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In-situ O-isotope analysis of relict spinel and forsterite in small (<200µm) Antarctic micrometeorites –

samples of chondrules & CAIs from carbonaceous chondrites

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Abstract

We report high-precision secondary ion mass spectrometer triple oxygen isotope systematics (95 individual analyses) from 37 micrometeorites (MMs) collected from South Pole-Water Well (SPWW), Antarctica. The study population focuses on unzoned coarse-grained (Cg) MMs (n=23) with both multiple (n=14) and single mineral (n=9) varieties investigated. We also analysed relict minerals in poikilitic cosmic spherules (n=13) and a single forsterite-fine-grained (Fg) MM. The target minerals investigated are primarily olivine (Fo=35–99%) and spinel. Textural, chemical and isotopic data confirm that both olivine and spinel grains have retained their pre-atmospheric O-isotope compositions, allowing inferences to be drawn about their development and parent body affinities. We separate the study population into three groups: spinel-free particles (consisting of CgMMs and PO cosmic spherules), spinel-bearing MMs and the single FgMM.

Olivine grains in spinel-free MMs vary between δ17O: -12.6‰ and +1.3‰, and δ18O: -9.6‰ and +7.9‰, and δ17O: -9.5‰ and +1.3‰ and define a slope-1 profile in δ16O–δ18O isotope space. They are most likely fragmented chondrules, with both type I and type II varieties represented. Their observed Mg#–δ17O distribution is best explained by a mixture of CM chondrules and either CR chondrules, Tagish Lake chondrules or WILD2 cometary silicates. One of these chondrules-like MMs has a substantially heterogeneous composition, characterised by a single olivine grain with a markedly δ16O-rich composition (Δ17O: -16.3‰), suggesting it is a relict silicate fragment of AOA material that was incorporated into the chondrule precursor.

We analysed 11 spinel grains in five spinel-bearing MMs. In all instances spinels are nearly pure MgAl2O4 with isotopically light (δ16O-rich) compositions (ranging from δ17O: -34.3‰ to -19.9‰, δ18O: -30.8‰ to +11.0‰, and Δ17O: -14.3‰ to -4.4‰). They are therefore δ16O-poor relative to spinel found in unzoned CAIs, indicating a different origin. Grains with high Cr2O3 contents (>0.5 wt%) are interpreted originating from Al-rich chondrule precursors, while low Cr2O3 spinels (<0.5 wt%) are interpreted as CAI-derived material affected by parent body aqueous alteration.
Finally, we report a single FgMM with a $^{16}$O-rich composition ($\delta^{17}$O > 0‰ and $\delta^{34}$O > +15 0‰). This particle adds to our growing inventory of water-rich C-type asteroid samples unified by their formation history which is characterised by accretion of abundant heavy water.

Our work strongly supports findings from earlier in-situ O-isotope studies, concluding that small MMIs overwhelmingly sample material from C-type parent bodies and that MgMMIs largely sample chondrules and, to a lesser extent, CAI material. The analysis of MgMMIs therefore provides insights into the primitive O-isotope reservoirs that were present in the early solar system and how they interacted.
1 Introduction

Micrometeorites (MMs) are among the smallest size fractions of extraterrestrial material (~50–2000 μm, Taylor et al., 1993; Geiss et al., 2008; Fedor and Corder, 2015). They are released from their parent bodies as dust and spiral inwards towards the Sun over geologically rapid timescales (<100 ka, Wyatt and Whipple, 1950; Gometsi et al., 1982). A small fraction of the inner solar system’s dust complex intersects Earth’s orbit and is captured by its gravity (Navroty et al., 2006). Infalling cosmic dust grains are subject to flash heating during atmospheric entry which results in the complete vaporization of most particles (Love and Brownlee, 1991). Those that do survive entry can be recovered from the Earth’s surface as MMs. They sample both asteroids and comets (Van Cittert et al., 2012; Cordier and Fedor, 2014; Neguchi et al., 2015) although the relative contribution from each source remains hotly debated (Brownlee, 2001; Plane, 2012).

Because unannealed micrometeorites (UMMs) retain mineral phases that formed prior to atmospheric entry, their study provides direct insights into the astrophysical conditions operating during the early solar system (Klock et al., 1989; Beckerling and Bischoff, 1995; Greshake et al., 1996) and the geological history of their parent bodies (Genge et al., 1997; Engel and Maurette, 1998; Suttle et al., 2019). Despite the advantages of studying UMMs, there are far fewer detailed investigations on unannealed particles than on cosmic spherules. This is primarily due to the limited number of MM collection sites that preserve highly viable UMMs as well as the difficulty in identifying UMMs within terrestrial sediment and the challenges associated with analysing small, scientifically valuable materials. Indeed, most MMs fall within the size range 50–300 μm making their collection practically challenging (Maurette et al., 1991; Brownlee et al., 1997; Taylor et al., 1995, 2000; Yada et al., 2004; Prasad et al., 2013, 2018).

Of the extraterrestrial dust collected from various environments (e.g., Antarctica, deep-sea sediments, and in the case of the smaller interplanetary dust particles [IDPs] the stratosphere) it is estimated that roughly half survive without significant melting (Love and Brownlee, 1991; Maurette et al., 1991; Taylor et al., 1998; Yada et al., 2004; Radawski et al., 2016a; Prasad et al., 2018; Rojas et al., 2021; Radawski et al., 2020a). The degree of atmospheric entry heating is a function of multiple variables. Numerical modeling demonstrates that particles with low entry velocities (<16 km s⁻¹) and low entry angles (<10°) are heated for longer times but at lower peak temperatures. These grains are therefore more likely to be unannealed (Love and Brownlee, 1991; Carillo-Sanchez et al., 2015). Additionally smaller MMs (<300 μm) preferentially survive as compared to larger ones. This is reflected in the dramatic change in the ratio of unannealed-to-melted particles at different size fractions, as demonstrated empirically by Taylor et al. (2007) from the South Pole Water Well (SPWW) collection and from comparison between different MM collections (e.g., Table 1 in Suttle and Fedor, 2020). Furthermore, the chemical composition and mineralogy of dust can also strongly affect survival rates, notably where the thermal decomposition of phyllosilicate in hydrated dust grains acts as an efficient heat sink, resulting in high thermal gradients (>200 K m⁻³) and the retention of low core temperatures (Genge, 2006; Genge et al., 2017). By contrast, aridous particles, large dust grains (>300 μm) and particles that enter the Earth’s resonance orbit with high entry velocity (>16 km s⁻¹) and high entry angles (>10°) will experience significant heating and corresponding chemical and isotopic alteration (Love and Brownlee, 1991; Radawski et al., 2016a).

Atmospheric entry heating not only affects the chemical composition but also the bulk O-isotope composition of MMs (e.g., Yada et al., 2005; Suavet et al., 2010; Cordier and Fedor, 2014; Van Cittert et al., 2017; Radawski et al., 2019, 2020b; Suttle et al., 2020; Goderis et al., 2020). This can potentially alter the O-isotopic composition of melted cosmic spherules. An alternative approach is therefore to use spatially resolved isotopic analysis to avoid MM mesostasis (defined as phases that formed during atmospheric entry via melting and recrystallization) and instead
analyse only relic\(^1\) mineral grains held either within unmelted particles (Greishake et al., 1996; Engrand et al., 1999; Gounelle et al., 2005; Matrajt et al., 2006) or cosmic spherules (Yedya et al., 2005; Svesta et al., 2011; Rudraswami et al., 2015, 2016a). Relic phases are expected to largely retain their pre-atmospheric O-isotope composition and allow the origin of MM to be established.

In the present work, we focus on unmelted coarse-grained micrometeorites (CgMMs) and relic-grain-bearing (RGG) porphyritic (PO) cosmic spherules. We have performed 35 in-situ oxygen isotope analyses (using an ion microprobe [Cameca IMS-1270 at the CEPG-Nancy, France]) on 37 particles. Our study population includes olivine-bearing CgMMs presenting either as single mineral grains or mineral clusters. We also analysed spinel-bearing cosmic spherules. As a result, the main target phases investigated are olivine, spinel and, for context surrounding MM mesostasis.

