ is taken to be 1.4 ‰ and the $\delta^{18}O$ is taken to be 3.1 ‰ – values that are broadly representative of the PMG
olivine population (see Chapter 3). Using the asymptotic lower limit of 0.5000 (Young et al., 2016), the $\Delta^{17}O$ for this hypothetical sample is -0.149‰. In contrast, using the high-T upper limit of 0.5305 (Matsuhisa et al., 1978; Young et al., 2016), the $\Delta^{17}O$ for this sample is -0.243‰. This example is hypothetical but demonstrates how important it is to know and use an appropriate value for the fractionation exponent when evaluating MDF relationships. The use of an inappropriate $\lambda$, especially when comparing the planetary provenance of two samples from different geological environments, can result in the apparent presence of an isotopic disequilibrium where none actually exists (Young et al., 2002; Miller, 2002) or conversely, the interpretation of a common parent body where none exists. The actual value for $\lambda$ can vary between 0.5 and 0.5305 for oxygen, however natural systems typically only have fractionation relationships with exponents between 0.514 and 0.529 (Young et al., 2016). This number is temperature dependent (Cao & Liu, 2011; Pack & Herwartz, 2014), and for equilibrium MDF processes in igneous and high-T systems, mostly varies across a narrower range of values: from ~0.525 to 0.529 (Pack & Herwartz, 2014; Young et al., 2016). Analysis of such a system on Earth has yielded a $\lambda = 0.529 \pm 0.006$ for fractionation between spinel, olivine, orthopyroxene, and clinopyroxene minerals in mantle-derived lherzolite (Pack & Herwartz, 2014).

The $\Delta^{17}O$ results presented in this thesis use a fractionation exponent of 0.5262 in line with published work on high-T igneous lunar material in the same laboratory (Greenwood et al., 2018). This value is within the range of possible values for the type of high-T equilibrium fractionation expected in the samples analysed. Despite this, fractionation “envelopes” as presented by Young et al. (2016) and Kohl et al. (2017) (e.g. Figure 2.4) have been added to figures as required to better display fractionation relationships between phases over a range of values for $\lambda$. A measured $\lambda$ outside of the envelope 0.5 to 0.5305 cannot be a consequence of any known mass-dependent fractionation mechanism in the oxygen isotope system, it must therefore be a) a mass independent process acting on the studied system, b) a mixing line between two reservoirs, or c) in situ effects such as spallation. In practice, the range over which this applies in high-T samples could probably be reduced to 0.525 – 0.529 (Young et al., 2016), however given the relative lack of constraint for PMG formational environment for example, it is prudent to keep a broader range of “reasonable” values for $\lambda$ and therefore the absolute upper limit (0.5305) is presented on diagrams where relevant. A worked example demonstrating the temperature dependence of $\lambda$ is presented in Appendix 1.
2.1.2 Chromium

The oxygen stable isotope system is not the only system that can be applied as evidence for linking meteorites by parent body; $^{54}$Cr anomalies can also be used and are well known to exist amongst planets and differing meteorite types (Qin et al., 2011). Chromium has four naturally occurring isotopes: $^{54}$Cr (2.36%), $^{53}$Cr (9.50%), $^{52}$Cr (83.79%) and $^{50}$Cr (4.35%) (Trinquier et al., 2008; Schiller et al., 2014). The heaviest isotope, $^{54}$Cr, is typically produced by neutron-rich equilibrium processes occurring in type Ia supernovae (Trinquier et al., 2007; Schiller et al., 2014) and/or possibly in type II supernovae (Qin et al., 2011). The other three isotopes are the result of explosive oxygen and silicon burning in supernovae (Schiller et al., 2014). Yamakawa et al. (2010) used $\epsilon^{54}$Cr (see Equation 2.6) to estimate the heliocentric distance for the ureilite parent body; a linear relationship
between $\varepsilon^{54}$Cr and distance from the Sun is evident when data for Earth, Mars and 4 Vesta (HEDs) are plotted (Yamakawa et al., 2010).

Equation 2.6

$$\varepsilon^{54}Cr \ (\text{in parts per } 10^4) = \left( \frac{R_{\text{sample}}^{54}}{R_{\text{standard}}^{54}} - 1 \right) \times 10000$$

From Meier et al. (2014), where $R$ is:

Equation 2.7

$$R^{54} = \frac{^{54}Cr}{^{52}Cr}$$

Qin et al (2011) hypothesised that grains from a type II supernova may be a source of $^{54}$Cr. The heterogeneous distribution of the isotope is interpreted as being due to lack of time for its complete homogenisation in a mature solar nebula. As pointed out by Warren (2011), systematic injection of this extra-solar component may be the reason for the observed relationship between $\varepsilon^{54}$Cr and distance from the Sun. Given this relationship, $\varepsilon^{54}$Cr data for PMGs and IIIABs could be used to estimate their orbital distances at time of formation and evaluate a potential parent body link. Sugiura & Fujiya (2014) correlated $\varepsilon^{54}$Cr with accretion ages of meteorite parent bodies in the early Solar System and concluded that both the relationship between $\varepsilon^{54}$Cr and heliocentric distance, and the relationship between $\varepsilon^{54}$Cr and accretion ages, could be explained by injection of supernova-derived $^{54}$Cr-rich material into the outer Solar System and gradual transportation inward (Sugiura & Fujiya, 2014). Care must be taken with this approach, however. Cosmogenic $^{54}$Cr in galactic cosmic rays would affect the $\varepsilon^{54}$Cr value (Papanastassiou & Chen, 2011; Sugiura & Fujiya, 2014) and if so, meteorites with greater cosmic ray exposure ages would have elevated $\varepsilon^{54}$Cr values.

The relatively recent identification of two Solar System isotopic reservoirs has fuelled investigation into the relationship between isotopic signatures and heliocentric distance (see Figure 2.5). Warren (2011) identified an isotopic dichotomy in Solar System materials that has been interpreted as inner and outer Solar System reservoirs (e.g. Warren, 2011; Kruijer et al., 2017). In the case of metal-rich meteorites, Cr isotope work (e.g. Papanastassiou & Chen, 2011; Warren, 2011; Scott, 2017; Kruijer et al., 2017) has led to the interpretation that Eagle Station pallasites and five magmatic iron meteorite
groups formed in an outer Solar System reservoir and thus record elevated $\varepsilon^{54}\text{Cr}$ values see Figure 2.5; Figure 2 in Warren, 2011) (Scott, 2017; Kruijer et al., 2017).

![Diagram of ε^50Ti vs ε^54Cr](image)

Figure 2.5 – A plot of ε^50Ti vs ε^54Cr for various Solar System materials highlighting the carbonaceous reservoir (outer Solar System) and the non-carbonaceous reservoir (inner Solar System). From Warren (2011).

This reservoir is thought to have been separated from the inner Solar System reservoir by the early formation of Jupiter which blocked mixing between the two populations (Kruijer et al., 2017; Kleine et al., 2020). This suggests that differentiated planetesimals were forming early on in the history of the Solar System and were also forming outside of the orbit of Jupiter.

2.1.3 Hafnium-Tungsten system

The extinct $^{182}\text{Hf} - ^{182}\text{W}$ radiogenic decay system is an important tool when evaluating differentiation timescales. The half-life of this radiogenic decay (8.9 ± 0.1 Myr) is of the same order as the likely timescales of accretion and differentiation processes, and Hf – which is produced by both the rapid neutron capture ($r$) and slow neutron capture ($s$) processes – acts in a strongly lithophile manner (Kleine et al., 2009). By contrast, W behaves in a moderately siderophile manner during differentiation and as such is partitioned preferentially into planetesimal cores (Kleine et al., 2004;
Both Hf and W are highly refractory elements and are therefore thought to have been present in chondritic ratios and abundances in early forming planetesimals (Halliday & Lee, 1999; Kleine et al., 2004). This means that chondritic Hf-W compositions should provide an approximation of those compositions in larger planetary objects (Kleine et al., 2009). During metal-silicate separation and core-formation, Hf is confined to the mantle whereas W is partitioned into the core (Kleine et al., 2009). As $^{182}$Hf behaves in a lithophile manner, its presence in silicate minerals will be considerably higher than in coexisting metals. Consequently, following differentiation and decay, the ratio of the daughter isotope $^{182}$W relative to other W isotopes should be higher in the silicate than the metal due to its higher initial $^{182}$Hf content. The amount by which W migrates to the core is dependent on its metal-silicate partition coefficient which, in turn, is dependent on factors such as P-T conditions, oxygen fugacity, and the composition of the silicate melt (Kleine et al., 2009). As a result of the above-mentioned factors, the W composition of silicate and metal portions of planetary bodies can vary both between different planetesimals, and also within a single body over the duration of core formation (Kleine et al., 2009). This, combined with the observation of some large fractionations resulting from variable Hf compatibility in different rock-forming minerals (e.g. Kleine et al., 2005c as cited in Kleine et al., 2009), means that the Hf-W system has great utility as a chronometer for core formation and mantle differentiation (Kleine et al., 2009). Published W results for the IIAB, IID, IIIAB, and IVB iron meteorite groups all give differentiation ages of $-0.2 \pm 1.2$ Myr ($\Delta T_{CAI}$) (Markowski et al., 2006, 2006b) showing that core separation in metal-rich meteorites occurred very early in the history of the Solar System. Finally, the initial $^{182}$Hf abundance in the early Solar System was high (Halliday & Lee, 1999), meaning that $^{182}$W is often present in measurable quantities in meteorites and planetary materials. The W isotope composition of samples is typically reported in epsilon ($\varepsilon$) notation, or parts per ten thousand relative to a standard (see section 2.1.2).

### 2.2 Sample Selection

Samples selected for analysis in this study were primarily chosen based on the following criteria: 1) they sample either a PMG, a IIIAB iron meteorite, or another group with the potential to aid interpretation, and 2) they contain a sufficient amount of an oxygen-bearing mineral to allow for high precision laser-assisted fluorination (see section 2.5) to be carried out. There were a few exceptions, the most notable being the Bushveld samples that were analysed in order to provide a terrestrial
magnatic comparison to PMGs. The Open University’s meteorite collection contains some pallasite olivine separates that were used for some analyses presented in this thesis (see Appendix 2). Further samples were obtained from the Natural History Museum in London, the Naturhistorisches Museum Wien (Vienna), the Smithsonian Institute, and the Chicago Field Museum. Appendix 2 lists the sources of the samples. Finally, the slices of Sericho, Seymchan, and Fukang were sourced from reputable meteorite dealers including Bob Haag, Bruno Fectay, and Carine Bidaut.

2.2.1 Sample criteria for O analysis

When selecting PMGs for oxygen isotope analysis, samples containing both olivine and chromite were targeted in order to test the impact hypotheses (see Chapter 1) for pallasite formation. The IIIAB iron samples were required to contain chromite, the most abundant oxygen bearing phase. Such samples were found with far less frequency than in PMG samples. The most effective way of finding chromites in IIIABs involved first looking for troilite inclusions with which the spinel is typically associated.

The terrestrial samples that were analysed were kindly donated by Dr. D. van Niekerk (Rhodes University, South Africa). They were crushed and prepared using an agate mortar at the Open University. These terrestrial samples were from the Bushveld Igneous Complex (BIC) in South Africa. The samples comprised three rock types: norite, pyroxenite, and a mixture of pyroxenite and chromitite. These samples were obtained with the aim of testing inter-mineral values for $\lambda$ in a terrestrial high-T environment where a common planetary provenance for all minerals was in no doubt. Given that the BIC is the largest layered intrusion in the world (Schouwstra et al., 2000) and the fact that the BIC is an economic deposit, there is a relative abundance of samples compared with other, more remote complexes.

2.2.2 Sample criteria for Cr analysis

In selecting PMG samples for Cr-isotope analysis, a number of criteria had to be met: 1) both chromite and olivine had to be available from the samples, 2) samples covering a range of chromite compositions had to be chosen to investigate whether observed differing Al-content is representative of a different petrogenesis, 3) sufficient sample material had to be available to facilitate olivine analysis (between 500 mg and 1 g), and chromite analysis (a few mg). Of these criteria, the quantity
of available olivine had the largest impact on sample selection. Fortunately, samples were available to meet all of the above criteria. Those selected were olivines from Sericho, Seymchan, Fukang, and Hambleton as well as chromites from Sericho, Seymchan, Fukang, Hambleton, and Brenham. Initially, Brenham olivine was also selected for analysis but unfortunately had been glued to a metal plate prior to acquisition and was thus left out as it was impractical to separate the olivine.

2.2.3 Sample criteria for Hf-W analysis

The sample selection for Hf-W analysis was primarily dependent on three criteria: 1) sufficient olivine and metal to allow for analysis (approximately 5 g of olivine, 1 g of metal) from the same samples to allow for direct metal-silicate comparison, and 2) a range of HSE contents in the metal suggestive of differing degrees of melt evolution. The samples selected for this analysis were Fukang and Seymchan, the latter having an order of magnitude higher Ir than the former. The silicate samples showed evidence of terrestrial contamination and so their data are not incorporated into this study. The silicate analyses yielded terrestrial W isotope signatures and contained a higher concentration of W than was in the pallasite metal, a clear sign of terrestrial contamination. The cause of this contamination is not clear, but it is possible that at some point prior to sample acquisition the meteorite had been cut with a W-carbide saw or some similar material. It seems likely that a small amount of dust or debris from such a tool had become trapped or caught in one of the fractures in the olivine. This conclusion is supported by the fact that the measured W concentration in olivine for both samples was even higher than was expected in the pallasite metal and displayed terrestrial isotopic signatures. There was no such contamination issue with the Fukang and Seymchan metal samples.

2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) analysis was carried out on some of the samples over the duration of this project. The primary purpose of these analyses was characterisation of mineral phases prior to other analysis by microprobe or laser-assisted fluorination. This was achieved using both EDX spectra and BSE images of minerals of interest. The instrument used was the FEI Quanta 200 3D at the Open University. The EDX detector on the system is an Oxford Instruments X-MAX with an 80mm² window. The acceleration voltage used was typically 20 kV at a working distance
of 15 mm to allow for optimal EDX signal. Any figures in which the beam conditions or working distance are not as outlined above have the information specifically stated either on the image or in the figure caption.

2.4 Electron probe microanalysis

A Cameca SX100 Electron Probe Microanalyser (EPMA) was used for quantitative characterisation of major element compositions in the meteorites studied. In all analyses the machine was used with an Open University pre-set set-up: an acceleration voltage of 20 keV, a beam current of 20 nA, and a beam diameter of 1 μm. The elements routinely measured were Na, K, Mg, Ca, Mn, Fe, Al, Cr, Si, and Ti. Analyses have a precision of ± 0.02 wt %. Standard calibration procedure mirrored that followed in Stephe n et al. (2019) with the exception of Cr. Initial analysis of PMG chromite yielded low microprobe totals; this was rectified by changing Cr standard from chromite to crocoite.

2.5 Laser-assisted fluorination

2.5.1 Introduction

The oxygen isotope analyses that form the focus of this work were conducted using laser-assisted fluorination at the Open University, U.K. following an established procedure (e.g. Miller et al., 1999; Greenwood et al., 2017). A sample loaded into the sample holder and the overall set-up at the Open University are shown in Figures 2.6 and 2.7, respectively. A schematic diagram is shown later in Figure 2.8.

Laser-assisted fluorination currently affords the highest precision available for oxygen isotope analysis with a recent study displaying precision (2 SD) of ± 0.053 ‰ (δ¹⁷O), ± 0.095 ‰ (δ¹⁸O), and ± 0.018 ‰ (Δ¹⁷O) (Starkey et al., 2016). The technique is restricted to bulk analyses. For the purposes of this project, laser-assisted fluorination is the most suitable technique; identification of small differences in Δ¹⁷O in differentiated planetary materials requires very high precision which necessitates the use of laser-assisted fluorination. Fortunately, the samples analysed in this study are well distributed in meteorite collections and are therefore easy to acquire. They also contain relatively coarse crystals of olivine and chromite.
Figure 2.6 – An image taken using the laser camera. This shows a partially reacted sample of Brenham chromite following an initial 3 mm beam reaction, note the light green CrF$_3$ precipitate around the edge of the sample.

The laser-assisted fluorination technique employed in this study uses BrF$_5$ as a reactant coupled with laser heating to liberate oxygen from mineral samples. The reaction with forsterite olivine (Kusakabe et al., 2004) is:

Equation 2.8

$$Mg_2SiO_4 + 3BrF_5 \rightarrow 2MgF_2 + SiF_4 + 2O_2 + 2BrF_3 + \frac{1}{2}Br_2 + \frac{1}{2}F_2$$

For chromite, this reaction is likely similar:

Equation 2.9

$$2FeCr_2O_4 + 9BrF_5 \rightarrow 2FeF_2 + 4CrF_3 + 4O_2 + 9BrF_3 + F_2$$

One of the products, CrF$_3$, forms a green crystalline solid that can sometimes be seen coating the bottom of the well when chromites are reacted (Figure 2.6).
2.5.2 Loading samples

The samples were loaded into wells (Figure 2.6) in a Ni sample holder using tweezers and guided by observations using a reflected light microscope. The typical amount of sample material loaded was \( \sim 1.8 \) mg for olivine and \( \sim 1.2 \) mg for chromite. For the olivine, this number is not as important because high yields can be obtained with any reasonable weight. With chromite, however, this is especially important. Initial analyses using > 1.6 mg of chromite consistently gave oxygen yields \( \sim 10\% \) lower than expected from mineral stoichiometry. This is probably because a large amount of debris was created during the reaction that occluded the well and made a complete reaction of the sample almost impossible. This has a significant effect and fractionates the oxygen isotopes, shifting \( \delta^{18}O \) by up to 2 \( \% \) towards lighter \( \delta \) values (see Figure 2.16). Conversely, the amount of chromite reacted needs to exceed \( \sim 1 \) mg or there is a risk that the O pressure will be too low (<150 \( \mu \)g O) to enable laminar flow in the mass spectrometer. If this is the case the microvolume can be employed to get a result, however this is a single lower precision measurement and was only used in this project for the ES chromite analysis. The microvolume allows for very small volumes of gas to be analysed. A potential weighing error can be introduced into the procedure at this stage. If the sample weight is recorded incorrectly, the subsequent calculation of oxygen yield will be inaccurate.

After the samples are loaded in wells in the sample tray, the tray is placed in the sample chamber in the laser housing (Figure 2.7). This sample chamber is in two parts and rests on a copper gasket. The removable upper half of the sample chamber contains a circular window of BaF\(_2\) measuring 38 mm in diameter and 3 mm in depth. This removable half is placed over the sample tray and tightened in place and then brought down to a vacuum pressure of \( 10^{-7} \) mbar. Heater tape is then wrapped around the sample chamber and Al foil placed over as an insulator. The sample chamber is left to bake out at around 80 °C overnight in order to remove any moisture from the system. After baking out overnight, the heater tape is removed and the sample chamber is wrapped in Al foil. It is then allowed to cool from around 80 °C to 50 °C. At 50 °C, the foil is removed and the chamber is allowed to cool to room temperature. When this has been achieved, the obsidian standards in the sample tray are fused using a Photon Machines Inc. CO\(_2\) Fusion Laser (Figure 2.7). This is done under vacuum by increasing the laser power to \( \sim 1.7 \) W which is sufficient to melt obsidian under high-vacuum. Different valve sequences are used at various stages of sample analysis and are documented here for
completeness. The initial valve configuration for the gas clean-up line is M3, M4, MB, M6, M7, M2, and V9 (see Figure 2.8 for reference) are closed, all other valves are open.

Figure 2.7 – The laser-assisted fluorination set-up at the Open University. (Left) Displayed here are the laser chamber, gas clean-up line, and mass spectrometer. (Right) This shows the set-up inside the laser chamber, the sample chamber itself is shown as an inset. Modified from Greenwood et al (2017).

Figure 2.8 – A schematic diagram showing the gas clean-up line and laser chamber at the Open University. The valves closed when the line is not in use are M3, M4, MB, M6, M7, M2, and V9. The sample chamber is inside the laser chamber.
2.5.3 Leak Check

Following the loading of the sample tray, fusing of the obsidian, and heating overnight, valve V5 is closed and the KBr turned down to 23 V (110 °C). Prior to releasing any BrF₅ into the sample chamber, a leak check is performed to ensure that the system is properly sealed. This is done by first closing V1, V7, V13, and V14 and taking a background pressure reading at the baratron. After ten minutes has elapsed, the pressure is taken again and compared with the earlier reading. If the second reading is higher than the first, it indicates that there may be a leak. If a leak is detected, the cell is removed and refitted.

2.5.4 Blanks

The system is then purged using BrF₅ aliquots in order to remove any adsorbed moisture on cell and sample surfaces. This is done until the oxygen blank is < 6 µg O₂, usually this requires two blanks of 20 minutes each. This is achieved by closing valves V1 and V12 and preparing an aliquot of the reactant BrF₅ equal to around 427 mbar. This aliquot is cycled by freezing onto trap 1 using liquid N₂, waiting until the BrF₅ has frozen down, opening valve V12 to allow any non-condensed gas to be pumped away, then closing the valve. This acts as a clean-up step for the BrF₅. The next step is removal of the N₂ dewar from trap 1. Following N₂ removal, the trap is heated to room temperature or just above using a hairdryer. This procedure is repeated twice. On the third repetition, valves V2, V4, V12, and V13 are closed and trap 1 is heated up. This mobilises the BrF₅, which expands into the sample chamber (Figure 2.8) at a pressure of around 227 mbar. Once this has happened, the manual valve MS is closed to seal the BrF₅ in the sample chamber and the liquid N₂ replaced on trap 1. This step freezes down the BrF₅ that has expanded through the pipes between trap 1, trap 2, and valves M6 and V2. Following freezing down, a timer is set for 20 minutes. After the time has elapsed, valves V7, V14, and V1 are closed, and V2 is opened. The manual MS valve is then opened allowing the gas from the sample chamber to expand into trap 2, which is cooled to liquid N₂ temperatures to trap waste BrF₅, for two minutes. After two minutes, V4 is opened for 9 minutes. This allows the gas through the heated bed of KBr which removes any F₂ gas and creates KF and Br₂ with the latter then being frozen down on trap 3 (Greenwood et al., 2017), which is also cooled with liquid N₂. Following this 9-minute step, an additional minute is timed during which all traps are topped up and then a pressure reading is taken at the baratron. This is the first time that the amount
of oxygen liberated during reaction can be calculated. After this has been recorded, the blank gas is pumped away by opening V1, V7, V13, V12, and V14. After a few minutes, following the recovery of the vacuum, the procedure can be repeated for the second 20-minute blank.

After the two 20-minute blanks, the line is left overnight to pump down and stabilize. Overnight, the KBr is turned up to 25 V (140 °C). This drives off any waste gas that has not been pumped away. The blank procedure is repeated with a single 5-minute blank the following day, prior to reacting the first sample.

2.5.5 Running a sample

The valve sequences for running a sample are similar to those used for BrF₅ blanks. To begin, V5 is closed, the KBr turned down to 23 V, and the molecular sieve turned down to 8 V. A BrF₅ aliquot is cycled twice, then V2, V4, V12, V13 are closed and trap 1 is heated. The BrF₅ expands along the line into the sample chamber and the pressure reaches around 227 mbar, valve MS is then closed to seal BrF₅ of pressure 227 mbar into the sample chamber. The N₂ is replaced on trap 1, condensing all BrF₅ not in the sample chamber. The sample is then lasered (Figure 2.9). The lasering technique varies depending on the sample being reacted.

2.5.5.1 Obsidian and silicates

Obsidian standards and silicate samples react easily during laser heating, the laser beam diameter is set at 3 mm and the laser power slowly increased to ~12 W (25% power). The obsidian often takes a few minutes to fully react, minerals such as olivine and pyroxene take typically a little less. After it has reacted, the beam diameter is reduced to 1 mm and the laser increased from 0 to 10 W (20%) quickly to react any residual unreacted material. Whilst the power is approximately the same, the power density of the 1 mm beam is ~8x higher than the 3 mm beam.

2.5.5.2 Chromites

Initial analyses of the chromite samples were conducted in the same manner as the obsidian and the silicates. Using this technique, the oxygen yield measured during laser fluorination was typically 5-15% lower than stoichiometric chromite according to EPMA analysis (Figure 2.16). This has a significant impact on δ¹⁸O and δ¹⁷O but little to no impact on Δ¹⁷O as the fractionation owing to this effect is mass-dependent.
After a long period of experimentation, the methodology for reacting chromite was refined. The beam diameter for chromite reaction was reduced to 400 μm and the power increased very rapidly to 16.6 W. This means that the power density in the well is considerably higher when reacting chromites compared with silicates, ~10x greater than for the 1 mm beam step at 10 W. This is important because the initial analyses (3 mm beam) were hampered by the formation of reacted detritus in the sample well, stopping the beam effectively reacting the sample. Using the new technique (400 μm beam), this issue was largely overcome. However, a shortcoming of this technique is that to be fully effective it requires that the samples of chromite loaded are one or two chips equalling around 1.2 mg. If the chromite samples are a powder it is much more difficult to react as rapidly increasing laser power has a tendency to dislodge fine sample material out of the well. If the sample is scattered out of the well the results are typically fractionated. This is because some material is only partially reacted and this results in an isotopically fractionated sample gas. In
the worst case it could also contaminate other samples in neighbouring wells or even adhere to and crack the BaF$_2$ window which means that the whole tray must be discarded. This risk was mediated throughout this study by reacting chips of chromite rather than powder where possible. Where not possible, the powdered chromite was separated by several wells from the nearest sample and run last to negate the risk of contamination. This new technique for reacting chromite gives consistently improved yields (Table 2.1). Section 2.8 shows the differing yield of chromite analyses obtained using the two techniques.

### 2.5.5.3 Sample gas clean-up

Following the reaction of the sample, valves V7, V14, and V1 are closed, and V2 is opened for two minutes to allow the gas to expand into and through trap 2. Valve V4 is then opened for 9 minutes during which time the molecular sieve is cooled down to liquid N$_2$ temperatures. After this step, the 1-minute top-up time is added as described in the blanks section. After topping-up the traps, the baratron pressure is recorded. This allows a calculation of the oxygen yield. The pressure recorded is in mbar and is converted to yield (%) in the following manner.

1) The final pressure (mbar) of liberated O$_2$ is recorded at the baratron

2) This value is converted to µg O$_2$ by multiplying by a calibration factor of 209. This calibration factor was determined using silicates where confidence was high that a full reaction had taken place and all O$_2$ was liberated.

3) The yield is then calculated by dividing the mass of O$_2$ (mg) by the mass of the sample (mg) and multiplying by 100.

The conversion factor of 209 is an approximation based on experiments conducted internally on different minerals and calibrated following any structural changes to the system. Once the yield has been recorded, V7 is then opened for 8 minutes. During this time, the O$_2$ freezes onto the molecular sieve which is filled with 13X molecular sieve pellets. After the 8-minute step, V8 is closed and the gas is trapped on the molecular sieve between valves V8 and V9. The rest of the line is then opened up to allow any non-condensed gas in the system to be pumped away. The molecular sieve is then heated up to 75 °C over 4 minutes by removing the liquid N$_2$ and using heater tape. Once 75 °C is reached, V9 is opened and the gas is expanded into a ThermoFinnigan MAT 253 Dual Inlet Isotope
Ratio Mass Spectrometer (IRMS). After allowing the gas two minutes to equilibrate in the IRMS, V9 is closed and V8 opened, returning the line to its initial configuration for the next sample.

2.5.5.4 Micro volume

For samples where a very small amount of gas is liberated, the microvolume can be employed to get a single run of 10 sample to reference comparisons. This was done just once in this study for the Eagle Station chromite sample. There are several minor deviations from the standard procedure when using the micro volume. Firstly, prior to the sample gas reaching trap 2, any BrF$_5$ that is present on trap 2 is moved to trap 4, a trap adjacent to and separated by a manual valve from trap 2 that is not used during standard analyses. This is done by freezing trap 4 to liquid nitrogen temperatures and heating trap 2 with valves 2, 4, and 13 closed. Secondly, the sample gas is allowed to freeze down onto the molecular sieve, which contains silica gel that absorbs O$_2$ at liquid nitrogen temperatures, for 10 minutes rather than 8 minutes to ensure no loss of analyte O$_2$. Finally, the gas is heated in the small microvolume and expanded into the same half of the changeover block in the mass spectrometer via a capillary bypassing the bellows. The very small volume of the micro volume ensures that the pressure of the O$_2$ remains sufficiently high for laminar flow. The sample gas is then analysed as normal.

2.5.6 Mass Spectrometry

Sample gas from the clean-up line is expanded into a ThermoFinnigan MAT 253 Dual Inlet IRMS with an m/Δm ~200. In a single run in the IRMS samples are analysed 10 times against the reference gas (O$_2$-10), which is in turn calibrated to VSMOW. Typically, each sample in this project was run 6 times to provide necessary internal precision (60 sample to reference comparisons total taking ~1 hour) unless otherwise stated in data tables (e.g. Table 3.5, Table 3.6, Table 3.7, Table 5.1). When analysing chromite, the initial run was set up to search for an interfering mass, NF$_2^+$ at mass 52. Whilst NF$_2$ itself does not affect the measurement of O$_2$ molecules (masses 32, 33, and 34), its presence indicates the fragmentation of NF$_3$ and therefore that an ion of NF$^+$ (mass 33) is also present. The very low abundance of $^{17}$O (0.038% of Solar System oxygen) and the high precision of the measurements means that even trace amounts of NF can have a detrimental effect on isotopic
results. On the very rare occasions that NF$_2$ was detected during this project, the measurement was rejected and therefore the $\delta^{17}$O values, and by extension the $\Delta^{17}$O values are reliable.

2.6 Acid Washing

Meteorite finds can have vastly different terrestrial ages and may have experienced weathering in considerably different terrestrial environments. An extreme example is that of the IIAB iron meteorite Lake Murray which was found in 1933 embedded in undisturbed Cretaceous sandstone, having presumably fallen during deposition (Buchwald, 1975). Comparing this with another IIAB, Sikhote Alin, which was an observed fall in what was then the Soviet Union on February 12$^{th}$ 1947 (Buchwald, 1975), gives a range of terrestrial ages for the IIAB group of at least 66 Myr. Whilst the samples analysed in this study are unlikely to have terrestrial ages within even two orders of magnitude of Lake Murray, there may be hundreds or even thousands of years between the terrestrial ages of the finds, as well as totally different weathering environments. In order to remove any terrestrial weathering or oxidation that the samples may have developed, the samples were acid treated (Figure 2.10) prior to analysis following the procedure of Ali et al. (2016; 2018). This involves the treatment of samples with 6M HCl at 70°C for 2-3 minutes (Ali et al., 2016). Early in the project, in order to test whether HCl washing had any effect on oxygen isotope results, both pristine and weathered olivines from pallasites were analysed before and after washing. In the case of Somervell County, where a lot of sample material was available, a “very dirty” set was also run. Eagle Station olivines were run in addition to PMG olivines as their large deviation from the TFL ($\Delta^{17}$O = ~-5‰) would mean that any influence on oxygen signature imparted by the HCl would be relatively easy to detect. Figure 2.11 shows HCl treated and non-HCl treated results for olivine from the same meteorites. The $\Delta^{17}$O of the acid treated olivines is not resolvable from those which were not treated. The non-HCl treated samples have an average $\Delta^{17}$O of -0.200 ± 0.015 ‰ (2σ), and the samples with HCl treatment -0.197 ± 0.016‰ (2σ). Acid treatment of olivine crystals as outlined in Ali et al. (2016) has no measurable impact, at least in these samples, on $\Delta^{17}$O. It has therefore been used in sample preparation to eliminate the possibility of terrestrial contamination. There may be a subtle effect on $\delta^{18}$O in the acid treated samples as the measured range of values is larger (Figure 2.11).
Figure 2.10 – A photomicrograph showing the condition of clean Brenham olivine in this study following treatment with 6M HCl at 70°C for 2-3 minutes (as in Ali et al., 2016).

Figure 2.11 – A comparison of HCl and non-HCl treated PMG olivines. There is no resolvable difference in $\Delta^{17}$O, nor any appreciable change in analytical precision. The $\delta^{18}$O values do seem to have a greater range in the HCl treated samples. Errors are 2 standard error of the mean.

The average $\delta^{18}$O of the acid washed samples is $3.103 \pm 0.404$ (2$\sigma$) and that of the untreated samples is $3.129 \pm 0.179$ (2$\sigma$). The two acid washed data points with the lightest $\delta^{18}$O values are from the same pallasite, Brahin. Given the fact that this $\delta^{18}$O variation seems to be sample specific, coupled with the tightening of the range of PMGs $\delta^{18}$O values over the duration of this project, it is possible
that the increased range of values in HCl-treated samples is the result of poor reaction during analysis rather than any actual effect on oxygen isotopes. If there is a real effect, it must affect δ¹⁷O too in a mass-dependent manner, as evidenced by the unresolvable Δ¹⁷O values.

Samples of Eagle Station olivine were analysed both at the beginning and end of this project. Acid treatment as described was conducted on those early samples (n = 2) but not the later olivine sample (n = 1). Figure 2.12 shows a measurable difference between acid-treated and non-treated olivine for Eagle Station.

![Figure 2.12 – Comparison of acid-treated Eagle Station olivine and non-treated Eagle Station olivine. Note that the non-treated olivine is offset toward the TFL. Errors are 2 standard error of the mean. The errors are larger on the acid-treated samples because only 30 analyses were run against the reference gas, not 60 as is the case for the non-treated sample.](image)

Given this difference, HCl treatment does appear to negate the effects of the alteration of olivine oxygen isotope composition by terrestrial weathering. In the case of the PMG, the difference between non-treated and acid-treated samples is not resolvable. The ES olivine, because it is ~25 times farther from the TFL in isotope space, is ~25 times more sensitive to the effects of terrestrial contamination and does show a resolvable difference when acid-treatment is used to remove weathering. These results support the use of HCl for removing terrestrial contamination (Figure 2.12) in this study.
2.7 Obsidian Standard, instrument precision, and variation over time

For analysis of planetary materials in the area of isotope space close to the TFL, the precision required for resolution of mass-fractionation lines is very high. Figure 2.13 shows the variation in $\Delta^{17}$O in obsidian standard analyses over the duration of the project, Figure 2.14 shows the variation in $\delta^{18}$O for the same analyses. Both figures highlight that there is no resolvable difference in either $\delta^{18}$O or $\Delta^{17}$O over the duration of the study. The reproducibility displayed in Figure 2.15 is excellent. The mean $\delta^{18}$O over the duration of the project was 7.339 ‰ ($\pm$ 0.080 ‰, 1σ) and for $\Delta^{17}$O the mean was -0.015 ‰ ($\pm$ 0.010 ‰, 1σ). The mean values for $\Delta^{17}$O (Figure 2.13 and Figure 2.15) are non-zero. This is because the $\Delta^{17}$O values in this study were calculated using $\lambda$ = 0.5262, a slope appropriate for igneous systems (e.g. Greenwood et al., 2018), and the absolute value of $\Delta^{17}$O is dependent on the fractionation exponent used. The precision (2σ, n=52) for obsidian $\delta^{18}$O over the whole duration of the project is $\pm$0.160 ‰, $\Delta^{17}$O is 0.021 ‰ (2σ), and $\delta^{17}$O is 0.085 ‰ (2σ).

![Figure 2.13 – Obsidian $\Delta^{17}$O over the duration of the project. Errors are 2 standard error of the mean. The mean $\Delta^{17}$O is -0.015 ‰ and one standard deviation is 0.010 ‰.](image-url)
Figure 2.14 – Obsidian δ¹⁸O over the duration of the project. Errors are 2 standard error of the mean but are smaller than the data points. The mean δ¹⁸O is 7.339 ‰ and one standard deviation is 0.080 ‰.

Figure 2.15 – Obsidian standard δ¹⁸O vs. Δ¹⁷O displaying excellent reproducibility. Errors are 2 standard error of the mean for both δ¹⁸O and Δ¹⁷O. Mean values for δ¹⁸O and Δ¹⁷O as well as associated uncertainties are given in the captions for Figure 2.13 and 2.14.
Overall, both the reproducibility and the consistency over time of the obsidian standard results demonstrate the excellent precision available through the laser-assisted fluorination technique. The $\Delta^{17}O$ results are comparable with those quoted by Starkey et al. (2016), the $\delta^{17}O$ and $\delta^{18}O$ results are slightly lower precision due to the inclusion in this study of the first obsidian analysed in each tray. This first obsidian is likely to have a higher blank contribution and was excluded from data presented in Starkey et al. (2016).

2.8 Fractionation of oxygen isotopes during reaction of chromite

Initial reaction of chromite samples, both PMG and IIIAB, was done using the same beam conditions as are used for olivine. The oxygen yield obtainable via this method was significantly lower than the expected yields calculated for select chromites using EPMA. This is almost certainly caused by the creation of a large amount of debris during the lasering of chromite that can cause unreacted material to be trapped amongst the debris. This prevents this trapped sample material from being reacted and results in sub-optimal oxygen yields. When using the initial beam conditions, the chromite was undergoing partial reaction and then was covered by reaction products. This resulted in fractionation between the chromite sample and the $O_2$ liberated by between 1.5 – 2 ‰ $\delta^{18}O$ (see Figure 2.16) and a correspondingly smaller fractionation in $\delta^{17}O$. Given that the fractionation in these cases is mass-dependent, the effect on $\Delta^{17}O$ was negligible – i.e. later optimized samples show minor, if any, $\Delta^{17}O$ differences from their pre-optimized counterparts. In order to address the low yield and fractionation, a new set of beam conditions were developed to allow for rapid and complete reaction of the sample prior to its being obscured (see section 2.5.5.2). The total oxygen yields for these optimized samples were consistently between 25 and 30%. This is between 5 and 10% higher than when using the prior technique (Table 2.1) and approaches expected stoichiometric yields. Crucially, a complete reaction was observable with no reaction products obscuring unreacted sample material. Using the optimized technique, the 400 µm beam has the ability to penetrate the reaction products which allows for the full reaction of the chromite samples. Any difference between expected yield and measured yield is therefore likely due either to weighing errors or underestimation of O content in EPMA analyses. This underestimation could arise from $Cr^{2+}$, and therefore the oxide $CrO$, being measured as $Cr_2O_3$ in EPMA. This would overestimate oxygen content in the sample and is in keeping with expectations at low $fO_2$ conditions (e.g. Roeder & Reynolds, 1991).
The observed fractionation in the low-$\delta^{18}$O PMG chromite subgroup follows a $\lambda$ of $0.5297 \pm 0.0038$ (2 SE). The high-$\delta^{18}$O subgroup follows a $\lambda$ of $0.5256 \pm 0.0078$ (2 SE). Both of these fractionation exponents are within the expected range for high-T mass-dependent fractionation. Table 2.1 shows differences in yield obtained using initial beam conditions and the subsequent 400 µm beam. Only chromite samples analysed using both techniques are presented for comparison.

Table 2.1 shows a general increase in average yield from 21.9% using initial beam conditions to 26.4% using the optimized beam conditions. Whilst even under optimized conditions, the full expected yield is often not liberated, the $\delta$ values do not appear to be fractionated. This is because the 400 µm beam allows for definite reaction of all material in the sample wells where the 3 mm beam did not. As a result of this, there is likely to be another reason for the consistent ~3 wt% deficit.
in yield compared with expected values. This may be the result of the presence of Cr\(^{2+}\) where stoichiometric yield calculations assume Cr\(^{3+}\) or it could mean that the conversion factor estimate (section 2.5.5.3) of 209 used to measure yield is less appropriate for chromite than for olivine and obsidian. Regardless of the cause, the optimized 400 µm analyses enable the whole chromite sample to be reacted and therefore ensure that the results are not fractionated by instrument effects.

Table 2.1 – The average yields for initial and optimized analyses for chromite. The optimized technique allowed for consistently higher average yields except for Wonyulgunga. This was likely the result of a weighing error during sample loading in the initial run, as only 1 sample was run initially. The initial yields were analyses using the 3 mm beam technique. The optimized yields were analyses using the 400 µm beam technique. The asterisk denotes a known weighing error.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Class</th>
<th>Initial yields (% O)</th>
<th>Avg. δ(^{18})O (‰)</th>
<th>Optimized yields (% O)</th>
<th>Avg. δ(^{18})O (‰)</th>
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<tbody>
<tr>
<td>Augusta County</td>
<td>IIIAB</td>
<td>17.2 (n=1)</td>
<td>6.294</td>
<td>22.4 (n=2)</td>
<td>7.230</td>
</tr>
<tr>
<td>Sacramento Mountains</td>
<td>IIIAB</td>
<td>21.2 (n=2)</td>
<td>0.242</td>
<td>22.2 (n=2)</td>
<td>1.138</td>
</tr>
<tr>
<td>Owens Valley</td>
<td>IIIAB</td>
<td>20.4 (n=3)</td>
<td>-2.621</td>
<td>25.5 (n=2)</td>
<td>-0.994</td>
</tr>
<tr>
<td>Wonyulgunga</td>
<td>IIIAB</td>
<td>28.0 (n=1)</td>
<td>-1.523</td>
<td>25.8 (n=2)</td>
<td>0.726</td>
</tr>
<tr>
<td>Mount Edith</td>
<td>IIIAB</td>
<td>18.2 (n=1)</td>
<td>-2.111</td>
<td>23.8 (n=1)</td>
<td>-1.472</td>
</tr>
<tr>
<td>Cape York</td>
<td>IIIAB</td>
<td>18.8 (n=1)</td>
<td>7.412</td>
<td>25.4 (n=2)</td>
<td>7.746</td>
</tr>
<tr>
<td>Bear Creek</td>
<td>IIIAB</td>
<td>19.6 (n=2)</td>
<td>-0.957</td>
<td>25.7 (n=2)</td>
<td>0.950</td>
</tr>
<tr>
<td>Fairview</td>
<td>IIIAB</td>
<td>20.2 (n=2)</td>
<td>-1.594</td>
<td>25.3 (n=1)</td>
<td>0.579</td>
</tr>
<tr>
<td>Puente del Zacate</td>
<td>IIIAB</td>
<td>22.9 (n=1)</td>
<td>-1.007</td>
<td>25.4 (n=2)</td>
<td>0.840</td>
</tr>
<tr>
<td>Brahín</td>
<td>PMG</td>
<td>22.5 (n=2)</td>
<td>-0.953</td>
<td>26.7 (n=1)</td>
<td>0.949</td>
</tr>
<tr>
<td>Unnamed Tibetan</td>
<td>PMG</td>
<td>22.2 (n=2)</td>
<td>0.163</td>
<td>37.7 (n=1)*</td>
<td>1.121</td>
</tr>
<tr>
<td>Imilac</td>
<td>PMG</td>
<td>26.9 (n=2)</td>
<td>0.910</td>
<td>29.0 (n=2)</td>
<td>1.953</td>
</tr>
<tr>
<td>Brenham</td>
<td>PMG</td>
<td>22.9 (n=5)</td>
<td>-1.136</td>
<td>26.8 (n=3)</td>
<td>0.871</td>
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<tr>
<td>Sericho</td>
<td>PMG</td>
<td>24.3 (n=3)</td>
<td>-1.246</td>
<td>25.4 (n=2)</td>
<td>1.256</td>
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<td>Seymchan</td>
<td>PMG</td>
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<td>Hambleton</td>
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<td>22.2 (n=2)</td>
<td>-1.260</td>
<td>26.8 (n=2)</td>
<td>1.113</td>
</tr>
</tbody>
</table>

2.9 Chromium isotope analyses

2.9.1 Chemistry

Four PMG olivine and 5 chromite samples were prepared for Cr isotope analysis using a technique modified from Yamakawa et al. (2009) at the Institute for Planetology in Münster, Germany. The
sample preparation and analysis were performed by and under the direction of J. Schneider. Initially
the samples were dissolved in 2:1 HF:HNO$_3$ followed by Aqua Regia to remove any residual
fluorides. For the chromites this was done with the aid of a pressure “bomb” using 2 ml of
concentrated HNO$_3$ at 190°C for 96 hours. Three stages of column chemistry were subsequently
employed for the olivine samples, the first two were used for the chromite samples. In the case of
the olivines, the second stage had to be repeated two additional times in order to remove Mg from
the sample solution. Following dissolution, the samples were dried down on a hotplate and then 500
μl 6 M HCl was added and the vials closed for 1 hour at < 100 °C. This process was repeated three
times, the final time with 1 ml 6 M HCl.