2 Oxygen isotopes in chondritic materials

Chondritic meteorites are isotopically heterogeneous (Clayton et al., 1977; Jones et al., 2004; Ushikubo et al., 2012; Marrocchi et al., 2018b). Their respective components display distinct and well-characterised O-isotope ranges. Chondrules and refractory inclusions (Ca-, Al-rich inclusions [CAIs] and a mesoband olivine inclusions [AOAs]) have compositions that plot either on or close to the carbonaceous chondritic anhydrous mineral (CCAM) line (Clayton and Mayeda, 1999) or the Primitive Chondritic Mineral (PCM) line (Ushikubo et al., 2012). These lines have slopes of approximately 1 in \(\delta^{18}O-\delta^{17}O\) isotope space (in detail: ~0.94 and ~1 for the CCAM and PCM lines, respectively). They reflect a fundamental mass-independent process that was operating in the solar nebula as the first solid phases condensed to form CAIs and were later followed by flash melting and cooling of solid precursors to form chondrules.

This process can be interpreted as mixing between \(^{16}\)O-rich and \(^{18}\)O-poor reservoirs or partial exchange of oxygen between a solar-like \(^{16}\)O-rich refractory silicate and a \(^{18}\)O-poor nebula gas (either SiO or SiO\(_2\) gas) during transient chondrule heating, melting and recycling events (e.g., Yu et al., 1995; Young and Russell, 1998; Bridges et al., 1999; Jones et al., 2004; Chausidon et al., 2005; Rudraswami et al., 2011; Ushikubo et al., 2012; Tennen et al., 2013, 2015, 2018; Marrocchi and Chausidon, 2015; Marrocchi et al., 2018a, b; Simon et al., 2019; Boéman et al., 2020; Krot et al., 2020). Individual chondrules often contain modest O-isotope variation (less than a few \(\%\)). However, relic grains with isotopically light values (potentially as low as \(\delta^{18}O-\delta^{17}O \approx -50\%\)) occur at low abundances. They are interpreted as earlier generations of chondrule silicates, some of which appear to have been derived from CAI material. Meanwhile, heavier isotope compositions, found in most chondrule silicates plot along the slope-1 (CCAM or PCM) lines and close to the Terrestrial Fractionation Line (TFL). Their compositions indicate later generation crystals formed by progressive melting and interaction with nebula gases (Krot et al., 2006; Chausidon et al., 2008; Chauviard et al., 2018).

By contrast, the fine-grained matrix in chondrites as well as any secondary minerals (formed by parent body processes) tend to have O-isotope compositions that plot off the slope-1 lines, shifted to heavier \(^{18}\)O-poor compositions. These phases instead define shallower lines with slopes >0.52 and <1 in \(\delta^{18}O-\delta^{17}O\) isotope space (Rowe et al., 1994; Clayton and Mayeda, 1999; Yurimoto et al., 2008; Ireland et al., 2020). They are generally interpreted as evidence of parent body alteration resulting in the equilibration of \(^{18}\)O-rich anhydrous silicates (within chondrules/CAIs/AOAs) with a \(^{18}\)O-poor, isotopically heavy water-ice component (e.g., Clayton and Mayeda, 1999; Chauviard et al., 2018).

\(^1\) Note, use of "relic grain" with respect to chondrule silicates is distinct from the use of "relic grain" often used in studies of CMMs. In MM papers "relic" is often used to draw a distinction between grains that survived unmelted ("relic") and mesostatic material that melted, homogenised and isochronalised during atmospheric entry. By contrast, when referring to chondrule histories, relic grains refer to grains that survived through episodes of chondrule melting and crystallization.
Spinel is a crucial refractory mineral in early solar system objects, often found as a component of CAIs and, to a lesser extent, in chondrules (Maryama et al., 1999; Maryama and Yumoto, 2003; Rudraswami et al., 2011). It melts at high temperature >2000 °C and is also relatively resistant to later parent body alteration (Greenwood et al., 1994). Primary spinel grains (MgAl₂O₄) are rarely found in MMs (Taylor et al., 2012). They are distinct from the abundant small iron-rich spinel grains that form in MMs during atmospheric entry (resulting in the formation of magnetic thin films on annealed and scoriaceous MMs; Toppo et al., 2001). Owing to their low abundance only a few primary spinels have been analyzed (Taylor et al., 2012). We also study relics of olivine grains, they are likewise resistant to O-isotopic exchange during atmospheric entry due to relatively slow diffusion kinetics and relatively large grain sizes (Yada et al., 2005). Detailed in situ O-isotope analyses of UMMs (and especially spinel-bearing particles) are limited in literature (Englal et al., 1999; Gounelle et al., 2005; Matrajt et al., 2006; Rudraswami et al., 2015, 2016a; Debreci et al., 2019), as such the current study aims to provide new data on their origin, formation and relationship to phases found in primitive chondrites.

3 Sample collection

The MMs were vacuumed from the bottom of the South Pole water well (SPWW), ~100 m beneath the new surface. The well with a diameter of ~24 m and depth of ~15 m has a potential to retrieve a large source of preserved extraterrestrial particles with low terrestrial contamination. The depositional age of the MMs studied (mounts SP005, SP006 and SP007) was between ~800 to 1100 A.D (Taylor et al., 2007). The MMs were mounted in epoxy and then polished to expose their approximate maximum interior surface area. The particles were examined using back-scattered electron (BSE) imaging to facilitate the classification and the identification of mineral phases following the methodology of Geiss et al. (2008). The oxygen isotope and chemical composition of target phases in selected MMs were subsequently analysed. Our study population includes 37 particles (Table 1), comprising a mix of un annealed/discohesive CgMMs (n=23) and RG Porphyritic (PO) cosmic spherules (n=13). In addition, we analysed a single scoriaceous fine-grained micrometeorite (FgMM) (SP007-P257).

4 Analytical techniques

4.1 Electron microscopy

The high-resolution back-scattered electron images (BSE) of carbon-coated polished MM interiors were obtained by scanning electron microscope (SEM, JEOL JSM 5800LV) equipped with an Oxford Instruments energy dispersive spectrometer (EDS, ISIS300s: National Institute of Oceanography, Goa) and using the INCA software. Backscattered electron images were used to classify particles and identify phases for oxygen isotope analysis. Supporting geochronological data on selected phases were acquired using a Cameca SX Five Electron Probe Micro Analyzer (EPMA at National Institute of Oceanography, Goa) fitted with four wavelength-dispersive x-ray spectrometers. The chemical analyses of particles under electron probe were performed at an accelerating voltage of 15 kV, a beam current of ~12 nA and a beam width of ~1–2 μm. Further analytical details for the EPMA work are given in Rudraswami et al. (2015). Based on the preliminary electron microscopy characterization, we selected 95 spots mostly on olivine and spinel phases for in-situ O-isotope analysis. Chemical data for all phases analysed by EPMA are given in supplementary material (Appendix A).

4.2 Ion microprobe analyses

Triple O-isotope analyses were acquired using a secondary ion mass spectrometer – the Cameca IMS-1270 instrument located at CRFG-Nancy, France. A detailed description of the analytical method was previously reported in Rudraswami et al. (2019). This study used a focused Cs⁺ ion beam with a primary current of ~1 nA and beam size of ~5 μm at the sample surface. Analyses achieved a mass resolving power of ~2500
for $^{18}$O and $^{16}$O ions, while an improved resolving power of ~7000 was required for the measurement of $^{18}$O ions to avoid measuring the interference of $^{16}$CH⁻ on the $^{18}$O ion peak. Secondary ion signals were measured using Frenkel caps for $^{16}$O and $^{18}$O ions, while an electron multiplier was used for $^{17}$O. The instrumental mass fractionation for olivine and spinel grains were corrected using terrestrial standards (San Carlos olivine and Buma spinel, respectively). There are no matrix effects in measured olivine grains arising due to variable chemical compositions of natural samples. However, the magnitude of these effects are small and, in most instances, the Mg content of target minerals were close to the composition of the analytical standard (Jia et al., 2017). We report O-isotope data in standard δ notation. Ratios of $^{18}$O/16O and $^{16}$O/18O are given as $\delta^{18}$O = [(18O/16O)sample / (18O/16O)NIST] - 1] × 1000‰. $\Delta^{17}$O, which represents the deviation from the terrestrial fractionation, has been calculated as $\Delta^{17}$O = $\delta^{17}$O − 0.52 × $\delta^{18}$O. The error reported was determined by the reproducibility of multiple standard analyses for $\delta^{13}$C propagated to errors in individual measurements. All errors in this study are quoted to the 2σ level (Table 2) and range between 0.3‰ and 0.9‰ for $\delta^{13}$C, between 0.5‰ and 1.5‰ for $\delta^{18}$O and between 0.4‰ and 1.2‰ for $\Delta^{17}$O. Mica-zonites were mounted close to the centre of their polished block to avoid large instrumental mass fractionation effects arising between samples and standards (Kim et al., 2000). For each sample one or more spots were carefully selected for ion microprobe analysis depending on the size of mineral surface (supplementary material—Appendix B).

5 Results

5.1 Petrographic details of MMNs

Most of the CgMMNs (examples shown in Fig. 1) have spherical shapes and, in section view, have a centrally located rounded grain cluster composed predominantly of forsterite grains (FeO95.5–99.5, median = FeO11.1) with or without minor pyroxene, Fe-Ni metal (as kamacite), Fe-sulphides and, in rare instances silicate glass of pre- or atmospheric origin (e.g., SP05 P1015 [Fig. 1b]). These unaltered cores are mantled by a well-developed layer of mesostasis, termed an igneous rim (Geeg, 2006). In addition, most of the CgMMNs have an outer discontinuous shell of magnetite rim on the particle exterior (Toopski et al., 2001). Both igneous rims and magnetite rims are extensively documented in the literature and form during atmospheric entry by partial melting. As such igneous and magnetic rims are routinely used as diagnostic evidence in the classification of unaltered/orbicular MMNs, as distinct from cosmic spherules (Geeg, 2005; Geeg et al., 2012; van Grunderbeen et al., 2012). They are also useful guidelines which visually mark the boundary between the particle’s melted exterior and its unaltered (but thermally altered) interior (Geeg, 2006). By definition cosmic spherules have experienced more thermal processing than the unaltered CgMMNs (Geeg et al., 2005). They lack igneous/magnetic rims and are instead dominated by mesostasis (which may take the form of quench-cooled Ca-rich glass, euhedral Fe-rich olivine phenocrysts, magnetic dendrites and/or a nanocrystalline groundmass of Fe-rich olivine). However, relict grains can be confidently identified by their anhedral shapes, darker Z-values in BSE images (indicating more Mg-rich compositions), minor element compositions enriched in Cr, Mn and Ca and by the presence of normal zonation (Fe-rich rims on Mg-rich cores) indicating growth of new Fe-rich olivine onto the margins of relict grains during atmospheric entry (Swade, 1992; Beckerling and Bischoff, 1995; Geeg et al., 2005).

Nine of the CgMMNs contain a single mineral grain (examples shown in Fig. 2). This is distinct from the "typical" CgMM texture that have multiple minerals. As a result, the single mineral MMNs are treated somewhat separately in this manuscript and assigned their own subgroup: CgMM-2M. In all instances the mineral phase is forsterite. As with the typical CgMMs, the single mineral varieties also contain igneous and magnetic rims along their exterior. In addition, some grains have a high density of submicron-sized Fe-oxide grains along their grain margins. These are magnetic crystals that formed during atmospheric entry by flash heating under an oxidizing regime, they can form either by sub solidus oxidation of olivine, leading to the exsolution of magnetite (Cordier et al., 2018) or by melting and recrystallization in an oxidizing environment (Blanchard and Cunningham, 1974). Finally, some of the CgMM-2M have thin melt veins that have penetrated into towards their cores — further evidence of thermal processing during atmospheric entry.
We also analysed eleven spinel inclusions from seven spinel bearing MMs (two CgMMs and five PO cosmic spherules [examples shown in Fig. 3]). Spinel grains range in size from 10 to 40 µm and often appear as skeletal crystals either held inside a host olivine crystal (as in SP005-P522 [Fig. 3a]) or embedded directly within mesostasis (as in SP005-P583 [Fig.3b]). In all instances spinels are Mg-Al varieties with stoichiometries approximated by MgAl₂O₄ and containing minor FeO (0.3–15 wt.% as well as trace of Cr₂O₃ (0.2–2.0 wt.%) and TiO₂ (0.1 wt.%, except in SP007-P164).

One of the particles we analysed (SP007-P257) is a MgMM with a partially melted, scoriation texture. The core preserves relict fine-grained matrix with a relatively Mg-rich composition (Mg₂<sub>1.4</sub>Si₃<sub>0.5</sub>Al₂<sub>0.5</sub>O₇<sub>1.0</sub>) and contains both Fe-sulphides and small Mn-rich anhydrous silicates. It therefore exhibits a C1 texture in the classification scheme of Van Schmus and Wood (1957), indicating its parent body was hydrated carbonaceous chondrite (CC). The relict matrix is enclosed by a well-developed vesicular igneous rim and a thin but continuous magnetite rim.

5.2 O-isotope data

We performed 71 O-isotope analyses (Fig. 4) on anhydrous silicate grains, of which 68 were on forsterite grains and three were on low-Ca pyroxenes (Table 2). Except for a single grain (within particle SP005-P351 [Fig. 1a]) with a distinctly δ¹⁸O-rich composition (δ¹⁸O = -28.2‰, δ¹⁷O = -22.8‰ and Δ¹⁷O = -16.3‰), all the anhydrous silicates fall within a narrow range in δ¹⁸O–δ¹⁷O isotope space. Their δ¹⁸O values vary between -12.0‰ and +3.5‰, δ¹⁷O values vary between -9.0‰ and +7.5‰ and Δ¹⁷O values vary between -9.5‰ and +9.6‰ (Fig. 4). As such this population can be collectively considered as consistent with the trends defined by the primordial CCAM and PCM reference lines, although several individual data points are slightly mass fractionated off this trendline towards heavier values (Fig. 4).

Nine analyses plot slightly below the CCAM line, shifted to marginally more δ¹⁸O-poor values and many of the forsterite analyses plot close to the intersection of the slope-1 lines with the TFL. After considering the maximum 2σ variation in measurement uncertainties, 10 analyses have Δ¹⁷O values >3‰ (i.e. above the TFL), while 52 analyses have Δ¹⁷O values <3‰ (i.e. below the TFL). The remaining nine analyses are within error of the TFL and thus have compositions statistically indistinguishable from a Δ¹⁷O=0‰ value.

By comparison, the O-isotope compositions of 11 spinel grains occupy a larger spread in δ¹⁷O–δ¹⁸O isotope space. Their δ¹⁷O values vary between -34.6‰ and -9.9‰, δ¹⁸O values vary between -30.8‰ and +11.0‰ and Δ¹⁷O values vary between -18.3‰ and +4.4‰ (Figs. 4 & 5). All spinel grains thus have compositions that fall below the TFL and, in many instances their compositions are significantly more δ¹⁸O-rich than the olivine grains studied here (Fig. 5). This relationship is best demonstrated in MMs where both spinel and forsterite are present (Fig. 5). In almost every instance spinel grains have isotopically lighter δ¹⁸O-enriched compositions than their corresponding olivine grains. Interestingly, however, we also note that, while most spinel grains show minimal isotopic variation, analyses on three spinel grains in the PO cosmic spherule SP005-P440 (Fig. 5c) cover a wide O-isotope range, with one of the spinel analyses (Δ¹⁷O = -6.6‰) having a more δ¹⁸O-poor composition than the MM’s mesostasis (Δ¹⁷O = -109‰).