Stage 1 – Anion removal

The initial stage of column chemistry was conducted predominantly to remove Fe. One millilitre of
AG1-X8, 200-400 (10 ml Biorad®) resin was added to each column. After this had settled, the
columns were cleaned. The cleaning consisted of three stages: an initial 10 ml of 3 M HNO$_3$ was
added to each column, followed by 18 ml of Milli-Q H$_2$O (hereafter MQ) and finally 12 ml of 6 M HCl. The columns were then conditioned with a further 5 ml of 6 M HCl each. The samples were
loaded in 1 ml 6 M HCl and this was collected after passing through the column. The 6 M HCl was
then added three further times in 1 ml steps and finally in a 2 ml step and collected in with the sample.
This cut was then labelled “Cr I”. Following the initial collection of the Cr, the matrix cut was taken
and collected in a separate vial. This comprises predominantly Cu, Fe, and Zn.

Following the steps described above, the Cr I samples were in 6 ml 6 M HCl in a 7 ml vial. They
were then left at 90 – 95 °C overnight to dry down after which concentrated HCl drops were added.
These were then also allowed to dry down. Prior to loading the columns for the second stage, 0.4 ml
of 6 M HCl was added to each vial after which they were closed for 12 hours and left on a hot plate
at 120 °C. Finally, 2 ml MQ was added just prior to loading so that the sample was in 2.4 ml 1 M
HCl.

Stage 2 – Cation (Cr) separation

New columns were prepared and 0.3 ml of AG50W-X8, 200-400 (10 ml Biorad®) resin was added.
The cleaning steps consisted of an initial addition of 16 ml 6 M HCl followed by two additions of 16
ml MQ. Conditioning of the columns was achieved using first 2 ml of 1 M HCl which was then backwashed, this involved using a pipette to take up a small amount of HCl and forcibly expel it under the HCl fluid level to disturb the resin. After the backwashing, a further 2 ml 1 M HCl was added. The sample was loaded in 2.4 ml 1 M HCl (as detailed above at end of stage 1). A further 3.6 ml 1 M HCl was added to collect the Cr II cut. After collection, the matrix cut was collected separately using 4 ml 2 M HCl, primarily for Ni. After this stage, Cr II was in 6 ml 1 M HCl. The sample was then checked for element concentrations using a ThermoScientific XSeries II Quadrupole Inductively Coupled Plasma Mass Spectrometer. In the case of the olivine samples, as described above, it was necessary to repeat this whole stage two additional times to remove the high amounts of Mg present. In the case of the chromite samples, stage 3 was not necessary as there was a high enough concentration of Cr present after stage 2 had been completed.

Stage 3 – Cation (Cr) clean-up

New heat shrink tube columns were prepared and 0.3 ml of AG50W-X8, 200-400 (10 ml Biorad®) resin was added. The cleaning steps consisted of an initial input of 9 ml 6 M HCl, followed by two steps of 7 ml MQ. The second of these MQ steps was backwashed to ensure the resin was well settled. Subsequent conditioning of the columns was achieved using two stages of 3 ml 0.5 M HNO₃. Following these steps, the sample was loaded in 3 ml 0.5 M HNO₃. The matrix cut was then taken using 1 ml 0.5 M HNO₃ to capture residual Na and Ti, followed by 3 ml 0.5 M HF for Al, Ti, and V. The columns were then washed with 6 ml 1 M HCl which removed residual Fe, Ni, Mn, and Mg. After the matrix cut, the final Cr cut (Cr III) was taken using 10 ml 2 M HCl. At this stage the sample was in 10 ml 2 M HCl.

The final step was organic removal. Initially, four drops of aqua regia (AR) was added twice and then dried down at 130 °C, then two drops of concentrated HNO₃ and one drop of H₂O₂ was added twice and dried down at 80 °C. This was followed by conversion to HCl for the loading solution and the addition of two drops of concentrated HCl after which the sample was dried down at 120 °C. The samples were then taken up in 6 M HCl to create a 500 ppm loading solution. This was left to sit for a minimum of one hour before it was loaded on to the filament.
2.9.2 Sample loading

Two microliters of 500 ppm sample solution (1 μg of sample) was added on the centre of previously outgassed Re filaments. The outgassing process was conducted > 2 days prior to this in order to allow time for the filament to oxidize. This step was conducted to ensure that the loaded drop of sample solution had sufficient friction to remain on the filament. The filament was heated at 0.7 A until the sample had dried then 1 μl of 1000 ppm Al solution was added immediately on top of the sample and left to dry at 0.7 A. After the sample and solution had dried, 2 μl of a Si gel-H₃BO₃ mixture was added. Again, this was dried at 0.7 A. When it had nearly dried, another 1 μl of the mixture was added ensuring adequate coverage of the sample. After drying down, the current was increased to 1.2 A and the sample mixture allowed to homogenise for 30 seconds. The current was then increased to 1.8 A and allowed to homogenise for 5 seconds. The filaments were then loaded onto the mounting wheel carefully and then placed in a ThermoScientific Triton Plus Thermal Ionisation Mass Spectrometer (TIMS) for analysis.

2.9.3 Radiometric decay and cosmic ray exposure corrections

The Cr isotopic composition of iron meteorites, and by extension pallasites, is a combination of native, cosmogenic, and radioactive nuclides (Liu et al., 2019). The short-lived $^{53}$Mn-$^{53}$Cr decay pathway ($T_{1/2} = 3.7$ Myr) has the potential to affect the $\varepsilon^{53}$Cr value of a sample by elevating the $^{53}$Cr content (Qin et al., 2010; Liu et al., 2019). This effect is negligible in the chromite samples analysed in this study as the Mn/Cr ratio is so small (see section 3.2.1.2). In the olivine samples analysed, where the Mn/Cr ratio is > 1, this effect must be corrected for as appreciable amounts of $^{53}$Mn may have been present relative to native $^{53}$Cr.

Prolonged exposure to galactic cosmic rays (GCR) can have significant effects on the Cr isotopic composition of a meteorite sample (Qin et al., 2010). These effects arise because all four Cr isotopes can be produced through spallation of target nuclides of Ni and Fe but are only seen in $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr ratios (Birck & Allègre, 1985b as cited in Qin et al., 2010). These cosmogenic effects are particularly noticeable in samples that have high Fe (or Ni)/Cr ratios and long cosmic ray exposure (CRE) ages (Qin et al., 2010). The relationship between CRE age and number of cosmogenic nuclides is treated as linear, assuming that GCR flux and energy is relatively constant over time (Liu...
There are several methods that seek to correct for this effect. The method adopted in this study is to back-calculate the pre-GCR affected $\varepsilon^{54}\text{Cr}$ composition of PMG olivines using a calculated slope of $3.90 \pm 0.03$ in $\varepsilon^{54}\text{Cr} - \varepsilon^{53}\text{Cr}$ space (Liu et al., 2019). No CRE correction is applied to PMG chromite on the basis of its very low target nuclei to Cr ratios. After implementing this correction, it was noticed that the difference between PMG chromite and individual PMG olivines was a function of the Mn/Cr ratios in those olivines and therefore the mineral phases were likely unresolvable or from the same Cr isotope reservoir (Chapter 3). The Mn-Cr age obtained for PMG was generated following this observation using ICPMS PMG olivine data. The PMG chromite compositions plot at the base of this line. Isochrons were created in ISOPLOT and using the temporally well-resolved LEW 86010, an angrite, as a time anchor (Lugmair & Shukulyukov, 1998).

2.10 Hf-W isotope analyses

Four samples from two PMGs were analysed with the help of and under the direction of J. Hellmann at the Institute for Planetology in Münster, Germany. The samples selected were a metal and silicate separate from the meteorites Fukang and Seymchan. These pallasites were chosen for two main reasons: firstly, there is an order of magnitude difference in the Ir content of the metal in the two samples, $0.043 \mu g \cdot g^{-1}$ in Fukang (Conolly et al., 2006) and $0.676 \mu g \cdot g^{-1}$ in Seymchan (van Niekerk et al., 2007), and secondly enough sample material was available from both the silicate and metal fractions for the analyses to be conducted.

2.10.1 Sample preparation and dissolution

The silicate and metal phases were mechanically separated at the Open University prior to analysis. This was achieved by wrapping the sample in several layers of Teflon and gently tapping with a hardened steel hammer to break the sample up. This material was subsequently separated using reflected light microscopy in a clean room. Following separation of the silicate and metal phases, any residual resin (the samples were bought from a meteorite dealer and had been resin coated) coating the pieces was removed using tweezers. The silicate fraction for each meteorite was then ground using an agate mortar and pestle and subjected to 5 rounds of magnetic separation in which a magnet was passed over the powder in order to separate any potentially contaminating metal shavings. In total, 5.74 g of olivine from Seymchan and 4.14 g of olivine from Fukang were
processed at the Institute for Planetology, University of Münster, Germany as well as around 1.5 g of metal from both pallasites.

The silicate samples were digested in a 2:1 mixture of HF-HNO$_3$ (24 ml per gram) at 120 °C for approximately 48 hours. Following drying down and converting into chloride form, the samples were dissolved in 40 ml 6 M HCl-0.06 M HF and 10% aliquots were taken for Hf and W concentration measurements. The metals were dissolved in 32 ml 10:5:1 HNO$_3$-HCl-HF also at 120 °C for approximately 48 hours. These samples were then dissolved in 60 ml 6 M HCl-0.06 M HF and aliquots of 12.5% for Pt and 3% for Hf and W concentrations were taken. These aliquots were spiked with a $^{180}$Hf – $^{183}$W spike for isotope dilution in order to obtain precise Hf and W concentrations.

2.10.2 Column chemistry and high field strength element (HFSE) separation

The initial column chromatography was conducted using a column volume of 18 ml and a volume of 4 ml of BioRad® AG 1x8 (200-400) resin. These columns were then cleaned sequentially using first 18 ml of 3 M HNO$_3$, then 18 ml of a mixture of 6 M HNO$_3$ – 0.2 M HF, then two washes with 4 ml H$_2$O, and finally 18 ml of a mixture comprising 6 M HCl – 1 M HF. The columns were then equilibrated by filling twice with 0.5 M HCl – 0.5 M HF. Once this was completed, 75 ml of the samples were loaded in 0.5 M HCl – 0.5 M HF. This was followed by rinsing in 10 ml of 0.5 M HCl – 0.5 M HF after which the HFSE cut was eluted using 15 ml of a 6 M HCl – 1 M HF mixture.

The second stage of column chromatography used columns of volume 10 ml and resin of volume 1 ml. Initial cleaning was conducted using the same procedure as in the first stage chemistry except with 10 ml acid mixtures instead of 18 ml and with two washes of 1 ml H$_2$O instead of two washes of 4 ml. The column was then equilibrated with 10 ml 1 M HF applied in two stages of 5 ml. The HFSE cut obtained in the first stage was dissolved in 6 ml 0.6 M HF mixed with 0.4% H$_2$O$_2$ and added to the column. This sample was then rinsed for removal of Ti, Hf, and Zr using 10 ml of a mix of 1 M HCl-2% H$_2$O$_2$. The column was then rinsed 3 times: first using 2 ml H$_2$O, then using 9 ml 8 M HCl – 0.01 M HF, and finally using 0.5 ml of 6 M HCl – 1 M HF. The W was then eluted using 8.5 ml of 6 M HCl – 1 M HF. Following this step, the column was rinsed using 2 ml H$_2$O and then Mo was eluted using 3 M HNO$_3$. The samples were then dried down.
The anion exchange chromatography used columns of the same size as the second stage column chromatography and the same volume of BioRad® AG 1x8 (200-400) resin. The initial cleaning stage was identical to that of the second stage chromatography. Following cleaning, the columns were equilibrated using 10 ml 0.5 M HCl – 0.5 M HF. Following this, 1.5 ml of the sample was loaded in 1 M HCl – 0.5 M HF and rinsed twice: initially with 1 ml 0.5 M HCl – 0.5 M HF, and subsequently with 5 ml 1 M HF. The Hf was then eluted using 4 ml 8 M HCl – 0.01 M HF and finally the W was eluted using 5 ml 6 M HCl – 1 M HF. The samples were then loaded into a ThermoScientific Neptune Plus MC-ICP-MS for high precision isotope measurements and analysed by J. Hellman using IfP procedures (e.g. Kruijer et al., 2017).

2.10.3 Pt Corrections

Platinum isotope analyses were carried out by F. Spitzer at WWU Münster using the ThermoScientific Neptune Plus MC-ICP-MS at the University of Münster. Analyses were performed on the same samples prepared for Hf-W measurements using the technique described in Kruijer et al. (2013). Analysis of Pt in conjunction with W allows for correction of $^{182}\text{W}/^{184}\text{W}$ for cosmic ray spallation effects as Pt isotopes exhibit large GCR-induced anomalies that are correlated with $^{182}\text{W}/^{184}\text{W}$ variations (Kruijer et al., 2013). The negative correlation between $\varepsilon^{182}\text{W}/^{184}\text{W}$ and $\varepsilon^{192}\text{Pt}$ is used to calculate pre-exposure $^{182}\text{W}/^{184}\text{W}$ values by York (1966) regression (e.g. Kruijer et al., 2013). The $^{192}\text{Pt}$ measured is formed by β decay of $^{192}\text{Ir}$, following neutron capture (Kruijer et al., 2013).
3 MAIN-GROUP PALLASITE RESULTS

3.1 Introduction

The history of investigation into PMG composition and a literature review of potential formation environments are covered in Chapter 1. This chapter presents the results of SEM, EPMA, as well as O, Cr, and W isotope analyses on PMG samples in this study. These samples were then assigned to subgroups on the basis of textural, isotopic, and compositional data. These subgroups provide a framework for the detailed interpretation of these results that can be found in Chapter 4.

3.2 Petrology

The petrology conducted in this study focused around a small subset of pallasite samples that were available for analysis. Slices of the PMGs Seymchan, Sericho (Figure 3.1), and Fukang were analysed in detail using SEM and EPMA techniques. Additionally, a chip of Mount Vernon (Figure 3.2), and a chip of Brenham chromite from the chropal region were analysed in the same manner.

Figure 3.1 – Photographs of slices of a) Seymchan and b) Sericho used in this study. Olivine, FeNi metal, troilite, and chromite are visible in these slices. Triple junctions between angular olivine grains can be seen on the image of Sericho (right). Fragmental olivine is highlighted in Seymchan (left), rounded and angular olivines are highlighted in Sericho (right).
3.2.1 Olivine

Olivine in PMGs can be subdivided on textural and compositional metrics (e.g. McKibbin et al., 2019). In this study, analysis of the major element composition of olivine was restricted to four PMG slices that were available and of the right size. These four slices, along with classifications of 15 other PMGs based on images, are grouped based on their olivine texture and compared with published classifications. Major element analysis of pre-separated olivine grains was not carried out because no context was available for the results.

3.2.1.1 Texture

Olivine morphology in pallasites has usually been divided into three groups – angular, fragmental, and rounded (Scott, 1977; Boesenberg et al., 2012). All three of these groups are visible in the analysed samples (Figure 3.1). The sample of Sericho exhibits rounded and angular olivine whilst Seymchan has angular, rounded, and fragmental. Both Fukang and Mount Vernon contain angular olivine with some micro-scale rounding present in the latter (see Figure 3.2). It is important to compare the textural classification of those samples analysed in this study (see Table 3.1) with previous work (e.g. Scott, 1977; Boesenberg et al., 2012; McKibbin et al., 2019) to establish whether the observed textures are in agreement. The fragmentary nature of the PMG meteorite record, coupled with inter-sample heterogeneities, mean that textural classification of PMGs in isolation may not be representative of the broader population. The textural classifications for 19 olivines are listed in Table 3.1. This subset of 19 PMGs has been chosen because it is olivine from these, as well as a few additional samples for which no textural information could be found, that have been analysed for oxygen isotopes in this study (see section 3.3.1). The oxygen isotope analyses of these PMGs therefore samples a spread of pallasite olivine textures.

Figure 3.2 demonstrates the different olivine textures routinely found in PMGs. Angular olivine can be seen in Mount Vernon, the unnamed Tibetan pallasite (UTP), and Acomita with the latter two also containing fragmental olivine. The angular olivine in Mount Vernon exhibits some micro-scale rounding of grain corners (Figure 3.2). The Brenham example in Figure 3.2 demonstrates rounded olivine. Sample heterogeneity and the relatively small sizes of samples available means that there can be inconsistencies between the classification of the same samples reported by different studies.
An example of this is the classification of Marjalahti (see Table 3.1); fragmental olivine is reported for the meteorite by McKibbin et al. (2019) but was not reported in the sample studied by Scott (1977). It is worth highlighting that Scott (1977) records Marjalahti as mixed angular olivine which means they may be “highly elongated with sharp corners”.

Table 3.1 – Textural classification of MG pallasite olivines used in this study with literature classifications where available. Classifications were done using high-resolution photographs of slices from the Field Museum, Chicago, and the samples in the OU collection. A = angular, F = fragmental, R = rounded, A(A) is “mixed angular grains” and denotes samples with irregular angular olivines (Scott, 1977). * denotes a tentative classification based on an image search where neither a high-resolution photograph or sample was available. In some cases, no images or information on texture could be found.

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<th>Pallasite name</th>
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Figure 3.2 – Four images illustrating how textural classifications were attributed; Mount Vernon (top left), Acomita (top right), the unnamed Tibetan pallasite (bottom left), and Brenham (bottom right). The Mount Vernon sample was donated by Robert Haag to the OU collection and is 17 mm across from left to right, the Acomita image, the unnamed Tibetan pallasite image, and the Brenham image were provided by the Philipp Heck. The red arrows highlight fragmental olivine, the blue arrows highlight angular olivine. The angular edges of an olivine in Mount Vernon (top left) have been highlighted with white lines. Note the rounding of the corners between these white lines.

This raises the pertinent question of where highly elongated angular olivines end and fragmental olivines begin and emphasises a major shortcoming in subdividing PMGs on the basis of olivine texture in isolation. Despite this potential pitfall, there is a reasonable degree of consistency between the textures determined in this study and those previously reported allowing this potentially important feature to be employed in understanding the formation environment and sample variability. The metal-silicate ratio may play an important role in determining which texture will be prevalent in a sample as pallasites with grains preferentially isolated in metal will have more rounded olivine (e.g. Solferino et al., 2015; Solferino & Golabek, 2018). This in turn may be related to the area of
formation within the PMG parent body. The relationship between olivine textures and other petrological indicators is explored further in section 3.4 and in Chapter 4.

### 3.2.1.2 Composition

The composition of the olivine in the four pallasites analysed by EPMA in this study is broadly consistent with the expected PMG range of Fo values (e.g. Boesenberg et al., 2012): olivine cores from Sericho, Seymchan, Fukang, and Mount Vernon have compositions of Fo$_{88}$, Fo$_{90.2}$, Fo$_{86.3}$, and Fo$_{88.3}$ respectively (see Table 3.2). The Fo$_{90.2}$ value recorded for Seymchan is higher than has been reported for other pallasites (e.g. Scott, 1977, Boesenberg et al., 2012; McKibbin et al., 2019), and marginally higher than the Fo$_{89}$ previously reported for Seymchan (McKibbin et al., 2019). Using the Fo values and MnO concentrations, the slices analysed in this study can be attributed to subgroups based on the framework of McKibbin et al. (2019), outlined in Chapter 1 (Table 3.3). Table 3.2 tabulates the compositional data of olivine from four PMG slices: Sericho, Seymchan, Fukang, and Mount Vernon, and reveals the typical pattern that PMG olivines exhibit decreasing MnO, FeO, and Cr$_2$O$_3$ from cores to olivine-metal or olivine-chromite rims. Concentrations of Na$_2$O, K$_2$O, CaO, Al$_2$O$_3$, and TiO$_2$ are consistently low across all samples. The Na$_2$O component appears to be marginally higher in Fukang, most noticeably at the olivine-metal boundary, than in the other PMGs where it is at or below detection limit (0.02 wt %).
Table 3.2 – Average compositional data (EPMA) for olivines in the studied slices. O is olivine core, O-M is olivine-metal rim, O-C is olivine-chromite rim. The n column denotes the number of analyses over which the average EPMA data is taken. The b.d. values are below detection limit (0.02 wt%).

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86
Table 3.3 – A breakdown of the subgroups of the analysed slices on the basis of EPMA and textural data. Those subgroups in bold are those assigned in this study. Where a subgroup was already attributed (McKibbin et al., 2019) this has been added for comparison. Seymchan is classified as transitional by McKibbin et al. (2019) on the basis of Fe/Mn ratios.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Fo-Fa</th>
<th>MnO (wt%)</th>
<th>Textural class</th>
<th>Assigned subgroup</th>
<th>Lit subgroup (McKibbin)</th>
</tr>
</thead>
<tbody>
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<td>Sericho</td>
<td>F0_88</td>
<td>0.19</td>
<td>AR</td>
<td>Low-MnO</td>
<td>Low-MnO</td>
</tr>
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<td>F0_90.2</td>
<td>0.23</td>
<td>ARF</td>
<td>Low-MnO</td>
<td>Transitional</td>
</tr>
<tr>
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<td>0.31</td>
<td>A</td>
<td>Common</td>
<td>Common</td>
</tr>
<tr>
<td>Mount Vernon</td>
<td>F0_88.3</td>
<td>0.26</td>
<td>A</td>
<td>Common</td>
<td>N/A</td>
</tr>
</tbody>
</table>

3.2.2 Chromite

The PMG chromite analysed in this study is compositionally and texturally variable. Chromite was analysed using SEM and EPMA in 5 samples: Sericho, Seymchan, Fukang, and Mount Vernon, as well as a sample of Brenham chromite from the region defined by Wasson et al. (1999) as chropal (see Chapter 1 for definition). In addition to these samples there are high resolution images of PMGs from the Field Museum and Smithsonian Institution from which chromite was sourced for O-isotope analysis. As a consequence of the nature of many of these additional samples in which the chromite was present, no samples suitable for analysis by EPMA were available and only in some cases was it possible to analyse in situ using SEM. This is due to the samples being either too large and precious to cut to size for EPMA analysis or the chromite availability being insufficient to allow for the required mounting and polishing as well as subsequent oxygen isotope analysis.

3.2.2.1 Texture

Chromite in the analysed PMGs can be cautiously separated by texture into two groups, although the likelihood is that there is a continuum between both “end-members”. The first group is characterised by chromite forming large, globular polycrystalline masses in Seymchan and Brenham (e.g. Wasson et al., 1999; Wasson & Choi, 2003) (see Figure 3.3). These chromite masses can be large and, in some cases, replace the metal in the pallasite textures (e.g. Wasson et al., 1999; Figure 1.8). In contrast to these large masses, PMG chromite can also be smaller and generally more angular. Both Fukang and Mount Vernon exhibit such chromite (see Figure 3.4 and Figure 3.5).
Figure 3.3 – A mosaic of X-ray elemental maps for Cr (in red) overlaid on a mosaic of BSE tiles (in greyscale) from the slice of Seymchan. Note 1) the considerably larger size and extent of this chromite compared with that in Fukang (Figure 3.4) or Mount Vernon (Figure 3.5), and 2) the predominant blob-like morphology of the chromite. This chromite is near end-member in composition and can be seen enclosing olivine in some places in this sample in a manner reminiscent of the chropal texture described in Brenham (highlighted by white arrow) (Wasson et al., 1999). The black arrow highlights chromite edges that are very straight and angular.

The Seymchan chromite (Figure 3.3) is large, near end-member in composition (see section 3.2.2.2), and can be seen encompassing olivine in a manner similar to that in the chropal regions of Brenham (e.g. Wasson et al., 1999). Contrastingly, the Mount Vernon chromite is much smaller and texturally and compositionally most similar to the chromite seen in Fukang (Figure 3.4). The Mount Vernon chromite does show much less prominent reverse zoning of Cr than does Fukang. Whilst the chromite in Seymchan is generally more globular (Figure 3.3) than in Fukang or Mount Vernon (Figure 3.4 and Figure 3.5, respectively), there are also angular edges and corners (see black arrow on Figure 3.3).
Figure 3.4 – A BSE image of the Fukang chromite analysed in this study. The chromite-metal boundary in this sample displays a somewhat more angular texture than that of the Seymchan chromite (see Figure 3.3).

Figure 3.5 – A BSE image of chromite in Mount Vernon. The fractured area on the top-left of the image has probably been created by terrestrial weathering. Note the smaller size of chromites in Figure 3.4 and 3.5 compared to Seymchan.
This difference in texture that may be present between different PMG chromite is not as pronounced as the corresponding compositional variation (section 3.2.2.2) and may be related to the size and orientation of the chromite grains of interest. This raises the possibility that both angular and rounded chromite, or perhaps a continuum of chromite textures, could be present in all PMG but are not consistently sampled. Furthermore, as is the case to a lesser extent for PMG olivine textures, the subdivision of chromite textures is somewhat ambiguous and without detailed image analysis could be dependent on the interpreter’s definition of what is angular and what is not, or differences in chromite orientation relative to sectioning. As a result of these factors, the texture of chromite is not considered when assigning subgroups to PMGs (see section 3.3.3). In order to incorporate the texture into a classification scheme a much bigger selection of much larger samples would be required.

### 3.2.2.2 Composition

Important information about the formation of the chromites in pallasites is recorded in their chemical compositions. A key compositional indicator in this regard is the Al-content, which is highly variable in PMG chromites (see Table 3.4). Chromite in the samples of Brenham, Sericho, and Seymchan has very low Al-contents (< 2 wt%, see Table 3.4). Similarly, on basis of the EDX spectrum in Figure 3.6, Hambleton chromite also contains very little Al. Chromite in the pallasites Fukang and Mount Vernon, however, exhibits appreciable Al-contents (> 7 wt%, Table 3.4). Figure 3.6 shows the stark difference in the Al-content between Hambleton and Fukang chromites. On the basis of this difference the PMGs can be divided into two groups by their chromite Al-contents: a high-Al group consisting of Fukang and Mount Vernon, and a low-Al group containing Seymchan, Sericho, Brenham, and Hambleton (see Table 3.4).

Irrespective of the amount of Al\(_2\)O\(_3\) present, the distribution of Al\(_2\)O\(_3\) across an individual chromite grain remains fairly consistent from core to rim in different meteorites with the notable exception of Fukang (see Figure 3.7), which exhibits a gradual increase in Cr\(_2\)O\(_3\) and corresponding decrease in Al\(_2\)O\(_3\) from core to rim. This is likely due to the relative availability of the two 3+ cations and may record a change in the composition of the surrounding melt over time.
Figure 3.6 – Top - EDX spectrum for a small chip of Hambleton chromite. This spectrum was taken to check mineralogy prior to laser-fluorination and shows the conspicuous absence of a significant Al component. The red arrow shows the location of the Al peak. Bottom - a spectrum from high-Al Fukang chromite is provided for comparison.

Table 3.4 (overleaf) – EPMA average compositional data for the analysed PMG chromites. C = core, C-M rim = chromite-metal rim, C-O rim = chromite-olivine rim. Bren. = Brenham. Bracketed L and S refer to large and small chromite grains respectively if applicable (e.g. Sericho). Seymchan has two core analyses (from two different chromites). The n column denotes the amount of point analyses that make up each average. Measurements listed as b.d. are below the detection limit (0.02 wt%).
<table>
<thead>
<tr>
<th>Details</th>
<th>Bren.</th>
<th>Mount Vernon</th>
<th>Fukang</th>
<th>Seymour</th>
<th>Sericho</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>C-M rim C</td>
<td>C-O rim C-M rim C</td>
<td>C</td>
<td>C-O rim C-M rim C</td>
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<tr>
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<td>15 15 20</td>
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<td>10 12 20</td>
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<td>6.60 6.98 9.58</td>
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<td>6.32 7.70 6.56</td>
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<td>7.42 8.41</td>
<td>10.98 8.55 19.09</td>
<td>1.51</td>
<td>1.39 1.61 1.39</td>
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<tr>
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<td>62.37 61.58</td>
<td>57.86 61.56 49.65</td>
<td>70.01</td>
<td>70.12 70.81 71.57</td>
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<td>0.15 0.18</td>
<td>0.07 0.07 0.08</td>
<td>0.11</td>
<td>0.07 0.11 0.11</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>0.15 0.20</td>
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<td>0.08</td>
<td>0.05 0.10 0.06</td>
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<tr>
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<td>99.10 99.12</td>
<td>98.78 99.49 98.93</td>
<td>99.46</td>
<td>99.89 100.37 100.98</td>
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</table>
The same \( \text{Cr}_2\text{O}_3 \) enrichment is seen at both chromite-olivine and chromite-metal rims. Although it is slightly more prominent in Fukang, a similar but considerably less prominent \( \text{Cr}_2\text{O}_3 \) vs \( \text{Al}_2\text{O}_3 \) profile is actually present in all the analysed chromites. Sericho, Seymchan, and Mount Vernon all show an enrichment in \( \text{Cr}_2\text{O}_3 \) by roughly 1 wt% on chromite rims compared with chromite cores. Again, this enrichment is most pronounced on chromite-metal rims (see Table 3.4) and is likely due to the relative availability of the two 3+ cations. This zoning may be recording a change in the composition of surrounding melt over time, or two-stage growth of the chromite with this initial core crystallising from an earlier and compositionally distinct melt to that from which the chromite rim crystallised (Chapter 4).

![Figure 3.7](image.png)

Figure 3.7 – A profile showing \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) variation between the core and rim of Fukang chromite over a distance of approximately 1.5 mm. Note the covariation evident where Cr increases and Al decreases.

The samples analysed using EPMA can be separated into two groups based on Al-content: those with very low Al, and those with variable amounts of Al. These subgroups correlate with \( \delta^{18}\text{O} \) values for PMG chromites (section 3.3.2) and with existing subgroups defined by olivine texture and composition (see McKibbin et al., 2019). A breakdown of these Al-defined PMG subgroups can be found in Table 3.8 along with the corresponding classification from McKibbin et al. (2019) and
relevant δ¹⁸O isotope data (see section 3.3.2). MgO, MnO, SiO₂, and TiO₂ concentrations are non-zero and remain fairly constant across the analysed PMG chromite samples (Table 3.4).

3.3 Oxygen isotopes in Main-Group pallasites

3.3.1 Olivine

Oxygen isotope analyses were performed on 62 olivine samples from 21 different PMGs using laser-assisted fluorination. Of these samples, 15 olivines from 8 different PMG were analysed in conjunction with corresponding chromite to allow for direct comparison (section 2.5). The mean values for all 62 PMG olivines analysed are: δ¹⁷O = 1.458 ± 0.188 ‰ (2σ), the δ¹⁸O = 3.144 ± 0.364 ‰ (2σ), and the Δ¹⁷O = -0.195 ± 0.018 ‰ (2σ) (Figure 3.8, Table 3.5). This is indistinguishable from the average values for the 15 samples run in tandem with the optimized PMG chromites: δ¹⁷O = 1.510 ± 0.167 ‰ (2σ), δ¹⁸O = 3.248 ± 0.318 ‰ (2σ), and Δ¹⁷O = -0.197 ± 0.014 ‰ (2σ). Where a direct comparison between optimized chromite data and corresponding olivine is required in this thesis (e.g. Figure 3.17, see Chapter 4), it is this 15-sample subset that is used because both phases were run in the same sample trays. This was done to eliminate any risk that instrument drift over time may have affected the data; whilst there is no evidence for any such drift, the precaution was taken to be absolutely sure.

The Δ¹⁷O values obtained for PMG olivine in this study are consistent with those obtained by Greenwood et al. (2006; 2015) when the same fractionation exponent is used (0.5247). The mean Δ¹⁷O reported by Greenwood et al. (2015) is -0.187 ± 0.016 ‰ (2σ). If λ = 0.5247 (as opposed to the 0.5262 used throughout this thesis) is used to calculate Δ¹⁷O for olivine in this study the results are -0.190 and -0.192 for all 62 olivines and the 15 olivines with corresponding chromite analyses respectively with the same standard deviation as above (0.014 ‰ 2σ). The 2σ for δ¹⁷O and δ¹⁸O are greater than those expected from obsidian standards analysed over the duration of this study (n = 52, 0.085 ‰ and 0.160 ‰ for δ¹⁷O and δ¹⁸O respectively, see Chapter 2) by a factor of ~2. This shows that whilst the PMG olivine are not as isotopically homogenous as the internal obsidian standard, which was chosen for its homogeneity, they still show a high degree of isotopic homogeneity.
Table 3.5 (continued overleaf)– The oxygen isotope results for the 62 PMG olivine samples analysed in this study. Those samples in bold are the optimized samples run in conjunction with chromite from the same samples. The samples in italics are those for which no corresponding chromite was run. The UTP sample is the unnamed Tibetan pallasite, 2 SE is 2 standard error of the mean, and \( \Delta^{17}O \) has been calculated using \( \lambda = 0.5262 \). The \( n \) column refers to the number sample reference comparisons that for each sample. Average values for the whole population and the optimized population are given at the bottom of the table with underlined errors of 2 standard deviation. Oxygen isotope results are given in \( \% \).

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<th>PMG</th>
<th>O content wt%</th>
<th>( \delta^{17}O )</th>
<th>2 SE</th>
<th>( \delta^{18}O )</th>
<th>2 SE</th>
<th>( \Delta^{17}O )</th>
<th>2 SE</th>
<th>HCl</th>
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<td>2.894</td>
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<td>30</td>
</tr>
<tr>
<td>Brahin</td>
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<td>1.533</td>
<td>0.014</td>
<td>3.314</td>
<td>0.010</td>
<td>-0.209</td>
<td>0.014</td>
<td>y</td>
<td>30</td>
</tr>
<tr>
<td>Brahin</td>
<td>48.2</td>
<td>1.481</td>
<td>0.016</td>
<td>3.212</td>
<td>0.008</td>
<td>-0.207</td>
<td>0.017</td>
<td>n</td>
<td>30</td>
</tr>
<tr>
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<td>1.397</td>
<td>0.013</td>
<td>3.022</td>
<td>0.006</td>
<td>-0.192</td>
<td>0.013</td>
<td>n</td>
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</tr>
<tr>
<td>Brahin</td>
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<td>1.531</td>
<td>0.018</td>
<td>3.292</td>
<td>0.005</td>
<td>-0.199</td>
<td>0.019</td>
<td>y</td>
<td>60</td>
</tr>
<tr>
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<td>1.483</td>
<td>0.013</td>
<td>3.177</td>
<td>0.004</td>
<td>-0.187</td>
<td>0.013</td>
<td>n</td>
<td>60</td>
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<tr>
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<td>1.660</td>
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<td>3.535</td>
<td>0.005</td>
<td>-0.198</td>
<td>0.018</td>
<td>y</td>
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<tr>
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<td>1.545</td>
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<td>0.011</td>
<td>-0.194</td>
<td>0.013</td>
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</tr>
<tr>
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<td>0.014</td>
<td>3.276</td>
<td>0.006</td>
<td>-0.200</td>
<td>0.014</td>
<td>y</td>
<td>30</td>
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<tr>
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<td>0.007</td>
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<td>0.019</td>
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</tr>
<tr>
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<td>1.482</td>
<td>0.016</td>
<td>3.185</td>
<td>0.005</td>
<td>-0.193</td>
<td>0.016</td>
<td>n</td>
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</tr>
<tr>
<td>Esquel</td>
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<td>1.472</td>
<td>0.012</td>
<td>3.197</td>
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<td>-0.208</td>
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<td>0.013</td>
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<td>60</td>
</tr>
<tr>
<td>Finmarken</td>
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<td>1.538</td>
<td>0.011</td>
<td>3.309</td>
<td>0.004</td>
<td>-0.201</td>
<td>0.011</td>
<td>y</td>
<td>60</td>
</tr>
<tr>
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<td>0.013</td>
<td>3.110</td>
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<td>-0.214</td>
<td>0.013</td>
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</tr>
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<td>0.004</td>
<td>-0.196</td>
<td>0.015</td>
<td>y</td>
<td>60</td>
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<td>0.014</td>
<td>3.406</td>
<td>0.005</td>
<td>-0.200</td>
<td>0.014</td>
<td>y</td>
<td>60</td>
</tr>
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<td>Glorieta Mountain</td>
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<td>1.423</td>
<td>0.014</td>
<td>3.063</td>
<td>0.006</td>
<td>-0.188</td>
<td>0.014</td>
<td>y</td>
<td>60</td>
</tr>
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<td>Glorieta Mountain</td>
<td>38.8</td>
<td>1.408</td>
<td>0.014</td>
<td>3.052</td>
<td>0.005</td>
<td>-0.196</td>
<td>0.013</td>
<td>y</td>
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<tr>
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<td>1.501</td>
<td>0.015</td>
<td>3.213</td>
<td>0.005</td>
<td>-0.187</td>
<td>0.015</td>
<td>y</td>
<td>60</td>
</tr>
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<td>1.590</td>
<td>0.012</td>
<td>3.389</td>
<td>0.005</td>
<td>-0.192</td>
<td>0.013</td>
<td>y</td>
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<td>-0.182</td>
<td>0.012</td>
<td>y</td>
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<td>0.011</td>
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<td>0.005</td>
<td>-0.192</td>
<td>0.011</td>
<td>y</td>
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<tr>
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<td>1.548</td>
<td>0.014</td>
<td>3.320</td>
<td>0.008</td>
<td>-0.197</td>
<td>0.014</td>
<td>y</td>
<td>60</td>
</tr>
<tr>
<td>Imilac</td>
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<td>1.555</td>
<td>0.016</td>
<td>3.356</td>
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<td>-0.209</td>
<td>0.016</td>
<td>y</td>
<td>60</td>
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<td>Imilac</td>
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<td>1.452</td>
<td>0.013</td>
<td>3.151</td>
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<td>-0.205</td>
<td>0.013</td>
<td>y</td>
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<tr>
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<td>1.348</td>
<td>0.009</td>
<td>2.922</td>
<td>0.004</td>
<td>-0.188</td>
<td>0.009</td>
<td>y</td>
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<td>Jepara</td>
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<td>1.224</td>
<td>0.011</td>
<td>2.709</td>
<td>0.005</td>
<td>-0.200</td>
<td>0.012</td>
<td>y</td>
<td>50</td>
</tr>
<tr>
<td>Krasnojarsk</td>
<td>49.2</td>
<td>1.433</td>
<td>0.015</td>
<td>3.109</td>
<td>0.006</td>
<td>-0.201</td>
<td>0.015</td>
<td>n</td>
<td>40</td>
</tr>
<tr>
<td>Krasnojarsk</td>
<td>46.7</td>
<td>1.377</td>
<td>0.014</td>
<td>2.996</td>
<td>0.006</td>
<td>-0.198</td>
<td>0.016</td>
<td>n</td>
<td>40</td>
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<tr>
<td>Lipovsky</td>
<td>47.0</td>
<td>1.371</td>
<td>0.010</td>
<td>2.984</td>
<td>0.008</td>
<td>-0.198</td>
<td>0.010</td>
<td>y</td>
<td>60</td>
</tr>
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<td>2.955</td>
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<td>0.016</td>
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<td>Marjalahti</td>
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<td>1.356</td>
<td>0.015</td>
<td>2.922</td>
<td>0.008</td>
<td>-0.181</td>
<td>0.015</td>
<td>y</td>
<td>60</td>
</tr>
<tr>
<td>Mount Vernon</td>
<td>47.5</td>
<td>1.312</td>
<td>0.012</td>
<td>2.839</td>
<td>0.005</td>
<td>-0.181</td>
<td>0.013</td>
<td>y</td>
<td>60</td>
</tr>
<tr>
<td>Mount Vernon</td>
<td>44.3</td>
<td>1.517</td>
<td>0.012</td>
<td>3.242</td>
<td>0.009</td>
<td>-0.188</td>
<td>0.013</td>
<td>y</td>
<td>40</td>
</tr>
</tbody>
</table>
The δ17O and δ18O values for PMG olivines are comparable to the 2σ precision of δ17O for the obsidian standard (0.021 ‰) suggesting that whilst there may be some minor variability in δ17O and δ18O across different PMG olivine outside of measurement precision, there is no offset from a homogenous fractionation line. The 2σ variation for δ17O and δ18O is slightly greater than for PMG olivines analysed by Greenwood et al. (2015) which gave δ17O and δ18O 2σ values of 0.128 ‰ and 0.236 ‰ respectively. This is perhaps due to the presence of several outliers that can be seen on Figure 3.8 (e.g. Brahin, Jepara, Brenham –Table 3.5) that may be recording small heterogeneities in the oxygen isotope composition of the PMG olivine or it could be because the dataset is almost three times larger than that in Greenwood et al. (2015). There is no correlation between δ18O and oxygen yield (Figure 3.9) suggesting that fractionation during reaction is not the cause of the variability as was observed in PMG chromites prior to optimization of the technique (see section 3.3.2).
Figure 3.8 – Oxygen isotope data for 62 samples of olivine from 21 PMGs analysed in this study. Error bars are 2 standard error of the mean.