We collected ten analyses on mesostasis regions within MMs. Seven were from cosmic spherules that had δ¹⁷O values vary between -11.7‰ and +15.1‰, δ¹⁸O values vary between -3.6‰ and +30.9‰ and Δ¹⁷O values between -10.9‰ and +1.2‰ (Fig. 4). Only two analyses plot along the slope-1 reference lines, while five have values closely associated with these slope-1 lines but are located slightly below the CCAM – shifted
to heavier $^{18}$O-poor compositions. The remaining three mesostasis analyses have distinct compositions with $\delta^{18}$O values $>$15‰ and $\Delta^{17}$O values close 0‰.

We also obtained four analyses on single FgMM (SP007-P257, Fig. 6), collecting these analysis regions at the particle’s relict fine-grained matrix and a single analysis within the particle’s igneous rim (mesostasis analysis). This MM has an unusually $^{18}$O-poor composition with mean average values of $\delta^{18}$O: +11.9‰, $\delta^{17}$O: +21.8‰ and $\Delta^{17}$O: +0.6‰.

5.3 Correlation between chemical and oxygen isotopic compositions of minerals

In a Mg$\#$-$\Delta^{17}$O plot (Fig. 7A) olivine grains span the range defined by type I and type II chondrules. However, no overall trend is apparent based on MM classification (CpMM vs. CpMM-SM vs. PC cosmic spherules). By contrast, if spinel-bearing and spinel-free MMs are compared (Fig. 7B) it can be seen that in spinel-bearing MMs forsterite grains always have a highly restricted compositional range in both chemistry and O-isotopes. Anhydrous silicate grains in spinel-free MMs ($n=66$) vary in Mg$\#$ between 59.5–99.5 with all but one analysis plotting within the $\Delta^{17}$O range: −7‰ to +21‰. By contrast, in spinel-bearing MMs anhydrous silicates ($n=5$) were exclusively forsterites with distinctly Mg-rich compositions (Fo$>98.5$) and a $\Delta^{17}$O range of: −10‰ to −4‰ (Fig. 7B). Another notable feature is the observation that all anhydrous silicates with $\Delta^{17}$O values $>$0‰ have Mg$\#$$<85$.

We compared the Ca abundance (Ca$_{100}$ wt %) against O-isotope composition ($\Delta^{17}$O values) for the 11 spinel grains analysed (Fig. 8). They separate into two distinct groups: a low $\Delta^{17}$O (< −8‰)/low Ca$_{100}$ (< 0.5 wt %) group and a high $\Delta^{17}$O (> −3‰)/high Ca$_{100}$ (> 10 wt %) group.

6 Discussion

6.1 Effects of atmospheric entry heating

Previous studies have investigated the bulk O-isotope composition of MMs. As a result, the modification of a particle’s pre-atmospheric O-isotope composition is well-studied both for melted cosmic spherules (Yada et al., 2005; Stauvet et al., 2010; Cordier and Folco, 2014; Yan Giahe et al., 2017; Godin et al., 2020; Radasumawithi et al., 2020b) and unmelted/sesrioclastic particles (Kiechle et al., 2020). Two effects operate: (i) mass-dependent fractionation, arising due to the preferential evaporation of light oxygen ($^{16}$O) shifts a particle’s bulk composition to isotopically heavier values and (ii) O-isotope exchange with terrestrial oxygen present within the stratosphere (whose value is conventionally given as: $\delta^{18}$O: +11.8‰, $\delta^{17}$O: +23.5‰, $\Delta^{17}$O: −0.42‰ [Thermes et al., 1995]) results in the progressive equilibration of the particle’s bulk composition with that of the stratospheric composition. Stauvet et al. (2010) suggested that mass-dependent fractionation and isotopic exchange with terrestrial oxygen contribute approximately equally. However, more recent work, analysing a larger population of cosmic spherules ($n=137$) observed a statistically robust correlation between a MM’s $\delta^{18}$O composition and its peak temperature (as inferred from cosmic spherule quench textures) (Radasumawithi et al., 2020b). This strongly suggests that mass-dependent fractionation dominates over mixing with stratospheric oxygen, even once particles achieve a molten state.

Thus, even in the most extreme scenario where a MM experiences high peak temperatures, long duration heating and significant alteration of its original $\delta^{18}$O values the particle will still retain the approximate $\Delta^{17}$O value of its precursor. This is because mass-dependent fractionation shifts the particle’s composition to heavier values along a 0.52 slope line, leaving its $\Delta^{17}$O value unaffected (Yada et al., 2005; Stauvet et al., 2010,
2011; Rudraswami et al., 2015, 2016, 2020b). Furthermore, significant alteration of a sample’s Δ17O value (by mixing with stratospheric oxygen) is unlikely as this requires a change of ~10‰ in δ18O to achieve a corresponding change of ~1‰ in Δ17O (Rudraswami et al., 2015).

Finally, modifications to O-isotope signatures in relic grains will be even less extreme than those observed for bulk analyses because experimentally determined O-isotope diffusion rates in olivine grains are extremely low, even at high temperatures (~50% equilibration achieved between olivine and vacuum when temperatures are held at the boiling point for 72 h; Davis et al., 1983). This knowledge combined with the observation that MMs are typically heated for <10s provides little opportunity for isotopic exchange between a relic mineral grain and silicate melt or indeed with atmospheric air.

The O-isotope signatures measured from relic forsterite and spinel in the present study can therefore be confidently assigned to pre-atmospheric processes, while O-isotope values obtained from MM mesosoles will have been altered in δ18O, being shifted to higher δ18O values but will retain the approximate Δ17O composition of their parent body.

6.2 The parent body affinities of MMs

We split the studied MMs into four populations and discuss their petrographic and O-isotope data and inferred parent bodies separately: (i) spinel-free CgMMs and RGB PO cosmic spherules (section 6.2.1), (ii) relic silicates in chondrules derived MMs (section 6.2.2), (iii) spinel-bearing MMs (section 6.2.3) and (iv) the FgMM (section 6.2.4).

6.2.1 Spinel-free CgMMs & RGB PO cosmic spherules – samples of chondrules

We investigated 21 spinel-free CgMMs (including nine particles dominated by a single mineral [CgMM-SM]). The petrographic properties of these particles are consistent with refractory minerals found in chondritic meteorites. Among the CgMMs with a grain aggregate texture both their mineralogy and chemical compositions are indistinguishable from chondrules (or fragments thereof), being composed primarily of Mg-rich (Mg#>70) anhydrous silicates and containing minor Fe-Ni metal, Fe-sulphides and/or silicate glass. Meanwhile the CgMM-SMs varieties may represent a single mineral grain derived from a chondrule, or a matrix-hosted isolated ahydrous silicates (which have close relationships with chondrules; e.g., Jocher et al., 2021). The O-isotope compositions of all our forsterite and pyroxene plot on, or close to, the slope-1 reference lines and within the O-isotope range most commonly associated with chondrules (Fig. 4). As such both their chemical and isotopic properties support a link to matrix-hosted anhydrous silicates and chondrule-derived silicates. We also investigated eight spinel-free RGB PO cosmic spherules. However, both chemically and isotopically the forsterite grains in the cosmic spherules are compositionally indistinguishable from their corresponding phases found in the unmelched CgMMs studied here (Fig. 7A). This indicates that relic forsterite grains in both MM types (UMMs and cosmic spherules) can be treated together as a single population.

The relationship between mineral chemistry and O-isotope composition in chondrules can be evaluated using an Mg#-Δ17O plot (Fig. 7). These plots provide insights into the conditions that existed in different chondrule-forming regions within the protoplanetary disk. Chondrules from the inner solar system (e.g. Scott et al., 2010) non-carbonaceous chondrite (NC) meteorites (the Ordinary, Eucrite, KENSION and RUMANUTI groups) show a relationship between Mg# and Δ17O composition (Kita et al., 2010, Weisberg et al., 2011, Nagashima et al., 2015; Miller et al., 2017). By contrast, chondrules from outer-solar system CCs demonstrate a correlation between Mg# and Δ17O. Reduced high-Mg type I chondrules (Mg#>90) generally have ~17O-rich compositions (with Δ17O between ~10‰ and 0‰, and averaging ~5‰), while oxidized low-Mg type II
chondrules (Mg#<90) generally have $^{18}$O-poor compositions (Δ$^{17}$O ~ -2‰) (Ushikubo et al., 2012, Tennert et al., 2013, 2015, 2018, Chaumard et al., 2018; Herweg et al., 2018; Ushikubo and Kimura, 2021). The formation of isotopically heavy type II chondrules are interpreted as evidence of extreme dust enrichment (Tennert et al., 2013; Herweg et al., 2018) or interaction between the chondrule-forming reservoir and either a $^{18}$O-poor gas phase (Schnieder et al., 2013) or the addition of $^{18}$O-poor water-ice onto chondrules prior to remelting (e.g. Schnieder et al., 2013; Herweg et al., 2013; Chaumard et al., 2018). Furthermore, multiple high-precision studies have collectively demonstrated that different subgroups of CR show subtle variations in their Mg#-Δ$^{17}$O distribution (see Fig. 4 in Ushikubo and Kimura (2021) as an example). Most notably, type II chondrules with Δ$^{17}$O>0‰ (and up to Δ$^{17}$O: -2‰) are found in the CR chondrites (Schnieder et al., 2013; Tennert et al., 2015) in Tagish Lake (TL) (Ushikubo and Kimura, 2021), the TL-like meteorites W51600 and MET 00432 (Yamanobe et al., 2018) and in the WIL22 silicates (Nakashima et al., 2012; Joswiak et al., 2014; Dousoufley et al., 2017). These $^{18}$O-poor (Δ$^{17}$O>0‰) chondrules are associated only with outer solar system D-type asteroids and cometary materials and therefore appear to have been produced at large heliocentric distances.

Micrometeorites sample a range of dust-produced small bodies. However, by comparing the Mg#-Δ$^{17}$O distribution of our spinel-free MMs (Fig. 7), which represent chondrule fragments against equivalent data from various chondrule groups (Fig. 4 in Ushikubo and Kimura, 2021) we can evaluate which parent bodies these MMs are sampling. Our MM population shows minimal overlap with the ranges measured for OC chondrules, which generally have Mg#>70 and Δ$^{17}$O > -6.5‰. Instead, over the type I chondrule range (Mg#<90) our MM population most closely matches the spread defined by CO, CM and Asker Ötive chondrules (Δ$^{17}$O < -2‰) and with a slight positive correlation (Ushikubo et al., 2012; Tennert et al., 2013; Chaumard et al., 2018). Meanwhile, over the type II chondrule range (Mg#<90) our MM population includes a large variation in Δ$^{17}$O (-5‰ to +2‰) which is generally inconsistent with a CO-CM range and is instead similar to the CR chondrites, TL and the TL-like meteorites and cometary silicates. Thus, although we cannot assign any individual MM to a specific chondrule group this technique allows an estimation of the provenance of the population as a whole. Nevertheless, OC precursors are relatively abundant amongst the coarse size fractions of MMs with sizes >300 µm, many studies support the concept that the smaller size MMs are overwhelmingly dominated by CC precursor, our work also support this observation. We conclude that these spinel-free MMs are chondrule fragments from CC chondrules. They most likely sample a mix of CM and either CR, TL-like or cometary materials.

6.2.2 Relict silicates in chondrule-derived MMs

Rare $^{18}$O-rich olivine grains are found within otherwise isotopically homogenous (Δ$^{17}$O < 2‰) papyrritic chondrules in both CC and OC meteorites (Jones et al., 2004; Krot et al., 2006; Kita et al., 2010, Ushikubo et al., 2012; Marrocche et al., 2018b, 2019; Schnieder et al., 2020). They are interpreted as relict minerals which survived (potentially multiple) transient melting and recrystallization events during chondrule formation (Jones, 1996). Depending on the magnitude of their $^{18}$O-enrichment they could be derived from either an earlier generation of chondrule (e.g., Type I grains held within a Type II chondrule; Ruzicka et al., 2008) or from a more refractory CAI/ACA source (Jones et al., 2004; Marrocche et al., 2019).

In this study we identified a single MM - SP005-P351 (Fig. 1a) hosting a forsterite grain with a distinctly $^{18}$O-rich composition (Δ$^{17}$O: -28.2‰, δ$^{18}$O: -22.6‰ and Δ$^{18}$O: -16.3‰; Fig. 4, Fig. 9). This composition is within the range reported for CAIs and AOAs (Tennert et al. 2018). The other forsterite grain analysed in this particle had an O isotopic composition (Δ$^{17}$O: +0.2‰, δ$^{18}$O: +4.3‰, and Δ$^{18}$O: -2.0‰), consistent with chondrule olivine found in CCs. Particle SP005-P351 is therefore best interpreted as a type I chondrule fragment from a CC precursor which contains a single relict olivine grain originating from a refractory inclusion. The relict silicate was most likely derived from an AOA (rather than a CAI) because olivine is common in these inclusions (and rare in CAIs).
Isotopically light relict chondrule silicates often have Mg-rich compositions (Mg#>90 [Fe=10]) (Hervig and Steele, 1992; Leshin et al., 1997; Hiyagon, 1999; Ushikubo et al., 2012; Tenner et al., 2013, 2015). However, olivine grains with high Fe contents and low δ17O values (δ17O enrichment) have also been identified (Jones et al., 2004; Ushikubo et al., 2012). These Fe-rich relict olivines may have originally started out as Mg-rich varieties but experienced advanced Mg-Fe equilibration with their host chondrule melt, while also retaining their initial δ17O-rich signature. This is possible because solid-state diffusion rates for Mg-Fe ratios are orders of magnitude faster than the diffusion rates of O-isotopes (Dohmen et al., 2007; Chakraborty et al., 2010). As a result, although the identification of the relict δ17O-rich grain in SP03-P351 was relatively straightforward (both due to its high-Mg chemistry and extremely light δ17O values), this is not always the case. Some of the other olivine grains with less extreme compositional variation may also be relict silicates from earlier generations of chondrules. Since the O-isotope compositions of relict grains often fall within the same range as the chondrules (namely between ~6‰ and ~2‰; e.g., Rudraswami et al., 2011; Tenner et al., 2013) and chemical composition cannot be used as a reliable indication. The only way to confidently identify additional relict grains is to collect multiple silicate analyses on different grains within a single chondrule (or in this case chondrule-like MM) and determine if the O-isotope range is either homogeneous (Δ17O < 2‰) or heterogeneous (Δ17O > 2‰), with heterogeneous compositions implying the existence of relict grains. Using this criterion (Fig. 9) we demonstrate that no other MM appears to contain relict grains, since all olivine particles have O-isotope variability Δ17O ≤ 2‰ (Fig. 9).

6.2.3 Spinel-bearing MMs—samples of CaS and Al-rich chondrules

There are three types of spinel found in chondritic materials: (i) primary spinels formed in the nebula, prior to the accretion of chondrules; (ii) secondary spinels formed on the parent asteroid by precipitation from fluids and (iii) spinels formed during atmospheric entry by oxidation and crystallization of a chondrule melt. Primary spinel grains have predominantly Mg-Al compositions (MacPherson et al., 1988; Zhang et al., 2020a), while secondary spinels have Ca- and Fe-rich compositions (Touma et al. and Buseck, 1985; Grossman and Brearley, 2005; Zolotov, 2012) and spinels formed during atmospheric entry appear as Ni-bearing magnetite and are located exclusively in the mesostasis of unmelted MMs or as magnetic grains in the fusion crusts in larger meteorites (Genge and Grady 1999; Toppani et al., 2001). All the spinels analyzed in this study have Mg-Al chemistries and primitive, δ17O-rich compositions. They are therefore interpreted as primary spinels.