Figure 3.9 – Oxygen yield vs \( \delta^{18}O \) for the 62 analysed PMG samples. The black dotted line is a trendline through the data. The very low yields are likely due to weighing errors.
The high degree of Δ^{17}O homogeneity is in direct contradiction to the findings of some recent studies (e.g. Ziegler & Young, 2007; Ali et al., 2013; 2014; 2018). Ali et al. (2018) identified a high-Δ^{17}O (Δ^{17}O = -0.166 ± 0.014 ‰ 2σ) and a low-Δ^{17}O (Δ^{17}O = -0.220 ± 0.009 ‰ 2σ) population offset by around 0.05 ‰. Of the high-Δ^{17}O population, olivine from Acomita, Brenham, Finmarken, Imilac, Marjalahti, and Somervell County has been analysed in this study. Of the low-Δ^{17}O population, olivine from Brahin, Esquel, Fukang, Hambleton, Krasnojarsk, and Seymchan has been analysed as part of this study. The samples from the high-Δ^{17}O group identified by Ali et al. (2018) analysed in this study have an average Δ^{17}O = -0.195 ± 0.019 ‰ (2σ), whilst those in the low-Δ^{17}O subgroup have an average Δ^{17}O = -0.197 ± 0.017 ‰ (2σ). Figures 3.10 and 3.11 provide a comparison of δ^{18}O and Δ^{17}O results between this study and that of Ali et al. (2018), the Δ^{17}O results in the latter study have been recalculated with λ of 0.5262 for direct comparison. There is no resolvable difference between olivines from meteorites in different subgroups as defined by McKibbin et al. (2019) (see Figure 3.12).

Figure 3.10 – A histogram comparing olivine δ^{18}O results of this study with that of Ali et al. (2018). Note the normal distribution of the binned δ^{18}O data reported in this study.
Figure 3.11 – A histogram comparing olivine $\Delta^{17}O$ between this study and that of Ali et al. (2018). Note the single normal distribution of $\Delta^{17}O$ values in this study compared with the two populations in Ali et al. (2018).

Figure 3.12 – A comparison of the oxygen isotope results for PMG olivine subdivided according to McKibbin et al. (2019). This figure does not include results for Jepara, Lipovsky, Santa Rosalia, Somervell County, or UTP as no subgroup is attributed to them by McKibbin et al. (2019). Seymchan is classed as Low-MnO on this figure. The black dashed lines show the mean $\Delta^{17}O$ values for the high-$\Delta^{17}O$ and low-$\Delta^{17}O$ populations reported by Ali et al. (2018).
The common PMG subgroup encompasses analysed samples from Esquel, Glorietta Mountain, Imilac, Marjalahti, Mount Vernon, and Fukang. The average isotope results of the olivine in this subgroup is $\delta^{17}\text{O} = 1.445 \pm 0.163 \%_o$ (2σ), $\delta^{18}\text{O} = 3.123 \pm 0.331$, $\Delta^{17}\text{O} = -0.196 \pm 0.020 \%_o$ (2σ).

Samples analysed for the low-MnO subgroup consist of Brahin, Hambleton, Seymchan, and Brenham. The average results for this subgroup are indistinguishable from the common subgroup olivine which has $\delta^{17}\text{O} = 1.468 \pm 0.208 \%_o$ (2σ), $\delta^{18}\text{O} = 3.165 \pm 0.405 \%_o$ (2σ), and $\Delta^{17}\text{O} = -0.196 \pm 0.015 \%_o$ (2σ). If the olivines run in conjunction with the optimized chromite are separated, the olivine corresponding to high-$\delta^{18}$O chromite (see section 3.3.2) has $\delta^{17}\text{O} = 1.515 \pm 0.127 \%_o$ (2σ), $\delta^{18}\text{O} = 3.268 \pm 0.234 \%_o$ (2σ), $\Delta^{17}\text{O} = -0.203 \pm 0.014 \%_o$ (2σ). The olivines corresponding to the low-$\delta^{18}$O chromite have $\delta^{17}\text{O} = 1.508 \pm 0.184 \%_o$ (2σ), $\delta^{18}\text{O} = 3.239 \pm 0.351 \%_o$ (2σ), $\Delta^{17}\text{O} = -0.194 \pm 0.011 \%_o$ (2σ). These two groups will be examined in more detail when interpreted in terms of their relationship to their respective chromites in Chapter 4.

3.3.2 Chromite

Initially, 21 chromite samples from 9 different PMGs were analysed using laser-assisted fluorination using the same technique as was used for olivines. The results of the (non-optimized) chromite reactions and a comparison with later optimized reactions are shown in Chapter 2. The initial chromite results are not discussed further in the context of PMG interpretation due to the fractionation imparted by the 3 mm beam technique (Chapter 2). Using the 400 µm optimized technique, 15 samples from 8 PMG were analysed (Figure 3.13). The results appear to show either a sparsely sampled $\delta^{18}$O continuum or two resolvable groups (Figure 3.13). If the results are split into two groups on the basis of Al-content, a high-Al/high-$\delta^{18}$O group and a low-Al/low-$\delta^{18}$O group are resolvable (Figure 3.13). The high-$\delta^{18}$O chromite group has $\delta^{17}\text{O} = 0.858 \pm 0.285 \%_o$ (2σ), $\delta^{18}\text{O} = 2.032 \pm 0.552 \%_o$ (2σ), and $\Delta^{17}\text{O} = -0.211 \pm 0.008 \%_o$ (2σ). This high-$\delta^{18}$O group contains four of the analysed samples from two PMGs, Fukang and Imilac. The low-$\delta^{18}$O group has average values: $\delta^{17}\text{O} = 0.333 \pm 0.214 \%_o$ (2σ), $\delta^{18}\text{O} = 1.046 \pm 0.407 \%_o$ (2σ), and $\Delta^{17}\text{O} = -0.218 \pm 0.016 \%_o$ (2σ). The $\Delta^{17}$O values for the two chromite groups are indistinguishable (Figure 3.13). The low-$\delta^{18}$O group contains Brahin, Brenham, Hambleton, Sericho, Seymchan, and an unnamed Tibetan pallasite (currently unclassified).
Figure 3.13 – Oxygen isotope data for optimized PMG chromite displaying the low-δ¹⁸O group (red) and high-δ¹⁸O group (yellow). Errors are 2 standard error of the mean.

Figure 3.14 – A plot of δ¹⁸O vs. Al₂O₃ (wt%) for PMG chromites excluding Hambleton and unnamed Tibetan pallasite for which no EPMA data was obtained. Compositional data from this study (Brenham, Seymchan, Sericho, Fukang) and averages from Bunch & Kiel (1971) (Imilac), and Boesenberg et al. (2012) (Brahin).

Figure 3.14 shows the relationship between Al₂O₃ and δ¹⁸O for the optimized PMG chromites. The low-Al group is relatively restricted in Al₂O₃ content (< 3 wt%) and a range in δ¹⁸O extending from
0.705 to 1.431 ‰. The high-Al group has a much greater range in Al-content (~8 – 20 wt% Al₂O₃) and ranges in δ¹⁸O from 1.737 to 2.416 ‰. As outlined in Chapter 2, prior to the optimization of chromite analysis, the δ¹⁸O of chromite analysed was found to increase with increasing yield. This is not the cause of the δ¹⁸O range observed in the optimized samples (Figure 3.15). Figure 3.15 shows that there is no relationship between oxygen yield and δ¹⁸O in the optimized samples. This suggests that the observed range in δ¹⁸O is not the result of partial reaction or instrument-induced mass-fractionation.

The high-δ¹⁸O chromite is associated with higher Al composition – Imilac average Al₂O₃ = 7.95 wt% (Bunch & Kiel, 1971) and Fukang 8.55 – 19.60 wt% – relative to the low-δ¹⁸O group. This in turn is also reflected in the petrographic subgroups identified by McKibbin et al. (2019). Both high-δ¹⁸O samples, Fukang and Imilac, belong to the common group PMG whilst Brahin, Brenham, Hambleton, Sericho, and Seymchan (the latter defined as transitional by McKibbin et al. (2019) but as low-MnO in this study – see Table 3.3) belong to the low-MnO subgroup. Compositional data is not available.
for the unnamed Tibetan pallasite, although on the basis of this δ¹⁸O difference it seems likely that it is compositionally aligned with the low-MnO subgroup. No oxygen isotope data was obtained for chromite from pallasites sampling the high-FeO subgroup defined by McKibbin et al. (2019) due to lack of availability either of sample material, or chromite (in the case of Rawlinna). Table 3.6 shows the oxygen isotope results for PMG optimized chromite analysed in this study.

Table 3.6 – Oxygen isotope results for optimized PMG chromite analysed in this study. All oxygen results are given in ‰.

<table>
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<th>PMG</th>
<th>Yield %</th>
<th>δ¹⁷O 2 SE</th>
<th>δ¹⁸O 2 SE</th>
<th>Δ¹⁷O 2 SE</th>
<th>HCl? n</th>
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<td>0.293</td>
<td>0.949</td>
<td>-0.206</td>
<td>0.020 n</td>
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<tr>
<td>Brenham</td>
<td>25.5</td>
<td>0.421</td>
<td>1.190</td>
<td>-0.205</td>
<td>0.019 y</td>
</tr>
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<td>Brenham</td>
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<td>0.716</td>
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</tr>
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<td>0.705</td>
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<td>0.021 y</td>
</tr>
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<td>Fukang</td>
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</tr>
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<td>2.416</td>
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</tr>
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<td>1.241</td>
<td>-0.228</td>
<td>0.018 y</td>
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<td>2.169</td>
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<td>0.021 y</td>
</tr>
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<td>1.431</td>
<td>-0.224</td>
<td>0.020 y</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>-0.211</td>
<td>0.016 y</td>
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</table>

3.3.3 Main-Group pallasite farringtonite oxygen isotope composition

Olivine and chromite are not the only pallasite phases that have been measured in this study. A sample of farringtonite (Mg₃(PO₄)₂) from Sericho was also analysed (Figure 3.16). Farringtonite is relatively rare in PMG and probably crystallised late from a pocket of trapped melt (Hsu, 2003). The oxygen isotope composition of this farringtonite is δ¹⁷O = 1.876 ± 0.013 (2 SE), δ¹⁸O = 3.971 ± 0.004 (2 SE), and Δ¹⁷O = -0.211 ± 0.013 (2 SE) (Table 3.7).

Table 3.7 – Oxygen isotope results for the Sericho farringtonite analysed in this study. All oxygen results given in ‰.

<table>
<thead>
<tr>
<th>PMG</th>
<th>Yield %</th>
<th>δ¹⁷O 2 SE</th>
<th>δ¹⁸O 2 SE</th>
<th>Δ¹⁷O 2 SE</th>
<th>HCl? n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sericho</td>
<td>45.3</td>
<td>1.876</td>
<td>3.971</td>
<td>-0.211</td>
<td>0.013 y</td>
</tr>
</tbody>
</table>

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The $\Delta^{17}$O value measured is between those measured for Sericho olivine and chromite and has a higher $\delta^{18}$O than both other phases (see Figure 3.16).

Based on the textural relationship between farringtonite and the other PMG phases, as well as the low rare earth element (REE) concentrations (Davis & Olsen, 1991; Hsu, 2003), it is likely that farringtonite in PMG forms late (Boesenberg et al., 2012), after olivine has crystallised but prior to the solidification of the metal melt.

### 3.4 Re-defining PMG subgroups

Previous studies have provided useful insights into the origin of pallasites through identification of sub-groups within the population based on a number of parameters (Scott, 1977; Wasson et al., 1999; McKibbin et al., 2019). In light of new oxygen isotope data reported in this study, it is desirable to review the definition and members of the sub-groups in the PMG meteorite population. Table 3.8 gives a breakdown of subgroups for PMGs analysed in this thesis.
Table 3.8 – The chromite Al subgroup, δ^{18}O subgroup (see section 3.3.2), and McKibbin et al. (2019) classification of the PMGs for which oxygen isotopes in chromite were analysed in this study. Subgroups denoted with an * were defined using data from Boesenberg et al. (2012), those with an † using data from Bunch & Keil (1971), and those with ‡ were defined by McKibbin et al. (2019). For samples not studied by McKibbin et al. (2019), the classification was applied using EPMA data and/or images of sample slices from the Field Museum compiled during this study. Those with question marks are tentative classifications made on the basis of other characteristics – e.g. Mount Vernon chromite was not analysed for O-isotopes yet on the basis of a) the high-Al content in chromite, and b) the McKibbin classification, it is predicted that it would belong to the high-δ^{18}O chromite subgroup. Samples for which chromite was neither run at optimized conditions for oxygen isotopes or analysed using EPMA are given in italics and are low confidence. In some cases, no information is available. UTP is unnamed Tibetan pallasite.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Chromite Al subgroup</th>
<th>δ^{18}O subgroup</th>
<th>McKibbin et al. (2019) classification</th>
<th>Designation (this thesis)</th>
<th>Conf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brahin</td>
<td>Low-Al*</td>
<td>Low-δ^{18}O</td>
<td>Low MnO</td>
<td>PMG-low</td>
<td>High</td>
</tr>
<tr>
<td>Brenham</td>
<td>Low-Al</td>
<td>Low-δ^{18}O</td>
<td>Low MnO</td>
<td>PMG-low</td>
<td>High</td>
</tr>
<tr>
<td>Fukang</td>
<td>High-Al</td>
<td>High-δ^{18}O</td>
<td>Common</td>
<td>PMG-high</td>
<td>High</td>
</tr>
<tr>
<td>Hambleton</td>
<td>Low-Al</td>
<td>Low-δ^{18}O</td>
<td>Low MnO‡</td>
<td>PMG-low</td>
<td>High</td>
</tr>
<tr>
<td>Imilac</td>
<td>High-Al†</td>
<td>High-δ^{18}O</td>
<td>Common‡</td>
<td>PMG-high</td>
<td>High</td>
</tr>
<tr>
<td>Mount Vernon</td>
<td>High-Al</td>
<td>High-δ^{18}O?</td>
<td>Common</td>
<td>PMG-high</td>
<td>Med</td>
</tr>
<tr>
<td>Sericho</td>
<td>Low-Al</td>
<td>Low-δ^{18}O</td>
<td>Low MnO</td>
<td>PMG-low</td>
<td>High</td>
</tr>
<tr>
<td>Seymchan</td>
<td>Low-Al</td>
<td>Low-δ^{18}O</td>
<td>Transitional/Low MnO</td>
<td>PMG-low</td>
<td>High</td>
</tr>
<tr>
<td>UTP</td>
<td>Low-Al?</td>
<td>Low-δ^{18}O</td>
<td>Low MnO‡</td>
<td>PMG-low</td>
<td>Med</td>
</tr>
<tr>
<td>Marjalahti</td>
<td>High-Al?</td>
<td>High-δ^{18}O?</td>
<td>Common‡</td>
<td>PMG-high</td>
<td>Low</td>
</tr>
<tr>
<td>Esquel</td>
<td>High-Al?</td>
<td>High-δ^{18}O?</td>
<td>Common‡</td>
<td>PMG-high</td>
<td>Low</td>
</tr>
<tr>
<td>Glorietta Mountain</td>
<td>High-Al?</td>
<td>High-δ^{18}O?</td>
<td>Common‡</td>
<td>PMG-high</td>
<td>Low</td>
</tr>
<tr>
<td>Rawlinna</td>
<td>?</td>
<td>?</td>
<td>High-FeO‡</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Pavlodar</td>
<td>?</td>
<td>?</td>
<td>Anomalous‡</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Finnmarken</td>
<td>High-Al?</td>
<td>High-δ^{18}O?</td>
<td>Common‡</td>
<td>PMG-high?</td>
<td>Low</td>
</tr>
<tr>
<td>Lipovsky</td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Jepara</td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Somervell County</td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Krasnojarsk</td>
<td>Low-Al?</td>
<td>Low-δ^{18}O‡</td>
<td>Low MnO‡</td>
<td>PMG-low?</td>
<td>Low</td>
</tr>
</tbody>
</table>
The low-Al PMGs correspond to low-\(\delta^{18}O\) PMGs which, in turn, correspond to the low MnO olivine-based subgroup identified by McKibbin et al. (2019). Similarly, the PMGs with high-Al chromite are also those with high-\(\delta^{18}O\) chromite and are classified as common subgroup (McKibbin et al., 2019). The oxygen isotope composition of olivine from samples defined as high-FeO (Rawlinna) and anomalous (Pavlodar) by McKibbin et al. (2019) was analysed but due to a lack of chromite from these PMGs, no subgroup could be assigned to either sample. The olivine from both Rawlinna and Pavlodar is isotopically unresolvable from that of all other PMGs (see Figure 3.12). Future work investigating isotopic variations in PMGs should seek to fill these gaps.

To simplify the relationships shown in Table 3.8, the following two subgroups are defined:

**PMG-low** – low Al content in chromite (Low-Al subgroup), \(\delta^{18}O\) around 1 ‰ (Low-\(\delta^{18}O\) subgroup – see section 3.3.2), \(\sim F_{88.91}\), and MnO < 0.25 wt%, predominantly rounded olivine but with some angular and some fragmental (low MnO subgroup as defined by McKibbin et al., 2019). This group includes Brahmin, Brenham, Hambleton, Sericho, Seymchan, and the unnamed Tibetan pallasite for which oxygen isotope analyses have been completed on both olivine and chromite.

**PMG-high** – high Al content in chromite (High-Al subgroup), \(\delta^{18}O\) > 1.5 ‰ (see section 3.3.2), and olivine composition of around \(F_{87.88}\), approximately 0.30 wt% MnO, and texturally predominantly angular olivine but with some occasional rounded and fragmental grains (common PMG as defined by McKibbin et al., 2019). This group includes Fukang and Imilac for which oxygen isotope analyses have been completed on both olivine and chromite.

### 3.5 Main-Group pallasite oxygen isotope disequilibrium

Whilst the PMG olivine analysed in this study is homogeneous in \(\Delta^{17}O\) and the chromite is split into two groups with indistinguishable \(\Delta^{17}O\) values, a comparison of the isotopic composition of these phases shows a measurable \(\Delta^{17}O\) offset between the silicate and spinel minerals (see Figure 3.17). The majority of chromite from PMGs plots outside the envelope of possible mass-dependent fractionation from the olivine (see section 2.1.1.2).
Figure 3.17 – Oxygen isotope data for the PMG-low olivine, chromite, and farringtonite analysed in this study. The lighter green diamonds are those PMG olivines that correspond to PMG-low chromite, the darker green are those olivines sampling the PMG-high subgroup. The $\lambda$ used in $\Delta^{17}$O calculation is 0.5262 after Greenwood et al. (2018).

Figure 3.17 shows the oxygen isotope relationship between PMG olivine and other phases. A critical finding of this study is that the PMG chromite isotopic composition falls outside of the envelope of possible mass dependent fractionation relative to coexisting olivine, denoted by the dashed black lines on Figure 3.17. A fractionation line steeper than 0.5305 is required to connect the two phases (Figure 3.17). The envelope of possible mass-fractionation is the area between the asymptotic lower limit for mass-dependent oxygen isotope fractionation, 0.5, and the high-T upper limit, 0.5305 (see Young et al., 2016). In practice, mass-dependent fractionation lines do not approach either value but rather may vary between around 0.525 and 0.529 in high-T igneous systems (Pack & Herwartz, 2014; Young et al., 2016). This range is shown on Figure 3.18. The slope required to connect all analysed olivine and chromite for PMG is $0.5350 \pm 0.0028$ (2 SE) which is >2 standard error above the high-T upper limit and > 4 standard error above the maximum likely high-T $\lambda$, 0.529. In light of the aforementioned compositional differences that allow for subdivision of PMG samples, it is better to separate the PMG $\lambda$ on the basis of the subgroups defined above (section 3.4). For the PMG-high
subgroup (Figure 3.17) the slope is shallower, 0.5312 ± 0.0070 (2 SE) and is within error of the high-
T upper limit and the likely range of high-T mass-fractionation.

Figure 3.18 – Oxygen isotope composition of analysed PMG phases with the envelope of likely high-T mass-
fractionation (0.525 – 0.529). This envelope is between the solid black lines and is highlighted with a blue arrow, the
area between the dotted black lines is the region of all possible, albeit mostly improbable, mass-fractionation (0.5 –
0.5305). A legend for the data can be seen on Figure 3.17.

For the PMG-low subgroup, however, the slope is 0.5364 ± 0.0030 (2 SE) and is approximately 4
standard error above the high-T upper limit and ~5 standard error above realistic high-T igneous
fractionation exponents (0.529). This is impossible through any known igneous process.

Table 3.9 – The fractionation exponents required to connect PMG olivine and chromite by mass-fractionation on Figure
3.17. Those values highlighted in bold are within error of possible high-T mass-fractionation exponents, those in italics
are outside of the possible envelope of mass-fractionation.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>$\lambda$ (high-T limit = 0.5305)</th>
<th>2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>All olivine – All chromite</td>
<td>0.5350</td>
<td>0.0028</td>
</tr>
<tr>
<td>PMG-high</td>
<td><strong>0.5312</strong></td>
<td>0.0070</td>
</tr>
<tr>
<td>PMG-low</td>
<td>0.5364</td>
<td>0.0030</td>
</tr>
</tbody>
</table>
The slopes displayed in Table 3.9 are all above the high-T limit for mass-fractionation. The slope encompassing all PMG olivine and chromite analysed must be treated with caution as there are two distinct chromite isotopic populations. As a result of this, interpretation must be based on the other values. The PMG-low required \( \lambda \) is around 4 standard error above the high-T upper limit and therefore these minerals appear to be in isotopic disequilibrium and may represent two separate and unrelated isotopic reservoirs (see Chapter 4). For the PMG-high samples the slope is less well constrained and has a 2 standard error range from 0.5241 to 0.5383. This encompasses the entire range of expected high-T igneous mass-dependent fractionation (0.525 – 0.529) and therefore these minerals may be in equilibrium or have undergone some degree of equilibration.

3.5.1.1 T-testing of the disequilibrium between \( \Delta^{17}O \) values

To evaluate whether the identified disequilibrium is statistically significant using the steepest possible slope of mass-fractionation, a two-tailed student’s t-test for two independent samples of the \( \Delta^{17}O \) results for optimized olivine and chromite data was conducted having recalculated \( \Delta^{17}O \) with \( \lambda = 0.5305 \) (the high-T upper limit). The null hypothesis was that the populations were the same, the alternative hypothesis was that they were different. The results of the statistical tests are shown in Table 3.10.

Table 3.10 – Details of the two-tailed t-tests carried out on olivine and chromite populations. The XLSTAT plugin for Microsoft Excel was used for computation. P values in italics are statistically significant at SL 0.05 (95%), those in bold are not.

<table>
<thead>
<tr>
<th>Difference</th>
<th>All ol-chr (optimized)</th>
<th>PMG-high (optimized)</th>
<th>PMG-low (optimized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (Observed value)</td>
<td>3.625</td>
<td>0.285</td>
<td>4.269</td>
</tr>
<tr>
<td>[t] (Critical value)</td>
<td>2.048</td>
<td>2.550</td>
<td>2.104</td>
</tr>
<tr>
<td>Degrees of freedom</td>
<td>27.980</td>
<td>5.139</td>
<td>17.664</td>
</tr>
<tr>
<td>p-value (two-tailed)</td>
<td>0.001</td>
<td>0.787</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Significance level alpha</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

If all optimized data are used, there is a statistically significant difference between \( \Delta^{17}O \) (\( \lambda = 0.5305 \)) in co-existing olivine and chromite in PMGs. This difference does not tell the full story, however. Taken further, if the PMG-high are tested in the same manner, there is no statistically significant
difference. In this case, the p-value (0.787) is greater than the significance level alpha (0.05, 95%), meaning that the null hypothesis cannot be rejected. In the case of the PMG-low population, the p-value is < 0.000, meaning that there is a statistically significant difference between the olivine and chromite populations.

A Monte Carlo simulation was conducted on XLSTAT using $10^6$ simulations on the PMG-low minerals with $\Delta^{17}$O recalculated with $\lambda = 0.5305$ in order to establish if the disequilibrium remains statistically significant at larger sample sizes. The computed p-value is 0.001, smaller than the significance levels for both 0.05 and 0.01 (95% and 99% respectively), showing that the presence of a statistically significant disequilibrium in $\Delta^{17}$O at all possible $\lambda$ values is robust.

### 3.6 Oxygen isotope systematics of the Eagle Station pallasite group

In order to help evaluate the significance of the $\Delta^{17}$O disequilibrium observed in PMGs, chromite and olivine from Eagle Station were obtained from NHM Vienna and analysed using the same technique as was employed for PMGs. The Eagle Station pallasites are a separate group to PMGs and belong to the carbonaceous reservoir that is likely from the outer Solar System (Warren, 2011). One replicate of chromite and two of olivine was analysed. The average result of the two olivine analyses is: $\delta^{17}$O = -6.592 ± 0.078 (2$\sigma$), $\delta^{18}$O = -3.033 ± 0.076 (2$\sigma$), and $\Delta^{17}$O = -5.016 ± 0.039 (2$\sigma$).

The blank-corrected chromite result was: $\delta^{17}$O = -7.501 ± 0.034 (2 SE), $\delta^{18}$O = -4.831 ± 0.031 (2 SE), and $\Delta^{17}$O = -4.981 ± 0.032 (2 SE) – see Figure 3.19. This blank correction is required on ES chromite due to the very small amount of sample gas that was liberated from the sample during analysis using the microvolume. The blank correction was applied by taking the measured blank on the morning that ES chromite was analysed (1.46 µg of O$_2$) as the blank contribution for the sample (118.3 µg of O$_2$ was measured). This means that ~1.23% of the recorded O$_2$ was blank. The oxygen isotope composition of this blank is taken to be atmospheric O$_2$ values: $\delta^{17}$O = 12.08 ‰, $\delta^{18}$O = 23.88 ‰, and $\Delta^{17}$O = -0.410 ‰ ($\lambda = 0.5262$) (Luz & Barkan, 2005). The corrected ES value is then calculated by assuming that 1.23% of the measured $\delta$ values was O$_2$ of atmospheric composition and subtracting it from the data. It is not necessary to apply this procedure to the analysed PMG (or IIIAB) chromite because the volume of gas liberated renders the blank contribution insignificant.
The Eagle Station olivine and chromite are connected by a slope of $0.5076 \pm 0.0385$ (2σ), which is within error of all possible mass-dependent fractionation values. The error on this slope is very large due to the low number of data points, and is in fact indistinguishable from a mass fractionation line of 0.5262 considered typical for igneous systems. Future analyses are needed to better constrain this slope in Eagle Station.

3.7 Bushveld Igneous Complex – A terrestrial comparison

In order to evaluate the possibility that some mineral-specific crystal or anharmonic effect is causing the $\Delta^{17}$O offset in PMG-low samples, comparable mineral samples from a broadly analogous high-T terrestrial environment were analysed using laser-assisted fluorination. The samples chosen were from the Bushveld Complex in South Africa and comprised two rock types – norite, and pyroxenite with abundant chromite (Figure 3.20).
Figure 3.20 – Oxygen isotope results from pyroxenite and norite samples from the Bushveld Complex, South Africa. Of key importance is the possible difference in Δ$^{17}$O, although small, between the pyroxenite olivine and Cr-spinel.

Ca-plagioclase and orthopyroxene was analysed from the norite sample, and olivine, orthopyroxene, and chromite were analysed from the pyroxenite sample (see Figure 3.20). Table 3.11 displays the data from these analyses.

The Δ$^{17}$O standard deviation for each individual mineral average is below instrument precision (0.021 ‰) suggesting that each mineral is isotopically homogenous with respect to Δ$^{17}$O. With the exception of the pyroxenite Cr-spinel and olivine, the minerals are also isotopically homogenous within instrument precision for δ$^{17}$O and δ$^{18}$O (δ$^{17}$O = 0.085, δ$^{18}$O = 0.160 (2σ)). The identification of δ$^{18}$O variability greater than instrument precision in olivine and chromite in Bushveld samples is consistent with the same observation for PMG minerals. This may be the result of small-scale sample variability. The slope of mass-fractionation for the pyroxenite whole rock is 0.5298 ± 0.066 (2 SE), consistent with expected high-T mass-fractionation λ values. Similarly, the whole rock λ for norite is 0.5300 ± 0.0255 (2 SE), again within error of high-T mass-fractionation. The error on λ for the Bushveld samples is poorly constrained compared with PMG samples because there is both smaller δ$^{18}$O variability and fewer data points.
Table 3.11 – Oxygen isotope results for Bushveld samples analysed in this study. Errors are 2 standard error of the mean. Rows in bold are average values with errors presented as 2 standard deviation (underlined).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Yield</th>
<th>δ^{17}O 2 SE</th>
<th>δ^{18}O 2 SE</th>
<th>Δ^{17}O 2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norite</td>
<td>Ca Plag</td>
<td>49.4</td>
<td>3.483 0.016</td>
<td>6.687 0.004</td>
<td>-0.031 0.017</td>
</tr>
<tr>
<td>Norite</td>
<td>Ca Plag</td>
<td>48.0</td>
<td>3.499 0.015</td>
<td>6.688 0.005</td>
<td>-0.015 0.015</td>
</tr>
<tr>
<td>Norite</td>
<td>Ca Plag</td>
<td>47.4</td>
<td>3.507 0.014</td>
<td>6.698 0.009</td>
<td>-0.012 0.013</td>
</tr>
<tr>
<td>Norite</td>
<td>Ca Plag</td>
<td>48.9</td>
<td>3.490 0.016</td>
<td>6.692 0.007</td>
<td>-0.025 0.015</td>
</tr>
<tr>
<td>Norite</td>
<td>Opx</td>
<td>47.0</td>
<td>3.241 0.016</td>
<td>6.196 0.004</td>
<td>-0.014 0.016</td>
</tr>
<tr>
<td>Norite</td>
<td>Opx</td>
<td>46.7</td>
<td>3.182 0.020</td>
<td>6.115 0.005</td>
<td>-0.031 0.020</td>
</tr>
<tr>
<td>Norite</td>
<td>Opx</td>
<td>46.4</td>
<td>3.239 0.013</td>
<td>6.202 0.005</td>
<td>-0.020 0.014</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Cr-spinel</td>
<td>31.5</td>
<td>2.353 0.019</td>
<td>4.546 0.006</td>
<td>-0.036 0.019</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Cr-spinel</td>
<td>29.1</td>
<td>2.311 0.016</td>
<td>4.468 0.008</td>
<td>-0.037 0.017</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Cr-spinel</td>
<td>30.2</td>
<td>2.114 0.019</td>
<td>4.083 0.006</td>
<td>-0.033 0.019</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Olivine</td>
<td>45.5</td>
<td>3.024 0.015</td>
<td>5.805 0.004</td>
<td>-0.027 0.015</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Olivine</td>
<td>44.0</td>
<td>3.251 0.015</td>
<td>6.212 0.005</td>
<td>-0.013 0.015</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Olivine</td>
<td>43.3</td>
<td>3.166 0.013</td>
<td>6.050 0.007</td>
<td>-0.013 0.014</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Opx</td>
<td>53.9</td>
<td>3.369 0.017</td>
<td>6.471 0.004</td>
<td>-0.031 0.017</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Opx</td>
<td>39.8</td>
<td>3.371 0.015</td>
<td>6.465 0.005</td>
<td>-0.025 0.015</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Opx</td>
<td>47.4</td>
<td>3.328 0.020</td>
<td>6.395 0.014</td>
<td>-0.032 0.016</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Opx</td>
<td>46.9</td>
<td>3.368 0.014</td>
<td>6.487 0.008</td>
<td>-0.041 0.014</td>
</tr>
<tr>
<td>Norite</td>
<td>Ca Plag</td>
<td>3.495</td>
<td>0.018</td>
<td>6.691 0.008</td>
<td>-0.021 0.015</td>
</tr>
<tr>
<td>Norite</td>
<td>Opx</td>
<td>3.221</td>
<td>0.054</td>
<td>6.171 0.079</td>
<td>-0.022 0.014</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Cr-spinel</td>
<td>2.259</td>
<td>0.209</td>
<td>4.366 0.404</td>
<td>-0.035 0.004</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Olivine</td>
<td>3.147</td>
<td>0.187</td>
<td>6.022 0.334</td>
<td>-0.017 0.013</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Opx</td>
<td>3.359</td>
<td>0.071</td>
<td>6.455 0.071</td>
<td>-0.032 0.011</td>
</tr>
</tbody>
</table>

3.8 Main-Group pallasite chromium isotope composition

Chromium isotope analyses were conducted on olivine samples from 4 PMG at IfP in WWU, Münster (Table 3.12). The olivines analysed were samples from PMG-low meteorites Seymchan and Sericho, and PMG-high meteorite Fukang (see Chapter 2 for details). Hambleton olivine was also prepared but analysis failed because too little Cr was separated during the column chemistry stage. Hambleton was the first olivine sample to be prepared and resultantly its failure helped improve the process by necessitating the addition of multiple stages of column chemistry (see section 2.9). Chromium isotopes were also measured for 5 chromite samples from PMGs. The samples analysed were Hambleton, Fukang, Seymchan, Brenham, and Sericho (Table 3.13). Figure 3.21 shows the chromite and uncorrected olivine Cr isotope results for PMGs analysed in this study. The olivine data are consistent with the results for Brenham olivine ($\varepsilon^{53}$Cr = 0.86 ± 0.08, $\varepsilon^{54}$Cr = -0.06 ±
0.11) from Qin et al. (2010) and when corrected are consistent with Krasnojarsk olivine $\varepsilon^{54}$Cr (-0.72 ± 0.10) analysed by Trinquier et al. (2007).

**Table 3.12 – Cr isotope results for PMG olivines analysed in this study.** Errors are the 95% confidence interval for the measurements except for those underlined which are the 2σ errors for the population.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Phase</th>
<th>Wt (g)</th>
<th>Fe/Cr</th>
<th>$\varepsilon^{53}$Cr ±</th>
<th>$\varepsilon^{54}$Cr ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hambleton</td>
<td>Olivine</td>
<td>0.121</td>
<td></td>
<td>1.69 ± 0.4</td>
<td>0.14 ± 0.5</td>
</tr>
<tr>
<td>Seymchan</td>
<td>Olivine</td>
<td>0.630</td>
<td>695.8</td>
<td>0.54 ± 0.14</td>
<td>0.04 ± 0.08</td>
</tr>
<tr>
<td>Sericho</td>
<td>Olivine</td>
<td>0.948</td>
<td>270.9</td>
<td>1.07 ± 0.1</td>
<td>-0.16 ± 0.19</td>
</tr>
<tr>
<td>Fukang</td>
<td>Olivine</td>
<td>0.707</td>
<td>349.1</td>
<td><strong>1.10</strong> ± <strong>0.94</strong></td>
<td><strong>0.01</strong> ± <strong>0.25</strong></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>Olivine</strong></td>
<td></td>
<td></td>
<td><strong>1.10</strong> ± <strong>0.94</strong></td>
<td><strong>0.01</strong> ± <strong>0.25</strong></td>
</tr>
</tbody>
</table>

**Table 3.13 – Cr isotope results for PMG chromites analysed during this study.** Errors are the 95% confidence interval for the measurements except for those underlined which are the 2σ errors for the population.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Phase</th>
<th>Wt (g)</th>
<th>Fe/Cr</th>
<th>$\varepsilon^{53}$Cr ±</th>
<th>$\varepsilon^{54}$Cr ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hambleton</td>
<td>Chromite</td>
<td>0.00271</td>
<td>-0.15</td>
<td>0.07 ± 0.07</td>
<td>-0.8 ± 0.10</td>
</tr>
<tr>
<td>Seymchan</td>
<td>Chromite</td>
<td>0.00261</td>
<td>0.31</td>
<td>-0.09 ± 0.07</td>
<td>-0.53 ± 0.13</td>
</tr>
<tr>
<td>Sericho</td>
<td>Chromite</td>
<td>0.00254</td>
<td>0.33</td>
<td>0.03 ± 0.07</td>
<td>-0.4 ± 0.13</td>
</tr>
<tr>
<td>Fukang</td>
<td>Chromite</td>
<td>0.00384</td>
<td>0.45</td>
<td>0.04 ± 0.10</td>
<td>-0.57 ± 0.20</td>
</tr>
<tr>
<td>Brenham</td>
<td>Chromite</td>
<td>0.00394</td>
<td>0.30</td>
<td>-0.04 ± 0.07</td>
<td>-0.44 ± 0.13</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>Chromite</strong></td>
<td></td>
<td><strong>-0.04</strong></td>
<td><strong>0.14</strong></td>
<td><strong>-0.49</strong></td>
</tr>
</tbody>
</table>

The Cr isotope system is susceptible to overprinting through both cosmic ray spallation and radiometric decay (see section 2.1.2). Details for correction of these effects can be found in Chapter 2. This spallation and radiogenic overprinting has a negligible effect on chromite Cr isotope composition due to the very high ratio of Cr to spallation target nuclei (e.g. Fe, Ni) in PMG chromite; in contrast the PMG olivine data must be spallation corrected (Figure 3.22). Figure 3.22 shows the spallation correction for PMG olivines using the slope defined by Liu et al. (2019) back to their likely initial $\varepsilon^{54}$Cr composition calculated using the average for PMG chromite. This procedure corrects for the $^{54}$Cr and $^{53}$Cr excess imparted by GCR spallation (Liu et al., 2019). The spallation-corrected olivine values, plotting along the black line representing initial $\varepsilon^{54}$Cr composition in Figure 3.22, were then corrected for $\varepsilon^{51}$Cr excess produced by $^{53}$Mn $\rightarrow$ $^{53}$Cr decay. The positions of the spallation-corrected olivine in Figure 3.22 correlate with the Mn/Cr ratio based on olivine core compositions.
For Seymchan, this value is 16.28, for Fukang it is 8.03, for Brenham it is 6.6 (Qin et al., 2010), and for Sericho it is 0.24. ICPMS analyses of dissolved olivines from Fukang, Seymchan, and Sericho yield Mn/Cr ratios of 8.48, 15.14, and 3.90 respectively, in general agreement with EPMA data. The ICPMS Mn/Cr data was then plotted against $\varepsilon^{53}\text{Cr}$ using the Excel add-in ISOPLOT by J. Schneider at WWU, Münster. This yielded an isochron as shown in Figure 3.23. The good correlation evident in Figure 3.23 suggests that the $\varepsilon^{53}\text{Cr}$ composition of the PMG olivines analysed is directly dependent on their initial $^{53}\text{Mn}/^{52}\text{Cr}$ ratio, the now extinct $^{53}\text{Mn}$ would have been present in the same relative proportion to the stable $^{55}\text{Mn}$ in each sample.

![Graph showing Cr isotope data for olivine and chromite analysed in this study. The chromite is treated as initial composition for both isotope ratios. The olivine is elevated in both $\varepsilon^{53}\text{Cr}$ and $\varepsilon^{54}\text{Cr}$, suggesting both GCR spallation and Mn-Cr decay effects. The Brenham olivine data (smaller blue circle) is from Qin et al. (2010).]
Figure 3.22 – A modified version of Figure 3.21 showing initial olivine composition in ε⁵⁴Cr obtained by back-calculating using a slope of 3.90 (Liu et al., 2019). The initial ε⁵⁴Cr composition of the reservoir is taken from the average chromite composition. Also shown are the GCR slopes projected for Sericho and Fukang chromite. The Brenham olivine data (small blue circle) is taken from Qin et al. (2010).

When PMG chromite is excluded from the calculation, the isochron yields an age of 4557.8 Myr (+5/-2.5), corresponding to ΔTCAI of 10.2 +5/-2.5 Myr. If chromite is included, the age calculated from Mn-Cr systematics is indistinguishable: 4557.6 ± 1.6 Myr, or 10.4 ± 1.6 Myr after CAIs, consistent with the absolute Mn-Cr age for the Omolon PMG of 4558 ± 1.0 Myr (Lugmair & Shukolyukov, 1998). These ages are isotopic closure ages, the significance of which is discussed in Chapter 4.
3.9 Main-Group pallasite Hf-W results

Hf-W analyses were successful on two metal samples from PMG, Fukang and Seymchan. The W isotope results, along with the Pt isotope results used to correct for CRE effects, are shown in Table 3.14. The model ages calculated from these results are shown in Table 3.15 and Table 3.16. CRE correction was carried out by F. Spitzer at WWU, Münster.

The results displayed in Table 3.15 and Table 3.16 show that when corrected for mass-independent effects and cosmic ray exposure, the PMG samples have $\Delta T_{\text{CAI}}$ W isotopic closure ages within error of each other and ranging between 0.5 (± 1.0) and 1.6 (± 1.1) Myr. The data presented in Table 3.16 have been further corrected for nucleosynthetic effects relative to those corrections applied to data in Table 3.15. This further correction yields ages that are problematic to interpret because they apparently pre-date CAIs. However, correction for nucleosynthetic effects is typically only applied to samples from the carbonaceous (outer Solar System) reservoir (F. Spitzer pers. comm, 2019) and...
as such can be discounted for the PMGs which are members of the non-carbonaceous (inner Solar System) reservoir on the basis of $\varepsilon^{54}\text{Cr}$ and $\varepsilon^{50}\text{Ti}$ results (e.g. Warren, 2011). Resultantly, the model ages presented in Table 3.15 are taken to be correct.
Table 3.14 – W and Pt isotope data for Seymchan and Fukang.

<table>
<thead>
<tr>
<th>ID</th>
<th>Sample</th>
<th>W (ppb)</th>
<th>N</th>
<th>$\varepsilon^{182}$W (6/3)</th>
<th>95% confidence</th>
<th>$\varepsilon^{182}$W (6/4)</th>
<th>95% confidence</th>
<th>$\varepsilon^{183}$W (6/4)</th>
<th>95% confidence</th>
<th>$\varepsilon^{184}$W (6/3)</th>
<th>95% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>BU01</td>
<td>Seymchan</td>
<td>309.9</td>
<td>7</td>
<td>-3.32</td>
<td>0.05</td>
<td>-3.42</td>
<td>0.06</td>
<td>-0.07</td>
<td>0.03</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>BU02</td>
<td>Fukang</td>
<td>184.4</td>
<td>5</td>
<td>-3.75</td>
<td>0.10</td>
<td>-3.60</td>
<td>0.06</td>
<td>0.12</td>
<td>0.08</td>
<td>-0.08</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3.15 – W isotope data corrected for mass-independent effects and cosmic ray exposure.