Primary Mg-Al spinel grains are highly refractory minerals. They formed either as condensates of nebular gas composition at temperatures below 1500°C (Lodders, 2003) or during crystallization of Al-rich chondrule melts (Kot et al., 2002; MacPherson and Huss, 2005; Touma et al., 2007; Kot et al., 2009). Spinel in CAIs were likely some of the earliest minerals to form in the solar nebula (Lodders, 2003; Kot et al., 2009). Conversely, their presence in chondrules is interpreted as evidence of CAI material being transported into chondrule-forming regions and becoming consumed as chondrules experienced multiple episodes of melting, crystallization and interaction with the surrounding nebula gas and dust (Marty et al., 1999; Kot and Kel, 2002; MacPherson and Huss, 2005).

The O-isotope compositions of Mg-Al spinels in chondrules plot on, or close to, the slope-1 reference lines and fall within the isotopic range (δ17O: −25‰ to 2‰) [Fig. 7 in Kot et al., 2009; Zhang et al., 2020a]. Isotopically light values (δ17O < −2‰) are consistent with pristine unaltered CAIs, while those affected by asteroidal alteration have compositions in the range: −20‰ < δ17O < +2‰ (Deich et al., 2004; Kot et al., 2009; 2019; Zhang et al., 2020a). Additionally, isotopically light compositions (δ17O < −2‰) were produced where CAI-derived spinels were incorporated into (Al-rich) chondrules (Kot et al., 2009; Zhang et al., 2020a). These grains would have been subjected to high-temperature partial melting during chondrule-heating events, leading to incomplete O-isotope exchange between the
spinel grain and their host chondrule melt and/or with the surrounding nebula gas. Such reactions produced heavier $^{16}$O-poor compositions (relative to pristine CAIs), with $\Delta^{17}$O values between $-20\%$ and $-5\%$ being characteristic (Maryama et al., 1999; Russel et al., 2000; Krot et al., 2009, 2019; Zhang et al., 2020b).

Meteorites containing Mg-Al spinel grains are very rare (<1%: Gebe et al., 2018; Taylor et al., 2012). We analysed seven spinel-bearing MMs (two were previously analysed by Taylor et al., 2012; SP005-P339 and SP007-P104), using 11 independent analyses on separate spinel grains (Fig. 8, 10 & 11). For a single particle (SP006-P102) the target spinel grain was too small to analyse, so only the surrounding MM mesostasis was investigated isotopically. Our measured spinels plot on, or close to, the slope-1 reference lines (except for which are slightly deviated from this trend [Figs. 4 & 10]) and vary from $\Delta^{17}$O: $-16.3\%$ to $-4.4\%$. Several Mg-Al spinel-bearing MMs with associated O-isotope data (Figs. 10 & 11) have been published previously (Kurt et al., 1994a) and Hoppe et al. (1995) reported data for three spinel-bearing MMs (with particle IDs: MM92/15-23, MM94-1 #23, and MM94-4 #36), they were Mg-Al spinels with O-isotope compositions in the range: $-19.2\%$ to $\Delta^{17}$O: $-10.5\%$. Later, Engrand et al. (1999) reported two spinel-bearing Mg-Al spinels (92-12C-23 and 94-4b-5), whose spinels had $\Delta^{17}$O compositions of $-20.7\%$ and $-15.8\%$, respectively. The particle with the most negative $\Delta^{17}$O content (92-12C-23) also contained a small amount of melilite (a mineral found exclusively in pristine and minimally altered CAIs). Most recently Taylor et al. (2012) reported Sgr spinel in two spinel-bearing cosmic dust spheres with spinel compositions of $\Delta^{17}$O: $-19.8\%$ and $\Delta^{17}$O: $-14.8\%$, respectively. However, one of the MM SP005-P440 has oxygen isotope data deviated to right side of slope-1 line, while the other spinel particles are closer to CCAM line (Fig. 5e) indicating that spinel in this particle had undergone thermal processing such as evaporation, melting and re-crystallization analogous to fractionation and unidentified nebular isotope anomalies (FUN) CAIs that follow trends parallel to the TFL (Thiim et al., 2008). This suggests the precursor of this CAI experienced isotopic exchange with nebular gas, thereby altering its original isotopic compositions (Thiim et al., 2008; Makaide et al., 2009).

All Mg-Al spinel grains reported from MMs to date (both in the literature and in this study) have $^{18}$O-depleted ($\Delta^{17}$O $> -20\%$) compositions (Fig. 5A), outside the range reported for pristine CAIs. In Fig. 5A we demonstrated that two populations of spinels exist a low Cr$_2$O$_3$ group and a high Cr$_2$O$_3$ group. The low-Cr population are likely CAI-derived spinel that have been affected by parent body aqueous alteration. This interpretation is based on two factors: (i) low-Cr contents (Cr$_2$O$_3$ ≤ 0.5 wt.%) are typical of CAI-derived spinel (as opposed to the spinels found in Al-rich chondrules, which are otherwise Cr-enriched [Maryama and Yurimoto, 2003; Radhakrishnan et al., 2011]). Furthermore (ii) most previously reported low-Cr spinels are found in hydrated Mg-Al spinel crystals. Surrounding particle textures therefore offer context. Among the literature several spinels in hydrated Mg-Al spinel crystals are reported. These Mg-Al phyllosilicates (or their thermal decomposition products) are observed mantling the Mg-Al spinel phase. They therefore experienced an episode of protracted parent body aqueous alteration which could have affected spinel grain’s isotopic composition, similar to those reported by Zhang et al. (2020b) from CO chondrites.

By contrast, spinel grains with high-Cr contents most likely originate from an Al-rich chondrule precursors. In both SP005-P322 and SP005-P392 their spinel grains are enclosed by magnesium olivine crystals and have $\Delta^{17}$O values that fall within the typical range of type I chondrules in CCs. Furthermore, elevated Cr abundances (Cr$_2$O$_3$ ≥ 0.5 wt.%) in spinels are characteristic of Al-rich chondrules (Maryama and Yurimoto, 2003; Radhakrishnan et al., 2011). Finally, we note that the origin of spinels in SP005-P440 are less clear. This particle contains three spinel with high Cr content (Cr$_2$O$_3$: 0.3, 0.3 and 2.0 wt.%, Fig. 8) and O-isotope compositions vary fractionated from the slope-1 reference lines (Fig. 5e).
6.2.4 The FgMM SP007-P257

Particle SP007-P257 is dominated by a dark Mg-rich matrix and contains small Fe-sulphides and a residual anhydrous silicate grains. Inside the igneous rim Fe-sulphides occur as rounded beads that abut vesicles. These textures attest to sulphide decomposition at temperatures between 800–1100°C (Greshake et al., 1993; Taylor et al., 2011). The particle’s matrix also shows evidence of phyllosilicate dehydration cracks although a vesicular texture dominates. During atmospheric entry phyllosilicates dehydrate at relatively low temperatures (~350–500°C) and subsequently recrystallize to form a groundmass of anorthoclase plagioclase (Suttle et al., 2017). At heating enhances the formation of vesicular matrix is associated with peak temperatures >1200°C (Toppini et al., 2001; Taylor et al., 2011). Thus, although the relict matrix inside this MM did not melt, it experienced significant thermal reprocessing. This MM’s mineralogy and texture are typical of sorogenic FgMMs.

Previous research has demonstrated a clear link between FgMMs and hydrated CC materials (Kurat et al., 1994b; Engrand and Maurette, 1994; Genge et al., 1997; Taylor et al., 2012; Bodyakov et al., 2018; Suttle et al., 2019, 2020b). It is therefore reasonable to assume that SP007-P257 derives from a hydrated CC precursor and as such we have compared its O-isotope composition against a wide range of hydrated CC precursors (Fig. 6A).

Three spot analyses were collected within the relict fine-grained matrix of particle SP007-P257 (Fig. 6B), they have δ18O-poor compositions characterized by δ18O: +8.8‰ to +14.2‰, δ17O: +17.5‰ to +23.8‰, and Δ17O: -0.5‰ to +1.9‰. The single massecrystallite analysis, collected within the sample’s igneous rim, revealed a composition of δ18O: +10.0‰, δ17O: +16.9‰, and Δ17O: +1.2‰. Atmospheric entry heating would have mass-fractionated the composition of SP007-P257 to higher δ18O values, although interestingly the massecrystallite analysis exhibits the lowest δ18O composition, implying that mass-dependent fractionation has not significantly affected this MM’s composition and also that the sample’s pre-atmospheric O-isotope composition was characterised by high δ18O values (+15‰).

The four analyses on SP007-P257 span a wide compositional range that partially overlaps with the fields of the CI chondrites and the newly defined CY chondrites (Kur et al., 2019) as well as the composition of Tagish Lake and the composition of a organic-rich clast held within the Zag meteorite (Kebukawa et al., 2019). Particle SP007-P257 may therefore be related to one of these parent bodies or sample a different object that has a similar O-isotope composition. However, based on the MM’s petrography this sample is unlikely to be directly related to any of these lithotypes (for example SP007-P257 lacks sufficient sulphides to be related to the CIs, contains anhydrous silicates which are very rarely found in CIs and lacks both organics and carbonates which are common components of the Zag xenolith and the Tagish Lake meteorite respectively (though their absence may be a result of atmospheric entry heating)).

In recent years there has been a significant increase in the number of reported hydrated CC lithologies whose O-isotope compositions plot on or above the TFL (Δ17O: >0‰) and have δ18O values >+10‰ (Kur et al., 2019; Goosch et al., 2018; Kebukawa et al., 2019, Suttle et al., 2020b). They represent a diverse set of water-rich C-type asteroids whose heavy bulk O-isotope compositions appear to be related to either the accretion of abundant 16O-poor water (Charnier et al., 2018; Suttle et al., 2020; Mannocchi et al., 2018a) and/or affected by parent body thermal metamorphism (Iwamoto et al., 2013; King et al., 2019). Data from SP007-P257 adds to this growing inventory as another sample of ungrouped water-rich isotopically heavy C-type asteroid.
7 Implications

Previous studies of unheated CgMMs show that many of these particles are chondrules or fragments of chondrules (Engaard et al., 1999; Genge et al., 2002; Genge, 2006; Van Goolen et al., 2012; Prasad et al., 2016; Diao et al., 2020; Radwanii et al., 2020) or in rare instances CAIs and AOAs (Kurat et al., 1994a; Hoppe et al., 1995; Greshake et al., 1996, Taylor et al., 2012). In addition, a small fraction of CgMMs, those containing olivine/pyroxene grains with both high Mg (Mg# > 93) and high Mn (MnO > 0.5 wt.%) compositions may have extremely refractory mineral aggregates similar to those reported from the comet Siding Spring (Iquo et al., 2013; Nozoki et al., 2015).

We identified material from both chondrules (spinel-free MMs) dominated by Mg-rich olivine and whose O-isotope compositions plot on the slope-1 reference lines between Δ17O ±6‰ and +4‰ and CAIs/AOAs (Mg-Al spinel-bearing MMs with or without olivine whose spinel) grain compositions plot on the slope-1 reference lines with Δ17O values < -4‰). Although our results support the conclusions of previous in-situ O-isotope studies on forsterite grains in MMs (Engaard et al., 1999; Gounelle et al., 2005; Mortaj et al., 2008, Radwanii et al., 2015) – namely that most small CgMMs are fragments of chondrules, primarily from CC parent bodies – we have also extended interpretations beyond this well-established paradigm by identifying both type I and type II chondrule varieties and through the recognition of a relict silicate grain with a δ18O-rich composition that suggests it was derived from an OA precursor.

Analysis of MM containing Mg-Al spinels also supports earlier work (Kurat et al., 1994a; Hoppe et al., 1995; Greshake et al., 1996, Taylor et al., 2012) which concluded these MM are CAI material. Building upon these inferences we note that most CAI-derived spinel grains show O-isotope evidence of partial exchange with a δ18O-poor reservoir and are therefore not pristine CAI material. Furthermore, spinel grains with the highest O-isotope compositions (Δ17O > -8‰) also exhibit minor element Cr enrichment (Cr > 0.2 wt.%) suggesting interaction with parent body fluids. We conclude that most Mg-Al spinel grains are fragments of aqueously altered CAIs and derived from hydrated C-type asteroids.

8 Conclusions

Olivine is the dominant mineral in all types of MM, while Mg-Al spinel grains are relatively rare. Their high melting points mean that forsterite and spinel grains frequently survive atmospheric entry without melting or significant sub-solidus alteration, ensuring that their pre-atmospheric chemical and O-isotope signatures are preserved. Except for mesosiderite phases, data in the present study has not experienced significant alteration due to atmospheric entry. Our main conclusions are:

1. The diversity in O-isotope compositions measured here showcase the heterogeneity in solar system materials. Compositions reported from small MM (< 200μm) parallel the range observed from primitive chondrites.
2. Spinel-free CgMMs (and RGB PO cosmic spherules) have clear chemical, textural and O-isotope links to chondrules. They appear to be sampling a mix of CM-like and other CR-like, Tagish Lake-like or carbonaceous materials.
3. In chondrule-like MM, relict grains representing earlier generations of chondrule silicates can be identified by analyzing multiple olivine grains in the same sample and testing for isotopic heterogeneity (Δ17O > 2‰). This technique identified a relict silicate derived from a CAI/AOA precursor.
4. Mg-Al spinels in MM are very rare (< 1% of MM). Based on their δ18O-depleted compositions none of the grains analysed here are unheated CAI-derived spinels. Instead, spinels with high Cr2O3 contents (> 0.5 wt.%) and δ18O-poor compositions (Δ17O > -3‰) probably originate from
Al-rich chondrules while spindles with low CaO (<0.5 wt.%) and modest 18O-depletions (−20‰ ≤ △17O ≤ −8‰) are interpreted as CAI-derived spindles affected by a later period of parent body aqueous alteration.

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10 List of figures & tables

Table 1. Particle classifications for the 37 MMs analysed in this study.

Table 2. The oxygen isotope compositions of mineral phases and mesostasis collected by ion microprobe on 37 MMs.

Fig.1. – Representative BSE images of unmelted CgMMS and RGB PO cosmic spherules.

Fig.2. – Representative BSE images of unmelted CgMMS whose internal texture is dominated by a single mineral (of forsterite) – here termed CgMM-5M.

Fig.3. – Representative BSE images of spindel-bearing MMs.

Fig.4. – Plot showing all O-isotope data collected in this study.

Fig.5. – O-isotope compositions of spindel-bearing MMs.

Fig.6. – O-isotope data and BSE image of PgMM SP007-P257.

Fig.7. – Comparing Mg# and △17O composition in anhydrous silicates.

Fig.8. – Comparing △17O composition and Ca contents of spindels found in MMs.

Fig.9. – Investigating △17O variability in chondrule-like MMs.

Fig.10. – Oxygen isotope data from spinel minerals in spindel-bearing MMs.

Fig.11. – The histogram plot of △17O compositions of spinel grains.