<table>
<thead>
<tr>
<th>ID</th>
<th>Sample</th>
<th>$\varepsilon^{182}$W (6/4)</th>
<th>95% confidence</th>
<th>$\varepsilon^{183}$W (6/4)</th>
<th>95% confidence</th>
<th>$\Delta T$ (CAI)</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BU01</td>
<td>Seymchan</td>
<td>-3.31</td>
<td>0.10</td>
<td>0.04</td>
<td>0.07</td>
<td>1.6</td>
<td>1.1</td>
</tr>
<tr>
<td>BU02</td>
<td>Fukang</td>
<td>-3.43</td>
<td>0.10</td>
<td>0.23</td>
<td>0.10</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3.16 – W isotope data corrected for mass-independent effects, cosmic ray exposure, and nucleosynthetic effects.

<table>
<thead>
<tr>
<th>ID</th>
<th>Sample</th>
<th>$\varepsilon^{182}$W (6/4)</th>
<th>95% confidence</th>
<th>$\varepsilon^{183}$W (6/4)</th>
<th>95% confidence</th>
<th>$\Delta T$ (CAI)</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BU01</td>
<td>Seymchan</td>
<td>-3.36</td>
<td>0.10</td>
<td>0.04</td>
<td>0.07</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>BU02</td>
<td>Fukang</td>
<td>-3.75</td>
<td>0.18</td>
<td>0.23</td>
<td>0.10</td>
<td>-2.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>
4 MAIN-GROUP PALLASITE INTERPRETATION

4.1 Introduction

The results of petrological and isotopic analyses on PMG samples conducted in this study are presented in Chapter 3. This chapter evaluates those data presented in Chapter 3 in the context of PMG formation environments and processes active in the early history of the PMG parent body.

4.2 Petrology

4.2.1 Olivine compositional and textural relationships

The olivine compositional and textural relationships both between different PMG samples and within individual PMGs may prove crucial in understanding their formation histories. The primary olivine shape in pallasites appears to be the angular (A), euhedral olivine (McKibbin et al., 2019) that can form visible triple-junctions in 2-dimensions (see Figure 3.1 – right). This texture is subsequently invaded by pervasive FeNi metal which exploits channels of flow along grain boundaries, however in some cases the olivine forms large olivine clusters (e.g. Boesenberg et al., 2012). The progressive invasion of metal seems to be the process by which olivine clusters are broken up, which in turn allows the formation of rounded (R) olivine grains during cooling. This probably occurs by the modification of pre-existing angular olivine crystals following their isolation in an Fe-Ni-S melt (e.g. Solferino et al., 2015; Solferino & Golabek, 2018). The final texture, fragmental (F) olivine, is probably formed by the mechanical break-up of the other two olivine types, possibly through their interaction with impact-induced shock waves (Wetherill, 1975; Boesenberg et al., 2012) or perhaps a violent ferrovolcanic process (e.g. Abrahams & Nimmo, 2019). Table 4.1 lists key compositional and textural indicators for PMGs. Data from this table are presented in Figure 4.1 and Figure 4.2.

The compositional metric used to evaluate olivine in this study is the Fo number. The first olivines to crystallise from a given melt composition are more Mg-rich than those crystallising later (Deer et al., 1966) meaning that the Fo-Fa value has utility in establishing how “primitive” particular olivine crystals are. The smaller radius of Mg$^{2+}$ relative to Fe$^{2+}$ means that the oxygen-cation bond is stronger in the former and it has a much higher melting temperature (Deer et al., 1966). The olivine in PMG is typically ~Fo$_{85}$–Fo$_{90}$ and therefore the liquidus temperature will be slightly lower than for
endmember forsterite. The Fo composition of PMG olivines are consistent with dunite and peridotite olivine compositions on Earth (Deer et al., 1966); additionally, olivine forming at low-pressure tends to be slightly more Fe-poor than that forming at high-pressure (Ford et al., 1983). This may be a contributing factor to the high Fo compositions of analysed PMG samples (see Chapter 3) as pressure conditions in the PMG parent body would have been considerably lower than mantle conditions on Earth (see section 4.6.3.2). The high Fo compositions, in combination with a host of other factors – the relatively slow cooling rates (e.g. McKibbin et al., 2016; Donohue et al., 2018; Yang et al., 2010) being a crucial one – strongly suggest that the olivine portion of PMG formed at depth and probably represents the mantle of its parent body.

In order to understand the relationship between olivine composition and depth in the PMG parent body, it is important to establish its relationship with cooling rate as more shallowly emplaced material will have cooled faster (Figure 4.1). The distribution of the data on Figure 4.1 indicates that at least when cooling through low temperatures (~870–990 K), there was no relationship between the PMG formation depth, for which metallographic cooling rate is presumably a proxy, and relative abundance of either angular or rounded olivine textures. There does appear to be a more restricted range in cooling rates for R and ARF (those with angular, rounded, and fragmental olivine) meteorites relative to angular PMGs. This may be evidence that PMGs with secondary olivine textures (e.g. R, F) are localised in part of the PMG parent body although data for a wider selection of samples is needed to verify this. There is also no compelling evidence for a relationship between olivine Fo composition and metallographic cooling rate, at least over the temperature range ~873–993 K (Yang et al., 2010; see Figure 4.1), suggesting that any relationship between mantle composition and depth in the PMG parent body was either not preserved or is complex. The textural classification does not take into account the absolute numbers of angular and rounded grains in given meteorites but rather the dominant texture. This means that there may be a relationship that remains unnoticed between the absolute amount of olivine grains of a certain texture and cooling rate. This would be very difficult to investigate without very large sample sizes and was impossible to do effectively in this study.
Table 4.1 – Olivine textural and compositional data, metallographic cooling rate, and metal Au composition for a range of PMGs. Data calculated or taken from the following references, listed as superscripts: 1Boesenberg et al. (2012). 2McKibbin et al. (2019). 3Yang et al. (2010). 4Wasson & Choi. (2003). 5Ali et al. (2018). 6This study (bold). 7van Niekerk et al. (2007). 8Metbull photo gallery. 9Scott (1977). 10DellaGiustina et al. (2019). 11Boesenberg et al. (2018). The predominant olivine textures are angular (A), rounded (R), and fragmental (F) or some combination of these textures.

<table>
<thead>
<tr>
<th>Meteorite name</th>
<th>Predominant olivine texture</th>
<th>Olivine composition (Fo)</th>
<th>Metallographic cooling rate (K Myr(^{-1}))</th>
<th>2σ Au in metal (µg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acomita</td>
<td>AF</td>
<td>87.7(^5)</td>
<td></td>
<td>2.73(^4)</td>
</tr>
<tr>
<td>Admire</td>
<td>AF</td>
<td>87.7(^1), 87.9(^9)</td>
<td></td>
<td>2.91(^4)</td>
</tr>
<tr>
<td>Ahumada</td>
<td>A</td>
<td>88.6(^1), 88.0(^5), 88.4(^9)</td>
<td></td>
<td>2.23(^4)</td>
</tr>
<tr>
<td>Albin</td>
<td>F</td>
<td>87.5(^9)</td>
<td></td>
<td>2.77(^4)</td>
</tr>
<tr>
<td>Brahin</td>
<td>ARF</td>
<td>88.1(^1), 88.4(^5), 88.3(^9)</td>
<td></td>
<td>3.02(^4)</td>
</tr>
<tr>
<td>Brenham</td>
<td>R</td>
<td>87.6(^1), 87.8(^5)</td>
<td>6.5(^3)</td>
<td>1.4(^3)</td>
</tr>
<tr>
<td>Dora</td>
<td>A</td>
<td>87.1(^9)</td>
<td>4.7(^3)</td>
<td>1.9(^3)</td>
</tr>
<tr>
<td>Esquel</td>
<td>A</td>
<td>88.1(^1), 88.4(^5), 88.3(^9)</td>
<td></td>
<td>2.05(^4)</td>
</tr>
<tr>
<td>Finmarken</td>
<td>A</td>
<td>86.8(^8)</td>
<td>18.2(^3)</td>
<td>2.4(^3)</td>
</tr>
<tr>
<td>Fukang</td>
<td>AR</td>
<td>86.0(^6), 86.1(^5)</td>
<td></td>
<td>2.55(^10)</td>
</tr>
<tr>
<td>Giroux</td>
<td>A</td>
<td>89.0(^5), 89.2(^9)</td>
<td>6.8(^3)</td>
<td>1.5(^3)</td>
</tr>
<tr>
<td>Glorieta Mountain</td>
<td>A</td>
<td>86.3(^1), 86.8(^9)</td>
<td>2.5(^3)</td>
<td>1.4(^3)</td>
</tr>
<tr>
<td>Huckitta</td>
<td>F</td>
<td>87.7(^2), 87.3(^9)</td>
<td></td>
<td>1.72(^4)</td>
</tr>
<tr>
<td>Imilac</td>
<td>AF</td>
<td>86.9(^1), 87.3(^5), 87.7(^9)</td>
<td></td>
<td>2.25(^4)</td>
</tr>
<tr>
<td>Krasnojarsk</td>
<td>R</td>
<td>87.6(^5), 87.8(^9)</td>
<td></td>
<td>2.41(^4)</td>
</tr>
<tr>
<td>Marjalahti</td>
<td>AF</td>
<td>88.8(^1), 88.1(^9)</td>
<td></td>
<td>1.84(^4)</td>
</tr>
<tr>
<td>Molong</td>
<td>AR</td>
<td>88.6(^1), 88.1(^9)</td>
<td></td>
<td>2.55(^4)</td>
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<tr>
<td>Mount Vernon</td>
<td>A</td>
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<td></td>
<td>2.51(^4)</td>
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<tr>
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<td>AF</td>
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<td>2.57(^4)</td>
</tr>
<tr>
<td>Otinapa</td>
<td>AF</td>
<td>86.3(^1), 86.5(^9)</td>
<td></td>
<td>2.57(^4)</td>
</tr>
<tr>
<td>Pavlodar</td>
<td>R</td>
<td>87.8(^1), 87.3(^9)</td>
<td></td>
<td>1.13(^4)</td>
</tr>
<tr>
<td>Phillips County</td>
<td>AR</td>
<td>82.1(^9)</td>
<td></td>
<td>4.03(^4), 2.81(^4)</td>
</tr>
<tr>
<td>Rawlinna</td>
<td>R</td>
<td>84.1(^9)</td>
<td></td>
<td>2.30(^4)</td>
</tr>
<tr>
<td>Sericho</td>
<td>AR</td>
<td>87.8(^8)</td>
<td></td>
<td>2.52(^1)</td>
</tr>
<tr>
<td>Seymchan</td>
<td>ARF</td>
<td>90.0(^6), 88.4(^5)</td>
<td>7.1(^3)</td>
<td>1.5(^3)</td>
</tr>
<tr>
<td>South Bend</td>
<td>A</td>
<td>87.7(^5)</td>
<td>8.9(^3)</td>
<td>1.4(^3)</td>
</tr>
<tr>
<td>Springwater</td>
<td>R</td>
<td>82.0(^1), 82.5(^5), 82.1(^9)</td>
<td>5.1(^3)</td>
<td>1.4(^3)</td>
</tr>
<tr>
<td>Thiel Mountains</td>
<td>R</td>
<td>87.4(^9)</td>
<td></td>
<td>2.67(^4)</td>
</tr>
</tbody>
</table>
Figure 4.1 – Fo composition of olivine vs. low-T metallographic cooling rates for angular olivine dominated, rounded olivine dominated, and mixed (plus fragmental) pallasites. Errors are 2 sigma uncertainty. Cooling rate data from Yang et al. (2010). The Fo number for the samples was calculated from data from Boesenberg et al. (2012) and Ali et al. (2018), as well as microprobe analyses from this study. The pallasites in the rounded group (R) are Brenham and Springwater, the angular group (A) contains Glorieta Mountain, Giroux, Finmarken, and South Bend. The ARF (angular, rounded, fragmental) sample is Seymchan. The Seymchan datapoint with the thick border has a Fo calculated using the EPMA data from this study. The Fo number of the Seymchan with a thin border has been calculated using data from Ali et al. (2018).

Figure 4.2 shows the relationship between olivine composition and evolution of the corresponding metallic melt for the same PMG samples shown in Figure 4.1. Figure 4.2 shows a negative correlation between the degree of melt evolution, for which Au abundance is a proxy (see section 1.2.1.1), and the Fo of olivine for 8 PMGs. In contrast to the similar cooling rates observed for ARF and R samples in Figure 4.1, the two textural subgroups plot at either end of the metal evolution trend on Figure 4.2. This relationship is not evident in the more complete dataset displayed on Figure 4.3. The more evolved metal appears to be preferentially associated with olivine that has lower Fo, i.e. is more Fe-rich. Given that the more evolved metal also typically exhibits slower cooling rates (Yang et al., 2010; Boesenberg et al., 2012) it seems possible that olivines with lower Fo formed at greater
depth. This could be explained if more Fe relative to Mg was available for incorporation into olivine at greater depths in the mantle, as may be the case in a differentiated body containing an Fe-rich core, although it is not clear to what extent Fe would be exchanged between immiscible silicate and metal melts. The propensity for olivine forming at higher pressure to be more Fe-rich than that forming at low pressure (Ford et al., 1983) may also be a causal factor.

The relationship on Figure 4.2 could also be explained if the PMG olivines equilibrated over time with the Fe metal. The olivines that were present in the FeNi metal melt for longest would have equilibrated to a greater degree and exhibit more Fo-poor compositions. If the metal were crystallising, the more evolved melt would then contain olivines that had a greater timescale to equilibrate, giving rise to the observed distribution. Another possible cause could be crystallisation of FeO by McKibbin et al. (2019). Seymchan appears twice. A key is displayed on Figure 4.1.
under different $fO_2$ conditions. Olivines such as those in Springwater (see Figure 4.2) with lower Fo (higher Fe-content) may have formed in a more oxidising environment. This is further supported by the fact that the metal associated with high-FeO PMGs contains higher Ni contents (McKibbin et al., 2019) which suggests Fe may have been lost from the metal to the olivine. Whilst this is a possibility, it seems counter-intuitive that $fO_2$ would increase with depth during the differentiation of a planetesimal. When a wider selection of PMGs are considered, the trend identified in Figure 4.2 appears to be most prominent in PMGs with angular olivine and is less well defined in other textural groups (see Figure 4.3). The relationship between olivine composition and Au content in metal for the entire population of Table 4.1 is shown in Figure 4.3.

Figure 4.3 – Olivine composition (Fo) vs. Au of metal ($\mu$g g$^{-1}$) for all PMGs in Table 4.1. Again, the data highlights a broad negative relationship between melt evolution (increasing to the right on this figure) and Fo composition of PMG olivine. Some samples have duplicate Fo values from different literature sources (e.g. Imilac) whilst Phillips County has duplicated Au values. As a result of this, several samples appear more than once. PAV indicates Pavlodar samples referenced in the text, SPR indicates Springwater, and RAW indicates Rawlinna.

Figure 4.3 shows a similar though less well-defined trend to the subset of data presented in Figure 4.2 and again suggests that there is a tendency for PMGs olivine with higher Fo values to be
associated with less evolved PMG metal. At first glance, it appears that the rounded olivines may have an offset trend compared with other olivine textures however there is a core of rounded olivines that plot near the centre of the negative trend defined by the other textures and the rounded olivine data contains Rawlinna as well as three duplicates of Springwater which are defined as High-FeO PMG by McKibbin et al. (2019). The rounded olivine data also includes two duplicates of Pavlodar which has anomalously low Au contents (Table 4.1). Overall, the rounded PMGs seem to span almost the whole range of both olivine composition and metal Au contents. The reported correlation between fragmental olivine abundance and metal melt evolution (Boesenberg et al., 2012) is not seen on Figure 4.2 or Figure 4.3. Figure 4.3 shows a general negative trend between olivine composition and metal melt evolution for PMGs dominated by angular olivine. Deconvoluting the data by simplifying the subgroups on Figure 4.3 can help identify relationships between metal composition and olivine texture. Figure 4.4 displays a simplified diagram where angular olivine (primary texture) has been left as in Figure 4.3 but AR has been combined with R, and any samples with any fragmental olivine (ARF, AF) have been assigned to the F group.

Figure 4.4 shows that angular PMG olivines form a well-defined negative trend between olivine composition and metal melt evolution. This trend is not readily apparent for any PMGs containing rounded olivine (R) or where fragmental olivine (F) is present. This suggests that the Fo composition of the primary angular olivine decreases with increasing degrees of melt evolution (increasing Au content) and therefore more primitive olivine is associated with more primitive metal in PMGs, at least initially. Subsequent processes that give rise to the rounding of primary angular and fragmental olivine (e.g. Solferino et al., 2015; Solferino & Golabek, 2018) and similarly the fragmentation of both angular and rounded olivine appear to add considerable scatter to the initial angular trend. This could be caused by localised movement of the metal melt induced by impact shock in the case of PMGs with fragmental olivine, or by variable metal-hosted non-metal (e.g. S) contents – which affect Au partitioning behaviour (see Figure 1.2) – in the case of PMGs where rounding has occurred. However, both of these suggestions are highly speculative and would require further detailed study of olivine texture vs. metal composition to verify.
Figure 4.4 – A simplified version of Figure 4.3 with PMGs combined into 3 groups. The angular olivine PMG is the primary olivine texture and so remains unchanged. The dotted region highlights the negative relationship between olivine Fo and metal Au in angular PMGs. All PMG with any fragmental olivine at all (including ARF, AF) have been combined into the F subgroup. Any PMG with any rounded olivine (including AR) except ARF samples have been combined into the R subgroup.

The reported relationship between the least fractionated metal and an increased abundance of fragmental olivine (Boesenberg et al., 2012) might be evidence that fragmented olivine formation is more sensitive to formation environment than are rounded or angular olivine. This relationship is not obvious on Figure 4.3 and Figure 4.4. This might be because the trend identified by Boesenberg et al. (2012) refers specifically to a higher proportion of PMGs with less fractionated metal containing significant fragmental olivine than those with fractionated metal. This does not mean that those samples containing a portion of fragmental olivine will be classified as fragmental pallasites because whilst they may contain a readily identifiable portion of fragmental olivine, it may not be the dominant texture. Similarly, different abundances of fragmental olivine in different samples of the same meteorite could also serve to complicate this trend.
If the fragmental olivine is the by-product of energetic mixing of metal and silicate or is formed by impact shock waves, it seems reasonable that it would be more abundant closer to the mixing or impact site and therefore should show a relationship with metallic cooling rates. It may also show a relationship with metal composition if the degree of metal melt evolution varies over the area proximal to the impact/mixing site. In light of the reported correlation between fragmental olivine and degree of metal melt evolution as well as the discovery that primitive metal cooled faster than evolved metal (Boesenberg et al., 2012), it follows that fragmental olivine should be preferentially associated with more rapidly cooled PMGs and therefore more shallowly emplaced samples. This is consistent with the formation of fragmental olivine by impact shockwaves as has been suggested previously (e.g. Wetherill, 1975) and is not consistent with ferrovolcanism as a mechanism for their formation (e.g. Abrahams & Nimmo, 2019) as the latter model would likely result in a higher proportion of fragmental olivine at greater depth where the energy would be greatest. A direct comparison of metal melt evolution (Au) and metallographic cooling rate can be seen in Figure 4.5.

Figure 4.5 – Au content of metal (µg g⁻¹) vs. metallographic cooling rate (K Ma⁻¹) for PMGs. See Table 4.1 for refs. Finmarken.is denoted by FIN.
Figure 4.5 shows a general negative relationship between degree of metal melt evolution (µg g\(^{-1}\) Au) and the low temperature (~873–993 K) metallographic cooling rate suggesting that more evolved melt cooled slower than less evolved melt, consistent with reported Ir vs cooling rate observations (Boesenberg et al., 2012). This suggests that more evolved melt cooled at greater depths and is compliant with inward crystallisation of PMG metal. An exception to this trend is Finmarken which has an exceptionally high cooling rate for a PMG (Table 4.1, Figure 4.5).

In addition to textural and wider olivine compositional considerations, elemental variations across PMG olivine samples also have the potential to provide key information about their formation environment. Table 3.2 shows decreasing abundances of MnO, FeO, and Cr\(_2\)O\(_3\) from core to rim in analysed olivine samples. These decreases could be due to progressive lessening of Mn, Fe, and Cr abundances in the melt. There are several possible reasons for this, firstly the abundance of these elements might decrease as they were continually incorporated into olivine crystal growth. An alternative possibility is that it is caused by the crystallisation of other mineral phases, perhaps chromite, during olivine grain growth. In the latter case, the newly crystallising minerals would preferentially incorporate the Mn, Fe, and Cr depending on their partition coefficients. This would lead to an apparent decrease in the abundance of these elements toward the rims of olivine crystals.

A third possibility is that this decrease records melt escape. If the olivine crystallised from a silicate melt containing these elements, or was a restite in such a silicate melt (see section 4.6.3), then late stage replacement of that fluid with the metal melt might also give the observed zoning due to the reduced availability of Mn and Cr. In this scenario, the trend in Fe content requires a slightly different interpretation as the PMG metal is not Fe-poor. Despite the high-Fe content of the metal melt, \(f_{O_2}\) conditions may have significantly decreased with the replacement of silicate melt by the reduced metal melt (see section 4.6.2) resulting in lower amounts of Fe incorporation into the olivine. If pockets of silicate melt containing Si, O, and Mg, remained adsorbed on olivine grain boundaries and incorporated Fe from the surrounding metallic melt, the observed zoning in the olivine could be explained. This is similar to the proposed mechanism for generating phosphoran olivine overgrowths (e.g. Boesenberg et al., 2012). Alternatively, some degree of re-equilibration between crystallised olivine and newly-injected metallic melt may have exchanged Mg with Fe between olivine rims and the metallic melt. Crystallisation of chromite from the melt surrounding the olivine would increase...
the Mg/Fe ratio in the melt as the Fe would be incorporated into crystallising chromite. This could give rise to the observed difference between Fe and Mg contents across olivine grains.

4.2.2 Chromite compositional and textural relationships

In addition to the olivine, chromite textural and compositional indicators have the potential to provide insight into PMG formation environments. The difference between the smaller, perhaps more angular chromites (e.g. Figure 3.4 and Figure 3.5) and the larger globular chromites as seen in Seymchan (e.g. Figure 3.3) and Brenham (e.g. Wasson et al., 1999) could be the result of crystallisation of the former from a silicate melt or silicate-influenced metallic melt, whilst the latter crystallised from the FeNi metal. It is difficult to defend this suggestion, especially as some IIIAB irons exhibit very angular chromites (e.g. Fehr & Carion, 2004) despite clearly having crystallised from FeNi metal. Combined with the fact that the relative rarity of PMG chromites may create sampling biases, this means that interpretations based on chromite textural differences may be unreliable and interpretation of chromite petrogenesis based on a textural evidence should be done cautiously and not without accompanying compositional data. With this in mind, a summary of the Al abundance of chromite cores based on literature data and analyses in this study is shown in Figure 4.6 (data available in Appendix 3).

The slight difference in Al content between PMG-low samples from literature and those from this study (Figure 4.6) is likely attributable to the different samples analysed. If there is an instrument-induced difference between the PMG-low Al and Cr contents between this study and literature sources, it does not affect the interpretation as there is still a clear offset between PMG-low and PMG-high data. The PMG-low samples analysed in this study consist of Sericho, Seymchan, and Brenham, only the latter of which is included in the literature data (see Appendix 3). As described in Chapter 3 when defining PMG subgroups, there is a clear distinction between the chemical trends of PMG-low and PMG-high chromite visible on Figure 4.6. The Al abundance results indicate that the chromite in PMGs appears to have crystallised out of the metal, although some chromite likely crystallised in the presence of at least some silicate melt. The near end-member composition of some PMG chromite and its similarity to magmatic iron meteorite chromite (see Figure 4.6, section 5.2) appears broadly correlated with prevailing globular textures (e.g. Seymchan, Brenham) and strongly
suggests crystallisation from the metal in the absence of appreciable amounts of silicate melt. Whilst almost end-member, the greater spread in PMG-low chromite Al-content than in IIIAB irons (Figure 4.6) does suggest that there may have been small quantities of Al-bearing silicate melt present during chromite crystallisation.

Figure 4.6 – A cross plot showing the chromite compositions of various PMG subgroups compared to IIIAB irons. The spinel component (3+ cation) co-varies. Note the PMG-low subgroup have near end-member, IIIAB-like compositions consistent with an absence of silicate melt presence during crystallisation. The PMG-high subgroup, however, exhibits a wide range of Al\(_2\)O\(_3\), suggesting variable abundance of silicate melt during crystallisation. Data from 1) this work (larger symbols), 2) Wasson et al. (1999), 3) Boesenberg et al. (2012), 4) Bunch & Kiel (1971). Appendix 3 tabulates these data.

The PMG-low chromite perhaps exhibits a weak positive relationship between Cr\(_2\)O\(_3\) and Al\(_2\)O\(_3\) on Figure 4.6 although this could be due to a small offset between EPMA data from this study and literature data, as discussed above. If there is a slight relationship, it suggests that the metallic melt from which PMG-low chromite crystallised varied slightly in Cr and Al contents. In this case, the higher abundance of Al\(_2\)O\(_3\) with Cr\(_2\)O\(_3\) may be a crystallisation trend as both cations are incompatible in crystallising FeNi metal; if this is the case, it is unclear what cations are replacing Al and Cr in the
spinel 3+ site. If this is the case it is present over a very restricted compositional range. In contrast to the PMG-low chromite, the chromite in Fukang and to a lesser degree, Mount Vernon, contains appreciable Al$_2$O$_3$ (see Table 3.4) which is interpreted as a tracer for silicate melt presence during formation. This difference between PMG-low and PMG-high chromite also encompasses literature data and is clear on Figure 4.6. There is no relationship between Al content and Mg content evident in PMG chromite (Figure 4.7).

As highlighted in Figure 4.6 for PMG-low and PMG-high subgroups, the PMGs with rounded olivine (PMG-low) tend to have correspondingly low chromite Al contents (Figure 4.7). Given that the primary texture is likely angular olivine, this may be evidence that the rounding of olivine and the crystallisation of Al-poor chromite are linked, perhaps occurring in an Al-poor, S-bearing (e.g.}

![Figure 4.7](image-url)
Solferino et al., 2015; Solferino & Golabek, 2018) metal melt. Whilst the Fukang sample analysed in this study contained exclusively angular olivine, rounded olivine has been reported (McKibbin et al., 2019) and therefore Fukang does not adhere to this general pattern on Figure 4.7. The suggestion that PMG chromite did crystallise from the metal at a later time than olivine crystallisation is borne out in Figure 4.8, which shows no relationship between MgO content of PMG chromite and olivine Fo composition. There is a non-zero MgO content in all analysed and reported PMG chromites which suggests that either some Mg-bearing melt was present during their crystallisation, or perhaps is due to the proximity of molten metal and ~Fo$_{85-90}$ olivine from which Mg could be incorporated.

The injection of hot metallic melt into the pallasite-forming environment may have instigated some chemical re-equilibration between the olivine and metal as well as allowing for olivine rounding. If Mg and Fe exchanged between the olivine and the metal melt, it would give rise to the observed reverse zoning in olivines as well as provide some Mg for incorporation into crystallising chromites. The MgO content of IIIAB chromites, which formed in the absence of both silicate melt and silicate minerals, is essentially zero (see Appendix 3).

Figure 4.8 – Olivine composition (Fo) vs. MgO content in chromite for PMGs for which both data is available. Large symbols are data from this study, small symbols are literature data from Boesenberg et al. (2012), Wasson et al. (1999), and Scott (1977). The colours again denote the predominant texture of the olivine in each pallasite. Appendix 3 and Table 4.1 tabulate these data.
Figure 4.9 – Olivine composition vs. $\text{Cr}_2\text{O}_3$ content of co-existing chromite for PMGs where both data is available. Large symbols denote data from this study (except Brenham olivine composition), small symbols are literature data from Boesenberg et al. (2012), Wasson et al. (1999), and Scott (1977). The colours again denote the predominant texture of the olivine in each pallasite. The sample on the extreme left of the figure is Fukang. The dashed black lines separate the PMGs where rounded olivine has been reported from those where angular, and/or fragmental olivine is reported. The green trendline is for all data, the red trendline is for all data excluding Fukang. The $R^2$ values are colour coded to match the lines they describe. Appendix 3 and Table 4.1 tabulate these data.

There is no relationship between olivine composition (Fo) and MgO in chromite (Figure 4.8). A relationship might be expected had the minerals crystallised and incorporated Mg from the same melt; the Mg abundance in olivine appears entirely independent of that in co-existing chromite. This supports the interpretation that olivine was already solid during the silicate-metal mixing event as the composition of crystallising chromite is unaffected by the olivine Fo composition. There does appear to be a relationship between olivine Fo composition and chromite $\text{Cr}_2\text{O}_3$ (Figure 4.9) although this may be largely defined by the Fukang data point. Figure 4.9 shows a positive correlation between the $\text{Cr}_2\text{O}_3$ content of PMG chromite and the Fo composition of the co-occurring olivine, although when Fukang is ignored this trend is not obvious. If all data points are included, the trend is statistically significant (significance $F = 0.01$, SL = 0.05), although if Fukang is excluded this drops...
to being significant at the 90 % level (F = 0.09). Also visible is the prevalence of PMGs containing rounded olivine to contain chromite with high Cr₂O₃ contents indicating that olivine rounding preferentially occurred with increasing Cr content, likely representing an absence of a silicate melt component. Fukang is an exception to this (extreme left on Figure 4.9) although the Fukang sample analysed in this study contained no rounded olivine and therefore is not necessarily at odds with this interpretation. There is a corresponding weak negative correlation between olivine composition (Fo) and Al₂O₃ content of PMG chromite (Figure 4.10). This is perhaps unsurprising given the relationship on Figure 4.9 and the strong co-variation of Cr₂O₃ and Al₂O₃ in PMG chromite seen in Figure 4.6.

Figure 4.10 – Olivine composition (Fo) vs. Al₂O₃ content (wt%) of co-occurring chromite for PMGs where both data are available. Large symbols denote data from this study (except Brenham olivine composition), small symbols are literature data from Boesenberg et al. (2012), Wasson et al. (1999), and Scott (1977). The colours again denote the predominant texture of the olivine in each pallasite. The sample on the extreme right of the figure is Fukang. The AF PMG with very low Al₂O₃ is Marjalahti. The dashed black lines separate the PMGs where rounded olivine has been reported from those where angular, and/or fragmental olivine is reported. Appendix 3 and Table 4.1 tabulate these data.

The trend on Figure 4.10 supports the interpretation of Figure 4.9. The PMGs with rounded olivines (Fukang excepted) are associated with chromite containing lower Al₂O₃ contents. This provides further support for the rounding of PMG olivines in the metal characterised by the absence of
significant quantities of silicate melt (e.g. Solferino et al., 2015; Boesenberg et al., 2012) from which the crystallising chromite could incorporate Al. The correlations identified on Figure 4.9 and Figure 4.10 indicate a broad relationship between more primitive olivine (higher Fo) and a prevalence for the formation of end-member chromite in the PMGs for which data is available. The lack of an obvious relationship between cooling rate and olivine Fo composition (Figure 4.1) suggests that the covariance of Fo and chromite Cr\text{$_2$O$_3$} (and Al\text{$_2$O$_3$}) may be unrelated to formation depth and therefore the distribution of the Al-bearing silicate melt that was likely present during the formation of PMG-high chromite may also have been unrelated to depth. More cooling rate data for PMGs are needed to establish whether this is the case. Figure 4.11 and Figure 4.12 highlight the lack of a relationship between chromite Al and Cr contents and metal melt evolution (Au).

![Figure 4.11 – Chromite Cr\text{$_2$O$_3$} content vs metal melt evolution (Au) for PMGs where data for both is available. Large symbols are Cr\text{$_2$O$_3$} measurements obtained in this study, small symbols are literature data from Wasson et al. (1999), DellaGiustina et al. (2019), Boesenberg et al. (2012), Wasson & Choi (2003), and Scott (1977). The AR sample at ~50 wt% Cr\text{$_2$O$_3$} is Fukang. The dashed black lines separate the PMGs where rounded olivine has been reported from those where angular, and/or fragmental olivine is reported. Appendix 3 and Table 4.1 tabulate these data.](image)

No relationship between metal melt evolution and chromite composition is apparent on Figure 4.11 beyond the previously discussed tendency for PMGs containing rounded olivines (including ARF and AR) to have chromite with compositions closer to end-member. Again, Fukang is an exception
to this trend. Figure 4.12 is almost a mirror image of Figure 4.11 due to the strong covariation between Al and Cr in PMG chromites.

Figure 4.12 – Al₂O₃ content of PMG chromite vs. corresponding metal melt evolution (Au) for PMGs where data on both are available. Large symbols are Al₂O₃ measurements obtained in this study, small symbols are literature data from Wasson et al. (1999), DellaGiustina et al. (2019), Boesenberg et al. (2012), Wasson & Choi (2003), and Scott (1977). The anomalous AR sample at ~19 wt% Al₂O₃ is Fukang. The AF PMG in the rounded field is Marjalahti. The dashed black lines separate the PMGs where rounded olivine has been reported from those where angular, and/or fragmental olivine is reported. Appendix 3 and Table 4.1 tabulate these data.

In order to better understand the relationship between PMG-high chromite and the precursor melt, a comparison of Al and Cr content along a profile was performed on chromite in Fukang. The Cr content increases from core to rim (see Table 3.4, Figure 3.7) suggesting a gradual influx of Cr-rich material into the formation environment during chromite crystallisation and growth and/or a decrease in available Al for incorporation into the spinel crystal. This trend could be satisfied by the migration away and subsequent replacement of an early, Al-rich silicate melt with a Cr-rich metal melt. There may be a temporal constraint on this event as the displacement of silicate liquid by metal melt is
likely the event recorded by Mn-Cr systematics (see section 4.4). An enrichment of Cr\textsubscript{2}O\textsubscript{3} is also observed at both chromite-olivine and chromite-metal rims (Table 3.4), suggesting that the chromite may have been mobile in the metal melt until a late stage during crystal growth as a grain-boundary with solid olivine crystals should not otherwise show Cr enrichment. In summary, the propensity for higher Cr contents on chromite-mineral rims than in chromite cores is evidence that crystal growth of chromite likely occurred over a period of time during which Cr-rich fluid, most likely the metal melt, was progressively added. The Cr\textsubscript{2}O\textsubscript{3} enrichment observed at chromite-olivine grain boundaries is evidence that the chromite was both mobile until a relatively late stage during its growth and that it crystallised prior to the metal and did not exsolve from it. Had the chromite exsolved from the solid metal, Cr zoning would not be present at chromite-olivine mineral boundaries. In crystallising metallic melts with PMG-like S-contents, Cr has a partition coefficient <1 (see Chapter 1, Jones & Drake, 1983) and therefore would be enriched in the melt as crystallisation progressed. If chromite crystallisation and growth was cotemporaneous with metal crystallisation, the increasing proportion of Cr in the surrounding melt would enable ever higher amounts of Cr relative to Al to be incorporated in the growing chromite. If this is the case it may be that Fukang, in which the zoning is most pronounced, crystallised initially from – or in an environment influenced by – an Al-bearing silicate melt and subsequently grew in an evolving metallic liquid. The initial presence and subsequent decreasing availability of Al as chromite growth progressed could be explained by the gradual displacement of silicate melt by a denser metal melt, although the lack of other Al-bearing minerals in PMG suggest that if this occurred, the subsequent evolution of this displaced silicate melt is not recorded in the meteorite record. An inverse correlation identified previously between Al/(Al+Cr) and Fe/(Fe+Mg) in PMG chromite and interpreted to be the result of subsolidus processes (Boesenberg et al., 2012) may be recording this same progressive displacement of a Mg and Al-bearing silicate melt with Cr and Fe-enriched metal melts. The chromites in which the zoning is less pronounced perhaps crystallised at a later stage from metallic or metal-dominated melts where Al was present in reduced amounts. The correlation between Al-content and \(\delta^{18}O\) of PMG chromite seems to bear out the notion of varying degrees of silicate influence on chromite major element and isotopic composition (see section 4.6.5). The PMG-low chromites had considerably higher initial Cr\textsubscript{2}O\textsubscript{3} contents (see Table 3.4) and thus exhibit much less pronounced zoning. They likely formed
in an environment with little or no silicate melt present, perhaps only beginning crystallisation after the displacement of the initial silicate melt from which PMG-high chromite formed.

The Al composition of chromite in PMGs seems to be broadly correlated with both PMG olivine composition and texture and forms part of the definition of the subgroups previously identified (Figure 4.6, Figure 4.9, Figure 4.10, Table 3.5) although it seems to be independent of metal composition (Figure 4.11; Figure 4.12; McKibbin et al., 2019). As already discussed, the PMG-high subgroup contains chromite with variable but appreciable amounts of Al$_2$O$_3$, whilst the PMG-low chromites have very low Al-contents (Figure 4.6). There appears to be a relationship between the rounding of olivines, which is greater in the PMG-low subgroup (low-MnO in McKibbin et al., 2019) and lack of silicate melt present during chromite crystallisation. This is loosely borne out on Figure 4.9, Figure 4.10, Figure 4.11, and Figure 4.12 with the exception of Fukang, a PMG for which rounded olivine has been reported (McKibbin et al., 2019) but was not observed in the sample analysed in this study. A relationship between olivine rounding and near-end-member chromite that likely formed in the absence of appreciable silicate melt is certainly consistent with the idea that the degree of rounding is correlated with the residence time of olivine in metallic liquid (e.g. Solferino et al., 2015; Solferino & Golabek, 2018) and, in turn, with a range of conditions dictating pallasite formation in the parent body.

### 4.3 Isotope data and implications

#### 4.3.1 Olivine

##### 4.3.1.1 Oxygen

It has been suggested that PMG olivine formed either as a magma ocean cumulate (e.g. Buseck, 1977), or as a restite (McKibbin et al., 2013) on the basis of olivine trace element data (Mittlefehldt, 1999; 2005; Mittlefehldt & Herrin, 2010; McKibbin et al., 2013). A restite origin has been shown to be consistent with the chemical composition of Vestan harzburgites (Hahn et al., 2018). The oxygen isotope results presented in this study provide constraints on the PMG olivine formation environment.
The lack of an identifiable difference in oxygen isotopes between low-$\Delta^{17}$O and high-$\Delta^{17}$O samples as defined by Ali et al. (2018), and the lack of any difference on the basis of the petrographic subgroups defined by McKibbin et al. (2019) (see section 3.3.1), suggest that the mantle sampled by PMG olivine was well homogenised isotopically at the time of olivine crystallisation. Results from three separate laser-assisted fluorination studies of PMG olivine at the Open University show that PMG olivine is isotopically homogenous with respect to $\Delta^{17}$O (Greenwood et al., 2006; Greenwood et al., 2015; this study) which contrasts with the bimodality in PMG olivine $\Delta^{17}$O results identified by Ali et al. (2018). The study by Ali et al. (2018) was also conducted using BrF$_5$ laser fluorination and has comparable reported precision to the results in this study. The cause of the discrepancy between laboratories could be due to at least one of three things: 1) one or both of the setups is yielding incorrect or inconsistent results, 2) there are two $\Delta^{17}$O populations of PMG olivine, one of which is not sampled during the course of this study, or 3) the low-$\Delta^{17}$O population identified by Ali et al. (2018) is the same isotopic reservoir as represented by the PMG-low chromite in this study and the high $\Delta^{17}$O reservoir is the same as the PMG-low olivine. The first of these possibilities is highly unlikely given the excellent precision and reproducibility of internal standards in this study (see Chapter 2) and the study by Ali et al. (2018). The second potential cause is also unlikely. This is because PMG olivine from both $\Delta^{17}$O groups identified by Ali et al. (2018) have been analysed in this study and found to have no resolvable offset (see Figure 3.10, Figure 3.11). It is possible that two $\Delta^{17}$O olivine populations exist across the whole range of PMGs, are not sample-specific, and by chance olivine from one group is not sampled at all in the present study, although this seems incredibly unlikely on the basis of the number of olivines analysed (n = 62). A third possibility is perhaps the most likely. The $\Delta^{17}$O offset identified between PMG-low olivine and chromite in this study could be the same offset identified in olivine by Ali et al. (2018) although there is a slight difference in magnitude. If this is the case, a key difference between the studies is that the work presented herein reports homogenous olivine offset from co-existing chromite, whereas Ali et al. (2018) report a bimodal olivine distribution and did not analyse any chromite. The reported $\Delta^{17}$O offset between the average values for olivine subgroups in Ali et al. (2018) is $\sim$0.054 ‰ whereas the $\Delta^{17}$O offset between the average PMG-low olivine and chromite is smaller at $\sim$0.024 ‰. The PMG-low and PMG-high subgroups in this study both include high-$\Delta^{17}$O and low-$\Delta^{17}$O samples identified
by Ali et al. (2018) suggesting that there is no clear relationship between subgroups defined in the two studies. Overall, despite acid-washing PMG samples in a manner identical to that outlined by Ali et al. (2016; 2018; see Chapter 2) and having different operators use the laser-assisted fluorination set up, no bimodality has been identified. The cause of the discrepancy between a single homogenised Δ¹⁷O PMG olivine population (Greenwood et al., 2006; 2015; this study) and a bimodal distribution of well homogenised Δ¹⁷O populations (Ali et al., 2018) is unknown but may be some unidentified issue with data in the latter study.

The homogeneity in Δ¹⁷O identified in this study has implications for the plausibility of a restite origin for PMGs (see section 4.6.3). Given that PMG olivine is isotopically homogenous (Greenwood et al., 2006; 2015; see section 3.3.1), and assuming that any precursor material would be isotopically heterogeneous, the mantle of the PMG body must have been subjected to a high degree of partial melting. The viability of a restite origin model is therefore dependent on the diffusion rate of oxygen between olivine and silicate melt at high temperatures. Examination of oxygen diffusion rates in San Carlos (terrestrial) olivine has yielded the observation that crystal-induced differences in diffusion rate exist along the 010 and 100 directions (Ryerson et al., 1989). At comparable fO₂ conditions to PMG formation (~IW – Righter et al., 1990;), the oxygen diffusion rates in San Carlos olivine range from ~10⁻²¹ to 10⁻¹⁹ m² s⁻¹ for both the 010 and 100 directions over a temperature range of ~1473–1773 K, although diffusivity along the 010 direction is slightly faster (Ryerson et al., 1989). The fastest of these values, 10⁻¹⁹ m² s⁻¹ at around 1673 K, equates to 10⁻¹⁵ cm² s⁻¹ or around 1 cm² every 32 Myr. This is incredibly slow compared with the diffusion rate of oxygen in a metal melt (see section 4.6.3.2) and if accurate likely precludes the possibility that partial melting and oxygen diffusion could result in the high degree of oxygen isotopic homogeneity seen in PMG olivine. This diffusion coefficient can be extrapolated to higher temperatures. After Gerard & Jaoul (1989), the diffusion coefficient in olivine can be written as:

Equation 4.1

\[ D = D_0 e^{\frac{-E}{RT}} \left( \frac{PO_2}{P_0} \right)^m \]

where \( D_0 \) is pre-exponential diffusion coefficient, \( E \) is activation energy (318 KJ mol⁻¹), \( R \) is the ideal gas constant, \( T \) is absolute temperature, \( PO_2 \) is the partial pressure of oxygen, and \( P_0 \) is room
pressure, and $m$ is 0.34 (Gerard & Jaoul, 1989; Ryerson et al., 1989). If $PO_2$ is taken as $10^{-3}$ Pa, roughly equivalent to IW at a temperature of 1873 K (Ryerson et al., 1989) the diffusion rate of oxygen in olivine is $1.73 \times 10^{-17}$ m$^2$ s$^{-1}$ or approximately 5.5 cm$^2$ Myr$^{-1}$. This suggests that the diffusion rate increases dramatically (~176 times) with a 200 K increase in temperature and if extrapolated further, could be considerably faster still. Considering that high-T cooling rates in PMGs were on the order of 100-300 K Myr$^{-1}$ (Donohue et al., 2018), even if the temperature exceeded those studied by Ryerson et al. (1989) and Gerard & Jaoul (1989), it would not have remained so for longer than a few million years (see section 4.6.3.1). If the maximum temperature during PMG formation is taken as around 1973 K (Boesenberg et al., 2012), the olivine would have cooled to the temperature under which San Carlos olivine was analysed (1673 K) (Ryerson et al., 1989) in around 1 Myr. With this in mind, it seems unlikely that the isotopic homogeneity of PMG olivine could be formed through high degrees of partial melting of an isotopically heterogeneous precursor unless the diffusion rate increases further as temperatures approach ~2000 K. Therefore, PMG olivine could have formed as a restite if temperatures remained very high for a prolonged period of time, otherwise it likely formed as a cumulate from an isotopically homogenised magma ocean.

4.3.1.2 Chromium

Chromium isotope analyses were performed on olivine separates of the PMG-low samples Seymchan and Sericho, and the PMG-high meteorite Fukang. Additionally, literature data (Qin et al., 2010) for the PMG-low pallasite Brenham was used for further context (see section 3.8). Chromium isotopes are readily produced through the spallation of Fe and Ni nuclei after interaction with very high energy nucleons (Liu et al., 2019). These effects are most obvious in $\varepsilon^{54}$Cr, and produce a slope in $\varepsilon^{54}$Cr – $\varepsilon^{53}$Cr space of 3.90 ± 0.03 (Liu et al., 2019). The magnitude of the GCR-produced anomalies is greater in samples with higher Fe (or Ni)/Cr ratios as well as in those with long CRE ages (Qin et al., 2010). Given the much higher Fe/Cr ratios (~3 orders of magnitude greater) in the olivine samples, this effect will be considerably more pronounced than in the corresponding chromites analysed in this study. The $\varepsilon^{54}$Cr results are constant within error for all analysed PMG olivine although there is some spread in $\varepsilon^{53}$Cr composition (see Table 3.9, Figure 3.21). As reported in section 3.8, the $\varepsilon^{53}$Cr distribution of olivine samples corresponds to the Mn/Cr ratio in those olivines and is therefore interpreted as being an artefact of the decay of $^{53}$Mn to $^{53}$Cr and dependent on the
initial $^{53}\text{Mn}$ content of the samples. On this basis the PMG olivines analysed in this study, along with Brenham (Qin et al., 2010), appear to be isotopically homogenous with respect to $\varepsilon^{54}\text{Cr}$ and $\varepsilon^{53}\text{Cr}$ when corrected for GCR spallation and radiogenic decay of $^{53}\text{Mn}$.

4.3.2 Chromite

4.3.2.1 Oxygen

The $\delta^{18}\text{O}$ difference between PMG-low and PMG-high chromite, coupled with the correlated difference in Al composition (see section 4.2.2), is most likely explained by varying amounts of isotopically heavier silicate melt present during chromite crystallisation. For the PMG-high chromite, a significant amount of silicate melt was likely influencing crystallisation and growth. This melt provided a source of $\text{Al}^{3+}$ for incorporation into the spinel structure as well as an abundance of relatively $^{18}\text{O}$-rich oxygen. The PMG-low chromite likely crystallised in the absence of any significant amounts of this silicate melt, likely from the metal where Al-contents were low and the oxygen was isotopically lighter. This difference between the PMG subgroups perhaps corresponds to different areas of the parent body or different crystallisation times, the PMG-low chromite perhaps crystallising following displacement of the silicate melt. The lighter oxygen isotope composition of the metal in PMGs could be explained through oxygen diffusion between the silicate and metal reservoirs with the lighter O nuclei diffusing most effectively. The $\lambda$ values required to connect the olivine and chromite subgroups are much steeper than would be expected in such a case. An evaluation of possible causes for this is covered in sections 4.5 and 4.6.

The fact that the high-$\delta^{18}\text{O}$ chromites are also those with higher Al-contents is in line with expectations for chromite formation in the presence of $\text{Al}^{3+}$ and $\text{Cr}^{3+}$. The strength of the ionic bonds in the compounds $\text{Cr}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ are dependent on the interionic distance and electric charges (e.g. Goldschmidt, 1937; Faure, 1998). Here, the ionic charges are the same (3+) and therefore the bond strength is dependent on the interionic distance. The cation $\text{Al}^{3+}$ has a smaller interionic distance than does $\text{Cr}^{3+}$ (Goldschmidt, 1937) which corresponds to a higher bond strength. On the basis of the differences in interionic distance and therefore bond strength for $\text{Al}^{3+}$ and $\text{Cr}^{3+}$, chromite with a higher proportion of $\text{Al}_2\text{O}_3$ would be expected to exhibit higher $\delta^{18}\text{O}$ values. This is because the heavy isotopes of an element preferentially occupy the sites with stronger, lower-frequency bonds.
This may be evidence that the PMG-high chromite formed as a result of isotopic equilibration between the PMG-low chromite and a silicate isotopic reservoir of PMG olivine composition. The Al zoning in PMG-high chromite, however, suggests that this is not the case. The decreasing Al-content from core to rim suggests that the initial nucleation and growth of the chromite occurred in the presence of an Al-bearing silicate melt and subsequent progressive replacement of this melt with Cr-rich metallic melt occurred during crystal growth. This indicates that PMG-high chromite formed as a result of partial equilibration between the isotopic reservoirs of a silicate melt, likely in equilibrium with PMG olivine, and a later intruded metal melt with an oxygen isotope composition in line with that of PMG-low chromite. The lack of a statistically meaningful difference between PMG-high olivine and chromite lends further credence to the idea that PMG-high chromite in this group may sample an equilibrated melt between the statistically distinguishable PMG-low chromite and olivine composition. The results of the statistical tests are consistent with the calculation of fractionation exponents presented in section 3.5 and lend extra support to the conclusion that the PMG-low minerals are in isotopic disequilibrium whilst the PMG-high minerals are either in equilibrium or have partially equilibrated.

The PMG-low chromite results break high-T mass-dependent-fractionation rules for oxygen when compared to PMG-low olivine. This may be explainable in a few ways and is discussed below (sections 4.5 and 4.6). Overall, the fact that PMG-low chromite appears relatively well constrained in both δ¹⁸O and Δ¹⁷O (see section 3.3.2) suggests that the PMG-low metal was isotopically well-mixed and homogenous prior to mixing with the silicates. Given that the PMG-high chromite isotopic composition seems to be part way between the PMG-low chromite and the olivine populations, as well as the compositional indicators of the presence of silicate melt discussed above (section 4.2.2), it seems likely that it records some equilibration between the two reservoirs.

4.3.2.2 Chromium

In addition to the oxygen isotope analyses of PMG chromite, chromium isotopes were also obtained. The very low Fe/Cr ratios in PMG chromite analysed means that they can effectively be treated as unaltered by GCR spallation in ε⁵⁴Cr because the amount of Fe/Ni spallation-produced chromium nuclei is insignificant relative to the total Cr in the samples (Schneider pers. comm, 2019). Strong
support for the validity of this approach is the lack of apparent difference in Cr isotope composition between Seymchan and Brenham chromites (see Table 3.10), these meteorites have very different CRE ages of $30 \pm 4$ Myr and $156 \pm 8$ Myr, respectively (Herzog et al., 2015). As a result of this, the Cr isotopic composition of the analysed chromite is taken to be unaltered from the initial isotopic composition of the reservoir from which they formed. Similarly, the very low Mn/Cr ratio of the chromites (0.01 in Brenham, Fukang, Seymchan, and Sericho) means that there is also negligible contribution from the $^{53}$Mn-$^{53}$Cr decay pathway ($t_{1/2} = 3.7 \pm 0.4$ Myr) (Liu et al., 2019) and therefore there is no measurable effect from radiogenic decay in these samples. The PMG olivines, however, have both high Fe/Cr ratios and high Mn/Cr ratios meaning that the results are heavily affected by both GCR spallation effects and radiometric decay of $^{53}$Mn (see section 4.3.1.2). Both the chromite and olivine results for PMG fall in the non-carbonaceous Solar System reservoir (e.g. Warren, 2011) and therefore likely formed in the inner Solar System.

4.3.2.3 Estimation of PMG body heliocentric distance

There is some evidence that a linear relationship exists between $\varepsilon^{54}$Cr and heliocentric distance for differentiated bodies (Yamakawa et al., 2010). The Cr isotope analyses obtained for PMG chromites as part of this study allow the accretion distance of the PMG parent body to be estimated (Figure 4.13). The data for Figure 4.13 is presented in Table 4.2. The estimation of heliocentric distance from $\varepsilon^{54}$Cr seems to be valid only for the inner Solar System. Outer Solar System materials are enriched in nucleosynthetic heavy elements relative to inner Solar System samples, probably due to the early growth of Jupiter and subsequent lack of inner-outer Solar System mixing (e.g. Warren, 2011; Kruijer et al., 2017). When applied to the inner Solar System, a key assumption is that the bodies used to define the linear relationship, Earth, Mars, and 4 Vesta, accreted at their current heliocentric distances, or at least at the same relative distances apart in the protoplanetary disk. This assumption is not consistent with the idea of chaotic migration of Solar System bodies in models such as the Grand-Tack model (e.g. Walsh et al., 2011) and the estimated PMG heliocentric distance shown in Table 4.2 is dependent on the estimated heliocentric distance of the ureilite parent body, itself calculated using the same method and assumptions. As a result of these factors, it is unlikely that this method accurately reports heliocentric distance of formation but it is calculated for comparison with other inner Solar System bodies.
Table 4.2 – Heliocentric distance calculated using the equation displayed in Figure 4.13 for PMG samples.

<table>
<thead>
<tr>
<th>Sample/body</th>
<th>$\varepsilon^{54}$Cr (‰)</th>
<th>±</th>
<th>Heliocentric dist. (AU)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earth</td>
<td>0.02</td>
<td>0.04</td>
<td>1.00</td>
<td>Trinquier et al (2007)</td>
</tr>
<tr>
<td>Mars</td>
<td>-0.17</td>
<td>0.03</td>
<td>1.52</td>
<td>Trinquier et al (2007)</td>
</tr>
<tr>
<td>4 Vesta</td>
<td>-0.73</td>
<td>0.03</td>
<td>2.36</td>
<td>Trinquier et al (2007)</td>
</tr>
<tr>
<td>Ureilite parent body</td>
<td>-0.92</td>
<td>0.02</td>
<td>2.80</td>
<td>Yamakawa et al (2010)</td>
</tr>
<tr>
<td>Krasnojarsk</td>
<td>-0.72</td>
<td>0.01</td>
<td>2.41</td>
<td>Trinquier et al (2007)</td>
</tr>
<tr>
<td>PMG (sample not specified)</td>
<td>-0.7</td>
<td></td>
<td>2.37</td>
<td>Warren (2011)</td>
</tr>
<tr>
<td>Hambleton</td>
<td>-0.8</td>
<td>0.10</td>
<td>2.56</td>
<td>This study</td>
</tr>
<tr>
<td>Fukang</td>
<td>-0.57</td>
<td>0.20</td>
<td>2.14</td>
<td>This study</td>
</tr>
<tr>
<td>Seymchan</td>
<td>-0.53</td>
<td>0.13</td>
<td>2.06</td>
<td>This study</td>
</tr>
<tr>
<td>Brenham</td>
<td>-0.44</td>
<td>0.13</td>
<td>1.90</td>
<td>This study</td>
</tr>
<tr>
<td>Sericho</td>
<td>-0.4</td>
<td>0.13</td>
<td>1.83</td>
<td>This study</td>
</tr>
<tr>
<td>AVERAGE PMG</td>
<td><strong>-0.59</strong></td>
<td><strong>0.28</strong></td>
<td><strong>2.18 ± 0.51</strong></td>
<td>This study (calculated)</td>
</tr>
</tbody>
</table>

Figure 4.13 – $\varepsilon^{54}$Cr vs. heliocentric distance (AU) for PMG chromite. The linear relationship between Cr isotope composition and heliocentric distance has been defined on the basis of known values for Earth, Mars, and 4 Vesta (HEDs) (data from Trinquier et al., 2007), as well as the estimated position of the ureilite parent body (UPB) from $\varepsilon^{54}$Cr data (Yamakawa et al., 2010). PMG chromite $\varepsilon^{54}$Cr data from this study has been combined with a Krasnojarsk datapoint from Trinquier et al. (2007) and a PMG datapoint from Warren (2011) to determine an estimated heliocentric distance (yellow circle). The errors on PMG data are as outlined in section 3.8 or in Trinquier et al. (2007). The errors on the PMG average are $2\sigma$ for both heliocentric distance and $\varepsilon^{54}$Cr.
Estimation of the heliocentric distance for PMG samples has been calculated using the equation of the line Earth-Mars-4 Vesta-UPB in Figure 4.13. If the relationship reported by Yamakawa et al. (2010) is a real trend, then on the basis of the Cr isotope data, the PMG parent body accreted at approximately 2.18 ± 0.51 AU.

4.3.3 Metal

4.3.3.1 Tungsten

The ages obtained through W isotope analyses are consistent with those of Homma et al. (2019) and with the Al-Mg model age calculated by Baker et al. (2012) (see Figure 4.14). These data show that accretion and differentiation of the PMG parent body must have occurred very early in Solar System history. Combined with the age obtained through Mn-Cr systematics (see section 3.8), the W chronology provides excellent insight into the first 10 Myr of the history of the PMG parent body (see section 4.4).

4.4 Main-Group pallasite chronology

The chronological results from this study, both Hf-W and Mn-Cr, are consistent with previous work (see Figure 4.14). The W model ages record a very early differentiation event in the PMG parent body that is consistent with prior studies (Homma et al., 2018; 2019). Fukang and Seymchan metals were selected for Hf-W chronology on the basis of differing Ir contents (see section 2.10), and therefore degree of melt evolution, to establish whether any difference could be identified between differentiation ages. Despite the samples representing different stages of metal melt evolution, the differentiation ages are not resolvable. This could be because either 1) there was no resolvable time difference between silicate-metal separation for different metal melts, i.e. very rapid global metal-silicate separation or 2) silicate-metal separation predated the evolution of the metal melts and was unrelated to them.

The Mn-Cr age records the time at which any Mn mobility between olivine and other phases was closed; this may have been the crystallisation of the olivine, cessation of diffusion between olivine and a melt, or perhaps a temperature at which sub-solidus Mn exchange ceased. The Al-Mg system
closed around 1.24 Myr after CAI formation, an event which is thought to represent the crystallisation of olivine (Baker et al., 2012; see Figure 4.14).

If the Al-Mg closure event does represent crystallisation of PMG olivine, it is not consistent with Mn-Cr model ages (see Figure 4.14) unless they record a different event, perhaps the displacement of silicate melt by the metal melt. Baker et al. (2012) analysed Al-Mg systematics in Admire, Brenham, Molong, and Esquel. None of these samples has been investigated in terms of Mn-Cr and it may be that the time of crystallisation of PMG olivine was different in different parts of the parent body. To satisfy the Mn-Cr age from this study, as well as the Al-Mg age from Baker et al. (2012), the time over which olivine crystallisation was occurring would be approximately 9 Myr (Figure 4.14). Given that the high-T cooling rates of PMGs are estimated at 100-300 K Myr\(^{-1}\) (Donohue et al., 2018), this would require a wider variation in high-T cooling rates than has been thus far identified. Both of these requirements are difficult to envisage in canonical pallasite-forming environments such as a core-mantle boundary layer. More likely is that sub-solidus \(^{53}\text{Mn}\) exchange between olivine and another phase continued after olivine crystallisation and ceased when either a

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Figure 4.14 – PMG chronology based on Hf-W and Mn-Cr decay systems from this study compared with literature chronological data.
certain isotopic closure temperature – perhaps around ~1000 K (e.g. Goldstein et al., 2009b) – was passed or when the phases it was exchanging with were displaced. McKibbin et al. (2016) used Mn-Cr systematics on olivine rims to define an age of ΔT (CAI) ~1 Myr, however a weighted mean was used (only taking points with $^{55}\text{Mn}^{52}\text{Cr} > 20$) and therefore this age may be skewed. The likelihood that Mn-Cr exchange affected olivine rim compositions after crystallisation (Lugmair & Shukolyukov, 1998) also serves to complicate this. Furthermore, spallation effects were not considered and the use of a single collector means that no simultaneous mass-fractionation correction was performed by analysing other stable isotopes with ICP-MS (e.g. McKibbin et al., 2013), as is done when analysing on TIMS (Schneider, pers. comm, 2019). As a result of these factors, the early Mn-Cr age obtained by McKibbin et al. (2016) is not considered further in this study.

Mn-Cr systematics for the Omolon pallasite have been used to estimate a high-T cooling rate of ~50–100 K Myr$^{-1}$ (Lugmair & Shukolyukov, 1998) which is broadly consistent with, but marginally slower than, those calculated on the basis of diffusion profiles (Donohue et al., 2018). It is not clear exactly how the cooling rate has been estimated by Lugmair & Shukolyukov (1998) but their estimate is reinforced by the data in this study on the basis of the similarities in Mn-Cr age (Figure 4.14). Mn-Cr ages from Lugmair & Shukolyukov (1998) have subsequently been interpreted as recording the partial resetting of the initial Cr distributions, probably occurring during the mixing of the olivine and metal phases (McKibbin et al., 2013). If this is accurate, the data in this study supports the mixing event occurring around 10 Myr after CAI formation. This event would have displaced any precursor silicate melt with which the olivine was exchanging Mn, and effectively closed the Mn system by isolating olivines in a metallic melt in which Mn is incompatible. If this interpretation of the Mn-Cr age is correct, the metal in PMG was injected into the olivine significantly later than core-mantle separation. The time difference between the differentiation age and metal-injection age (Figure 4.14) seems at odds with the possibility of PMG formation during parent body differentiation or at a core-mantle interface.

4.5 Potential complications to oxygen isotope interpretation

Of critical importance when investigating candidate PMG formation environments are the findings of this study. The previously undiscovered presence of a statistically significant $\Delta^{17}$O disequilibrium
between minerals in PMG-low meteorites (see section 3.5) is of great importance when seeking to understand processes active in early planetesimals. Prior to the interpretation of the data collected over the duration of this project in the context of pallasite formation processes, it is important to first consider what potential complicating factors may be influencing the isotope data presented. These factors are addressed below in order from most likely to be affecting the results to least likely.

4.5.1 “Multi-step” or multiple stages of fractionation

A possible cause of the disequilibrium seen in PMGs could be mass-fractionation between the two phases and a third phase. This kind of multi-step fractionation is possible because there are a range of temperature-dependent slopes possible for oxygen mass-dependent fractionation processes (see Appendix 1; e.g. Sharp et al., 2018).

4.5.1.1 Farringtonite

The analysis of farringtonite, a third O-bearing phase in PMGs, allows limited testing of this hypothesis. The farringtonite sample is from Sericho (PMG-low) and so is compared with the PMG-low average compositions for olivine and chromite in order to evaluate this possibility; the PMG-high olivine and chromite are within error of a mass-dependent relationship and so no such process is required to satisfy the data. The required slope (i.e. lambda) to connect olivine and farringtonite, assuming they are in equilibrium, is 0.5116 ± 0.0142 (2 SE) (Figure 4.15). At face value this is well below the expected range for high-T mass-dependent fractionation (e.g. Young et al., 2016), and even outside of the range expected for geological materials taking low-T equilibrium and kinetic mass-dependent fractionation processes into account. This slope is not well constrained, however, and is within error of expected high-T mass-fractionation λ values. Only one oxygen isotope analysis of farringtonite was performed owing to the low abundance of this mineral in the analysed PMGs and resultantly, the slope relies heavily on that single point. If it is assumed that the point is representative of PMG farringtonite as a whole, the mineral is unlikely to be in equilibrium with the PMG olivine. The λ required to connect chromite and farringtonite in PMGs is 0.5283 ± 0.0058 (2 SE) which is within the expected range for high-T equilibrium mass-dependent fractionation. On this basis, and assuming that the olivine-farringtonite λ is accurate, it appears that the farringtonite
and the chromite plot on a mass-dependent fractionation line and the olivine is offset towards the TFL (Figure 4.15). There are two possible explanations for this behaviour:

1) PMGs represent two parent bodies, an impacted body represented by the olivine and an impactor represented by the metal from which both chromite and farringtonite crystallised, or

2) the minerals crystallised from a single isotopic reservoir in equilibrium but some as yet unknown effect offset the olivine from a mass-dependent fractionation line defined by chromite-farringtonite.

Given that the olivine is in disequilibrium with the chromite and probably with the farringtonite as well, it seems that multi-step fractionation between these three minerals cannot explain the observed results. Figure 4.15 shows this relationship in three isotope space. Farringtonite in PMG likely formed late (Boesenberg et al., 2012), probably utilising Mg from PMG olivine and P and O in PMG metal. The reaction for forming farringtonite may have been as follows (Olsen & Frederiksson, 1966; Fuchs, 1967; McKibbin et al., 2019):

Equation 4.2

\[
3Mg_2SiO_4 + 4P + 6Fe + 8O_2 = 2Mg_3(PO_4)_2 + 3Fe_2SiO_4
\]

\[
\text{Forsterite} + \text{Metal} = \text{Farringtonite} + \text{Fayalite}
\]

Farringtonite formation proceeding according to the reaction above would explain the documented propensity for its presence in PMGs containing lower olivine Fo numbers due to the conversion of some PMG olivine to more fayalitic compositions (McKibbin et al., 2019) as well as the oxygen isotope data when interpreted in the context of point 1, above.

On the basis of the probable crystallisation of farringtonite and PMG-low chromite from metal-hosted oxygen, combined with the unrealistic \( \lambda \) between PMG olivine and farringtonite (Figure 4.15), it seems unlikely that multi-step fractionation between olivine, chromite, and farringtonite could generate the observed \( \Delta^{17}O \) offset between PMG-low olivine and chromite. Given the relatively poorly constrained farringtonite result, however, such a mechanism cannot be completely discounted.
Figure 4.15 – A three-isotope plot showing the average composition of the three analysed O-bearing phases in PMG-low samples. Errors are 2 standard deviation for chromite and olivine, and 2 standard error for farringtonite (n=1). The dashed lines are the fractionation slopes connecting the phases. Slope 1, connecting chromite and olivine is > 0.5305 and so is impossible through known mass-dependent processes. Slope 2, connecting olivine and farringtonite, is 0.5116 which is too shallow for high-T equilibrium fractionation. Slope 3, connecting chromite and farringtonite, is 0.5283. This slope is within the range of high-T mass-fractionation and perhaps represents the oxygen fractionation line of the metal portion of PMGs. The $\Delta^{17}$O values were calculated using $\lambda = 0.5262$ and this is the reason that slopes steeper than this value appear positive and those shallower appear negative.

### 4.5.1.2 A fourth oxygen-bearing phase?

The presence of a fourth phase during crystallisation may be able to explain the distribution of isotopes between the three measured minerals. If this phase, in equilibrium with PMG-low olivine, had a mass-dependent fractionation slope of 0.525, the lowest end of likely high-T mass-fractionation slopes (Young et al., 2016), then the intercept with the metal mass-fractionation line (defined by PMG-low chromite – farringtonite (slope 0.5283)) would be at around 8.5 ($\%$) for $\delta^{18}$O (see Figure 4.16). This would require fractionation of > 5 per mil in $\delta^{18}$O between olivine and the fourth phase which seems highly unlikely given the high-T formation environment of PMGs and the fact that oxygen isotope fractionation between two phases decreases with increasing temperature (Criss 1999, Eqn 2.55b). To evaluate the likelihood of this, olivine-pyroxene equilibrium temperatures (Zheng,
1993; Bottinga & Javoy, 1973; 1975) for these intercepts were investigated using AlphaDelta (Beaudoin & Therrien, 2009). Pyroxene, or a silicate melt of similar composition, seems a likely candidate for an unknown fourth phase because as it is found in some pallasites (e.g. Bunch et al., 2005). Based upon typical equilibration equations for the olivine-pyroxene system (e.g. Zheng, 1993: Bottinga & Javoy, 1973; 1975), no practical temperatures can be set to generate a $\Delta^{18}O$ (difference in $\delta^{18}O$ between minerals) of 5 ‰, which is considered extremely large in the context of this system. Using the same $\Delta^{18}O$ for olivine – pyroxenite equilibria from 273-1473 K (Zheng, 1993; Zhao & Zheng, 2003), no result is possible (Beaudoin & Therrien, 2009), indicating that such a $\Delta^{18}O$ cannot result from equilibrium mass-dependent fractionation.

If $\lambda = 0.529$, a slope similar to that observed in terrestrial mantle minerals (e.g. Pack & Herwartz, 2014), is assumed between the olivine and a fourth phase the $\delta^{18}O$ intercept with the metal
fractionation line defined by chromite and farringtonite is at ~26% (i.e. the blue square on Figure 4.16). The Δ^{18}O (which is the difference between two δ^{18}O values) in this case is -29% from the olivine. The magnitude of this shift means that it is not possible through high-T equilibrium fractionation. Furthermore, only oxide minerals are usually lower in δ^{18}O than olivine following melt crystallisation (Eiler 2001; Valley 2003; cited in Bucholz et al., 2017) and therefore any fourth phase in equilibrium with both the metal-hosted minerals and the olivine would be expected to have higher δ^{18}O than the olivine. This restricts the range of slopes for mass-dependent equilibrium fractionation between olivine and any fourth phase to shallower than that of the metal fractionation line (Figure 4.16). Given that the range of high-T equilibrium mass-dependent fractionation slopes extends between 0.525 and 0.529 (Young et al., 2016), the shallowest of these will intersect the chromite-farringtonite fractionation line with the smallest olivine-intersect Δ^{18}O. This means that in order to reduce the Δ^{18}O between olivine and any potential fourth phase, a slope of 0.525 seems the best candidate. As outlined above, however, even this case seems irreconcilable with high-T fractionation.

A fractionation line of 0.5305 from the olivine intersects the metal (chromite-farringtonite) fractionation line at -2.7‰ δ^{18}O (Δ^{18}O = -6.0) which again yields no result for an equilibrium temperature between olivine and pyroxene (Zheng, 1993; Bottinga & Javoy, 1973; 1975; Beaudoin & Therrien, 2009)). In summary, it is most unlikely that a fourth phase is in equilibrium with the olivine and metal-hosted minerals. The δ^{18}O shift from any intercept between the metal fractionation line and any realistic fractionation line on which the olivine might lie is not consistent with expected ranges for equilibrium at high temperatures.

4.5.2 Anharmonic effects

Another complicating factor that could be affecting oxygen isotope results is anharmonicity (Figure 4.17). Disparate anharmonic effects between the olivine and chromite in PMG-low samples may result in a slope steeper than is allowed through mass-dependent fractionation. A similar mechanism has been suggested previously for slight, apparently mineral-specific differences in Δ^{17}O although no detail on this candidate mechanism is proffered (Kohl et al., 2017). Additionally, investigation into the anharmonic contribution to fractionation in dissolved Li^+ ions in aqueous solution has led to
the determination that ln $\alpha^{7}_{\text{Li}}$ between the solution and phyllosilicate minerals is affected significantly by anharmonicity (Figure 5 a, b in Dupois et al., 2017). Whilst there is evidence for considerable deviation from the simple harmonic oscillator expected values in Li isotope fractionation (Dupois et al., 2017), no studies on anharmonic effects in oxygen at magmatic temperatures have been reported. Given that a similar but less pronounced offset is observable between Bushveld olivine and chromite (see Figure 4.18), it is possible that there is some such effect. The simple harmonic oscillator (SHO) approximation, upon which Urey’s (1947) and Bigeleisen & Mayer’s (1947) frameworks rely, is not realistic for molecules (Criss, 1999). Whilst it has great utility at low potential energies where quantum numbers are low, it assumes a parabolic potential energy curve (see Figure 4.17) with an infinite number of quantised energy levels that are evenly spaced (Criss, 1999) and does not accurately describe systems where quantum numbers are high. Given that high-T environments have more energy, it may be the case that the differences between SHO-modelled fractionation and reality increase with increasing temperature. In such a scenario, the SHO approximation may be considerably different to the reality (see Figure 4.17). If the PMG olivines are restites and did not crystallise from a magma ocean (see section 4.6.3), any difference in quantum numbers between different isotopologues as temperature increased may have resulted in preferential dissociation of certain molecules and redistribution of their isotopes. Whilst intuitively it seems that this process would be mass-dependent, it may be that the differences between SHO and the anharmonic oscillations in a crystal lattice result in some apparent disequilibrium between olivine and other minerals where none actually exists. The SHO approximation has no treatment for scenarios in which either 1) the molecule is broken into its constituent atoms, as can occur in kinetic mass-dependent fractionation processes, or 2) there is an increase in repulsive force if a molecule is compressed (Criss, 1999). Kohl et al. (2017) postulated that observed $\Delta^{17}_{\text{O}}$ offsets in tectosilicates (quartz and plagioclase) may be due to crystal-chemical differences arising from mineral-specific anharmonic effects. This does not seem to be reflected in plagioclase from the BIC analysed in this study (Figure 3.20). It may be the case, however, that some mineral-specific anharmonic effect is causing either a positive (i.e. upward) offset in $\Delta^{17}_{\text{O}}$ of olivine, or a negative (i.e. downward) $\Delta^{17}_{\text{O}}$ offset in chromite. Given that the $\lambda$ connecting the chromite and farringtonite in PMG-low is within the region of expected values, it seems more likely that it is the olivine that is subject to any mineral-
specific anharmonic influence if such an effect is present. This is an area of research that needs to be explored further as any such effect would be of critical importance, particularly in studies analysing whole rock samples, looking at inter-mineral fractionation, or comparing the oxygen isotopes signature of different minerals in the context of meteorite parent body relationships.

Figure 4.17 – An energy level diagram showing the differences between a simple harmonic oscillator (SHO, in red) and anharmonic oscillator (Morse potential, in green). Note that the energy levels are evenly spaced with increasing energy for SHO, but Morse potential sees a decrease in spacing as energy increases. The red and green numbers for SHO and Morse respectively are the quantised vibrational energy levels, the dissociation energy is shown as a dashed line, as is the zero-point energy (Z.P.E.). D1 and D2 are the energies required for dissociation factoring in Z.P.E. and the true dissociation energy respectively. The base of D1 corresponds to the lowest point of the SHO and Morse curves. Image recreated based on one from http://universe-review.ca/R15-33-harmonics.htm.

Analysis of inter-mineral fractionation from the Bushveld Igneous Complex (BIC), a high-temperature, igneous, terrestrial environment, were conducted to evaluate the possibility that the PMG disequilibrium is caused by some crystal-chemical or anharmonic effect. Immediately evident from the Bushveld analyses, and relevant to PMGs, is the similarity in the offset between olivine and
The $\Delta^{17}$O offset is calculated using $\lambda = 0.5262$.

<table>
<thead>
<tr>
<th>Mineral pair</th>
<th>$\Delta^{17}$O offset (‰)</th>
<th>$\lambda \pm 2$ SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine-chromite</td>
<td>0.018</td>
<td>0.5370 ± 0.0054</td>
</tr>
<tr>
<td>Pyroxene-chromite</td>
<td>0.003</td>
<td>0.5275 ± 0.0038</td>
</tr>
<tr>
<td>Olivine-pyroxene</td>
<td>0.015</td>
<td>0.5061 ± 0.0300</td>
</tr>
<tr>
<td>Pyroxenite all</td>
<td>N/A</td>
<td>0.5298 ± 0.0067</td>
</tr>
</tbody>
</table>

The similarity between the olivine-chromite $\lambda$ for the BIC pyroxenite and that for PMG-low minerals raises questions about the potential for some previously unknown effect resulting in $\Delta^{17}$O offsets in igneous minerals. If the olivine and chromite in the Bushveld pyroxenite are in equilibrium, it seems possible that such a process may increase the $\Delta^{17}$O of the olivine. If the olivine is ignored and the Cr-spinel and pyroxene taken to be in equilibrium, $\lambda$ is $0.5275 \pm 0.0038$ (2 SE) (see Figure 4.18). It is difficult not to draw parallels between the olivine $\Delta^{17}$O offset displayed on Figure 4.18 and that on
Figure 4.15, however the offset between olivine and pyroxene on Figure 4.18 is not statistically significant ($P = 0.57$). This is unsurprising given the restricted data set available.

![Graph showing oxygen isotope data for pyroxenite](image)

**Figure 4.18 – Bushveld oxygen isotope data for pyroxenite.** Note that there is a hint that the olivine may be offset from a mass-fractionation line ($\lambda = 0.5275$) connecting Cr-spinel and orthopyroxene (dotted black line). The $\lambda$ for $\Delta^{17}$O on this figure is 0.5262.

The Cr-spinel-orthopyroxene slope on Figure 4.18 is consistent with high-T equilibrium mass-dependent fractionation (e.g. Pack & Herwartz, 2014; Young *et al*., 2016) and also with the slope in PMG-low defined by chromite-farringtonite (see Figure 4.15). Given that in the case of the pyroxenite samples olivine almost certainly crystallised from the same melt, yet significantly steepens the $\lambda$ for the whole rock, it is reasonable to suggest that some crystal chemical or other process may offset olivine relative to the other phases on a three-isotope diagram (see Figure 4.15 and Figure 4.18). This same process, if it exists, may be what is affecting the pallasites. If this is the case, the chromite and the olivine in pallasites may be in equilibrium, stemming from a common isotopic reservoir. This would have severe implications for future oxygen isotope interpretation and mean that significant care must be taken in whole-rock and inter-mineral isotopic studies. There is no corresponding $\Delta^{17}$O offset identifiable in the very limited ES olivine-chromite dataset (Figure
3.19) meaning that even if an anharmonic or mineral-specific offset is present in PMG-low and BIC samples, it does not appear to be universal. Cano et al. (2020) recently attributed the proposed crystal chemical effects observed by Kohl et al. (2017) and Young et al. (2016) to crustal contamination in the BIC rather than some previously unknown process, however this interpretation cannot be extended to cover the PMG results in this study. Further investigation into the mechanics of olivine-chromite equilibria at high-T are warranted to identify if any such mineral-specific effect exists. In light of the possibility that an anharmonic effect may account for the observed variation in the BIC results, it is important to consider that such effects may have influenced the isotopic compositions of the PMG olivine-chromite system.

4.5.3 Crossovers

In very limited cases, it is possible for $\lambda$ to range from $-\infty$ to $+\infty$ in restricted cases where the fractionation factor ($\alpha$) for $^{17}\text{O}/^{16}\text{O}$ reaches 1 at different closure temperatures to that of $^{18}\text{O}/^{16}\text{O}$ for a given system (Skaron & Wolfsberg, 1980; Deines, 2003). The temperature range at which this occurs is typically very small (see worked example in Appendix 1), however if the samples reached equilibrium in this range, it is possible that the mass-fractionation line may be steeper than 0.5305. This is almost certainly not the cause of the disequilibrium for two reasons: 1) the chances of equilibrium being reached in such a small temperature range would probably be very low, however it is not known what this temperature range would be, and crucially 2) the fractionation factors $\alpha_{17/16}$ and $\alpha_{18/16}$ for all analysed PMGs are all positive which suggests that they are not in a crossover situation.

4.5.4 Nuclear field shift effect (NFSE)

Assuming that the olivine and chromite formed from a common isotopic reservoir, the oxygen isotope disequilibrium in PMGs could be the result of a mass-independent effect offsetting one or both phases from a mass-fractionation line. Given that the PMGs formed in a high-T, igneous environment, no consideration has been thus far been given to the possibility that mass-independent effects may impact isotope fractionation. Despite this, mass-independent effects are known to impact isotope fractionation of heavier elements such as U (Yang & Liu, 2016). The odd-numbered isotope $^{235}\text{U}$ has been found to diverge from the expected mass-dependent fractionation line delineated by
the even numbered isotopes of U (Fujii et al., 1989, 1989b). In these cases, a mass-independent component originating from differences in ground-state electronic energy causes offsets from expected mass-dependent fractionation trends. An investigation into the magnetic isotope effects of nuclear spin on isotope ratios in U has shown that they are negligible (Bigeleisen, 1996). The differences reported are caused by the nuclear field shift effect (NFSE) which relates to differences in nuclear shape and size (Yang & Liu, 2016). This effect is caused by variations in the arrangement of protons relative to neutrons in a nucleus of isotopes with odd mass numbers compared with those with even mass numbers (Fujii et al., 2006). These differences cause unevenness in the nuclear charge radii which gives rise to a mass-independent component to the electric field around different isotopes of the same element and in turn, to fractionation (Fujii et al., 2006). Nuclei with odd-numbered neutron counts react as though they are lighter nuclei in chemical exchange reactions as a result of the NFSE (Bigeleisen, 1996). The relationship between the NFSE and temperature is linear and inversely proportional. Mass-dependent fractionation effects also decrease with increasing temperature, this relationship is $1/T^2$ at high temperatures (Eqn 2.55b in Criss 1999). The NFSE decreases with temperature to a lesser degree, with a factor of $1/T$ (Yang & Liu, 2016). Consequently, it is conceivable that at high temperatures any NFSE would be more noticeable as mass-dependent effects would be smaller relative to any NFSE contribution. The contribution of such nuclear volume effects has been shown to be the dominant cause of equilibrium fractionation in $^{205}$Tl/$^{203}$Tl and $^{202}$Hg/$^{198}$Hg, accounting for up to a ~3 ‰ fractionation (Schauble, 2007). Mass-dependent effects on the same systems produce significantly smaller fractionation, 0.5–1 ‰ (Schauble, 2007).

The amount of NFSE is thought to increase with increasing difference in mean-square nuclear charge radius, $\delta <r^2>$, ($\delta <r^2> = <r^2>_{X'} - <r^2>_X$) where $<r^2>_X$ denotes the mean square nuclear charge radius of the heavy isotope of element X of a given nucleus. These radii do not increase linearly (or even necessarily increase) with increasing neutron number (see Figure 4.19) (Yang & Liu, 2016). This offset of odd numbered isotopes from the trend defined by even numbered isotopes of the same element is called odd-even staggering (King, 1984 as cited by Yang & Liu, 2016). The fact that the variation in mean square nuclear radius ($\delta <r^2>$) in odd-numbered uranium isotopes is non-linear with the change in $\Delta m/mm'$ (see Figure 4.20) is evidence that NFSE induces mass-independent
effects on isotope fractionation (Yang & Liu, 2016). Here, $\Delta m$ refers to the mass difference between the isotopes, $m$ and $m'$ are the masses of the lighter and heavier isotope respectively (Yang & Liu, 2016). This variation is less well constrained in oxygen isotopes (Figure 4.21) as there are only 3 stable isotopes of which one has an odd mass number. However, the $\delta \langle r^2\rangle$ between the odd and even numbered nuclei suggests that NFSE may be active in oxygen isotope fractionation.

Figure 4.19 – Root mean square nuclear charge radii vs mass number for the stable oxygen isotopes with which this study is concerned. Note that the $^{17}$O has a smaller RMS nuclear charge radius than simple extrapolation between the even numbered isotopes would suggest. Errors for $^{16}$O are standard deviation of the results tabulated in Fricke & Heilig (2004). Errors for $^{17}$O and $^{18}$O are those quoted by Fricke & Heilig (2004) and references therein.

Figure 4.20 – $\delta \langle r^2\rangle$ (fm$^2$) vs $10^3 \Delta m/mm'$ for isotopes of uranium (after Yang & Liu, 2016, Figure 2b). Here the offset of odd-numbered nuclei from the linear relationship seen in even numbered nuclei is clearer than in the oxygen diagram on
Figure 4.21. The red dotted line is the trendline of even-numbered nuclei. The data for this diagram was calculated using values from Fricke & Heilig (2004b).

![Diagram](image.png)

Figure 4.21 – A plot of $\delta^{18}$O vs $10^3\Delta m/mm'$ (where ' denotes the heavy isotope) for oxygen isotopes $^{16}$O, $^{17}$O, and $^{18}$O. Note the deviation from the trend exhibited by $^{17}$O. See Figure 2b in Yang & Liu (2016). The red dotted line represents the trendline for even numbered isotopes. The data for this diagram was calculated using values from Fricke & Heilig (2004a). The large offset for $^{17}$O indicates a mass-independent component that may be associated with the NFSE (see Fujii et al., 2009).

It is conceivable that the disequilibrium observed between olivine and chromite in PMGs is caused by disparate NFSE effects between the two minerals; because the magnitude of NFSE changes with temperature (Yang & Liu, 2016), it is possible that minerals with different crystallisation histories and temperatures may record mass-independent effects. In light elements, the NFSE has been thought to be too small to matter (Yang & Liu, 2016) although it may be that this effect is now detectable at the improved precision afforded by laser-assisted fluorination. Accurate methods for the calculation of NFSE in crystalline materials and melts do not, to date, exist (Yang & Liu, 2016).

4.5.5 Cosmic ray spallation

Another possible mechanism for generating the observed disequilibrium in PMG oxygen isotopes is cosmic ray spallation. The interactions between cosmic rays and minerals are known to affect some isotopic systems (Stauffer & Honda, 1962; Honda, 2002). Given the long CRE ages (> 200 Ma, see Herzog et al., 2015) of some PMGs, the potential for spallation-induced overprinting of the original
isotopic composition must be considered. Inelastic collisions of H with $^{20}\text{Ne}$, $^{24}\text{Mg}$, $^{28}\text{Si}$, and $^{56}\text{Fe}$ can produce $^{16}\text{O}$, $^{17}\text{O}$, and $^{18}\text{O}$ at different rates relative to their natural abundances (Longair, 1992) and therefore could conceivably alter the isotope composition of the PMG minerals, in which some of these target nuclei are common. Given the improved precision now achievable through the use of laser-assisted fluorination, it is possible that previously unseen effects may be creating secondary oxygen isotope signatures that are now measurable. Whilst accurate spallogenic production rates are not available for all of the elements or phases involved, it is possible to evaluate the likelihood of cosmic ray spallation-induced offsets using measured $\Delta^{17}\text{O}$ values and published CRE ages of some of the pallasites that have been analysed in this study (Figure 4.22).

![Figure 4.22](image)

**Figure 4.22** – Cosmic ray exposure ages (Myr) from Herzog *et al.* (2015) vs. $\Delta^{17}\text{O}$ of selected PMG olivines (this study), l-r Seymchan, Imilac, Brahin, Brenham. The black dotted line is the trendline through the data. X-errors are standard deviation of the CRE ages in Table 15 of Herzog *et al.* (2015) except where fewer than two ages are available (where the quoted error is taken). Y-errors are 2 standard deviation except for Brahin (where 2 standard error is taken because fewer than 2 samples were run).

Figure 4.22 and Figure 4.23 display CRE age vs $\Delta^{17}\text{O}$ for PMG minerals where both exposure age and isotope data are available. Despite there being a ~130 Myr difference in CRE ages between
Seymchan and Brenham (see Figure 4.22 and Figure 4.23), the $\Delta^{17}$O values for both the olivine and chromite of these two meteorites as well as those with intermediate CRE ages are unresolvable. This lack of any relationship between CRE age and $\Delta^{17}$O strongly suggests that despite the large CRE age variations in PMGs, there is no causal link between CRE age and the observed olivine-chromite disequilibrium.

Figure 4.23 – Cosmic ray exposure ages (Myr) from Herzog et al. (2015) vs. $\Delta^{17}$O (this study) for selected PMG chromites (as above for olivines). L-τ Seymchan, Imilac, Brahin, Brenham. The black dotted line is the trendline through the data. X-errors are standard deviation of the CRE ages in Table 15 of Herzog et al. (2015) except where fewer than two ages are available (where the quoted error is taken). Y-errors are 2 standard deviation except for Brahin (where 2 standard error is taken as fewer than 2 samples were run).

4.5.6 Instrument-induced offsets

Fractionation of $\delta^{18}$O results was observed in chromite analyses prior to the optimisation of the technique (see section 2.7). The fact that $\lambda$ values measured during laser-fractionation of PMG chromite are mass-dependent precludes it as a candidate for causing the isotopic disequilibrium between olivine and chromite in PMG-low samples. This is because the required $\lambda$ values for PMG-low and PMG-high minerals are both steeper than possible through mass-fractionation, although the latter is within error of a mass-fractionation slope. Given that the instrument-induced fractionation effects such as shown in Figure 2.11 are mass-dependent and the observed difference between olivine
and chromite phases in PMG is not mass-dependent, such an effect cannot be the cause of the disequilibrium.

4.6 Candidate formation environments for PMGs

Having considered a range of factors that might influence the observed oxygen isotope variations in PMGs (see section 4.5), this section explores various candidate formation environments and processes. This utilises both data obtained in this study and data from the literature.

4.6.1 PMG planetesimal size estimates

Estimates of sizes for the PMG parent body are variable. On the basis of low-temperature metallographic cooling rates, Yang et al. (2010) estimate that the PMG parent body was around 400 km in radius. This estimate assumes that the PMG body re-accreted from ~20 vol% of the core and ~40 vol% of the mantle of a larger body (around 950 km radius) following a hit-and-run impact (e.g. Asphaug et al., 2006). However, this model does not take the effects of regolith cover into account, and also assumes that the slowest cooled pallasites were positioned at the centre of the re-accreted body. If the oxygen isotope disequilibrium identified in this study, combined with cooling rate (e.g. Yang et al., 2010) and palaeomagnetic evidence (e.g. Tarduno et al., 2012; Nichols et al., 2016), is taken as evidence for two isotopic reservoirs mixed in a planetary impact (see section 4.6.5), both of the assumptions that PMGs cooled in the centre of the body and the assumed lack of regolith are likely to be false. Whilst any impact-injected metal could conceivably percolate through the mantle in a manner similar to that proposed for core-formation on 4 Vesta (e.g. Kieffer & Mittelfehldt, 2017), there is unlikely to be olivine in the core of the body because of the stark density contrast between it and the metal. Furthermore, if the shallow emplacement depths estimated for some PMGs on the basis of palaeomagnetic studies (e.g. Tarduno et al., 2012; Bryson et al., 2015; Nichols et al., 2016) are accurate, then coupled with the slow cooling rates at low-temperature (Yang et al., 2010), the evidence is consistent with a regolith-insulated parent body that was in the range of 200–400 km radius (e.g. Yang et al., 2010; Tarduno et al., 2012; Bryson et al., 2015; Solferino & Golabek, 2018). If PMGs are not generated in an impact and are instead formed through some differentiation process (e.g. Boesenberg et al., 2012), the estimate of parent body size would probably change very little. If the PMGs formed at depth, near the core-mantle boundary, then the parent body could be smaller.
than 200–400 km radius to produce the observed cooling rates given the same amount of regolith. In the case of an impact-injection formation of PMGs (section 4.6.5), the size of the impactor is unconstrained. Any impacting body would need to have been large enough to have undergone core separation during differentiation because it is this material that is mixed with PMG olivine. It would also probably have to have been smaller than the PMG body (200–400 km radius) for the latter to avoid destruction (e.g. Asphaug et al., 2006).

The estimates for the PMG parent body radius outlined above are similar to the measured value of the asteroid 4 Vesta of 262.7 ± 0.1 km (Russell et al., 2012) which may be the parent body for the HED meteorites (e.g. McSween et al., 2011). Given that 4 Vesta is thought to be a remnant protoplanet from the earliest stages of Solar System evolution (Russell et al., 2012) and therefore to have formed at the same time as the PMG parent body (see section 4.4), it is useful to use 4 Vesta as a point of reference. If it is assumed that the PMG parent body was similar in its internal make-up to 4 Vesta, the latter can be used to help calculate several characteristics that would have had an influence on PMGs. These characteristics include the oxygen content of the PMG core and the diffusion rate of oxygen in the PMG metal melt (see section 4.6.3.2).

4.6.2 Oxygen content

Analysis of the Salta and Springwater PMGs have yielded $f_{\text{O}_2}$ conditions of -0.5 log units below the iron-wüstite (IW) buffer and approximately equal to the IW buffer respectively (Righter et al., 1990). For the ES pallasites, there was a slightly higher partial pressure of oxygen, approximately 0.5 log units above the IW buffer (Righter et al., 1990).

If PMGs are a core-mantle boundary mixture, or a mechanical mixture of core and mantle material that originated from the same parent body, it should be possible to estimate the amount of oxygen that was in the PMG parent body following differentiation. PMGs are approximately 35% metal by volume of which ~5% is chromite, phosphates, and other accessory minerals (Yang et al., 2010). Given these values, and if it is assumed that the 5% is all metal-hosted chromite in order to create a higher bound for oxygen content in the core, then the PMG metal is ~14% chromite by volume. EPMA analyses of PMGs in this study show that the typical oxygen yield in stoichiometric chromite should be around 30%. Assuming that the metal component of PMGs has a density of ~7900 kg m$^{-3}$
(Britt & Consolmagno, 2003), and chromite has a density of 5090 kg m\(^{-3}\) (Deer et al., 1966), the
density of the metallic fraction, including the 14 vol% chromite, is around 7506 kg m\(^{-3}\) of which
around 9.5 wt% is chromite. If 30% of this chromite is oxygen, then there was around 2.8 wt% O in
the PMG metal which is marginally higher than, but broadly consistent with, the 2.5 wt% upper
bound suggested for Earth’s core (Ricolleau et al., 2011).

Size estimates for the PMG parent body place it in the same range as the asteroid 4 Vesta (see section
4.6.1). If it is assumed that the PMG parent body had the same internal structure as 4 Vesta, it would
be 9.3 volume percent core (Kiel, 2002). The crust is ignored for simplicity here so it is assumed
that the remaining 90.7 volume percent of the body is mantle. With the densities of the metal
component given above, and assuming an olivine density of 3400 kg m\(^{-3}\) based on studies of the
Earth’s upper mantle (Wang, 1970; Anderson, 1989), the average density would be around 3786 kg
m\(^{-3}\). For a body of 263 km radius with a core accounting for 9.3% of the volume, the core radius is
119 km and the mantle radius is 144 km. This equates to a core mass of 5.3 \times 10^{19} kg and a mantle
mass of 2.3 \times 10^{20} kg assuming the densities for each component outlined above. The total mass of
the body is therefore 2.9 \times 10^{20} kg, similar to the measured 2.6 \times 10^{20} kg for 4 Vesta (Russell et al.,
2012). This means that by mass the planetesimal was 18.5% core, similar to measured values for 4
Vesta (Russell et al., 2012) and consistent with H chondrite FeNi proportions (Korotev, 2019). The
responding mantle therefore accounts for 81.5% of the mass of the body. Given the wt% O
calculated in PMG metal (2.8 wt% - see above), and a value of 44% for olivine based on laser
fluorination yields and EPMA data, then if the PMG parent body were the same structurally as 4
Vesta, the total oxygen content for the PMG parent body, assuming it is 4 Vesta-like, is 36.37 wt%,
of which 35.84 wt% (98.5%) is in the mantle and 0.53 wt% (1.5%) is in the core. If the PMG metal
is representative of the bulk core, the silicate-metal partition coefficient for oxygen during parent
body differentiation was \sim 68. This assumes that all 5% of accessory minerals (Yang et al., 2010) in
PMGs is chromite containing 30 wt% O which likely overestimates metal oxygen content and as
such is a lower bound for silicate-metal partition coefficient.
4.6.3 Restite or incomplete homogenisation

4.6.3.1 PMG temperatures

The metal fraction of PMGs, rather than representing a planetary core, may record partially melted material beginning to settle during differentiation (Figure 4.24). Chondritic material likely formed the building blocks for the terrestrial planets (Jurewicz et al., 1993) and therefore chondritic partial melting experiments and similar studies are important in understanding how partial melting of this precursor material may be recorded in achondrites. There is no absolute evidence that chondrites do represent the precursor material of differentiated bodies sampled by achondrite meteorites although this stance is regularly adopted, in part due to the lack of non-chondritic primitive meteorites (McCoy et al., 2006). The minimum temperature at which FeNi + FeS start melting from chondritic material is as low as 1261 K (Tomkins, 2009) and basaltic silicate melts melt at between ~1323 and 1373 K (McCoy et al., 2006). It is therefore conceivable that precursor chondritic material, heated by radioactive decay of $^{26}$Al (Larson et al., 2016) and $^{60}$Fe (e.g. Moskovitz & Gaidos, 2011), underwent partial melting which resulted in the localised concentration of restite olivine, FeNi metal, and accessory phases after the removal of, for example, more buoyant basaltic silicate melts. In this scenario, the large density difference between the olivine and metal in pallasites suggests that they may have initially separated following melting and then been remixed; this remixing could then explain the presence of fragmental olivine in PMGs. Main group pallasites do provide some constraints on the maximum temperature reached. The presence of phosphoran olivine in some PMGs, which crystallised around 1523 K (Boesenberg et al., 2012), shows that the temperature must have been at least that high. When combined with the fact that the rounding of olivine predates co-existing phosphoran olivine crystallisation (Boesenberg et al., 2012) and that the rounding occurs during contact with FeS melt (Solferino et al., 2015; Solferino & Golabek, 2018), it is clear that whilst the metal could conceivably have melted at temperatures as low as 1261 K there must have been a prolonged period of time when olivine and metal were juxtaposed at temperatures that were well above this. It is not clear, however, that this temperature ever exceeded the olivine solidus and therefore the possibility that PMGs record restite olivine and partially melted FeNi metal must be examined.
Depending on the temperatures reached, partial melting (*e.g.* Figure 4.24) could preserve isotopic heterogeneity of precursor chromite and olivine. If the PMG parent body was not fully melted and homogenised, evidence of the primordial isotopic heterogeneity should be manifest in the metal and silicate phases. In PMGs, the oxygen isotope compositions of these phases are represented by the chromite and olivine, respectively. Given that Fo$_{90}$ olivine has a high liquidus temperature, ~1873 K at 1 atm pressure (Ashcroft & Wood, 2015) and perhaps up to 1973–2073 K (Bowen & Schairer, 1935), coupled with the very slow diffusion rate of oxygen between olivine and silicate melts (see section 4.3.1) it seems likely that any remnant heterogeneity would be preserved in the isotopic composition of PMG olivine unless the diffusion rate of oxygen increases very drastically from ~1873 K to ~2073 K. Partial melting experiments of both ordinary (H6) and carbonaceous (CV and CM) chondrites at reducing $f_{O_2}$ conditions (Ford *et al.*, 2008) and at conditions around IW (Jurewicz *et al.*, 1993) show that olivine crystals remain un-melted in the presence of other melt phases at temperatures of ~1573 K.

Figure 4.24 – Ongoing differentiation of silicate and metal. In this model, partially melted metallic melt is percolating through silicate restites. Figure from [http://www.jsg.utexas.edu/news/2017/12/trickle-down-is-the-solution-to-the-planetary-core-formation-problem/](http://www.jsg.utexas.edu/news/2017/12/trickle-down-is-the-solution-to-the-planetary-core-formation-problem/).

On the basis of results reported in the work herein this process is unlikely to be responsible for the PMGs for several reasons. The established oxygen isotopic homogeneity of PMG olivine (Greenwood *et al.*, 2006; 2015; this study - section 3.3.1) seems to preclude the possibility that the
mantle was not isotopically homogenised. This homogeneity spans a range of cooling rates (e.g. Yang et al., 2010) that likely correspond to formation depths, suggesting that it was widespread.

There is a reported bimodality in olivine oxygen Δ^{17}O compositions (e.g. Ali et al., 2018) – which this study was unable to reproduce – interpreted as two resolved mass-fractionation lines. Even this is not consistent with mixing or remnant isotopic heterogeneity but rather would support an impact mix of two well-homogenised isotopic reservoirs. On the basis of the homogeneity of the olivine isotopic composition, the PMG parent body interior was probably initially molten. Effective homogenisation of a restite would require relatively rapid diffusion of oxygen in olivine contrary to empirically-determined estimates (section 4.3.1.1). Models for heating by decay of $^{26}$Al estimate that bodies accreting within the first ~1.5 Myr of Solar System history could have had fully melted interiors, especially those of several hundred km radii (see Figure 4 in Sanders & Scott, 2012).

Tungsten isotope chronology from PMG metal shows that it was undergoing differentiation during this time period (see Figure 4.14) and had therefore already accreted. When the isotopic homogeneity of PMG olivine is coupled with the slow cooling rates of PMG metal (Yang et al., 2010), it leads to the conclusion that the PMG body was probably both initially molten, and relatively large. The PMG parent body had an active core dynamo (e.g. Tarduno et al., 2012; Nichols et al., 2016) and therefore must have undergone effective core separation which requires a minimum of 50% partial melting of silicates (Taylor, 1992). The maximum temperatures experienced by the PMGs have been estimated at ~1873–1973 K on the basis of the preservation of Al-Cr zoning in PMG chromites (Boesenberg et al., 2012), although given that there appears to be internal isotopic homogeneity in PMG olivine oxygen isotope composition that may require complete melting of the olivine, the temperature may have been even higher. In this case, the Al-Cr zoning may have been imparted by varying silicate:metal melt ratios during crystallisation and slow cooling of chromite rather than preservation of a precursor zoning profile. Whether the olivine fully melted or not, in order to effectively homogenise the oxygen isotope composition across all analysed PMG olivine samples, the temperature would have had to exceed 1673 K and probably 1873 K perhaps by a significant amount and for a prolonged period of time on the basis of experimental measurements of oxygen diffusion in olivine (Ryerson et al., 1989; Gerard & Jaoul, 1989). Oxygen diffusion measurements in San Carlos olivine were performed at the IW buffer (Ryerson et al., 1989). The $f_O^2$ of the PMG formation
environment was likely between 0.5 log units below the IW buffer and the IW (Righter et al., 1990), suggesting that the diffusion of oxygen at ~1673 K and 1873 K may have been slower still.

An investigation of the isotope equilibrium temperatures for olivine and chromite may also provide some insight into PMG formation temperatures. The earlier discussed possibility that PMG-high chromite underwent some high-T equilibration with a silicate melt that was in isotopic equilibrium with the olivine (see section 4.3.2.1) is potentially consistent with the calculation of the olivine-chromite equilibrium temperature of PMG-high minerals, 1733 K (Zheng, 1991; 1993; Beaudoin & Therrien, 2009) and suggests that if the phases are in equilibrium the temperature was at least this high. A similar investigation into the olivine-chromite equilibrium temperature for PMG-low minerals yields a temperature of 1206 K which is below the solidus temperature of both minerals, suggesting that they are unlikely to be in equilibrium. Given the standard deviation of δ¹⁸O over analysed samples for both the olivine and the chromite, however, caution must be used when interpreting based on this temperature. Calculating the maximum possible range of temperatures on the basis of δ¹⁸O errors yields a possible equilibrium temperature range for PMG-low of 1007–1528 K and for PMG-high 1252–2273 K. Given the established disequilibrium between PMG-low olivine and chromite (see section 3.5.1.1), only the PMG-high equilibrium temperatures might be relevant in constraining PMG formation temperatures although these temperatures are based on end-member chromite compositions and the Al-content of PMG-high chromite may have an effect on this temperature. Even if the temperature is not affected by the chromite composition, the > 1000 K range imparted by the large range in δ¹⁸O compositions of the chromite in these samples means that little can be gleaned from the data aside from a minimum temperature.

Experimental examination of the crystallisation temperature for pallasite-like metal has shown it to be 1753–1798 K (Donohue et al., 2018) which is difficult to reconcile with the presence of phosphoronic olivine in some PMGs. Where present in PMGs, phosphoronic olivine likely crystallised at around 1523 K and from a melt of identical composition (Boesenber et al., 2012). This suggests that by the time phosphoronic olivine was crystallising at ~1523 K from a P-enriched silicate melt (Boesenber & Hewins, 2010), the metal temperature was well below its crystallisation temperature (e.g. Donohue et al., 2018). In this scenario it is hard to envisage how P-rich silicate melt could still
be present except as late-stage melt pockets. In light of the observed melt out of FeNi metal and FeS at < 1273 K in chondrite partial melt experiments (Tomkins, 2009) it may be the case that the liquidus temperature for PMG metal has been overestimated. The presence of phosphoran olivine therefore suggests that either 1) the metal was solid at 1523 K and phosphoran olivine crystallised from a P-rich silicate melt in trapped pockets, perhaps adsorbed on olivine crystals, or 2) that P-rich silicate melt was present in small quantities and crystallised prior to the metal. A further possibility is that the P content of this melt depressed the liquidus temperature (e.g. Haack & Scott, 1993; Chapter 1), in which case there may have been localised melt pockets remaining after metal crystallisation. Without a concrete understanding of the non-metal content in PMGs during crystallisation, it is difficult to determine which of these is correct. However, the presence of phosphoran olivine as overgrowths rather than as discrete crystals suggests that it may have been present as trapped melt or adsorbed on to olivine crystals. In either case, after the phosphoran olivine crystallisation, the temperature did not again exceed ~1523 K (Boesenberg & Hewins, 2010; Boesenberg et al., 2012). The phosphoran olivine seems to be preferentially associated with PMGs exhibiting rounded olivine morphologies and forms on the crystal edges. As such, it seems likely that it formed after rounding with some silicate melt present (Boesenberg et al., 2012; McKibbin et al., 2019). Given that rounding is thought to form after isolation of olivine in FeS melt (Solferino et al., 2015; Solferino & Golabek, 2018), it seems likely that small pockets of P-enriched silicate melt remained throughout this period.

4.6.3.2 Diffusion rate of oxygen in molten metal

The chromites analysed also display a reasonably high degree of isotopic homogeneity within subgroups that is not consistent with preservation of prior mass-independent chondritic values (see section 4.3.2.1), although this could be explained by the much more rapid diffusion rate of oxygen in molten metal than in restite olivine. To calculate the diffusion rate of oxygen in molten iron, it is desirable to have a handle on the P-T conditions under which the diffusion is taking place, even though the rate is thought to be broadly independent of these conditions (Posner et al., 2017). To work out these conditions, the following assumptions are made.
- The PMG parent body radius is taken as approximately 263 km as has been proposed (see section 4.6.1).

- Pallasites formed at around 25 km depth (e.g. Nichols et al., 2016)

- The molten metal is above experimentally determined liquidus temperature, 1753–1798 K (Donohue et al., 2018) but lower than 1973 K which may be pallasite peak temperature (Boesenberg et al., 2012). The temperature used is 1915 K (Posner et al., 2017).

The overburden pressure is given by:

Equation 4.3

\[ P(Pa) = \rho gh \]

where \( \rho \) is density, \( g \) is acceleration due to gravity, and \( h \) is depth/thickness of overburden. The depth of pallasite formation is assumed to be 25 km (Nichols et al., 2016), although this is probably variable across the PMGs. The density of the overburden material is assumed to be 3400 kg m\(^{-3}\), broadly representative of peridotite in Earth’s upper mantle (Wang, 1970; Anderson, 1989). The acceleration due to gravity is given by:

Equation 4.4

\[ g = \frac{GM}{r^2} \]

where \( G \) is the gravitational constant, \( M \) is the mass of the body, and \( r \) is the radius from the centre of mass of the body. This last term is simply the planetesimal radius minus the formation depth. In order to get a realistic estimate for the mass of the PMG body, the mass and radius of an extant differentiated body of comparable size, 4 Vesta (radius = ~263 km), is used: 2.59076 x 10\(^{20}\) kg (Russell et al., 2012). This means that the acceleration due to gravity at 25 km depth for a PMG body of radius 263 km and mass equivalent to 4 Vesta equals:

Equation 4.5

\[ g = \frac{6.67 \times 10^{-11} \times 2.59076 \times 10^{20}}{(263000 - 25000)^2} \]

\[ = 0.31 \, ms^{-2} \]

Inputting the density, acceleration due to gravity, and depth into the overburden equation gives:
Equation 4.6

\[ P(Pa) = 3400 \times 0.31 \times 25000 = 25930926.17 \text{ Pa} = 26 \text{ MPa} \]

So rough P-T conditions of 26 MPa and 1915 K have been established for pallasite formation at 25 km depth in a 4 Vesta-like parent body. This can be inputted into the Arrhenius Model in order to obtain the diffusivity for O under these conditions. The Arrhenius Model is given by (Posner et al., 2017):

Equation 4.7

\[ D(P,T) = D_0 \exp \left( -\frac{\Delta H + P\Delta V}{RT} \right) \]

where \( D_0 \) is the pre-exponential diffusion coefficient (1.2 \( \times \) 10\(^{-7}\) m\(^2\) s\(^{-1}\) from Posner et al., 2017), \( \Delta H \) is activation enthalpy (50 ± 17 kJ mol\(^{-1}\) from Posner et al., 2017), \( \Delta V \) is activation volume (1.1 \( \times \) 10\(^{-7}\) m\(^3\) mol\(^{-1}\) from Posner et al., 2017), \( R \) is the universal gas constant (8.314 J/mol K from Posner et al., 2017), and \( T \) is the temperature (1915 K). For the conditions assumed:

Equation 4.8

\[ D(45 \text{ MPa, 1915 K}) = 1.2 \times 10^{-7} \exp \left( -\frac{50000 + 2.5931 \times 10^7 \times 1.1 \times 10^{-7}}{8.314 \times 1915} \right) \]

\[ = 5.19 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \]

This equates to 5.19 \( \times \) 10\(^{-5}\) cm\(^2\) s\(^{-1}\), or approximately 5 cm\(^2\) per day. The calculation uses inputs from Posner et al (2017) for 3 GPa pressure (the lowest investigated in that study) and as such is only a broad estimate. Despite this, the similarity between inputs for 3 GPa and 18 GPa (see Posner et al., 2017) as well as the possibility that diffusion rate of oxygen in liquid iron is largely independent of P conditions, mean that this is probably a realistic ball-park figure. This assertion is backed up by comparison of this figure with measured Arrhenius curves in Figure 5 of Posner et al. (2017).

The expected rapid diffusion of oxygen in molten FeNi metal calculated above has important implications for oxygen isotope equilibration between metal and silicate fractions of pallasites. Given that the diffusion is on the order of several cm\(^2\) per day, it is very likely that the oxygen isotopes would have equilibrated between the silicate and metal if they formed from melting of a common precursor.
Accounting for PMG formation at greater depth, e.g. at the core mantle boundary, the above calculation would change slightly. If the core radius of 4 Vesta (107–113 km, Russell et al., 2012) is used for the PMG body, the core-mantle boundary would be ~110 km from the centre of the body, radius 263 km. This equates to a depth of 153 km. In this calculation, the overburden density is again taken to be 3400 kg m\(^{-3}\), similar to the upper mantle density on Earth (Wang, 1970). Using the same procedure as used above, the acceleration due to gravity at the core-mantle boundary is 1.43 ms\(^{-2}\), and the overburden pressure is 743 MPa. Inputting these values into the Arrhenian model yields a diffusivity of 5.17 x 10\(^{-9}\) m\(^{2}\)s\(^{-1}\). This value is essentially the same as for the scenario above, roughly 5 cm\(^{2}\) per day. The similarity of these diffusivities is unsurprising given that diffusion rates of oxygen in liquid iron are thought to be largely independent of pressure (Posner et al., 2017), but it serves to illustrate that it is likely that the oxygen had equilibrated in the metal regardless of the formation environment. Even if the temperature for PMG metal melt is taken as the lowest possible value and based on chondritic partial melting experiments (Tomkins, 2009), corresponding to around 1261 K, the diffusivity is 1.01 x 10\(^{-9}\) m\(^{2}\)s\(^{-1}\) or approximately 0.87 cm\(^{2}\) per day. In summary, the reason for the chromite-olivine disequilibrium cannot be incomplete homogenisation of oxygen in the metal component of pallasites.

4.6.3.3  Implications

The maximum temperature during PMG formation was certainly above ~1523 K on the basis of the presence of phosphoran olivine (Boesenberg et al., 2012). Given that experimentally determined liquidus temperatures for PMG-like metal are in the region of 1753–1798 K (Donohue et al., 2018) combined with the fact that the oxygen isotope composition of PMG olivine is well-homogenised despite the incredibly slow estimates for diffusion rate at ~1673 K and ~1873 K, it seems likely that the temperature in PMGs exceeded ~1773 K perhaps by a considerable amount. The peak temperature estimate for PMGs of 1973 K (Boesenberg et al., 2012) cannot be constrained further using data from this study, although on the basis of the well-homogenised oxygen isotope composition of PMG olivine it seems likely that it crystallised from a homogeneous melt rather than homogenised as a restite. Depending on the liquidus temperature of olivine during precursor melting, this may have been above or below 1973 K.
The rough calculation of the oxygen diffusion rate in molten metal is convincing evidence against the observed olivine-chromite isotopic disequilibrium forming through lack of full homogenisation. A diffusion rate in the region of 1–5 cm$^2$ per day suggests that the metal melt would not have acted as a significant barrier to isotopic homogenisation over millions of years and therefore rules out the possibility that incomplete equilibration of oxygen between the metal and silicate in PMGs could be the cause of the isotope disequilibrium measured between olivine and chromite. The suggestion of rapid oxygen diffusion in PMG metal is borne out by the relatively well constrained oxygen isotope results for PMG-low chromite. By contrast, the very slow oxygen diffusion rate in olivine at similar temperatures (approximately 1 cm$^2$ in 32 Myr – see section 4.3.1.1) means that the olivine was likely fully melted and is not a restite. As a result of these factors, the PMG parent body likely homogenised isotopically during differentiation. If representative of the silicate and metal melts in equilibrium, the olivine and chromite in PMG-low samples should fall on a mass-dependent fractionation line. This means that an equilibrium fractionation exponent would be expected to describe this relationship, contrary to what is observed.

4.6.4 Core-mantle boundary or pallasite zone

The canonical formation environment for PMG formation is at a core-mantle boundary or similar metal-silicate interface (e.g. Boesenberg et al., 2012; McKibbin et al., 2019). Several arguments have been previously raised against this model (see Chapter 1). Nevertheless, such a formation environment is a key contender for PMG genesis. Some of these arguments are perhaps not wholly inconsistent with PMG formation in a core-mantle boundary. For example, the range in low-T cooling rates in PMG metal have been cited as evidence for the reaggregation of the PMG body after an impact and does not seem consistent with formation at a well-defined core-mantle boundary (Yang et al., 2010). However, in a small planetesimal with a relatively low gravitational gradient, it seems plausible that a core-mantle boundary might be less well defined than for larger bodies and perhaps account for the range in cooling rates. Palaeomagnetic evidence suggestive of PMG formation at very shallow depths (Tarduno et al., 2012; Bryson et al., 2015; Nichols et al., 2016) has recently been attributed to the effects of a locally variable magnetic field generated by a small convecting sulphide or phosphide inner core separated from PMG formation by crystallised core material (McKibbin et al., 2019) although the existence of these criteria in PMGs is speculative.
In a core-mantle boundary environment, a possible mechanism for the injection of metal into an overlying mantle is core-collapse or core-overturn. Asteroidal cores are known to have inwardly crystallised (Yang & Goldstein, 2006; Yang et al., 2008), and that the presence of non-metals such as S, P, and C, as well as incompatible elements such as O would increase in the residual melt as metal crystallisation progressed. In this scenario, it is possible that a progressively evolving melt enriched in lighter elements relative to crystallised metal surrounding it would either forcefully be ejected into the mantle in a manner similar to proposed ferrovolcanic processes (e.g. Johnson et al., 2019; Abrahams & Nimmo, 2019), or that the crystallised metal may collapse into the centre of the core, displacing and expelling the residual melt. Such events could be the mechanism by which metal and silicate were mixed in pallasites and would explain the prevalence of highly fractionated metal in PMGs (Wasson et al., 1999; Wasson & Choi, 2003). Subsequent crystallisation of this expelled melt as inter-cumulus liquid around lower mantle cumulate olivines could give rise to pallasite textures across a range of depths. The melt would then have to itself inwardly crystallise in order to satisfy the trend observed in PMG metal, with the amount of mature and evolved melt increasing with depth. There is a key problem with ferrovolcanism as a process for pallasite formation. The PMGs have typically very low S-contents (~2.34 wt%) with the exception of a very small set of meteorites: Hambleton, Phillips County, and Glorieta Mountain, that are likely sampling trapped S-rich melt pods (Buseck, 1977; Boesenberg et al., 2012). This does not appear consistent with the injection of a S-rich evolved metal melt into overlying olivine.

If local dynamo variability can generate the magnetic signatures detected in other studies (Tarduno et al., 2012; Bryson et al., 2015; Nichols et al., 2016) as suggested by McKibbin et al. (2019), then the range in PMG cooling rates could be explained by a core-collapse or ferrovolcanic process. However, the key finding from this study that remains a major barrier to PMG formation at a core-mantle boundary is the oxygen isotope disequilibrium between the metal-hosted chromite and the olivine (see section 3.5).

4.6.5 Multiple parent bodies – recording planetary growth?

Perhaps the most intriguing possibility is that the olivine and chromite minerals are recording different isotopic reservoirs corresponding to different parent bodies that were mixed in an impact.
Differences in $\Delta^{17}$O have long been used as a tool to trace the planetary provenance of meteorite groups (e.g. Clayton & Mayeda, 1996; Greenwood et al., 2006). The presence of a statistically significant difference in $\Delta^{17}$O values between PMG-low minerals may be evidence supporting an impact mixing model for pallasite formation such as has been proposed previously (e.g. Yang et al., 2010; Tarduno et al., 2012). Given that the PMG-low chromite probably crystallised from the metal in the absence of large quantities of silicate melt (see section 4.2.2), it is possible that the disequilibrium is the offset between the mantle oxygen isotope composition (olivine) of one planetesimal, and the oxygen isotope composition of a late-stage injected metal component (chromite) of a second planetesimal. This suggests that an impact injection of the core of a protoplanet into the mantle of another protoplanet (see Figure 4.25) or perhaps re-aggregation of disrupted planetary materials such as has been proposed in other impact scenarios (e.g. Yang et al., 2010) may be the mechanism by which pallasites are generated. If this is the case, pallasites record planetary growth rather than differentiation.

An impact-injection model similar to Figure 4.25 was first proposed by Tarduno et al. (2012) on the basis of palaeomagnetic data suggesting shallow emplacement of some PMGs. The utility of the model in Figure 4.25 is that it satisfies most requirements of a PMG formation mechanism. It can be invoked to explain the variations in low-temperature cooling rates (e.g. Yang et al., 2010) seen in metal portions of PMGs; the ranges in cooling rates would simply be a function of the depth at which the particular pallasite sampled the affected part of the parent body. The fact that the cooling rates are very slow at low temperature, 2.5–18 K Myr$^{-1}$ (Yang et al., 2010), means that the body in which pallasites cooled must have been relatively large or well-insulated if the PMGs were shallowly emplaced. The varying stages of melt evolution recorded in PMG metal are correlated with the cooling rate of the metal (Boesenberg et al., 2012). More evolved metal appears to have cooled slower, suggesting that the shallowly-emplaced melt crystallised earlier in a less-evolved state because it was shallower. This behaviour is consistent with an impact-injection type event and the fact that primitive, more shallowly emplaced PMG metal is reported to be associated with significant amounts of fragmental olivine (Boesenberg et al., 2012) generated as a result of relative proximity to impact site lends further support to this idea.
An event similar to that depicted in Figure 4.25 would be expected to give rise to heterogeneous metal-silicate ratios depending on the position of the PMG in question relative to large metal veins. Such heterogeneity is well documented in some PMGs (e.g. van Niekerk et al., 2007). The compositional variation observed in PMG chromites (see section 3.2.2.2) can be ascribed to variations in the amount of silicate melt present during crystallisation. This compositional difference correlates with chromite $\delta^{18}$O and also with subgroups defined on the basis of olivine composition and texture (see section 3.4). If some of the impacted body was re-melted during an impact, this silicate melt could provide both the Al-content observed in these chromites and the means by which they could partially equilibrate with the PMG olivine. The fact that predominantly angular olivine is typically associated with these chromites (see section 3.4) is consistent with this, the presence of silicate and not just metal melt may explain the less prevalent rounded olivine and chromite textures in these samples. The increasing Cr abundances from core to rim of PMG-high chromite, however, does not support equilibration with re-melted silicate material but rather initial equilibrium with a silicate melt and subsequent partial equilibration with injected metal (see section 4.2.2). This suggests that the PMG-high chromite may have formed initially as cumulate minerals with the olivine and undergone subsequent mobilization and growth following the injection of Al-poor metal. Finally, analysis of the rare earth element (REE) profiles in PMG phosphates has led to the conclusion that they likely did not form at great depth in the parent body but rather more shallowly (Davis & Olsen, 1991), which is also consistent with an impact-injection hypothesis for the metal emplacement. The model presented in Figure 4.25 is split into four stages. Stage A shows an impact injection of a protoplanetary core into the mantle of another body, the isotopic compositions of which are recorded by PMG-low chromite and olivine respectively. The largest of these bodies must have been several hundred km in radius to allow for the slow cooling rates observed in pallasites (e.g. Yang et al., 2010). Both of these bodies must have been fully differentiated at the time of impact on the basis of oxygen isotope $\Delta^{17}$O homogeneity in PMG-low olivine and chromite. The differentiation of the impactor is constrained by W isotope results from this study ($0.5 \pm 1.0$ to $1.6 \pm 1.1$ Myr after CAIs) and the crystallisation time of the olivine in the impacted body may be at $1.24$ Myr after CAIs on the basis of Al-Mg systematics (Baker et al., 2012). This latter age suggests that the impacted body was also fully differentiated before $\sim 2$ Myr after CAI formation.
Figure 4.25 – Impact injection model for PMG formation similar to one proposed previously (Tarduno et al., 2012). This figure is separated into four parts: A) impact between two differentiated bodies, the core of the smaller body is injected into the mantle of the larger body. B) over time, an insulating layer of regolith develops and the silicate and liquid metal cool together at depth. C) at the kilometre scale the metal-silicate distribution is heterogeneous, with some large metallic veins and some large olivine clusters. At the metre scale pallasite textures are as observed in meteorites. This depicts chromite (black mineral) and troilite (gold mineral) crystallising from the metal during cooling. D) an image of Seymchan (PMG-low) at sub-metre scale displaying the same textures seen in C, credit: Luc Labenne.
The impact probably occurred at around 10.2 (+5, -2.5) Myr after CAIs on the basis of the Mn-Cr systematics in PMG olivine analysed in this study (see section 4.4). The more precise age of 10.4 ± 1.6 Myr uses the PMG chromite as a compositional anchor and therefore is not appropriate for this model given that the chromite represents a different isotopic reservoir. The slow cooling rates of PMG metal at sub-solidus temperatures (Yang et al., 2010) suggests that the larger body must have remained intact for a significant period of time after the impact, which must have occurred when the injected core was still molten. This impact must have been very high energy to enable the injection of core material to ~50 km (e.g. Tarduno et al., 2012).

Stage B shows insulation by regolith (dark green) following the impact injection. Again, this insulation is necessary to account for the slow cooling rates of PMGs. In this model, metal at greater depth would cool slower and the melt would evolve more than at shallower depths as evidenced in the PMG meteorite record (e.g. Figure 4.5, Boesenberg et al., 2012). This is also the stage at which some partial equilibration may have occurred between the silicate and metal isotopic reservoirs to generate the chromite in the PMG-high sub-group. Localised melting of silicate country rock due to impact heating could account for the Al component and partially equilibrated oxygen isotope signature observed in PMG-high chromite but not for the increasing Cr content from core to rim. It seems likely on the basis of Al and Cr zoning in Fukang (see Figure 3.7) that the PMG-high chromite had already crystallised from a silicate melt that was later displaced by the injected metal. If the chromite crystal growth continued during and after metal injection, the increasing Cr abundance and decreasing Al abundance from core to rim could be explained. This would also explain the partial equilibration of the PMG-high chromite oxygen isotopes as the incorporated oxygen would have initially been derived from a silicate melt and increasingly from the metal during crystal growth. Any such displacement of Al-bearing melt with Cr-bearing melt must have been gradual on the basis of Figure 3.7, perhaps in an area where injected metal melt was percolating through.

Stage C shows large metal dykes at the kilometre scale. The ratio of metal to silicate would probably increase nearer to the impact site and these dendrite-like structures would increase in size. A model like this raises the interesting possibility that some iron meteorite groups may be sampling very silicate-poor areas in such an impact process. For example, Seymchan was first identified as a IIE
iron meteorite before reclassification as a PMG in 2007 (van Niekerk et al., 2007). This idea is explored further for IIIAB irons which are compositionally similar to PMG metal in Chapters 5 and 6. The smaller diagram in Stage C of this model highlights how the pallasite texture may form where metal invades pre-existing olivine masses, breaking them apart. This results in the rounding of some isolated olivines (e.g. Solferino et al., 2015; Solferino & Golabek, 2018; McKibbin et al., 2019).

The chromite, troilite, phosphate, and other accessory minerals then crystallise from this invading metal and therefore sample a different isotopic reservoir to the olivines. Stage D shows a sample of Seymchan with a clear metal vein hosting globular chromite.

An impact-injection model (Figure 4.25) is not the only impact mixing model that could account for the observed Δ\(^{17}\)O disequilibrium. Yang et al. (2010) published a model in which re-aggregation of two bodies disrupted by a hit-and-run planetary collision created pallasites with the observed range in cooling rates (see Chapter 1). This model makes many of the same predictions as the impact-injection models, however complete destruction and reaggregation cannot account for the continued presence of a core dynamo imparting a magnetic field in the PMG parent body until it cooled to ~630 K (Tarduno et al., 2012).

The apparent similarity between the corrected Cr isotopes of the metal-hosted chromite and the olivine from PMGs (see Figure 3.21) does not support the idea of derivation from multiple parent bodies but it does not necessarily preclude it either. A critical assumption in creating the isochron (Figure 3.23) and spallation correcting the olivine data is that both phases had indistinguishable initial isotopic compositions. Given that the Mn/Cr ratios correspond to the x-axis offset of the olivines in Figure 3.22, this seems a reasonable assumption. Assuming that it is correct, it may be that the Cr isotope system is not as sensitive to the small difference in isotopic composition as is the oxygen. This may be due to better mixing of Cr relative to O in the protoplanetary disk, or it may be that the sensitivity of Cr isotopes to planetary provenance differences in proximal feeding zones is insufficient to allow for measurable offsets at the current levels of analytical precision. There is also the possibility that the metal and silicate portions of PMGs formed from a common isotopic reservoir and that subsequent processes (see section 4.5) affecting O but not Cr have resulted in the observed disequilibrium.
4.7 Summary

This chapter has outlined the key compositional, textural, isotopic, and temporal relationships identified in PMGs both from this study, and from published literature. In summary, it seems likely that PMG olivine formed as a cumulate and crystallised at ~1.2 Myr after CAI formation (e.g. Baker et al., 2012). It is possible that the PMG olivine has a restite origin but this would require a significant increase in diffusion rates for oxygen at temperatures > 1873 K but below the olivine solidus and a very high degree of partial melting. The PMGs underwent core formation between ~0.5 and 1.6 Myr on the basis of W isotope chronology, although in light of the suggested impact mechanism for PMG formation, this data is recording the differentiation event on the impactor rather than the impacted body sampled by PMG olivine.

Given that there is a statistically significant $\Delta^{17}$O disequilibrium between metal-crystallised PMG-low chromite and co-occurring olivine, and barring the influence of some unknown anharmonic or mass-independent effect, it is likely that PMGs record an impact-mix of two differentiated protoplanets at ~10 Myr after CAI formation. In this case, PMG olivine records the isotopic signature of the impacted – and probably the larger – body. The PMG-low chromite records the isotopic signature of the impactor core, with the PMG-high chromite forming firstly as a cumulate mineral in the larger (impacted) body and then equilibrating with the Al-poor metallic melt as it was progressively added. The accretion of the impacting body may have occurred at ~2.18 AU on the basis of Cr isotopes but this is based upon a number of untested assumptions. The Cr isotope results for both PMG olivine and chromite show that they belong to the non-carbonaceous reservoir (e.g. Warren, 2011) and therefore likely accreted inside the orbit of Jupiter (e.g. Kruijer et al., 2017). The comparison of olivine-chromite fractionation relationships between extra-terrestrial and terrestrial igneous rocks yields an interesting result. Bushveld pyroxenite shows a similar offset in $\Delta^{17}$O between olivine and chromite and also requires a $\lambda$ that apparently breaks mass-fractionation laws. This may be due to multi-step fractionation between BIC minerals, although that has been shown to have been unlikely in PMG, or it could be an artefact stemming from the relatively few BIC olivine datapoints and associated uncertainty in the mean values. A similar offset is not seen in the Eagle Station data suggesting that any olivine-chromite specific fractionation effect may not be universal.
However, the Eagle Station dataset is very restricted and therefore there are significant errors to contend with in interpreting fractionation behaviour. Furthermore, the ES samples plot a long way from the TFL in isotope space, meaning that even very small terrestrial contamination would have a significant effect on the data. Future work is crucial to investigate whether there is an anharmonic or mass-independent effect at work in PMG and BIC minerals. If it can be demonstrated that there is such an effect, the PMG-low minerals may not be sampling separate isotopic reservoirs after all. The existence of apparent mass-independent influences on geological samples would have severe implications for a wide array of scientific disciplines including: cosmochemistry, geochemistry, archaeology, and climatology. On balance, considering the isotopic disequilibrium identified in this study, the variation in major element composition between PMG-low and PMG-high chromite suggestive of disparate origins, the range in cooling rates in PMG metal (Yang et al., 2010), and magnetic inclusions in olivine suggestive of shallow emplacement (Tarduno et al., 2012), an impact-injection model for PMG formation seems most likely.
5 IIIAB IRON RESULTS

5.1 Introduction

The IIIAB irons are the largest iron meteorite group (see Chapter 1) with 309 distinct meteorites (Goldstein et al., 2009). As a result of their compositional similarities with a precursor PMG melt it has been suggested that the two groups share a common parent body, sampling the core and core-mantle boundary (Wasson et al., 1999; Wasson & Choi, 2003; Scott, 2007). The possibility of a common parent planetesimal means that the two groups have the potential to yield detailed information about processes active in multiple parts of an early-formed planetesimal. This chapter presents the high-precision oxygen isotope analyses of chromite from IIIAB irons collected in this study.

5.2 Chromite texture and composition

The samples analysed in this study comprised small chromite mineral separates or powder; no samples were large enough to allow for EPMA analyses. Consequently, no new quantitative textural or compositional data could be acquired.

Chromite in IIIAB irons is often included within troilite (FeS) inclusions (e.g. Wasson et al., 1999) suggesting that it crystallises relatively late and probably from S-rich melt; all IIIAB chromite analysed in this study were extracted from chromite-troilite inclusions. The juxtaposition of chromite, sulphide, and phosphate minerals in Cape York is taken as an indication of the late-stage crystallisation of chromite, sulphide and phosphate from a melt and has even been used to estimate the orientation of the palaeo-gravitational gradient within the sample (Buchwald, 1971; 1975; Chabot & Haack, 2006). The texture of IIIAB chromite is variable and ranges from globular (Figure 5.1A) to very angular (Figure 5.1B). There appears to be no corresponding compositional variation as was tentatively identified in PMGs (Chapter 3); all IIIAB chromites analysed in this study are troilite-hosted and likely end-member FeCr$_2$O$_4$ (Figure 5.2), consistent with available literature compositions (e.g. Wasson et al., 1999; Bunch & Kiel, 1971; Fehr & Carrion, 2004). This is strong evidence that it crystallised in the absence of any silicate melt (e.g. Boesenberg et al., 2012).
Figure 5.1 – Examples of chromites in IIIAB irons. (A) A large globular chromite (black mineral highlighted by the red arrow) in a sample of Sacramento Mountains at the Smithsonian Institute. The inset is an enlarged image of the chromite. This is the sample from which the chromite analysed in this study was obtained. Note the associated troilite (green arrow). (B) – A large and very angular chromite, approximately 3 cm in longest dimension, (the large mineral highlighted by the red arrow) from Saint Aubin, slab size 20 x 13 x 0.5 cm (Fehr & Carrion, 2004).
5.3 Oxygen isotope results

Sixteen chromite samples from 9 IIIAB iron meteorites were analysed using laser-assisted fluorination at the Open University. The analysed samples appear to define three distinct groups on the basis of their oxygen isotope compositions (Figure 5.3). Given the lack of compositional variation in chromite cation content in IIIAB irons (e.g. Wasson et al., 1999; Fehr & Carrion, 2004), the subgroups identified in this study are distinguished purely on the basis of oxygen isotope composition of the samples. The first, low-$\delta^{18}O$ group, is designated Group 1. There is a group with higher $\delta^{18}O$, hereafter referred to as Group 2, and a third group that appears entirely offset in both $\delta^{18}O$ and $\Delta^{17}O$, hereafter termed Group 3 (Figure 5.3).
Figure 5.3 – Oxygen isotope composition of analysed IIIAB irons. There appear to be 3 distinct groups. The black dotted line is a trendline through all points with a slope ($\lambda$) of $0.5118 \pm 0.0034$ (2 standard error).

Group 1 consists of three chromite samples, two from Owens Valley and one from Mount Edith, and has average compositions of $\delta^{17}$O = $-0.78 \pm 0.31 \%$ (2σ), $\delta^{18}$O = $-1.15 \pm 0.55 \%$ (2σ), and $\Delta^{17}$O = $-0.170 \pm 0.039 \%$ (2σ). Group 2 comprises 9 chromite samples from 5 meteorites: Wonyulgunna, Bear Creek, Sacramento Mountains, Puente del Zacate, and Fairview. The average oxygen isotope results for this subgroup are $\delta^{17}$O = $0.28 \pm 0.25 \%$ (2σ), $\delta^{18}$O = $0.88 \pm 0.44 \%$ (2σ), and $\Delta^{17}$O = $-0.181 \pm 0.03 \%$ (2σ). Group 3 contains four chromite samples, two each from Augusta County and Cape York. The average oxygen isotope results are $\delta^{17}$O = $3.646 \pm 0.363 \%$ (2σ), $\delta^{18}$O = $7.488 \pm 0.693 \%$ (2σ), and $\Delta^{17}$O = $-0.286 \pm 0.042 \%$ (2σ). If the data from all three subgroups are included in a regression for $\lambda$, the slope is $0.5118 \pm 0.0034$ (2 SE) which is considerably shallower than the expected range from high-T mass-dependent fractionation (0.525–0.529, e.g. Young et al., 2016).

Table 5.1 is a complete list of optimized IIIAB results for this study.

Oxygen isotope results have previously been reported for 5 of the IIIABs for which data are presented in Table 5.1 and are broadly consistent, albeit at much lower precision as they were acquired using
the Ni-bomb technique (Clayton & Mayeda, 1996). These results have an average $\Delta^{17}O (\lambda = 0.52)$ of $-0.21 \pm 0.6 \%$, typically an order of magnitude less precise than the data of this study. The chromite results from the IIIABs analysed by Clayton & Mayeda (1996) typically have higher $\delta^{17}O$ and $\delta^{18}O$ values than those measured using laser-assisted fluorination (this study) and do not quote errors on the reported values.

Table 5.1 – Oxygen isotope data and subgroup allocation for the analysed IIIAB irons in this study. The errors (2 SE) are 2 standard error of the mean. $\Delta^{17}O$ calculated using $\lambda = 0.5262$.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>$\delta^{17}O$</th>
<th>2 SE</th>
<th>$\delta^{18}O$</th>
<th>2 SE</th>
<th>$\Delta^{17}O$</th>
<th>2 SE</th>
<th>Subgroup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mount Edith</td>
<td>-0.968</td>
<td>0.025</td>
<td>-1.472</td>
<td>0.009</td>
<td>-0.193</td>
<td>0.026</td>
<td>Group 1</td>
</tr>
<tr>
<td>Owens Valley</td>
<td>-0.770</td>
<td>0.018</td>
<td>-1.187</td>
<td>0.009</td>
<td>-0.145</td>
<td>0.018</td>
<td>Group 1</td>
</tr>
<tr>
<td>Owens Valley</td>
<td>-0.594</td>
<td>0.018</td>
<td>-0.802</td>
<td>0.010</td>
<td>-0.172</td>
<td>0.019</td>
<td>Group 1</td>
</tr>
<tr>
<td>Bear Creek</td>
<td>0.322</td>
<td>0.017</td>
<td>0.963</td>
<td>0.007</td>
<td>-0.184</td>
<td>0.017</td>
<td>Group 2</td>
</tr>
<tr>
<td>Bear Creek</td>
<td>0.312</td>
<td>0.020</td>
<td>0.937</td>
<td>0.007</td>
<td>-0.181</td>
<td>0.020</td>
<td>Group 2</td>
</tr>
<tr>
<td>Fairview</td>
<td>0.106</td>
<td>0.021</td>
<td>0.579</td>
<td>0.009</td>
<td>-0.199</td>
<td>0.021</td>
<td>Group 2</td>
</tr>
<tr>
<td>Puente del Zacate</td>
<td>0.229</td>
<td>0.017</td>
<td>0.766</td>
<td>0.007</td>
<td>-0.174</td>
<td>0.017</td>
<td>Group 2</td>
</tr>
<tr>
<td>Puente del Zacate</td>
<td>0.305</td>
<td>0.019</td>
<td>0.915</td>
<td>0.009</td>
<td>-0.176</td>
<td>0.020</td>
<td>Group 2</td>
</tr>
<tr>
<td>Sacramento Mountains</td>
<td>0.542</td>
<td>0.019</td>
<td>1.355</td>
<td>0.008</td>
<td>-0.170</td>
<td>0.020</td>
<td>Group 2</td>
</tr>
<tr>
<td>Sacramento Mountains</td>
<td>0.307</td>
<td>0.020</td>
<td>0.921</td>
<td>0.009</td>
<td>-0.178</td>
<td>0.019</td>
<td>Group 2</td>
</tr>
<tr>
<td>Wonyulgunna</td>
<td>0.096</td>
<td>0.017</td>
<td>0.576</td>
<td>0.008</td>
<td>-0.207</td>
<td>0.017</td>
<td>Group 2</td>
</tr>
<tr>
<td>Wonyulgunna</td>
<td>0.305</td>
<td>0.021</td>
<td>0.877</td>
<td>0.007</td>
<td>-0.156</td>
<td>0.022</td>
<td>Group 2</td>
</tr>
<tr>
<td>Augusta County</td>
<td>3.582</td>
<td>0.022</td>
<td>7.433</td>
<td>0.010</td>
<td>-0.321</td>
<td>0.023</td>
<td>Group 3</td>
</tr>
<tr>
<td>Augusta County</td>
<td>3.419</td>
<td>0.019</td>
<td>7.028</td>
<td>0.009</td>
<td>-0.272</td>
<td>0.019</td>
<td>Group 3</td>
</tr>
<tr>
<td>Cape York</td>
<td>3.921</td>
<td>0.021</td>
<td>8.004</td>
<td>0.011</td>
<td>-0.281</td>
<td>0.022</td>
<td>Group 3</td>
</tr>
<tr>
<td>Cape York</td>
<td>3.664</td>
<td>0.019</td>
<td>7.488</td>
<td>0.009</td>
<td>-0.268</td>
<td>0.018</td>
<td>Group 3</td>
</tr>
</tbody>
</table>

From a comparison of the data it seems that the Ni-bomb technique may be considerably less precise in $\delta^{17}O$ and $\delta^{18}O$ measurements than laser-fluorination. A key example of this is Cape York chromite which is reported as $\delta^{17}O = 0.77 \%$, $\delta^{18}O = 2.03 \%$, $\Delta^{17}O = -0.29 \%$ which is broadly consistent with the other IIIABs (Clayton & Mayeda, 1996). The results of this study, by contrast, show a clear difference in $\delta^{18}O$ between three discrete groups of IIIAB chromite as well as a large $\Delta^{17}O$ offset between two of those groups and the group containing Cape York (Table 5.1). A discussion of the implications of the oxygen isotope data presented, as well as an investigation into the presence of any correlated compositional data from the literature are presented in Chapter 6.
6 IIIAB IRON OXYGEN ISOTOPE INTERPRETATION

This chapter explores the implications of the IIIAB results presented in Chapter 5 and combines it with IIIAB petrology and chronology using previously published data. Timelines, possible formation environments, and the relationship to the PMG meteorites, which have similar metal compositions, are discussed.

6.1 IIIAB petrology

As stated previously, no new quantitative compositional data for IIIABs has been gathered in this study. The petrology that has been conducted is limited to characterisation of chromite textures in some IIIABs (Figure 5.1) and EDX characterisation of selected IIIAB chromites (Figure 5.2).

6.1.1 Chromite texture

Where chromite occurs in IIIAB irons it can exhibit varying degrees of angularity between samples. This range encompasses globular and rounded – in a similar manner to some PMG-low chromite (see Figure 5.1A) – as well as very angular chromite (Figure 5.1B). The presence of this spectrum of chromite textures in IIIAB irons (see Figure 5.1) which all exhibit end-member chromite compositions (e.g. Wasson et al., 1999; Fehr & Carrion, 2004) suggests that chromite texture cannot be used as an effective petrological indicator in these meteorites. The IIIAB chromite samples analysed in this study were surrounded by, or juxtaposed with troilite (e.g. Figure 5.1A) indicating that they all formed from late-stage melts; S is incompatible in crystallising FeNi metal and is therefore incorporated into FeS minerals at a very late stage (Chabot, 2004; see Chapter 1). No angular IIIAB chromites (e.g. Figure 5.1B) were obtained for analysis in this study.

6.1.2 Chromite composition

Chromite composition in IIIAB irons is consistently end-member with typically < 0.02 wt% Al$_2$O$_3$, < ~0.3 wt% MgO, and similarly low contents of other cations except for Fe and Cr (e.g. see Table 3 in Wasson et al., 1999). No new quantitative compositional analyses were conducted in this study due to the paucity of available chromite to make suitable polished samples, however Figure 5.2 shows EDX spectra for Bear Creek and Cape York chromites analysed in this study, both of which exhibit end-member chromite compositions. The composition of the IIIAB chromites, along with the
consistency of this composition, is strong evidence that they crystallised from a metallic melt with no interaction with a silicate melt (Fehr & Carrion, 2004; Boesenberg et al., 2012). This is in agreement with the established model of a core-forming environment for magmatic iron meteorite groups (Goldstein et al., 2009; Chapter 1). The lack of variation in IIIAB chromite composition, combined with the fact that all chromites analysed in this study were globular and picked out of troilite inclusions, means that whatever process controlled the observed variability in oxygen isotope composition appears to be entirely independent of compositional and textural factors. As no angular IIIAB chromite was analysed in this study, no conclusions on possible textural vs. isotopic relationships can be drawn.

6.2 IIIAB chronology and cooling rates

No new chronological data was collected for IIIABs as part of this study. Chronological information obtained from the $^{182}\text{Hf} - ^{182}\text{W}$ (Markowski et al., 2006), $^{187}\text{Re} - ^{187}\text{Os}$ (Cook et al., 2004), and $^{53}\text{Mn} - ^{53}\text{Cr}$ (Sugiura & Hoshino, 2003) decay schemes have been published previously. These literature ages provide some constraints on the evolution of the IIIAB core. Table 6.1 is modified from Goldstein et al. (2009) and lists the relevant ages for the IIIAB irons; these ages are displayed on Figure 6.1.

<table>
<thead>
<tr>
<th>Decay scheme</th>
<th>Inferred process</th>
<th>Age (Ma)</th>
<th>$\Delta T_{\text{CAI}}$ (Myr)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{182}\text{Hf} - ^{182}\text{W}$</td>
<td>Core-mantle separation</td>
<td>4567 ± 1.2</td>
<td>-0.2 ± 1.2</td>
<td>Markowski et al. (2006)</td>
</tr>
<tr>
<td>$^{187}\text{Re} - ^{187}\text{Os}$</td>
<td>FeNi metal crystallisation</td>
<td>4517 ± 28</td>
<td>50 ± 28</td>
<td>Cook et al. (2004)</td>
</tr>
<tr>
<td>$^{53}\text{Mn} - ^{53}\text{Cr}$</td>
<td>Closure of phosphates at ~1000 K</td>
<td>4563 ± 1</td>
<td>4.1 ± 0.5</td>
<td>Sugiura &amp; Hoshino (2003)</td>
</tr>
</tbody>
</table>

The W isotope data suggests that the IIIABs differentiated very early in Solar System history, either contemporaneous with, or more likely very shortly after, CAI formation (Markowski et al., 2006). This is consistent with published core-mantle separation ages for a host of other magmatic iron
meteorite groups (Goldstein et al., 2009) and within error of corresponding ages for the PMG samples analysed in this study (see Chapter 3). The Mn-Cr data for IIIAB irons were obtained from phosphates (Sugiura & Hoshino, 2003) and therefore the age has been interpreted as recording phosphate closure, probably at a temperature of ~1000 K (Goldstein et al., 2009). This is inconsistent with the Re-Os age, which is interpreted to record FeNi metal crystallisation (Goldstein et al., 2009) and records a much later event (Figure 6.1). Given that the decay constant for $^{187}$Re is poorly constrained (Goldstein et al., 2009), this later Re-Os age may be unreliable.

Figure 6.1 – A timeline of processes in IIIAB core evolution, as indicated by the ages summarised by a number of workers listed in Table 6.1 (see table for references). The errors for both core-mantle separation and phosphate closure ages are smaller than the datapoint.

The timeline presented in Figure 6.1 does not seem either internally consistent or consistent with the measured IIIAB cooling rates at temperatures of 56–338 K Myr$^{-1}$ (Yang & Goldstein, 2006). Whilst the maximum temperature for IIIAB irons is not known, partial melting experiments have shown that metal starts to melt out of chondritic precursor material at ~1261 K (Tomkins, 2009) and therefore the temperature must have been at least this high and probably considerably higher during core-mantle separation. Indeed, the liquidus temperature for the FeNi metal may be as high as 1753–1798 K, as has been suggested in PMGs (Donohue et al., 2018). At ~4 Myr after CAI formation the Mn mobility in IIIAB phosphates ceased (Sugiura & Hoshino 2003). If this represents the crossing of a
closure temperature at ~1000 K (Goldstein et al., 2009) it is considerably lower than FeNi metal melting temperatures in chondritic partial melting experiments (Tomkins, 2009), and vastly lower than those empirically determined for FeNi metal (Donohue et al., 2018). This suggests that the FeNi metal must have been solid when phosphate Mn closure occurred; a conclusion completely at odds with Re-Os age dating for metal crystallisation (Figure 6.1). Barring a reheating event recorded in Re-Os but not Mn-Cr systematics, this inconsistency suggests that at least one of the ages presented in Table 6.1 may be incorrect or recording a different event to that reported by Goldstein et al. (2009).

Given that Mn is partially compatible in sulphide melt (McKibbin et al., 2019), it may be that the Mn-Cr age is actually recording some sort of melt escape, perhaps the separation of a S-rich outer core at a later point than the initial core-mantle separation. In this scenario, the Mn would be concentrated in, for example, liquid FeS and removed from the IIIAB environment where the phosphates were forming. If this were the event recorded by the Mn-Cr systematics, the temperature could have been higher than 1000 K. In such a model, subsequent slow cooling after separation of a sulphide outer core would be compatible with the crystallisation of the metal significantly later (Figure 6.1). If this interpretation is correct, the separation of this S-rich melt component must have occurred over a very short timescale across the 5 IIIABs analysed by Sugiura & Hoshino (2003) to satisfy the very small variations in the Mn-Cr age (Table 6.1).

The low temperature cooling rates for IIIAB irons range from 56–338 K Myr\(^{-1}\) (Yang & Goldstein, 2006). This is relatively fast compared with those for PMGs (Yang et al., 2010) suggesting that the IIIAB core was partially exposed or less well insulated than the PMG forming environment during cooling through low temperatures. As the IIIABs are thought by many to sample a planetesimal core this means that either this planetesimal was smaller than the PMG parent body or had insulating material removed by impacts after the crystallisation of the FeNi metal. If the ages on Figure 6.1 are correct, removal of the insulating material could not have occurred prior to the metal crystallisation or initial temperatures would have to have been incredibly high to allow for ~50 Myr of cooling. Given that measured low temperature cooling rates ranging from ~2–18 K Myr\(^{-1}\) in PMGs is reported to be consistent with the progression from high temperature cooling rates of 100–300 K Myr\(^{-1}\) (Donohue et al., 2018), similar extrapolation of the IIIAB low temperature cooling rates (56–338 K Myr\(^{-1}\)) would yield incredibly fast and unrealistic high temperature cooling rates. The fact that the
PMG and IIIAB parent bodies may have been different sizes and had different histories means that such an extrapolation is not reliable, however.

6.3 Oxygen isotope composition

The presence of three distinct IIIAB iron sub-groups on the basis of oxygen isotopes (see Chapter 5) has not been previously reported. The fact that Group 3 seems to be well-defined in both $\Delta^{17}$O and $\delta^{18}$O and that Groups 1 and 2 are resolvable in $\delta^{18}$O suggests that the IIIABs analysed in this study sample at least two and perhaps three individual isotopic reservoirs and do not record continuous mixing between different reservoirs. This has important implications for the IIIAB irons and magmatic iron meteorites as a whole because it could record the failure of the IIIAB core to homogenise isotopically or may even be evidence that the chemical classification scheme is unable to resolve multiple parent bodies contributing to the IIIAB group of iron meteorites. The failure of the IIIAB core to isotopically homogenise would lead to differences in oxygen isotope results across IIIAB samples. Alternatively, it is possible that the three subgroups plot along a single shallow mass-dependent fractionation line. Whilst there is a clear $\Delta^{17}$O offset between Group 3 and the other IIIAB subgroups when high temperature $\lambda$ values are used, the slope of the trendline on which all three subgroups plot is actually consistent with kinetic mass-fractionation. This raises the possibility that a process such as diffusion could be imparting a shallower $\lambda$ than expected and if the distribution of oxygen isotopes in the IIIAB core was controlled by diffusion rather than typical high-T equilibrium mass-fractionation, the $\lambda$ of the system may be considerably shallower than expected from typical igneous systems (e.g. Pack & Herwartz, 2014; Young et al., 2016). These different mechanisms are evaluated in detail in sections 6.4 and 6.5.

6.4 Multiple isotopic reservoirs

This section investigates the possibility that IIIAB irons sample multiple parent bodies that are represented by separate oxygen isotope subgroups.

6.4.1 Multiple parent bodies

The distribution of IIIAB chromite on Figure 5.3 could be explained if the subgroups are sampling different parent bodies or isotopic reservoirs. Given that the minerals analysed are all chromite, the
comparison between different potential parent bodies is like-for-like, and therefore not affected by process-specific deviations in $\lambda$ or by inter-mineral fractionation as is the case for PMGs (see Chapter 4 for more details). On this basis, IIIAB endmember chromites from a single well-homogenised parent core would be expected to have well-homogenised oxygen isotope composition. Given that there appear to be 3 discrete subgroups (Figure 5.3), it is possible that there are as many as 3 distinct parent reservoirs for the analysed samples, or perhaps a single body sampled by Groups 1 and 2 and a second body sampled by Group 3.

The interpretation of multiple parent bodies for IIIAB irons is supported by the fact that Group 3 is distinct in $\Delta^{17}$O ($\lambda = 0.5262$) from both Groups 1 and 2. It is also offset by a large amount in $\delta^{18}$O (Figure 5.3) and a fractionation line connecting it with the other groups would be much shallower than expected through high-T fractionation (e.g. Young et al., 2016). There is no resolvable difference in $\Delta^{17}$O between Groups 1 and 2 and they only differ by $\sim 2$‰ in $\delta^{18}$O. As is evident from the metal-hosted chromite in PMGs (see Chapter 3), such a $\delta^{18}$O offset is possible for chromites of slightly different composition with differing parageneses. As a result, it is unclear whether the difference between Groups 1 and 2 is a result of fractionation, partial equilibration with another phase (e.g. PMG-high chromite in Chapter 3), or the sampling of different isotopic reservoirs that are unresolvable in $\Delta^{17}$O. This latter notion, that Groups 1 and 2 may sample distinct parent bodies, is much less robust than when applied to the difference between Group 3 with the other two. On balance, considering the compositional homogeneity of IIIAB chromite, it seems unlikely that the difference between Groups 1 and 2 is due to fractionation or partial equilibration. On the basis of the difference between Groups 1 and 2 and the third, offset group, it is possible that the analysed IIIABs sample up to three well-homogenised parent bodies. If this is the case, it suggests that care must be taken when classifying iron meteorites on a compositional basis, especially as Cape York (Group 3) has been used as evidence for dendritic inward crystallisation of the IIIAB core (e.g. Haack & Scott, 1993). It also means that there may be more planetary bodies represented in the iron meteorite collection than previously thought.
6.5 IIIAB oxygen isotope variations – possible mass-dependent fractionation processes?

This section evaluates possible mechanisms for generating the observed oxygen isotope distribution in a single isotopic reservoir.

6.5.1 Equilibrium mass-dependent fractionation

The meteorites in the IIIAB iron group likely formed in one or more planetary cores (e.g. Goldstein et al., 2009; see section 1.2.1) and therefore by fractional crystallisation under high-temperature conditions. This assertion is supported by an experimental investigation into FeNi metal liquidus temperatures (e.g. Donohue et al., 2018). Given that high-T mass-fractionation slopes range from 0.525–0.529 (Young et al., 2016), and a fractionation line connecting the IIIAB subgroups would have a slope of 0.5118 ± 0.0034 (2 SE), high-T equilibrium mass-fractionation is not a candidate for the observed distribution. Low-temperature equilibrium and kinetic processes, however, do yield shallower slopes than does high-T mass-fractionation, and often larger fractionations in δ\(^{18}\)O (e.g. Criss, 1999). The range controlled by low-T and kinetic processes extends from ~0.514 - ~0.525 (Young et al., 2016). Given that the IIIABs formed at igneous temperatures in a high-T environment it seems very unlikely that low-T equilibrium mass-dependent fractionation could be responsible for the observed distribution, however kinetic processes such as diffusion must be considered.

The diffusion of oxygen in molten metal has been shown to be very fast (see section 4.6.3) and may be the mechanism by which O homogenises in metallic melts. Diffusion is a non-equilibrium process (Criss & Farquhar, 2008) and could result in the shallow slope connecting the three IIIAB subgroups. The rapid rate of oxygen diffusion in metal melts means that homogenisation of oxygen isotopes in a core environment would be expected to occur relatively rapidly. This means that IIIAB chromite crystallising from a single melt should have homogeneous oxygen isotope compositions and not the heterogeneous δ\(^{18}\)O distribution that is observed. Possible mechanisms for generating the observed δ\(^{18}\)O distribution following diffusion of oxygen are explored in section 6.5.3.2.
6.5.2 Inter-mineral fractionation

Inter-mineral fractionation is not a possible cause of the observed distribution because the oxygen-bearing phases analysed for the IIIABs were all chromite. As already stated, it is possible that differing compositions of chromite in the subgroups may be responsible for the $\delta^{18}O$ offset although the reported compositions of IIIAB chromites are consistently end-member (e.g. Wasson et al., 1999; Fehr & Carrion, 2004). Without enough sample material to conduct EPMA analyses on the IIIAB chromite samples for which oxygen isotopes were measured, it is not possible to say definitively whether such a compositional difference exists but it seems very unlikely that it is the cause of the observed data distribution. Strong support for this perspective can be seen in Figure 5.2. The spectra for Bear Creek and Cape York chromite show no difference in major element composition despite sampling two isotopically different subgroups (Groups 2 and 3 respectively). On this basis, it seems highly unlikely that any compositional difference in IIIAB chromite is causing the observed distribution.

6.5.3 Incomplete homogenisation of the IIIAB core

As discussed in the context of PMGs in Chapter 4, the fact that all three sub-groups of IIIAB irons have well resolved $\delta^{18}O$ values seems to exclude the possibility that they could be randomly sampling the incomplete homogenisation of an isotopically heterogeneous precursor as the isotope compositions of the samples would be spread along a mixing line and not arranged in discrete groups as is the case. A key consideration in this regard is the potential for incomplete sampling in the meteorite record, it may be that if more IIIABs are analysed the three subgroups would extend to form a continuum. The observed distribution might arise if the three groups sample internally homogenised regions of the parent body. These regions may have been quite large, or in close proximity to each other. This is because despite the observed differences, the oxygen isotope compositions of the groups are similar compared with the range in achondrites and therefore may have been broadly representative of the IIIAB parent isotopic reservoir. This constraint could explain why Groups 1 and 2 are so similar in composition, for example. A model like this would require separation of the isotopic reservoirs between which no subsequent isotope fractionation or homogenisation could take place. If a heterogeneous precursor melted and individual reservoirs of this melt were isolated and then evolved and homogenised separately, it could perhaps explain the
observed clustering of the 3 subgroups along something approximating a kinetic mass-dependent fractionation line.

In order to identify whether there are differences in crystallisation histories of the subgroups, a comparison of the isotope results vs. the composition of IIIAB metal is conducted in section 6.5.3.1. Candidate mechanisms for isolating melt pools and arresting complete homogenisation are discussed in section 6.5.3.2.

6.5.3.1 IIIAB O-isotope relationship with chemical signatures

The IIIAB irons analysed in this study have a range of metal compositions. Iridium content is a key compositional indicator that is used as a proxy for fractional crystallisation (see section 1.2.1.1) and is therefore useful for establishing differing crystallisation histories for metal melts. Figure 6.2 shows Ir content vs $\delta^{18}O$ for the identified subgroups. The range in $\delta^{18}O$ observed in the samples analysed in this study contrasts with the range in results from Clayton & Mayeda (1996), where the $\delta^{18}O$ of IIIABs (including Cape York) were reported as ranging from 1.86 ‰ to 2.75 ‰. This discrepancy may be due to the increased precision afforded by the laser-assisted fluorination technique or perhaps different chromite was analysed by the two studies. The minerals analysed by Clayton & Mayeda (1996) included silicates, chromites, and phosphates, all of which were reported in the $\delta^{18}O$ range quoted above. Given that improvements in the precision of isotope analysis saw the identification of differences in isotope results where none had been reported previously (e.g. Greenwood et al., 2006), it may be that differences between IIIAB subgroups were not resolvable. The differences between the subgroups identified in this study are considerably larger than the $\delta^{18}O$ precision obtained by Clayton & Mayeda (1996) of $\sim$0.2 ‰ (2σ), however, suggesting that the difference may be the result of sample variability.

The analysed Group 1 IIIABs have very low Ir contents (see Table 6.2) and therefore likely represent an extensively fractionally crystallised later-stage melt. The range of Ir contents varies between the two analysed Group 1 samples by a factor of 10. Group 2 samples a wide range of degrees of fractional crystallisation, the Ir content ranges from 0.021 to 7.56 (see Table 6.2). This group may be representative of bulk IIIABs with Groups 1 and 3 sampling restricted pools of highly evolved and very primitive metal respectively at opposite extremes of fractional crystallisation.
Figure 6.2 – Iridium content (ppm) from literature sources vs. $\delta^{18}O$ data from this study. Whilst there a clear $\delta^{18}O$ separation between the groups, it is less evident in Ir. Ir data from Wasson (1999), Wasson et al. (1989), Scott et al. (1973), and Buchwald (1975). The error bars for Cape York Ir content are 2 st dev.

The Group 3 samples have Ir contents that vary by a factor of ~2. The fact that two of the Group 2 IIIAB samples have Ir contents around 0.02 ppm is evidence that the $\delta^{18}O$ difference between Group 1 and Group 2 samples is not simply the result of fractional crystallisation. If this were the case, a clear relationship between Ir content and subgroup would be expected. Similarly, the Ir contents of Group 3 preclude such a mechanism for the difference between Group 3 and Group 2. The Ir contents of these two subgroups overlap (Figure 6.2) suggesting that differences in melt evolution through fractional crystallisation is unlikely to be the sole cause of the $\delta^{18}O$ offset. It does not rule out the possibility that the IIIAB core was initially homogenising by diffusion and that a subsequent process, perhaps dendritic inward crystallisation (e.g. Haack & Scott, 1993), isolated pools of melt which then crystallised separately. The large range in Ir, particularly prevalent in Group 2, combined with the homogeneous oxygen isotope compositions of each group, is good evidence that the reservoirs were initially equilibrated (at least with respect to O) following isolation and subsequently evolved by
fractional crystallisation. A mechanism such as this could allow for a range of crystallisation stages to be sampled in each isolated melt pod but is difficult to reconcile with the restricted high-Ir contents of Group 3. This could be addressed if a) the initial Ir content was higher and therefore Group 3 represents an evolved melt (but less evolved than e.g. Group 1) or b) Group 3 samples an early-crystallising feature such as a dendrite. This latter explanation is unlikely because chromite crystallises late in IIIABs.

The HSE concentrations for different IIIAB subgroups (see Figure 6.2) do not show a relationship between subgroups and Ir content, although Group 3 does exhibit considerably higher Ir contents than Group 1. This might indicate it is sampling an earlier-crystallising melt. In this context, and considering the IIIAB core inwardly crystallised, the Group 3 IIIABs may have crystallised at a shallower depth. Another possibility is that differing non-metal contents affected crystallisation histories between the groups, either by depressing the liquidus of the melt, or by affecting the partition coefficient of HSEs (Chapter 1). Figure 6.3 shows $\delta^{18}$O vs. Os contents for IIIABs where information on both is available. Cook et al. (2004) identified a high-Os and a low-Os subgroup in IIIAB irons from which Cape York was distinct. No high-Os IIIABs have been analysed for oxygen isotopes, however both Wonyulgunna and Mount Edith (Groups 2 and 1 respectively) sample the low-Os group of Cook et al. (2004). This suggests that the subgroups identified in this study are not identical to those previously reported on the basis of Os contents (Cook et al., 2004).

Figure 6.3 shows that the samples from Groups 1 and 2 for which both Os and $\delta^{18}$O are available are unresolvable in Os content. Cape York, the only Group 3 sample for which Os content is reported (Cook et al., 2004), has $\sim 3$ orders of magnitude more Os than the samples from Groups 1 and 2. There is not a clear relationship between subgroup and metal Ni, Au, Ga, and Ge content (Table 6.2) although there does consistently appear to be a resolvable difference between Groups 1 and 3 in most compositional metrics. No such difference exists between Group 2 and either of the other subgroups, suggesting that the Group 2 samples may be representative of bulk IIIABs and the other two subgroups record crystallisation in isolated environments capturing different stages of melt evolution. This relationship is illustrated on Figure 6.4.
Figure 6.3 – Os content in ppb (Cook et al., 2004) vs. $\delta^{18}$O for IIIABs where both data is available. Cape York shows a clear and much higher Os content than the samples from Groups 1 and 2. Mount Edith and Wonyulgunna are both from the low-Os subgroup identified by Cook et al (2004).

Figure 6.4 – A cross plot of Ir vs. Ni for the IIIABs analysed for oxygen isotopes in this study. Note that there is a resolvable difference between Groups 1 and 3 in both Ni and Ir. Group 2 samples appear to plot in both Group 1 and Group 3.
Figure 6.4 highlights the relationship between the three subgroups discussed above and reconfirms that identified on Figure 6.2. The Group 2 samples span the whole range and are perhaps representative of bulk IIIABs, although no Group 2 samples plot in between Groups 1 and 3. Group 1 and Group 3 samples appear to be restricted to evolved and less evolved metal compositions respectively. This is consistent with the idea that Groups 1 and 3 sample restricted melt pools whilst Group 2 is more broadly representative of the whole range of IIIAB compositions.

Table 6.2 – Literature Ir data for the analysed IIIAB irons. Cape York is split into two: Agpalilik (Ag) and Savik (Sav). References are numbered as follows: Wasson (1999) = 1, Mullane et al. (2004) = 2, Wasson et al. (1989) = 3, Scott et al. (1973) = 4, Buchwald (1975) = 5. Os contents are from Cook et al. (2004), the Cape York (Ag) value is the average of the two samples reported in that work.

<table>
<thead>
<tr>
<th>IIIAB meteorite</th>
<th>Subgroup</th>
<th>Ir (ppm)</th>
<th>Ni (mg g⁻¹)</th>
<th>Au (ppm)</th>
<th>Ga (ppm)</th>
<th>Ge (ppm)</th>
<th>Os (ppb)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Owens Valley</td>
<td>Group 1</td>
<td>0.141</td>
<td>88.9</td>
<td>1.30</td>
<td>21.6</td>
<td>45.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mount Edith</td>
<td>Group 1</td>
<td>0.014</td>
<td>93.7</td>
<td>1.70</td>
<td>20.1</td>
<td>37.5</td>
<td>4.37</td>
<td>1, 2</td>
</tr>
<tr>
<td>Bear Creek</td>
<td>Group 2</td>
<td>0.021</td>
<td>99.8</td>
<td>2.21</td>
<td>19.1</td>
<td>32.8</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Fairview</td>
<td>Group 2</td>
<td>7.56</td>
<td>76.5</td>
<td>0.62</td>
<td>19.4</td>
<td>37.6</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Puente del Zacate</td>
<td>Group 2</td>
<td>1.4</td>
<td>82</td>
<td>20.6</td>
<td>40.5</td>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Sacramento Mountains</td>
<td>Group 2</td>
<td>6.7</td>
<td>78.2</td>
<td>19.2</td>
<td>36.6</td>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Wonyulgunna</td>
<td>Group 2</td>
<td>0.022</td>
<td>93.2</td>
<td>1.43</td>
<td>19.7</td>
<td>39.4</td>
<td>3.81</td>
<td>1</td>
</tr>
<tr>
<td>Cape York (Ag)</td>
<td>Group 3</td>
<td>2.95</td>
<td>83.1</td>
<td>0.99</td>
<td>19.9</td>
<td>37</td>
<td>4365</td>
<td>1</td>
</tr>
<tr>
<td>Cape York (Sav)</td>
<td>Group 3</td>
<td>5.6</td>
<td>77</td>
<td>0.57</td>
<td>19.7</td>
<td>36</td>
<td>2275</td>
<td>1</td>
</tr>
<tr>
<td>Augusta County</td>
<td>Group 3</td>
<td>8.9</td>
<td>81.2</td>
<td>18.4</td>
<td>35.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.5.3.2 Melt isolation by dendritic inward crystallisation

As outlined previously, the oxygen isotopic composition in IIIAB subgroups could be distributed along a mass-fractionation line assuming that it was controlled by a kinetic process such as diffusion (Figure 6.5). A regression through linearized IIIAB oxygen data yields a λ of slope 0.5118 ± 0.0034 (2 SE), within error of expected values for kinetic processes, 0.514–0.525 (Young et al., 2016). If
diffusion was the primary control on oxygen distribution in the IIIAB core, it is possible that the three subgroups sample a single parent body (see Figure 6.5).

Figure 6.5 – Oxygen isotope results for IIIAB irons normalised to $\Delta^{17}\text{O}$ calculated with $\lambda = 0.5118$.

If the IIIABs do sample a single core, the discrete groupings of samples in $\delta^{18}\text{O}$ require an explanation. One possibility is that initial melting homogenised the oxygen isotope composition of the IIIAB core and oxygen mobility was controlled initially by diffusion; it is not clear what might act as the driving force for such oxygen mobility. Subsequent isolation of pools of melt by dendritic inward crystallisation (e.g. Haack & Scott, 1993) then created segregated isotopic reservoirs that were loosely distributed along the initial diffusion-controlled fractionation line and homogenised in $\delta^{18}\text{O}$ separately (Figure 6.6). Crystallisation of chromite then incorporated oxygen trapped in these melt pods and gave rise to differing $\delta^{18}\text{O}$ compositions between different pods. These pods could not have been completely homogenised as there is considerable scatter in $\Delta^{17}\text{O}$, especially when compared to PMG chromite for example (see Figure 6.5, Figure 6.7). Assuming that the subgroups
identified in this study do sample isolated melt pods spaced along a diffusion-controlled mass-fractionation line, there remains the question of between what the metal-hosted oxygen was diffusing.

**Figure 6.6 –** A model showing the initial diffusion in a homogenised IIIAB core and subsequent dendritic inward crystallisation isolating melt pools. These isolated pools would exhibit different average δ\(^{18}\)O contents based on their distance along the diffusion gradient.

Oxygen is not incorporated into crystallising FeNi metal and therefore may have been diffusing out of the metal melt and into an oxygen bearing component, perhaps co-crystallising chromite or even overlying mantle minerals. Oxygen-bearing minerals are significantly less dense than is FeNi metal and therefore they would be buoyant in the IIIAB core. If diffusion were occurring between metal and these overlying O-bearing minerals, the oxygen isotope results have the potential to act as a depth gauge for their parent melt pods. Lighter isotopes diffuse faster than heavier isotopes (White, 2015) meaning that more \(^{16}\)O-enriched samples (lower δ\(^{18}\)O) may be recording increased diffusion influence. In the context of an isotopically well-mixed core diffusing oxygen with overlying O-bearing minerals, samples further from these minerals would be expected to exhibit less pronounced diffusion and therefore have higher δ\(^{18}\)O values (Figure 6.6). The primitive composition of Group 3 IIIABs does not fit this hypothesis. Group 3 has the highest δ\(^{18}\)O values and therefore in the context of this model should be furthest from the core-mantle boundary. The HSE content of Group 3 relative to the other subgroups suggests that it is the earliest crystallised, when coupled with the fact that the IIIAB core probably inwardly crystallised (e.g. Yang & Goldstein, 2006), the Group 3 IIIABs should
be the closest to the core-mantle boundary. The potential for a link between δ¹⁸O and depth could be tested by comparing cooling rate data for the different IIIAB subgroups. Unfortunately, the IIIAB cooling rate data published by Yang & Goldstein (2006) do not sample any of the same meteorites as were analysed in this study and so a direct comparison between oxygen isotope composition and cooling rate cannot be carried out. In light of the disparity between HSE content in Group 3 and the requirement of this model that it samples a shallower melt pool than the other IIIAB subgroups, it does not seem likely that all three groups are representative of three separate melt pools in the same core unless either 1) the core evolution was more complex than in Figure 6.6, or 2) some mechanism was generating the diffusion of oxygen into the IIIAB core. Both of these possibilities seem unlikely and therefore the simplest explanation is that Group 3 samples a different parent body to the other IIIAB subgroups, which may themselves sample multiple parent bodies.

6.6 Implications for a IIIAB-PMG link

On the basis that PMG metal is consistent with a ~80% fractionally crystallised IIIAB melt, as well as previously unresolvable oxygen isotope compositions (Clayton & Mayeda, 1996), it has been suggested that the two meteorite groups sample different regions of a single parent body (Scott, 1977b; Wasson & Choi, 2003; Dottin et al., 2018). This is testable using an oxygen isotope comparison of metal-hosted chromite from PMG and IIIAB samples analysed in this study (Figure 6.7). Figure 6.7 is a direct comparison of the oxygen isotope composition of PMG chromites and IIIAB chromites. The PMG chromites are clearly distinct in Δ¹⁷O from all 3 identified IIIAB subgroups and are offset below the possible mixing/mass-fractionation line that may connect the IIIAB subgroups. If all chromite for PMG and IIIAB is combined they define a slope (λ) of 0.5131 ± 0.0032 (2 SE). This slope is within error of that expected in low-T equilibrium mass-dependent fractionation and kinetic mass-dependent fractionation. Owing to the high-T environment in which iron meteorites and pallasites formed, the former possibility can be excluded. A kinetic process such as diffusion could be responsible for the observed PMG-IIIAB chromite slope but does not explain the distribution displayed on Figure 6.8, which shows the relationship between PMG and IIIAB minerals when Δ¹⁷O is recalculated using the best fit λ for all IIIAB and PMG chromite, 0.5131.
Figure 6.7 – A comparison of chromite oxygen isotope compositions for IIIABs and PMGs analysed in this study. The black dotted line is a trendline through the IIIAB data with a slope ($\lambda$) of $0.5118 \pm 0.0034$ (2 standard error).

Figure 6.8 – Oxygen isotope results of all IIIAB and PMG data with $\Delta^{17}O$ calculated using a $\lambda$ of $0.5131$ – the slope of best fit through all chromite data. The green line is $\lambda = 0.5131$, the red line is PMG best fit $\lambda = 0.5369 \pm 0.0034$ (2 standard error).
A mass-fractionation line of this slope is consistent with expected slopes for kinetic processes (Young et al., 2016). The interpretation of IIIAB subgroups as isolated metal pods within a single parent core could be extended to include the PMG chromite. Given that PMG metal is broadly consistent with fractionally crystallised IIIAB metal (Wasson et al., 1999; Wasson & Choi, 2003; Scott, 2007), it is possible that the PMG chromite is recording a melt pool of the IIIAB core that was injected into the overlying mantle (Figure 6.9).

Figure 6.9 – A model showing expulsion of a pressurised melt pool isolated by dendritic inward crystallisation into the deep mantle. The red box surrounds the possible pallasite forming zone.

The major issue with this model from an isotopic perspective is that there is still a marked difference in chromite composition between the IIIABs and the PMGs. Even where the PMG and IIIAB chromite data are juxtaposed on Figure 6.8, there is a noticeable difference in Δ$^{17}$O with little overlap. A further complication to the model on Figure 6.9 is the offset of PMG olivine (see Figure 6.8) along a line steeper than is possible through any known mass-fractionation process (Chapter 4). The
possibility for olivine-specific offsets is discussed elsewhere in this thesis (see Chapter 4). T-testing of the differences between PMG and IIIAB chromite $\Delta^{17}$O values was conducted in order to establish whether the offset discussed is statistically significant.

6.6.1.1 Statistical testing of PMG-IIIAB chromite differences

A student’s t-test on the differences in $\Delta^{17}$O values recalculated to the PMG-IIIAB chromite best fit $\lambda$, 0.5131 (Figure 6.8) between PMG-low chromite and Group 2 IIIAB chromite yields a statistically significant result (P value = 0.00017). This is strong evidence that the PMG chromite and IIIAB chromite are not from the same parent body if oxygen mobility in molten metal is controlled by diffusion and highlights a statistically significant $\Delta^{17}$O offset between the meteorite groups even when a shallow mass-fractionation slope is adopted.

The above statistical test takes the most likely scenario for a common PMG-IIIAB parent body and assumes that mass-fractionation in the IIIAB core was governed by diffusion. If the possibility of some low-T or kinetic process is discounted, interpreting Figure 6.7 through the lens of high-T mass-fractionation leads even more convincingly to the conclusion that all 3 IIIAB subgroups are distinct from the PMG chromite. T-testing (SL = 0.01) of PMG-low chromite vs. Group 1, Group 2, and Group 3 chromite subgroups $\Delta^{17}$O values ($\lambda = 0.5262$) yield p-values of 0.079, <0.0001, and 0.009 respectively. The difference between PMG-low and Group 2 IIIAB $\Delta^{17}$O ($\lambda = 0.5262$) values is statistically significant at a significance level alpha of 0.01 (99%) as is the difference between PMG-low and Group 3 IIIAB chromite. The PMG-low – Group 1 IIIAB chromite difference is not statistically significant although this is attributed to the relative lack of constraint (n=3) on Group 1 IIIAB $\Delta^{17}$O values as well as the relatively large standard deviation. The PMG-high chromite is not considered in the statistical tests as it may have initially formed from a different isotopic reservoir to PMG-low chromite and undergone subsequent partial equilibration (see section 4.3.2.1).

On the basis of the oxygen isotope results, it is possible that the IIIAB chromite Group 2 (average $\Delta^{17}$O = -0.181) sample the core of a body where the PMG olivine (average $\Delta^{17}$O = -0.195) samples the mantle. Measured metallographic cooling rate considerations, however, render this highly unlikely. The IIIABs, which would be from the core of the body, have cooling rates of 56–338 K Myr$^{-1}$ (Yang & Goldstein, 2006) whilst the PMGs, which in the mantle would be cooling at a
shallower depth, have cooling rates of 2–18 K Myr\(^{-1}\) (Yang et al., 2010). To satisfy these data, a model where the IIIABs form the core of the PMG body would have to have been stripped of its mantle (PMGs) prior to the sub-solidus cooling of the core. If the PMG-forming impact occurred at ~10 Myr after CAI formation, as is suggested by Mn-Cr systematics (see section 4.4), and the IIIAB iron (core) crystallisation occurred at ~50 Myr after CAI formation (see section 6.2), it is possible that this stripping could have happened in the ~40 Myr between PMG emplacement and IIIAB crystallisation. However, in light of the subsequent slow sub-solidus cooling required in the PMG metal (e.g. Yang et al., 2010), the PMGs would have to have been insulated for a considerable time after the metal injection. This is inconsistent with the sequence of events required to account for all cooling rate data. On balance, it is highly unlikely that any IIIAB subgroup and the PMG olivine formed in the same parent body.

### 6.7 Summary

The interpretation of both the IIIAB subgroups and their potential relationship with PMG chromite depends on what processes govern the fractionation of oxygen in core-forming environments. The IIIAB chromite plots roughly along a mass-fractionation line \( \lambda \) consistent with kinetic processes and therefore if a mechanism such as diffusion governs oxygen mobility in core environments then the IIIAB subgroups identified here may sample isolated residual melt pools of a single parent core (e.g. Figure 6.6). In this case, the enrichment in \( \delta^{18}O \) in more primitive, earlier-crystallising samples (Group 3), is not easily explainable and requires either complex evolution of the IIIAB core or suggests that Group 3 is not from the same parent body as Groups 1 and 2. If the data are treated as products of high-T mass-fractionation, the conclusion that there are at least 2 distinct parent bodies sampled by IIIAB chromites is inescapable. In this case, a single body is sampled by Group 3 chromite whilst Groups 1 and 2 originate from at least one different body, perhaps two. The difference between Group 1 and Group 2 IIIABs is less well resolved than that between either group and Group 3. If the oxygen isotope difference between Group 1 and Group 2 IIIABs is due to separation and parallel evolution of metal melts in the same planetesimal then there must have been very effective oxygen homogenisation prior to the separation of the two melts. The difference in \( \delta^{18}O \) between these two subgroups is difficult to explain by high-T mass-fractionation but may be
explained by the sampling of melt pools between which prior oxygen mobilisation had been controlled by diffusion.

The fact that Cape York has an oxygen isotope composition that is drastically different to the bulk of the IIIABs has implications for the past suggestion that the IIIAB core dendritically crystallised inwards (Haack & Scott, 1993). Whilst cooling rate vs. melt evolution data still supports the inward crystallisation of the IIIAB core (Yang & Goldstein, 2006), if the oxygen isotope data is interpreted as a high-T regime then Cape York is likely not from the same parent planetesimal as Group 1 or 2 IIIABs. In this case, there is no evidence that the IIIAB core dendritically crystallised. Furthermore, if the IIIAB chromites analysed in this study do sample 2 or even 3 distinct parent bodies, the effectiveness of the current chemical classification scheme for linking iron meteorites by parent body must be revisited; there may have been many more differentiated planetesimals in the early Solar System than is currently believed.

The PMG and IIIAB meteorite groups do not sample a common parent body as has been previously proposed (e.g. Scott, 1977b; Wasson & Choi, 2003; Dottin et al., 2018). Whilst Group 1 IIIAB chromites are not currently statistically resolvable from PMG chromite, the difference may become statistically significant were more data from the Group 1 IIIAB subgroup obtained.
7 REVISITING RESEARCH QUESTIONS AND IMPLICATIONS OF THIS WORK

The findings discussed in this thesis have answered the three key research questions identified in Chapter 1. This chapter discusses the wider implications for planetary science research of each of these research questions.

7.1 What is the role of impacts in pallasite formation?

7.1.1 Findings

Chapter 4 demonstrates possible isotopic evidence for the impact formation of PMGs. A key observation of this study is the presence of a statistically significant $\Delta^{17}$O offset between PMG-low olivine and chromite minerals and evidence for partial equilibration between the two minerals in PMG-high samples. The simplest interpretation of the data is that PMG samples are a mixture of minerals from two isotopic reservoirs brought together by some process, likely an impact. This is supported by other lines of evidence such as the range in PMG cooling rates (Yang et al., 2010) and the likelihood of shallow emplacement of some PMGs (Tarduno et al., 2012; Nichols et al., 2016).

If this is the case, impacts would have a critical role in pallasite formation as the process responsible for mixing the metal and silicate portions. There are several alternative hypotheses discussed in Chapter 4 that can partially explain some of the observations and need further investigation through future studies. The most plausible of these is the influence of an anharmonic, perhaps mineral-specific, mass-independent offset (see Chapter 4). If such a process were responsible for the observed disequilibrium then there is no requirement for impact-mixing of isotopic reservoirs in PMG formation; in this case the role of impacts in PMG formation is likely restricted to the fragmentation of precursor olivine grains through impact shockwaves. Although the statistics are poorer, the similar apparent $\Delta^{17}$O offset in Bushveld pyroxenite olivine-chromite relationships (see Chapter 3) seems to lend credibility to the idea that such a process could be responsible for the observed offset in PMG. This is not supported by the relationship between olivine and blank-corrected chromite in the limited Eagle Station pallasite group dataset which is within expected mass-fractionation bounds (see Chapter 4), although in this case the uncertainties are too large to provide any useful constraints on this discussion.
7.1.2 Implications

The identification of the $\Delta^{17}O$ disequilibrium has significant implications for the interpretation of pallasite formation environments and suggests that PMGs formed during the impact mixing of two differentiated planetesimals. The PMG group, then, may be providing a unique window into a period of planetary growth in the early Solar System rather than a record of differentiation processes at a core mantle boundary as has been previously suggested. The existence of numerous different pallasite groups in the meteorite record may indicate that such an impact-mixing process was widespread in the early Solar System and perhaps implies that core injection during impacts are a contributing factor to a second, later stage of core growth in already differentiated planetesimals. If such an impact-mixing process is responsible for the generation of the different pallasite groups, a significant amount of equilibration post-impact probably occurred in order to account for the similarity between olivine and chromite $\Delta^{17}O$ results in the PMG, as well as in the Eagle Station samples measured. In the Eagle Station parent body this equilibration would have had to have been greater than in the PMG parent body, resulting in no measurable offset in the samples analysed.

If the $\Delta^{17}O$ offset is not a record of impact-mixing but rather induced by some crystal chemical, anharmonic, or nuclear shift effect, there would be significant implications for the interpretation of oxygen isotope data in cosmochemistry. In the event that such an effect (or effects) are now resolvable at the increased precision afforded by laser-assisted fluorination, studies measuring oxygen isotopes at high precision must be exceptionally cautious when comparing data from different minerals, either from the same or from different meteorites. Other mass-independent effects, such as the magnetic isotope effect driven by differences in nuclear spin between isotopes, may warrant investigation in the future but are unlikely to impact geological materials (White, 2015; Yang & Liu, 2016) and were shown theoretically to be insignificant by Bigeleisen (1996) in U isotopes. An anharmonic or mass-independent effect has the potential to seriously affect both whole-rock and mineral-mineral studies seeking to link different meteorite groups unless the same minerals are used when comparing two samples. This means that in seeking to link meteorite groups by parent body, for example, the same minerals must be used from each sample in order to compensate for any anharmonic effect. In whole rock studies where this is not possible, care must be taken to ensure the same mineralogies are analysed in the same quantities for disparate samples. Further investigation
and an understanding of any such effect, if it exists, is absolutely critical for the future of both inter-
mineral fractionation studies as well as parent body determination as instrument precision advances.

7.2 Are PMGs and IIIAB irons from a common parent body?

7.2.1 Findings

As discussed in Chapter 6, the findings of this study show that IIIAB irons and PMG metal do not
sample a common parent planetesimal and it seems very unlikely that PMG olivine could share a
parent body with IIIAB irons on the basis of cooling rate evidence (e.g. Yang et al., 2006; 2010).
The oxygen isotope analyses on chromite from IIIAB iron subgroups and PMG-low samples strongly
suggests that there is no parent body relationship between the two groups as had been excogitated in
numerous prior studies (e.g. Buseck, 1977; Dottin et al., 2018).

7.2.2 Implications

The implications for this are fairly straightforward. The IIIAB irons and PMGs do not sample
different domains of a single parent body and therefore do not represent a combined record of early
planetary differentiation. Despite this, the similarities, both isotopic (e.g. Markowski et al., 2006;
Dottin et al., 2018; this study) and compositional (e.g. Buseck, 1977), between the two groups imply
that they formed in compositionally very similar parent bodies and at approximately the same time.
This leads to the conclusion that the inner Solar System was relatively well mixed. A consequence
of this is that whilst there is no direct genetic link between the PMGs and IIIABs, they can still inform
our understanding of deep planetary processes in early formed differentiated bodies. The possibility
that both PMG and IIIABs may sample multiple parent bodies themselves is a further consideration.
If PMGs sample at least two bodies (see Chapter 4) and IIIABs sample two or three bodies (see
Chapter 6), a pair of meteorite groups once thought to originate from a single planetesimal may
actually sample four or five separate differentiated bodies that are compositionally and isotopically
similar. This would mean that current estimates of the number of differentiated bodies represented
in the meteorite collection (e.g. Greenwood et al., 2017b; 2020) could be considerably
underestimated and that the meteorite record samples a greater number of the early Solar System
planetesimal population than has been previously thought. The fact that the PMG olivine is not
isotopically resolvable from *e.g.* Group 2 IIIABs is good evidence that distinct but isotopically unresolvable (at least presently) parent body reservoirs were present in the early Solar System.

### 7.3 What can PMGs and IIIABs tell us about parent body conditions?

#### 7.3.1 Findings

It seems likely that PMGs were formed sometime after differentiation during the collision of two such bodies. The W isotope data presented in Chapter 3 indicates that differentiation of the impacting PMG core occurred ~0.5–1.6 Myr after CAI formation. The injection of metal into the cumulate olivine occurred afterwards and likely corresponds to the Mn-Cr age of 10.2 (+5/-2.5) Myr, an interpretation based on the assumption that diffusion of Mn between PMG olivine and a silicate melt ceased at this time. This means that on the basis of the model ages for Mn-Cr and Hf-W decay schemes, metal-injection occurred some time after differentiation. The relatively homogenous PMG olivine oxygen isotope composition, coupled with the very slow rates of O diffusion in olivine crystals (see Chapter 4), strongly suggests that the PMG olivine crystallised as a magma ocean cumulate and is not a restite. On the basis of the somewhat controversial relationship between Cr isotope composition and heliocentric distance, the PMG parent bodies may have accreted at around 2.2 ± 0.5 AU. This is consistent with formation in what is now the inner asteroid belt.

The combination of textural, isotopic, and compositional factors to define the PMG-low and PMG-high subgroups should aid with future studies into PMG formation and evolution. The existence of these subgroups indicates that both silicate and metal melts were present in varying amounts in the PMG parent body during pallasite formation. Future work should seek to assign meteorites to the subgroups identified on the basis of compositional, textural, and isotopic relationships discussed in this and similar studies (*e.g.* McKibbin *et al.*, 2019). Subsequent evaluation can then be carried out in the context of formation processes.

The identification of three resolvable $\delta^{18}$O subgroups of IIIAB irons provides some additional constraints for our understanding of the evolution of planetary cores. The distinct isotopic reservoirs within the IIIAB population demand the need for a complex evolution of an asteroidal core involving the isolation of oxygen reservoirs in metal melt pools. These pools may have been isolated during dendritic inward crystallisation of a diffusion-controlled core. This interpretation supports that of
previous work; Haack & Scott (1993) proposed dendritic inward crystallisation as a controlling process during core evolution in small differentiated bodies. A possible and perhaps more likely alternative cause for the $\Delta^{17}$O offset between Group 3 IIIAB irons and the other two groups is differing planetary provenance. Given that to satisfy the $\delta^{18}$O and HSE data, a single-core model requires oxygen to be diffusing in to the IIIAB core, it seems more reasonable that the IIIAB subgroups identified in this study represent distinct planetary cores that accreted from the same, or similar, precursor material. In order to establish whether IIIABs sample several cores or a single complex core, further work into diffusion of oxygen in metal melts, as well as a detailed oxygen isotope investigation into other magmatic iron groups should be undertaken. If it can be demonstrated that the mobility of oxygen in molten FeNi is controlled by diffusion, and that a mechanism for the diffusion of oxygen into a metal core exists, it would support the model for isolation of melt pools during the dendritic inward crystallisation of the IIIAB parent core. Currently, however, it seems more likely that IIIABs sample several planetary bodies. By comparing the oxygen isotope results of chromite minerals from other magmatic iron groups, the presence or absence of other asteroidal cores displaying complex evolution in the early Solar System can be evaluated.

7.3.2 Implications

The interpretation that PMGs formed from a magma ocean rather than as a restite implies that relatively small bodies (200–400 km radius) may undergo global melting in the earliest stages of planetary formation. Coupled with the estimate for heliocentric distance, this finding has implications for the extent of planetary melting in the early Solar System and, in turn, perhaps the abundance of short-lived radioactive nuclides. When this is considered alongside the impact model for PMG formation it seems that impacts between sizable planetesimals were occurring in the inner Solar System at ~10 Myr after CAI formation. By this time, the bodies had already melted and differentiated. It may be that PMGs are a record of a later stage of planetesimal growth by the impacts of differentiated bodies.

There are several potential implications apparent from the IIIAB results in this study. Firstly, the dendritic evolution of small planetary cores recorded by IIIAB irons may have implications for the
dynamo characteristics of small bodies. Secondly, and looking further into the future to when commercial exploitation of asteroid resources may be more viable, a process such as dendritic inward crystallisation could also conceivably lead to the economic concentrations of various elements in asteroid cores. Concentrations of incompatible HSEs, for example, increase in the melt phase during metal crystallisation; melt pools trapped by dendritic inward crystallisation therefore have the potential to concentrate elements of economic interest and an understanding of the nature of the crystallisation of a parent body core would provide better constraints on where such deposits could be found. Finally, if the discrete isotopic subgroups identified in IIIAB irons relate to distinct parent bodies, then the chemical classification scheme currently used to group iron meteorites is not 100% effective at identifying parent body links. As discussed, this has implications for the estimated number of differentiated bodies present in the early Solar System; if the established magmatic iron groups actually sample several different planetesimals, there may have been significantly more such bodies in the early Solar System than is currently thought.
8 CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

This study has utilised SEM, EPMA, high-precision oxygen isotope analyses, Cr isotope analyses, and W isotope analyses to investigate the processes active in early-forming differentiated planetesimals. High-precision oxygen isotope analyses of PMGs have uncovered a widespread disequilibrium between olivine and Al-poor chromite in the samples classified as PMG-low. This disequilibrium seems to provide good support for relatively recent pallasite formation models that invoke impact-mixing of two planetesimals and as such, perhaps provides the best evidence yet that the PMG meteorite group records a period of planetary growth and not differentiation. Sixty-two olivine samples from 21 PMGs were analysed in conjunction with 36 chromite samples from 9 PMGs. Of this data set, 15 chromite samples from 8 PMGs were analysed using optimized conditions and have been compared directly with 15 olivine samples from the same 8 PMGs. The whole suite of olivine samples (n = 62) shows no evidence for bimodality as had been reported in published literature and instead display relatively homogenous isotopic signatures ($\delta^{18}O = 0.364 \, \text{‰} \, 2\sigma$, $\Delta^{17}O = 0.018 \, \text{‰} \, (2\sigma)$), even across subgroups. In order to counter significant challenges when reacting chromite, the technique for fluorinating chromite was optimized and a subsequent improvement in yield was observed. The chromite oxygen isotope data fall in two subgroups that are correlated with major element composition and are interpreted as being indicative of differing degrees of equilibration between two separate isotopic reservoirs; this conclusion is borne out by measured variations in $\lambda$ between minerals in the two PMG subgroups. The PMG-low olivine-chromite $\lambda = 0.5364 \pm 0.0030 \, (2 \, \text{SE})$, is approximately 4 standard error outside of the high-T upper limit, and the PMG-high olivine-chromite $\lambda = 0.5312 \pm 0.0070 \, (2 \, \text{SE})$, is within error of the high-T upper limit. There is a similar, although not statistically significant, offset between olivine and other minerals in terrestrial Bushveld Igneous Complex samples analysed and an olivine-chromite $\lambda = 0.5370 \pm 0.0054 \, (2 \, \text{SE})$. This provides some evidence that the olivine-chromite disequilibrium identified in PMG-low samples may be caused by some previously unknown crystal chemical, anharmonic, or nuclear effect, that may shift olivine “upward” in $\Delta^{17}O$ space relative to other minerals analysed. The number of Bushveld samples analysed are relatively few and as such, more analysis is required on terrestrial
material in order to constrain the existence and magnitude of any unknown effect. No disequilibrium is seen between analysed Eagle Station olivine and chromite; however, the sample set is very small and this requires further validation.

The Hf-W decay system has been employed to date the differentiation of the PMG parent body and yielded results consistent with contemporaneous work and previous studies; the PMG parent body(ies) differentiated very early in Solar System history (0.5–1.6 Myr $\Delta T_{\text{CAI}}$). Unlike for oxygen isotopes, chromium isotope analyses on both PMG olivine and chromite have not revealed a resolvable difference. This may be because Cr is less sensitive to planetary provenance than is oxygen, or it could be because some the disequilibrium identified in oxygen isotopes stems from some other effect, perhaps anharmonicity or NFSE. The Mn-Cr decay system has been used to date Mn closure in PMGs. On the basis of Cr isotopes in PMG olivine, this closure occurred at $\Delta T_{\text{CAI}} = 10.2 \pm 5/-2.5$ Myr which becomes 10.4 ± 1.6 Myr after CAIs if PMG chromite is used to constrain the isochron. This event is interpreted as the removal of Mn-bearing silicate melt during displacement with metal melt following PMG silicate and metal mixing. If the mixing event was the result of an impact, as may be demonstrated by the oxygen isotope results, this shows that sizable differentiated bodies were colliding within ~10 Myr of CAI formation.

The IIIAB iron meteorite results obtained using high-precision oxygen isotope analyses in this study fall into three resolvable and previously unreported subgroups. These subgroups can be connected along a fractionation line of $0.5118 \pm 0.0034$ (2 SE) which is too shallow for typical high-T equilibrium mass-dependent fractionation but may be imparted by a kinetic process such as diffusion. In this case, the three IIIAB subgroups may sample separated melt pools in a single planetesimal core evolving by dendritic inward crystallisation or a similar complex process. The HSE composition of the Group 3 IIIAB irons seems at odds with this interpretation, however, as the inwardly-crystallising IIIAB core should have more primitive samples exhibiting lighter $\delta^{18}$O compositions, the opposite to what is observed. To fit with the evidence that the IIIAB core crystallised inward, and therefore more evolved metal should be closer to the centre of the core, oxygen would have had to diffuse in to the core. This seems very unlikely. An alternate explanation for the observed oxygen isotope distribution is that the samples analysed represent at least two (and perhaps three) distinct
parent bodies. This would have significant implications for the iron meteorite classification scheme and current understanding of the evolution of the IIIAB core.

On the basis of the oxygen isotope data presented in this study, the IIIAB iron metal is not genetically related to PMG metal as has been proposed by numerous authors over a period spanning several decades. There is a statistically significant difference in $\Delta^{17}$O between bulk IIIABs and the PMG-low chromites that is not explainable if the metal from both meteorite groups originate from the same parent planetesimal. The data do not preclude the possibility that the IIIAB core formed the centre of the impacted PMG parent body (into which the PMG metal may have been injected), although this is difficult to reconcile with other factors such as cooling rate differences.

8.2 Future work

The results of this PhD project have identified a series of avenues that should be explored in future studies.

8.2.1 PMG impact model

The PMG impact model that appears to be supported by the oxygen isotope results from olivine and chromite presented in this study requires further testing. The analysis of more olivine and chromite samples from other pallasite groups is required in order to establish if this disequilibrium is common to all pallasite groups. If it is shown that this is the case, it would support the impact model hypothesis and suggest that Solar System-wide planetary growth was occurring by impact-injection of core material in the early Solar System. If not the case, it may be that partial equilibration between the silicate and metal reservoirs, as sampled by PMG-high chromite in PMGs, is further advanced or completed in other pallasite groups meaning that any disequilibrium is removed. This type of further investigation presents significant challenges, however. There are a limited number of pallasite samples in the meteorite record and only a relatively restricted subset of these contain the minerals of interest. As a result of the paucity of material, it may be difficult to get statistical evidence for such a process if the corresponding offsets in other pallasite groups are similarly small.
8.2.2 Anharmonicity/NFSE

The tentative identification of a possible olivine-specific $\Delta^{17}$O offset in the Bushveld Igneous Complex samples analysed in this study necessitates the investigation into the possibility that anharmonic, crystal-chemical, or nuclear field shift effects may impart non-mass-dependent signatures in oxygen isotope fractionation. Detailed studies testing the fractionation relationships between different igneous minerals are essential in order to establish whether there is such an effect although higher precision measurements may be required before this can be thoroughly investigated. The automation of a laser-assisted fluorination setup, allowing for a high volume of samples to be analysed per day, may help to overcome this issue and provide a statistically robust dataset. A problem with such a setup in this context is the care that must be taken when fluorinating chromites, for example, a procedure that really requires human oversight. A comparison of the theoretical fractionation relationships with empirically tested mineral-mineral relationships should also be pursued in order to determine if measurements deviate significantly from theory. This investigation would require computational chemistry software to calculate vibrational frequencies for chemical bonds in minerals to calculate key parameters using isotope fractionation theory (e.g. Urey, 1947) which could then be compared to high-precision oxygen isotope analyses. In this manner, the accuracy of the theoretical fractionation relationships could be tested and any deviations highlighted by empirical testing could be quantified and explored.

8.2.3 IIIAB investigation

In light of the identification of three previously undiscovered IIIAB subgroups in this project, a detailed oxygen isotope study of available oxygen bearing phases should be carried out in other magmatic iron groups. This would provide an insight into whether isotopic subgroups such as those identified are widespread in the iron meteorite record and would provide a framework by which the iron meteorite classification scheme could be re-evaluated if necessary. An investigation into the cooling rate characteristics of the subgroups identified in this study, as well as of any identified in the future, would help provide a better understanding of the evolution of the IIIAB core and the behaviour of oxygen with varying depth. This, coupled with further investigation into oxygen solubility, diffusion, and partitioning in FeNi metal melts would help determine whether there is a
relationship between oxygen isotope subgroup and depth which, in turn, would provide new insights into the evolution of asteroidal cores.
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APPENDICES

1 TEMPERATURE DEPENDENCE OF THE TERM $\lambda$

The temperature dependence of $\lambda$ is already established (Young et al., 2002; Young et al., 2016). The purpose of this appendix is to illustrate this temperature dependence with a simple example and to highlight possible shortcomings in the use of fractionation exponents as a temperature indicator.

1.1 A worked example

The framework for calculating fractionation relationships from statistical mechanics was pioneered independently by Harold Urey (Urey, 1947) and Jacob Bigeleisen & Maria Goeppert Mayer (Bigeleisen & Mayer, 1947) (method hereafter referred to as U-BM). In principle, it is possible to calculate the equilibrium constant ($K_{eq}$), the fractionation factor ($\alpha$) and therefore the fractionation exponent $\lambda$ (see Equation A2), between minerals in different geological environments. In practice, this requires very arduous calculation of many vibrational frequencies and necessitates the use of computational chemistry software to be achievable in a reasonable timescale (e.g. Huang et al., 2014; Cao & Liu, 2011). The calculation of isotope fractionation between smaller molecules, however, is relatively straightforward. Whilst an in-depth theoretical exploration of the fractionation behaviour between PMG minerals is outside of the scope of this thesis, this section demonstrates the utility of the U-BM framework in simple molecules and illustrates the temperature dependent nature of $\lambda$. This may provide insight into the need for similar theoretical investigation of the PMG olivine-chromite disequilibrium identified in this study. The following example applies the U-BM framework to a simple isotope exchange reaction. The example reaction (Equation A8) is taken from Chacko et al. (2001) but the calculations are extended to allow for the determination of $\lambda$ at different temperatures. Also demonstrated is the use of the harmonic oscillator approximation in calculating unknown vibrational frequencies for heavier isotopologues and therefore this section highlights possible shortcomings in the U-BM framework in situations where the anharmonic contributions are large (see Chapter 4).
For an isotope exchange reaction between phases A and B where * designates the presence of the heavy isotope(s) in that molecule:

Equation A1

\[ aA + bB^* = aA^* + bB \]

In this reaction, \( a \) and \( b \) are stoichiometric coefficients – e.g. for \( 2CO_2 + CO \), \( a \) would be 2 and \( b \) would be 1. To calculate \( \lambda \) for a given isotope exchange at a given temperature it is first important to understand the relationship between \( \lambda \) and \( \alpha \), the fractionation factor (Young et al., 2002) as shown by:

Equation A2

\[ \alpha^{17}_{16} = \left( \alpha^{18}_{16} \right)^{\lambda} \]

where \( \alpha \) is the fractionation factor, defined as (Ferronsky & Polyakov, 1982; Criss, 1991; 1999):

Equation A3

\[ \alpha = \left( \frac{K_{eq}}{K_l} \right)^{\frac{1}{ac}} \]

This definition differs slightly from some others (e.g. Chacko et al., 2001), but does not make the assumption that \( \alpha \) is the \( n^{th} \) root of \( K_{eq} \) (Criss, 1999). Here \( ac \) is the number of atoms exchanged and \( K_l \) is the limiting equilibrium constant at high-T between phases A and B:

Equation A4

\[ K_l = \left( \frac{\sigma^*}{\sigma} \right)_A a \left( \frac{\sigma^*}{\sigma} \right)_B b \]

here, \( \sigma \) refers to the symmetry number of the molecule, * designates the molecule containing the heavy isotope(s). \( K_{eq} \) is given by (Chacko et al., 2001):

Equation A5

\[ K_{eq} = \left( \frac{Q^*}{Q} \right)_A a \left( \frac{Q^*}{Q} \right)_B b \]

where \( Q^*/Q \) is the partition function ratio. The partition function is the product of rotational, translational, and vibrational behaviour of the molecule (Criss, 1999; Chacko et al., 2001).
materials, only the vibrational motion is available to molecules (White, 2015). Urey (1947) employed the Teller-Redlich spectroscopic theorem (see Criss, 1999; Chacko et al., 2001 for application to the full partition function equation) to simplify the equation for diatomic molecules to:

Equation A6

\[ \frac{Q^*}{Q} = \left( \frac{m^*}{m} \right)^{\frac{3r}{2}} \left( \frac{\sigma}{\sigma^*} \right) \left( \frac{u^*}{u} \right) \left( \frac{e^{-\frac{u^*}{2}}}{e^{-\frac{u}{2}}} \right) \left( 1 - e^{-u} \right) \left( 1 - e^{-u^*} \right) \]

where \( u = \hbar v/kT \). Here, \( h \) is Planck’s constant, \( k \) is Boltzmann’s constant, \( T \) is temperature in K, \( v \) is vibrational frequency, \( r \) is the number of isotopes being exchanged, and \( m \) is the isotopic mass. The latter term can be calculated from the relationship \( v = \omega c \) (Urey, 1947; Criss, 1991) where \( \omega \) is wavenumber in \( \text{m}^{-1} \). For polyatomic molecules, Equation A6 is more complex (Urey, 1947; Criss, 1991; Criss, 1999; Chacko et al., 2001; White, 2015) and takes the product over each vibrational mode \( i \). The \( 3n - t \) refers to the number of vibrational modes a molecule has, \( n \) is the number of atoms and \( t \) is 5 for linear polyatomic molecules and 6 for non-linear polyatomic molecules (Criss, 1999; Young et al., 2002):

Equation A7

\[ \frac{Q^*}{Q} = \left( \frac{m^*}{m} \right)^{\frac{3r}{2}} \left( \frac{\sigma}{\sigma^*} \right) \prod_{i} \left( \frac{u_i^*}{u_i} \right) \left( \frac{e^{-\frac{u_i^*}{2}}}{e^{-\frac{u_i}{2}}} \right) \left( 1 - e^{-u_i^*} \right) \left( 1 - e^{-u_i} \right) \]

The partition function equations are sometimes missing the mass term, these are called the reduced partition function (White, 2015). When applied to minerals, Equation A7 takes the product of \( 3n \) vibrational modes, where \( n \) is the number of atoms in the unit cell of a given mineral (Chacko et al., 2001).

From the above equations, the \( \lambda \) for fractionation between two molecules can be worked out if the equilibrium constant and fractionation factor for \(^{18}\text{O}/^{16}\text{O}\) and \(^{17}\text{O}/^{16}\text{O}\) are calculated independently and then combined in Equation A2. To illustrate this, the simple example fractionation factor calculation done by Chacko et al. (2001) has been extended below to calculate theoretical partition functions, equilibrium constants, fractionation factors and \( \lambda \) at 500 °C and 200 °C for exchanges of
${}^{16}\text{O}$ with both $^{17}\text{O}$ and $^{18}\text{O}$. Figure A1 shows the relationship between $\lambda$ and temperature for this reaction. The example given in Chacko et al. (2001) is the isotope exchange reaction:

Equation A8

\[
C^{18}\text{O} + \frac{1}{2}C^{16}\text{O}_2 = C^{16}\text{O} + \frac{1}{2}C^{18}\text{O}_2
\]

For this reaction, the symmetry numbers are 1 for both CO isotopologues and 2 for both CO$_2$ isotopologues and so cancel out. Chacko et al. (2001) present wavenumbers for the isotopologues at all vibrational modes for bonds with both the light and heavy isotope. Wavenumbers for bonds containing the heavy isotope are often not reported in the literature for oxygen owing to their relative rarity. In these cases, it is useful to use the relationship between vibrational frequency and reduced mass in a simple harmonic oscillator (Equation 4 in Chacko et al., 2001) to obtain the vibrational frequencies of bonds containing the heavy isotope. The simple harmonic oscillator (SHO) approximation is widely used:

Equation A9

\[
v^* = \sqrt{\frac{\mu}{\mu^*}} \nu
\]

where $\mu$ is the reduced mass. Calculating $v^*$ as above gives the same wavenumbers quoted in Chacko et al. (2001). The reduced masses must be calculated for several vibrational modes in polyatomic molecules (e.g. the CO$_2$ in this example). This is done using Equation A9 and the measured wavenumber for the given bond as well as calculating the reduced masses using the relevant equation based on the vibrational modes present in the molecule (see Figure 2 in Chacko et al., 2001). For CO$_2$ there are 3 available vibrational modes: symmetric stretching, bending, and asymmetric stretching (Chacko et al., 2001). The bending mode in CO$_2$ is degenerate, i.e. can be in multiple orientations – two in this case – and so must be counted twice (Figure 2 in Chacko et al., 2001). This means that the product in Equation A7 must be taken over 4 vibrational modes, which is equal to the $3n - 5$ expected for linear polyatomic molecules.

Use of Equation A7 for CO$_2$ and Equation A6 for CO gives $Q^*/Q$ values of 1.49690 and 1.22466 respectively for 18/16O and 1.23213 and 1.11058 for 17/16O. These numbers can be used to find
the equilibrium constant $K_{eq}$ and fractionation factor $\alpha$ for these exchanges. The symmetry numbers of the molecules in this example are equal across all of their isotopologues, therefore the $K_t$ term is equal to 1 (see Equation A3). Table A1 tabulates the results for partition function, equilibrium constant, and fractionation factor calculations.

Table A1 – Results for partition function, equilibrium constant, and fractionation factor calculations for the isotope exchange reaction given in Equation A8 at both 500°C and 200°C.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$Q^*Q_{(18/16)}$</th>
<th>$Q^*Q_{(17/16)}$</th>
<th>$K_{eq,18/16}$</th>
<th>$K_{eq,17/16}$</th>
<th>$\alpha,18/16$</th>
<th>$\alpha,17/16$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ 500°C</td>
<td>1.49690</td>
<td>1.23213</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO 500°C</td>
<td>1.22466</td>
<td>1.11058</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ 200°C</td>
<td>1.59338</td>
<td>1.27344</td>
<td>CO$_2$-CO (500°C)</td>
<td>0.999033</td>
<td>0.999490442</td>
<td>0.99806764</td>
</tr>
<tr>
<td>CO 200°C</td>
<td>1.26050</td>
<td>1.12763</td>
<td>CO$_2$-CO (200°C)</td>
<td>1.001417</td>
<td>1.00074299</td>
<td>1.00283773</td>
</tr>
</tbody>
</table>

Rearranging Equation A2 for $\lambda$ and inputting the values given above for 500°C:

Equation A10

$$\lambda = \frac{\ln(0.99898114)}{\ln(0.99806764)} = 0.5270$$

Similarly, at 200°C:

Equation A11

$$\lambda = \frac{\ln(1.00074299)}{\ln(1.00148653)} = 0.5242$$

The value reached in Equation A10 is consistent with the expected range of high-T equilibrium fractionation (Young et al., 2016), the value in Equation A11 with low-T equilibrium fractionation. This simple example demonstrates the utility of the U-BM method and highlights the potential of using statistical thermodynamics to calculate isotope exchange between phases. It also suggests that
measured fractionation exponents have the potential to be employed as thermometers in the future. Table A1 and Figures A1 and A2 highlight the temperature dependence of $\lambda$ in this example.

![Figure A1](image)

Figure A1 – Calculated fractionation exponent vs. temperature (K) for the exchange reaction in Equation A8. Note that as temperature increases, the $\lambda$ approaches the high-T upper limit, 0.5305. The black arrow highlights the approximate location of the crossover point for this reaction (Figure A2).

1.2 Crossovers

There are certain rare conditions under which the fractionation exponent can be outside the range of mass dependent fractionation (0.5–0.5305 for oxygen). These scenarios are called crossovers and arise from differences in the closing temperature ($T_c$) at which the fractionation factor for 17/16 and 18/16 reach unity for a given system (Skaron & Wolfsberg, 1980; Deines, 2003). Over the temperature range between the $T_c$ for the two fractionation factors, the $\lambda$ can extend from $+\infty$ to $-\infty$ (Skaron & Wolfsberg, 1980; Deines, 2003; Hayles et al., 2018). Even just outside of this temperature range, the $\lambda$ can be outside of the region of mass-fractionation, although the range of temperatures across which this effect is noticeable is usually very, very small. In the example of $^{18}C^{16}O + \frac{1}{2}^{16}C^{16}O_2 = ^{16}C^{16}O + \frac{1}{2}^{18}C^{18}O_2$ given above, the $T_c$ values are ~563 K for 17/16 and ~562.98 K for
18/16. In this range, λ could be any number. The values for λ would be outside the mass-fractionation range if equilibrium was reached at any temperature between ~560.3 K and ~563.6 K. Figure A2 highlights this crossover point in the $C^{18}O + \frac{1}{2}C^{16}O_2 = C^{16}O + \frac{1}{2}C^{18}O_2$ exchange reaction. It is unclear what this range is for different mineral-mineral fractionations although it is incredibly unlikely the samples analysed in this study reached and remained in equilibrium in such a small temperature range as would be required for crossovers to have an effect. Table A2 lists the calculated fractionation exponent at temperatures from 10 K to 5000 K.

![Fractionation exponents at temperatures from 500–600 K approaching the crossover (~563 K, see Chapter 1) for the above reaction. Note that the temperature dependence of λ does not apply very close to the crossover point (see Chapter 1 for definition). The solid black line is the high-T upper limit.](image)

The temperature dependence of λ is illustrated in Table A1, Table A2, and Figure A1 for a simple CO$_2$–CO exchange reaction. Whilst the exchange of oxygen between olivine and chromite in PMGs is considerably more complex, the possibility that an anharmonic or previously unknown mass-independent effect is generating an observed disequilibrium means that a similar theoretical investigation into the fractionation relationships between igneous minerals at T conditions consistent with PMG formation is timely.
Table A2 (continued overleaf) – Table of calculated fractionation exponents for increasing temperature for the exchange reaction in Equation A8.

<table>
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<tr>
<th>Temperature (K)</th>
<th>Calculated fractionation exponent</th>
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</tr>
<tr>
<td>50</td>
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<td>100</td>
<td>0.51890</td>
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</tr>
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<td>----------------------------------</td>
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<td>5000</td>
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# 2 LIST OF SAMPLES

Appendix 2 – A list of the samples presented in this thesis. PMG, PES, and IIIAB denote Main-Group pallasites, Eagle Station pallasites, and IIIAB irons, respectively. The abbreviation opx is orthopyroxene, Ca plag is calcic plagioclase.

The provenance column contains the abbreviations CFM (Chicago Field Museum), BCF (Bruno & Carine Fectay), R.H. (Robert Haag), SI (Smithsonian Institute), NHMV (Natural History Museum, Vienna), DvN (D. van Niekerk, Rhodes University, South Africa), and OU (meaning from Open University collection). The sample numbers are provided where relevant to ensure future work can draw direct comparisons with that presented here.

<table>
<thead>
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<th>Meteorite/Sample</th>
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<th>Provenance</th>
<th>Sample Number</th>
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<td>Olivine + chromite</td>
<td>CFM</td>
<td>ME 3382</td>
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<td>Olivine</td>
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<td>Cr spinel + olivine + opx</td>
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Appendix 3 – A table of Al, Cr, and Mg content in PMG and IIIAB chromites collating literature data and analyses from this study. The reference code is as follows: 1 = Wasson et al. (1999), 2 = Boesenberg et al. (2012), 3 = Bunch & Kiel (1971).

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<th>Meteorite</th>
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<th>Cr$_2$O$_3$</th>
<th>MgO</th>
<th>Total</th>
<th>Reference</th>
<th>Subgroup</th>
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