11 Supplementary material

Appendix A

Appendix B
12 References


Figure captions

Figure 1
Representative backscattered electron (BSE) images of CgMM and relict-grain bearing PO cosmic spherules analysed in this study: (a) SP005-P351, (b) SP005-P105, (c) SP005-P1042, (d) SP005-P109, (e) SP005-P1162, (f) SP005-P160, (g) SP007-P233, (h) SP005-P727, and (i) SP005-P728. Petrographic and chemical studies were done on some particles by Rudraswami et al. (2015), but not for oxygen isotope studies. The white circle with the number indicates the spot of oxygen isotope analyses and the corresponding data is provided in Table 2.

Figure 2
Representative backscattered electron (BSE) images of single mineral MMAs analysed using ion microprobe. Clinopyroxene is the dominant mineral and is analysed for oxygen isotope studies. (a) SP005-P339, (b) SP005-P730, (c) SP005-P743, (d) SP005-P1029, (e) SP007-P135, and (f) SP005-P95. Only petrographic and chemical studies were done on some particles by Taylor et al. (2012) (d) and Rudraswami et al. (2015) (a, b, c, d), but not for oxygen isotope studies.

Figure 3
The backscattered electron (BSE) images of spinel-bearing MMAs analysed using ion microprobe are shown. Spinel is rarely found in MMAs and is marked in BSE images along with olivine. (a) SP005-P522, (b) SP005-P583, (c) SP005-P440, (d) SP005-P392, (e) SP005-P164, and (f) SP005-P88. The abbreviation Sp. and Ol. stand for spinel and olivine, respectively. Only petrographic and chemical studies were done earlier by Taylor et al. (2012) and Rudraswami et al. (2015). Oxygen isotope analyses of spinel grains on SP005-P583 and SP005-P164 were done previously by Taylor et al. (2012) is repeated in the present study.

Figure 4
All 95 O-isotope analyses collected in this study, plotted in δ18O–δ17O isotope space. Forsterite grains are shown in blue with different shades denoting olivine grains hosted within unmelting CgMMs (light blue), CgMM-SM (dark blue) and relict olivine grains held within a PO cosmic spherules (medium blue). Analyses on spinel grains are shown in green, analyses from the single FgMM are shown in yellow while analyses on mesostasis regions are shown in red. Error bars are reported at the 2σ level. We also show the CCAM line (Clayton et al. 1977), Y&R line (Young and Russell, 1993) and the PCM line (Usuihise et al. 2012). Shaded regions mark the approximate domains occupied by reprocessed CAIs, chondrules within CCs (Tisserant et al. 2014) and chondrules within OCs (Clayton et al. 1991; Kie et al. 2010).

Figure 5
The Oxygen three-isotope ratios of spinel-bearing MMAs (A) SP005-P522, (B) SP005-P583, (C) SP005-P440, (D) SP005-P392, (E) SP005-P164, and (F) SP005-P88. The red circles denote spinel minerals, which are δ18O-enriched relative to their corresponding olivine grains (denoted by green squares). O-isotope data used in this plot is provided in Table 2. Except for SP005-P440 (C), most of the data plot close to CCAM line. The TPL is shown for reference.

Figure 6
Combined (A) O-isotope and (B) BSE image data from the coesiteeous FgMM SP007-P257. (A) O-isotope data are plotted in δ18O–δ17O isotope space alongside reference data from other hydrated CC materials. The four spot analyses collected on this MM have a δ18O-poor composition that
spans a wide compositional range. This range partially overlaps with the fields of the CI and CY chondrites as well as the CI-like dust reported in the Zag meteorite. The approximate locations of the four O-isotope analyses are marked on the BSE image and indicated in (A) by coloured digits. Reference data were obtained from: Clayton and Mayeda, 1999; Ivanova et al. 2016; Schrader et al. 2011, 2014; Goodrich et al. 2018; Kebabzadeh et al. 2019; Kimura et al. 2020; Joy et al. 2020; Suttle et al. 2020.

Figure 7
Combined chemical (Mg#) and O-isotope (Δ^{17}O) data for the 71 anhydrous silicates analysed in this study. Data is separated based on MM texture (A) or based on the presence/absence of (Mg, Al) spinel grains (B). There is no clear correlation based on MM texture. By contrast, spinel-bearing MMs always have high Mg compositions and Δ^{17}O values between -10‰ to -4‰. These spinel-bearing particles most likely sample CAI+AOA material, while the spinel-free MMs most likely sample chondrules (or matrix-hosted silicates). Assuming this is correct, a grain’s Mg/Δ^{17}O values can be used to infer whether it is a sample of a type I or type II chondrule. Both types are represented among the study population.

Figure 8
(A) The chemical (Cr_{2}O_{3}) abundance (wt%) and O-isotope composition (Δ^{17}O [‰]) of the 11 Mg-Al spinel grains analysed. Spinel analyses separate into two distinct populations. (B) Interpretation of the reported spinel composition by comparison against previously reported data. Fields for pristine CAIs, spinels in Al-rich chondrules (Zhang et al. 2020a) and spinels in aqueously altered FeGMMs (Kurat et al. 1994a; Hutter et al. 1995; Engrand et al. 1999) are shown.

Figure 9
Investigating Δ^{17}O variability in selected MMs. Assuming spinel-free CgMMs and RGB PC cosmic spherules are samples of chondrules, variability in a sample’s Δ^{17}O provides an indication of whether the chondrule was either isotopically homogeneous or heterogeneous (denoted by grey shading). Most chondrules are isotopically homogeneous (Δ^{17}O variability < 2%). Heterogeneity implies the presence of relict silicates derived from an earlier generation of chondrule crystallization. This may be either a previous chondrule silicate (not shown here) or in rare cases a silicate grain derived from a CAI+AOA precursor (as in the case of SP005-351, identified based on its H-O rich signature [Δ^{17}O < -10‰]). Note, only spinel-free MMs with grain cluster textures and which have more than one data point are shown. Thus, CgMM-SE particles and CgMMs with only one spot analysis have been omitted since isotopic heterogeneity cannot be investigated in these particles due to either insufficient data or insufficient mineral grains.

Figure 10
Oxygen isotope data from spinel minerals in spinel-bearing MMs. Plot includes data from this study along with literature data (Kurat et al. 1994a; Engrand et al. 1999; Taylor et al. 2012). Errors reported are 2σ. The TFL and CCAM line are shown for reference. Some of the analyses on SP005-P583 and SP005-P664 from this study were made on the same grains as Taylor et al. (2012).

Figure 11
The histogram plot of Δ^{17}O compositions of spinel grains in spinel-bearing MMs from the present study and from the literature (Kurat et al. 1994a; Engrand et al. 1999; Taylor et al. 2012). Our study has effectively doubled the number of spinel grains analysed within a MM host. Note, Δ^{17}O ≤ -20‰ are consistent with pristine CAIs, while H-O-depleted compositions (Δ^{17}O > -20‰) indicate reprocessed CAIs affected either by nebula processes (i.e. O-isotope exchange with nebula gas or silicate melts) or affected by parent body processing (i.e. thermal or aqueous alteration).
Fig 1.
**A) Data separated based on MM texture**

- Type II porphyritic chondrules
- Type I porphyritic chondrules & Type II chondrule relics
- Relict grains derived from CAI/AOA precursors: (range extends to ~ -25%)

**B) Data separated based on presence of spinel**

- Olivine in spinel-bearing MM have a restricted compositional range.

- Spinel-free MM
- Spinel-bearing MM
Isotopically heterogenous compositions imply the existence of relict silicate grains that preserve the composition of an earlier generation of chondrule silicates.
Figure 11

- Spinel grains with pristine O-isotope consistent with unaltered CAIs.
- Spinel grains whose O-isotope compositions may be affected by parent body alteration.
Table 1. Particle classifications for the 37 micrometeorites analysed in this study. Abbreviations are OL – olivine, Px – pyroxene, Mess. – mesostasis, Sp – spinel, Chr. – chromite, Sul. – Fe-sulphides and Fe-matrix – fine-grained matrix.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: