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Mass-independent fractionation of oxygen isotopes during thermal decomposition of divalent metal carbonates: crystallographic influence, potential mechanism and cosmochemical significance

Martin F. Miller\textsuperscript{a,*}, Jonathan R. Woodward\textsuperscript{b}, Edward Bailey\textsuperscript{c,1}, Mark H. Thiemens\textsuperscript{d}, Paul F. McMillan\textsuperscript{e}, Monica M. Grady\textsuperscript{a}, Caroline Kirk\textsuperscript{e,f}

\textsuperscript{a} Planetary and Space Sciences, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

\textsuperscript{b} Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo, 153-8902, Japan

\textsuperscript{c} Department of Chemistry, University College London, Gower Street, London WC1E 6BT, UK

\textsuperscript{d} Department of Chemistry and Biochemistry, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0356, USA

\textsuperscript{e} School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, UK

\textsuperscript{f} Earth Sciences, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

\textsuperscript{1} Present address: Department of Chemical Engineering, Imperial College London, Imperial College Road, Kensington, London SW7 2AZ, UK

\textsuperscript{*} Corresponding author at: Planetary and Space Sciences, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

\textit{E-mail address:} martin.miller@open.ac.uk (M. F. Miller)
ABSTRACT

Few physical or chemical processes defy well-established laws of mass-dependent isotopic fractionation. A surprising example, discovered two decades ago, is that thermal decomposition of calcium and magnesium carbonate minerals (conducted in vacuo, to minimise back-reaction and isotopic exchange) causes the oxygen triple-isotope compositions of the resulting solid oxide and CO$_2$ to fit on parallel mass-dependent fractionation lines in ln(1 + δ$^{17}$O) versus ln(1 + δ$^{18}$O) space, with anomalous depletion of $^{17}$O in the solid and equivalent enrichment of $^{17}$O in the CO$_2$. By investigating the thermal decomposition of other natural divalent metal carbonates and one synthetic example, under similar conditions, we find that the unusual isotope effect occurs in all cases and that the magnitude of the anomaly (Δ$^{17}$O) seems to depend on the room temperature crystallographic structure of the carbonate. A lower cation coordination number (as associated with smaller cation radius) correlates with a Δ$^{17}$O value closer to zero. Local symmetry considerations may therefore be influential. Relative to a reference fractionation line of slope 0.524 and passing through VSMOW, solid oxides produced by thermal decomposition of orthorhombic carbonates were characterised by Δ$^{17}$O = $-0.367 \pm 0.004$‰ (standard error). The comparable figure from rhombohedral examples was $-0.317 \pm 0.010$‰, whereas from the sole monoclinic (synthesised) specimen it was $-0.219 \pm 0.011$‰. The numerical values are, to some extent, dependent on details of the experimental procedure. We discuss potential origins of the isotopic anomaly, including the possibility of hyperfine coupling between $^{17}$O nuclei and unpaired electrons of transient radicals (the ‘magnetic isotope effect’). A new mechanism based on the latter process is proposed. The associated transition state is compatible with that suggested by recent quantum chemical and kinetic studies of the thermal decompositions of calcite and magnesite. An earlier suggestion based on the magnetic isotope effect is shown to be incompatible with the generation of a $^{17}$O anomaly, regardless of the identity of the carbonate. We cannot exclude the possibility that a Fermi resonance between states leading to dissociation may additionally affect the magnitude of Δ$^{17}$O in some cases. Our findings have cosmochemical implications, with thermal processing of carbonates providing a potential mechanism for the mass-independent fractionation of oxygen isotopes in protoplanetary systems.

Key words:
Oxygen triple isotopes; Mass independent fractionation; Carbonates; Thermal decomposition; Magnetic isotope effect; Cosmochemistry

1. Introduction

With few – though important – exceptions, chemical or physical processes that modify oxygen stable isotope distributions in nature, whether under equilibrium conditions or by kinetic mechanisms, cause the $^{17}$O/$^{16}$O ratio to change by approximately half the corresponding change in $^{18}$O/$^{16}$O. This is related to the mass difference between $^{17}$O and $^{16}$O (1.0042 Da) being approximately half that between $^{18}$O and $^{16}$O (2.0042 Da). Isotope ratio modifications that follow this pattern of proportionality are usually referred to as ‘mass-dependent’ fractionations and are described by well-established laws (Urey, 1947; Bigeleisen and Goeppert-Mayer, 1947; Bigeleisen and Wolfsberg, 1957; Young et al., 2002; Dauphas and Schauble, 2016). In contrast, Thiemens and Heidenreich (1983) reported that ozone generated by electrical discharge in molecular oxygen deviates from this relationship, with the $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios changing by an equal amount. Since this discovery of a chemically produced ‘mass independent’ (or ‘non-mass-dependent’) isotope effect, several other examples have been documented, usually involving gas phase photochemistry. These include the reaction of CO with the $\bullet$OH radical in Earth’s atmosphere (Huff and Thiemens, 1998; Röckmann et al., 1998); photodissociation of CO$_2$ (Bhattacharya et al., 2000) and of CO (Chakraborty et al., 2012). The occurrence of mass independent isotope effects in nature provides useful tracers and insights to the present and past atmosphere, climate and even the origin of life (Thiemens, 2013; Thiemens and Lin, 2019, 2021).

Surprisingly, thermal decomposition of calcium and magnesium carbonates is also associated with mass-independent fractionation of the oxygen isotopes (Miller et al., 2002), if the decomposition is conducted under vacuum, to minimise the potential for back-reaction and isotopic exchange between the resulting solid oxide and CO$_2$. Anomalous depletion of $^{17}$O in the solid oxide is accompanied by a corresponding enrichment of $^{17}$O in the CO$_2$. No generally accepted explanation for this finding has since been proposed. Here, we report an investigation of whether the unusual fractionation pattern occurs during thermal decomposition of other anhydrous divalent metal carbonates and consider whether the magnitude of the
isotopic anomaly relates to specific characteristics of the individual carbonates. Most of the empirical data were obtained shortly after the initial report, but have not been published hitherto. Some years later, we also tested a hypothesis based on a hyperfine coupling mechanism (proposed and subsequently published by Buchachenko, 2013) for explaining the experimental findings. Although that test and its outcome were mentioned at a conference (Miller et al., 2012), no data were reported in the abstract; neither have they been published since. We therefore present the details here, together with the (also hitherto unpublished) oxygen triple-isotope measurements of oxides from thermal decomposition of eight different divalent carbonate minerals, for comparison with the Ca and Mg examples reported by Miller et al. (2002).

On the basis of the Buchachenko (2013) mechanism, details of which are discussed below (Section 5.6), all divalent metal carbonates would be expected to exhibit mass-independent fractionation of the oxygen isotopes during the thermal decomposition process, unless the corresponding cation in the univalent state contains no unpaired electrons. In this case, the intermediate cannot be a radical pair and therefore its reactions are not spin-state selective. Because 

\[ \text{Cu}^{2+}, \text{Cu}^{+} \hspace{1cm} \text{Cu} \]  

has electronic configuration \([\text{Ar}]3d^{10}\), a definitive empirical test of the hypothesis was to perform controlled thermal decomposition of \( \text{CuCO}_3 \) \textit{in vacuo} and measure the oxygen triple-isotope compositions of the resulting \( \text{CuO} \) and \( \text{CO}_2 \). If the proposed mechanism is correct, no \( ^{17}\text{O} \) anomaly would be produced.

Unfortunately, \( \text{CuCO}_3 \) does not occur in nature. The first reliable synthesis – from heating the hydroxycarbonate minerals azurite and malachite at 500 ± 10 °C for approximately 21 hours duration in \( \text{CO}_2 \) atmosphere at 20 ± 1 kb pressure – was reported by Ehrhardt et al. (1973), with the structure being published the following year (Seidel et al., 1974). \( \text{CuCO}_3 \) is a grey, monoclinic crystalline solid (space group \( P\text{a}-\text{C}_{2}\text{\textit{s}} \), cation coordination number 5), reputedly stable in dry air at room temperature for several months. To conduct the experimental test, it was therefore necessary to first prepare a small quantity (~20 mg) of \( \text{CuCO}_3 \), based on the Ehrhardt et al. (1973) procedure.

2. Definitions and notation
Measurements of oxygen triple-isotope ratios are, by convention, reported as $\delta^{17}O$ and $\delta^{18}O$ values relative to a specific reference material, usually Vienna Standard Mean Ocean Water (VSMOW). With $^{17}R$ and $^{18}R$ as the abundances of the respective minor isotopes relative to the $^{16}O$ abundance, then by definition:

$$\delta^{17}O = \frac{^{17}R_{\text{sample}} - ^{17}R_{\text{reference}}}{^{17}R_{\text{reference}}} \quad \text{and} \quad \delta^{18}O = \frac{^{18}R_{\text{sample}} - ^{18}R_{\text{reference}}}{^{18}R_{\text{reference}}}$$

Because the magnitudes of the dimensionless quantities $\delta^{17}O$ and $\delta^{18}O$ are $<< 1$ in natural systems, their values are usually reported as parts per thousand (per mil, ‰). For two chemical entities or phases A and B at equilibrium, the fractionation factors for oxygen isotope exchange, defined by:

$$a^{17/16}_{A-B} = \frac{^{17}R_A}{^{17}R_B} = \frac{1 + \delta^{17}O_A}{1 + \delta^{17}O_B} \quad \text{and} \quad a^{18/16}_{A-B} = \frac{^{18}R_A}{^{18}R_B} = \frac{1 + \delta^{18}O_A}{1 + \delta^{18}O_B}$$

are related by:

$$a^{17/16}_{A-B} = (a^{18/16}_{A-B})^\theta$$

Although few experimental measurements of $\theta$ have been reported, calculations (Matsuhisa et al., 1978; Young et al., 2002; Cao and Liu, 2011; Dauphas and Schauble, 2016) for various equilibrium exchange reactions give a range from ~0.522 to a universal high temperature limit value of 0.5305.

Kinetic processes may be described by a comparable formalism (Young et al., 2002; Dauphas and Schauble, 2016). As noted by Young et al. (2002), the masses used to evaluate $\theta$ in such cases depend on the isotopic species in motion: reduced masses apply for breaking bonds whereas molecular or atomic masses apply for transport processes. The functional form of $\theta$ for kinetic processes involving a triple-isotope system is $\ln(\mu_1/\mu_2)/\ln(\mu_1/\mu_3)$, where $\mu_1$ are the reduced, molecular or atomic masses. For the simple case of Graham’s Law diffusion, $\theta$ varies according to the molecular mass of the diffusing entities, with limiting values of 0.501 and 0.516 (the latter for atomic oxygen in the gas phase). In the transition state theory of chemical kinetics, which describes activation energy-limited kinetic isotope fractionation, the corresponding $\mu_1$ terms relate to multiple atoms in complex motion along the reaction coordinate, modelled as a special vibrational mode with a negative force constant (and thus an ‘imaginary’ vibrational frequency). In general, as noted by Dauphas and Schauble (2016), for isotopic masses $m_1 < m_2 < m_3$, as in the oxygen triple-isotope
system, kinetic fractionation exponents are of smaller magnitude than the canonical high-T equilibrium value, 0.5305.

For a collection of natural carbonate samples (or silicate rocks or minerals, oxides or waters) differing in oxygen isotopic compositions, the distributions of $^{16}$O, $^{17}$O and $^{18}$O similarly conform to a power law relationship:

$$\frac{R_{\text{sample}}^{17}}{R_{\text{reference}}^{17}} = (1 + \gamma) \left( \frac{R_{\text{sample}}^{18}}{R_{\text{reference}}^{18}} \right)^{\lambda}$$

(4)

where $\lambda$ and $\gamma$ are empirical parameters. Whereas $\theta$ relates to a specific process, such as isotope exchange under equilibrium conditions, or kinetic fractionation, the exponent is usually designated as $\lambda$ when the process or cumulative processes are undefined or unknown. In linear format and expressed in terms of $\delta^{17}$O and $\delta^{18}$O values, as determined experimentally, Eq. (4) becomes (Meijer and Li, 1998; Miller, 2002):

$$\ln(1 + \delta^{17}O) = \lambda \ln(1 + \delta^{18}O) + \ln(1 + \gamma)$$

(5)

In some reports, $\ln(1 + \delta^{17}O)$ and $\ln(1 + \delta^{18}O)$ are designated as $\delta'^{17}$O and $\delta'^{18}$O respectively, following similar terminology introduced by Hulston and Thode (1965) in the context of sulphur multiple isotope ratios. The $\ln(1 + \gamma)$ term is a measure of any ordinate offset of the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ linear array from the zero point of the $\delta^{17}$O and $\delta^{18}$O scales, usually VSMOW. Defining $\Delta'^{17}$O = $\ln(1 + \Delta^{17}$O) as the magnitude of any inequality between the two sides of Eq. (5), this parameter represents the $\ln(1 + \delta^{17}O)$ offset of an individual sample from a reference mass fractionation line of slope $\lambda$ and ordinate offset $\gamma$. An empirical reference line, such as defined from a collection of samples, may be used; alternatively, the reference line may be of arbitrarily assigned slope ($\lambda_{RL}$) and ordinate offset ($\gamma_{RL}$). A value of 0.528 is commonly assigned to $\lambda_{RL}$ (and with $\gamma_{RL} = 0$), corresponding to the VSMOW-SLAP scale for $\Delta^{17}$O measurements (Schoenemann et al., 2013). SLAP is the Standard Light Antarctic Precipitation reference and has $\Delta^{17}$O defined to be zero on the VSMOW-SLAP scale. Thus,

$$\Delta^{17}$O = $\ln(1 + \delta^{17}$O) - $\lambda_{RL} \ln(1 + \delta^{18}$O) - $\ln(1 + \gamma_{RL})$$

(6)
Because the difference between $\ln(1 + \Delta^{17}O)$ and $\Delta^{17}O$ is below the measurement precision limit (~5 ppm) for $\Delta^{17}O < 3 \, \%_{oo}$, which is orders of magnitude greater than nearly all examples in nature, $\Delta^{17}O$ may be conveniently approximated as $\Delta''^{17}O$ without loss of accuracy. This is currently standard practice, for measurements at high precision. Alternatively, $\Delta^{17}O$ may be expressed (exactly) as:

$$\Delta^{17}O = \frac{1 + \delta^{17}O}{(1 + \gamma_{RL})(1 + \delta^{18}O)^{\gamma_{RL}}} - 1$$

Eq. (6), based on Miller (2002), has been widely adopted, with various assigned values of $\lambda_{RL}$ (as discussed by Hofmann et al., 2017), with or without the inclusion of a $\gamma_{RL}$ term. From a practical perspective, it is also useful to include a scaling factor of $10^3$ so that the logarithmic terms are then of similar magnitude to the corresponding $\delta^{17}O$ and $\delta^{18}O$ values reported as $\%_{oo}$. Linear regression of the $10^3\ln(1 + \delta^{17}O)$ versus $10^3\ln(1 + \delta^{18}O)$ data from a collection of samples differing in oxygen isotopic composition gives a ‘mass fractionation line’ of slope $\lambda$ and ordinate intercept $10^3\ln(1 + \gamma)$ specific to the particular group of samples. There is not necessarily an implied relationship between the individual samples. In practice, the ordinate intercept value $10^3\ln(1 + \gamma)$ may be approximated as $10^3\gamma$ without loss of accuracy. The magnitude of $\Delta''^{17}O$ is not necessarily of physical significance, as a proportion may be attributed to the divergence (or convergence) of the assigned reference line from the linear array formed by the specific group of samples under investigation. Furthermore, a non-zero value of $\Delta''^{17}O$ does not necessarily imply mass-independent fractionation.

The parameter $\Delta^{17}O$ was originally introduced by Clayton and Mayeda (1988) and defined on the basis of approximating the relationship between $\delta^{17}O$ and $\delta^{18}O$ as a linear function; a proportionality constant of 0.52 was usually adopted. For further information on oxygen triple-isotope systematics, see Miller and Pack (2021) and references therein.

3. Methods

3.1. Samples
Apart from CuCO$_3$, which was synthesised for this investigation, most of the single carbonate mineral specimens used in this study were supplied by the Natural History Museum, London. Sample details are given in Table 1. The use of natural samples ensured that the relationship between the $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios would conform to mass-dependent norms, prior to the commencement of thermal decomposition.

Oxygen triple-isotope characterisation of carbonates at high precision (to ~10 ppm or better for $\Delta^{17}$O) is challenging. Various alternative analytical procedures have been developed, or refined recently, as reviewed by Passey and Levin (2021) and by Fosu et al. (2020). For our investigation, we assign a reference line of slope ($\lambda_{RL}$) 0.524, with no offset from VSMOW (i.e., $\gamma_{RL} = 0$), as discussed below (Section 4.1.1). The $\Delta^{17}$O values of calcite reference materials NBS 18, NBS 19 and IAEA 603 as reported by Wostbrock et al. (2020), when recalculated with $\lambda_{RL}$ as 0.524, are −19, +11 and +12 ppm respectively, i.e. very close to zero. Similarly, the mean $\Delta^{17}$O of seventeen natural carbonates as reported by Fosu et al. (2020), relative to the same reference line, is 10 ± 11 ppm (standard error). This indicates that natural carbonates, including those used in our investigation, are characterised by $\Delta^{17}$O values which are very close to zero, on the basis of our assigned mass-dependent reference line.

Rhombohedral (trigonal) carbonates used in the investigation were CaCO$_3$ (calcite), MnCO$_3$ (rhodochrosite), FeCO$_3$ (siderite) and ZnCO$_3$ (smithsonite). These are characterised by cation coordination number 6 and space group $R3c$. Additionally, the MgCO$_3$ (magnesite) and Ca,Mg(CO$_3$)$_2$ (dolomite) samples from Miller et al. (2002) were included. The dolomite structure is characterised by space group $R3$.

Orthorhombic carbonates investigated were CaCO$_3$ (aragonite), SrCO$_3$ (strontianite), BaCO$_3$ (witherite) and PbCO$_3$ (cerussite). In such cases the cation coordination number is 9, according to Speer (1983), and the space group is $Pmcn$. Alía et al. (1997), however, assigned a cation coordination number of 8 to aragonite and aragonite-type structures. Single carbonates with cation radius larger than ~100 pm are generally characterised by the orthorhombic (aragonite) structure. Whereas oxides formed from thermal decomposition of Ca, Sr and Ba carbonates readily recombine with CO$_2$ on cooling, others (from Mg, Mn, Fe and Zn carbonates) recombine only at high partial pressures of CO$_2$ (Goldin and Kulikova, 1984). MnO can be handled in air without hydration or exchange (Sharma and Clayton, 1965).
3.2. Synthesis of CuCO$_3$

CuCO$_3$ was prepared (by EB) at University College London, using high pressure, high temperature reaction between laboratory reagent copper (II) carbonate hydroxide CuCO$_3$·Cu(OH)$_2$ and CO$_2$ produced *in situ* by thermal decomposition of silver oxalate, Ag$_2$(CO$_2$)$_3$. The latter was prepared by adding silver nitrate to oxalic acid solution; the resulting precipitate was washed in absolute ethanol and dried. Approximately 140 mg of silver oxalate was loaded into a platinum capsule which had been sealed at the lower end by spot welding. 80 mg of CuCO$_3$·Cu(OH)$_2$ was then added. A platinum disc of width slightly greater than the internal diameter of the capsule, and slightly bowed convex side towards the sample, was then placed over the CuCO$_3$·Cu(OH)$_2$. Above this, a cylindrical plug of hexagonal boron nitride was tightly fitted. The loaded capsule was then placed in a non-endloaded piston cylinder (‘QUICKPress’ model, ‘Depths of the Earth’, Cave Creek, Arizona, USA), and subjected to a pressure of 2 GPa and temperature of 500 °C for 21 hours. X-ray diffraction analysis showed that no azurite, malachite, copper metal or boron nitride were present in the resulting CuCO$_3$. The yield was ~18 mg, which was sufficient for three replicate thermal decomposition experiments.

3.3. Carbonate thermal decomposition procedure and oxygen triple-isotope measurements of the resulting solid oxides

Thermal decompositions of the carbonate mineral specimens, and subsequent determinations of the oxygen triple-isotope composition of the resulting solid oxide phase, were performed at the Open University. For all the rhombohedral and orthorhombic examples, single grains of ~60 μmol (mass ranging from 5.3 mg for magnesite to 16.7 mg for cerussite) were loaded in duplicate into a quartz glass tube (6 mm external diameter) that formed an integral part of a high vacuum system. After outgassing at 100 °C until a vacuum of ~10$^{-4}$ Pa was attained, samples were gradually heated, with constant pumping, until onset of thermal decomposition caused the pressure to rise to ~0.1 Pa, as monitored with a Penning gauge. The temperature was then held constant until CO$_2$ evolution essentially ceased, after which the temperature was increased in a carefully controlled manner until the pressure again increased to ~0.1 Pa. This incremental heating procedure was repeated over a period of several days. When no further evolution of CO$_2$ was detected, the
temperature was then increased to 900 °C whilst monitoring the pressure, to check that carbonate decomposition was complete. The quartz tube was then flame-sealed, under high vacuum, and the resulting ampoule transferred to a glove box flushed by dry, high-purity nitrogen. Ampoules were opened in this inert atmosphere and individual oxide grains (none of which had fragmented during the heating process) transferred into a fluorination chamber fitted with a barium fluoride window. The chamber was then sealed, still containing dry nitrogen, removed from the glove box, and coupled to the vacuum system of a facility for infrared laser-assisted fluorination of silicates or oxides. This procedure ensured that the metal oxide grains were not exposed to air. Fluorination of the grains was conducted using excess of BrF₅ vapour, after ensuring that the oxygen ‘blank’ was negligible. Details of the procedure have been described elsewhere (Miller et al., 1999; Miller et al., 2002). After purification of the ~30 μmol O₂ by cryogenic traps at ~196 °C and by adsorption/desorption to/from cryo-cooled 13X zeolite pellets, oxygen triple-isotope ratio analysis was performed using a VG Isotech PRISM III dual inlet mass spectrometer. The original δ¹⁷O and δ¹⁸O data were subsequently recalibrated to VSMOW, based on a recent inter-laboratory investigation (Miller et al., 2020), anchored to direct measurements of VSMOW and SLAP (Pack et al., 2016). It was found that, although the original δ¹⁸O data (and the Open University data reported in the initial study of 2002) were accurately on the VSMOW scale, the corresponding δ¹⁷O values needed adjusting by −0.012 ‰.

Because the initial report (Miller et al., 2002) had demonstrated that corresponding enrichment of ¹⁷O occurs in the CO₂ produced during thermal decomposition of carbonate examples (calcite and dolomite), accompanying ¹⁷O depletion in the solid oxide, we considered it unnecessary to demonstrate a similar finding for the thermal decomposition of the natural carbonate examples used in this investigation, if the solid oxide was shown to be characterised by ‘mass-independent’ oxygen isotopic composition.

3.3.1. Carbonate thermal decomposition in an applied magnetic field

Radical pair reactions can be influenced by external magnetic fields. Effects are normally observed within the magnetic flux density range of ~1 mT to a few T, as shown in Fig. 13 of Woodward (2002), although the

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¹ A slightly higher maximum temperature of ~940 °C was used for the thermal decomposition of witherite.
specific range for individual examples is usually much narrower. Turro et al. (1985) found that an applied magnetic field of 200 mT had no effect on $^{13}$C enrichment in the reactant remaining after partial photolysis of dibenzyl ketone in the solid phase, whereas the corresponding $\alpha^{17/16}$ decreased from $1.10 \pm 0.02$ to $1.05 \pm 0.02$ when the magnetic field was applied. If a mechanism based on the magnetic isotope effect is responsible for the anomalous isotopic fractionation of oxygen that occurs during the thermal decomposition of divalent metal carbonates, the magnitude of the anomaly ($\Delta^{17}$O) may be influenced by the presence of an applied magnetic field, of appropriate flux density. As an exploratory test, we therefore heated additional duplicate grains of two of the carbonate examples (siderite and cerussite) sequentially, with the samples located between the poles of an ion pump (fixed) magnet which provided a magnetic field of flux density ~250 mT.

For technical reasons, it was necessary to use a different extraction line from that used for the other decompositions of natural carbonate samples. Also in this case, the helical wire heating element was wound directly around the quartz tube containing the sample, with a ceramic tube positioned over the heating element to reduce heat loss and maintain temperature stability. This arrangement minimised shielding of the sample from the applied magnetic field. A lower temperature ramp rate was used, resulting in a more protracted decomposition period (approximately double that of the other examples). The $\Delta^{17}$O values of the resulting metal oxide grains were compared with those obtained by performing the thermal decomposition in an identical manner, using the same experimental facility, but without the applied magnetic field. We note that the heating wire element would also have generated a magnetic field, alternating at a frequency of 50 Hz, although with magnetic flux density probably < 3 mT; clearly negligible relative to the applied field for the present test. For comparison, the surface flux density of the Earth’s magnetic field at the location of the heating experiments is ~0.049 mT.

3.3.2. CuCO$_3$ thermal decomposition procedure and oxygen triple-isotope analysis of the decomposition products

For thermal decomposition of CuCO$_3$, a slightly different procedure was adopted than for the other carbonates. In this case, evolved CO$_2$ was also collected for oxygen triple-isotope measurements.
single grains, each of ~45 μmol (5.5 mg) were heated individually and sequentially in the same extraction line as used for testing the effect of an applied magnetic field. Individual grains were loaded and outgassed overnight at room temperature, after which the extraction line was sealed and any pressure rise during a period of 30 minutes recorded using a capacitance manometer. This was found to be 5 × 10^{-2} Pa; essentially negligible. Gradual heating of the CuCO_3 was then commenced, with released CO_2 being trapped in a borosilicate glass finger maintained at −196 °C by liquefied nitrogen. It was observed that thermal decomposition of the CuCO_3 commenced between 250 °C and 300 °C, with maximum gas evolution (corresponding to pressure of 0.8 to 1.2 Pa, uncorrected for blank) occurring at ~390 °C. The pressure subsequently decreased, to a minimum of 0.12 Pa, as the furnace temperature was gradually increased to 550 °C. Further heating, to 600 °C, caused a slight rise in pressure, attributed to the release of O_2 from CuO decomposition. At this stage, the furnace was switched off and allowed to cool slowly, for resorption of O_2.

An n-pentane/liquid nitrogen slush bath (−131 °C) was used to purify the CO_2 from any traces of water, after which the gas was transferred cryogenically to a borosilicate glass tube which was then flame-sealed. Similarly, the (quartz) extraction tube containing CuO from decomposition of the carbonate was also flame-sealed, under vacuum, as for the other carbonates in this investigation. The CuCO_3 decomposition procedure was completed within one hour. Fluorination of the CO_2 was conducted at the University of California San Diego (UCSD), by reaction for 45 hr with a 1,000-fold excess of BrF_5 in a Ni tube at 800 °C (Bhattacharya and Thiemens, 1989), to give complete conversion to O_2 and CF_4. Isolation and purification of the O_2 for triple-isotope ratio analysis at UCSD was conducted as described previously (Miller et al., 2002).

3.4. Determinations of δ^{18}O, thermal decomposition temperature profiles, phase purity and elemental compositions of the natural carbonates

Whereas the respective δ^{18}O values of the carbonates were not of particular significance for this investigation, as it was the Δ^{17}O values of the solid oxides formed during thermal decomposition that were primarily of interest, measurements of the δ^{18}O values of the carbonate specimens were made for completeness, using the long-established method of temperature-controlled reaction with concentrated
H$_3$PO$_4$ (McCrea, 1950) and isotope ratio measurements of the released CO$_2$, in conjunction with appropriate fractionation factors.

To compare the relative thermal decomposition profiles of the carbonate minerals as a function of temperature, thermogravimetric analysis (TGA) was conducted (by MMG), using a Netzsch TGA system (model STA 449 C) in conjunction with evolved gas analysis (EGA) using a Hiden HPR20 quadrupole mass spectrometer. Fine-grained samples were loaded into a Pt bucket (with lid) and heated in a flow of helium (53.8 mL min$^{-1}$), at a ramp rate of 0.5 °C min$^{-1}$ to 1000 °C, except for witherite, which was heated to 1200 °C. In all cases, the thermal decompositions profiles would not be expected to be identical to those during the protracted thermal decompositions conducted for isotope ratio measurements of the decomposition products, because of the much slower and variable temperature ramp rates during the latter process. In a kinetic study of the thermal decomposition of calcite, Wang et al. (2017) showed that the decomposition profile was shifted to higher temperatures when the calcite was heated in a flow of nitrogen (30 mL min$^{-1}$) rather than in vacuum (10$^{-3}$ Pa); the same authors found that a similar shift – though of much smaller magnitude – also occurred when the ramp rate was increased from 7.5 to 10 °C min$^{-1}$. A comparative assessment under controlled and constant conditions does, however, provide useful information on the relative stabilities of the carbonates investigated in this study.

For determining the phase purity of the carbonate mineral specimens, X-ray powder diffraction analysis was performed (by CK) at the Natural History Museum, London, using a Nonius diffractometer with Cu K$_\alpha$ radiation and an INEL CPS120 detector. Elemental compositions of the carbonate minerals were determined by electron probe microanalysis at the Open University, using a Cameca SX100 instrument.

4. Results

4.1. Oxygen triple-isotope measurements

4.1.1. Oxides formed from the rhombohedral and orthorhombic carbonates

A compilation of the oxygen triple-isotope data from this investigation is provided in Table 2. From the respective mean values of replicate measurements of the ten solid oxides produced by thermal decomposition
of the natural anhydrous carbonates, a linear array of slope $0.5243 \pm 0.0011$ (standard error) can be derived in $10^{3}\ln(1 + \delta^{17}O)$ versus $10^{3}\ln(1 + \delta^{18}O)$ space, with ordinate intercept of $-0.343 \pm 0.023$ relative to VSMOW, as shown in Fig. 1. The slope of the array is in accord with mass-dependent fractionation, but the magnitude of its displacement from VSMOW identifies isotopically anomalous behaviour during the thermal decomposition process. It is evident that all the natural carbonates investigated here exhibit such behaviour.

Lower scatter of individual data points about $10^{3}\ln(1 + \delta^{17}O)$ versus $10^{3}\ln(1 + \delta^{18}O)$ regression lines – leading to lower standard error values associated with the respective slope and intercept – has been reported from measurements on silicates: for example, 0.0004 from replicate measurements (also conducted using the same Open University facility) of eight eclogitic garnets (Rumble et al., 2007) and similarly from measurements of fifteen diverse natural silicates conducted at the University of Okayama (Tanaka and Nakamura, 2013). This indicates that the divalent metal oxide data may be subject to small, second-order effects, although variation between replicates contributes to the observed degree of scatter. In the initial report (Miller et al., 2002), coincidentally, the triple isotope regression line given by replicate measurements of CaO produced from thermal decomposition of calcite reference materials NBS 18 and NBS 19 was $0.5241 \pm 0.0009$, with the corresponding value for the evolved CO$_2$ being $0.5239 \pm 0.0009$. Those two essentially parallel mass-dependent fractionation arrays were separated by a $10^{3}\ln(1 + \delta^{17}O)$ value of 0.41. For the present investigation, we therefore assign a reference line slope value $\lambda_{RL}$ of 0.524 and set $\gamma_{RL}$ to be zero, for defining $\Delta^{17}O$ in Eq. (6). This avoids the magnitude of $\Delta^{17}O$ being dependent (as an artefact) on the associated $\delta^{18}O$ value, in contrast to reporting our $\Delta^{17}O$ data on the VSMOW-SLAP scale ($\lambda_{RL} = 0.528$, $\gamma_{RL} = 0$), for example.

With reference to Table 2, duplicate grains of siderite heated together in the presence of an applied magnetic field, strength ~0.25 T, produced FeO characterised by $\Delta^{17}O$ values of $-0.293$ and $-0.299$ ‰, whereas in the absence of an applied magnetic field the corresponding data were $-0.286$ and $-0.297$ ‰. All these results are identical, within measurement precision. Measurements of the two other duplicate FeO grains from siderite decomposition reported in Table 2 were conducted earlier, using a different extraction line and less protracted heating period. The observation that significantly more negative $\Delta^{17}O$ values ($-0.394$
and –0.405 ‰) were obtained during those earlier measurements is probably due to the use of different experimental conditions, illustrating the sensitivity of the magnitude of Δ¹⁷O to details of the carbonate decomposition procedure. Further evidence is provided by the consistently smaller magnitude of Δ¹⁷O when metal oxides were generated by infrared laser heating of carbonate samples (calcite, magnesite, dolomite) during a period of only 1–2 hours, rather than when a much slower and more controlled rate of heating, by tube furnace, was adopted (Miller et al., 2002). Clearly, there are several variables that need to be controlled individually before substantive conclusions can be made.

Although duplicate grains of cerussite were also heated in the presence/absence of an applied ~0.25 T magnetic field, as for the siderite, the conclusive finding that the presence of the applied magnetic field had no effect on the Δ¹⁷O value of the FeO produced from siderite, together with poorer Δ¹⁷O reproducibility of PbO duplicates produced in the presence of the applied magnetic field (–0.353 and –0.322 ‰ respectively), led to the PbO duplicates produced in the absence of the applied magnetic field not being analysed for oxygen triple-isotope composition.

From the data compilation in Table 2, metal oxides derived from thermal decomposition of the six different calcite isotype minerals (rhombohedral structure) were characterised by a mean Δ¹⁷O value of –0.317 ± 0.010 ‰ (standard error). This compares with –0.367 ± 0.004 ‰ for the metal oxides formed from the four aragonite isotypes (orthorhombic carbonates). If the final batch of replicate results for siderite and cerussite (identified with an asterisk in Table 2) are excluded, because of the slightly different experimental conditions of thermal decomposition, then the respective mean values become –0.329 ± 0.017 and –0.374 ± 0.008 ‰. Also, the regression line shown in Fig. 1 then becomes slightly steeper: 10³ln(1 + δ¹⁷O) = (0.5248 ± 0.0013)10³ln(1 + δ¹⁸O) – (0.363 ± 0.028).

4.1.2. CuO and CO₂ formed from thermal decomposition of the synthesised CuCO₃

The relationship between the oxygen triple-isotope compositions of the CuO and CO₂ formed from the three replicate thermal decompositions of individual grains of CuCO₃ is illustrated in Fig. 2. From mass balance considerations, the δ¹⁷O and δ¹⁸O values of the CuCO₃ may be inferred, from which the corresponding Δ¹⁷O value relative to the assigned reference line is seen to be indistinguishable from zero.
For comparison, recent measurements at the Open University of two widely-used silicate standards for oxygen isotope measurements, San Carlos olivine and University of Wisconsin garnet (UWG-2) respectively, gave $\Delta^{17}\text{O}$ values of $-0.020 \pm 0.003$ and $-0.023 \pm 0.001 \%$, when recalculated from the corresponding values on the VSMOW-SLAP scale as reported by Miller et al. (2020). The CuCO$_3$ synthesised for this investigation clearly conforms to mass-dependent distribution of the three oxygen isotopes. A $\delta^{18}\text{O}$ shift of $-2.4 \%$ was associated with complete thermal decomposition of the CuCO$_3$ to CuO, together with the $\delta^{18}\text{O}$ value of the evolved CO$_2$ being 1.2 % greater than in the CuCO$_3$. The corresponding fractionation line slope in $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ space is $\sim 0.61$ (0.602 from decomposition experiment #2 data; 0.623 from decomposition experiment #3), which nearly exceeds the maximum theoretical value of 0.5305 associated with mass-dependent fractionation (Matsuhisa et al., 1978; Young et al., 2002; Dauphas and Schauble, 2016). Although the $\Delta^{17}\text{O}$ value of the resulting CuO ($-0.219 \pm 0.011 \%$) is more positive than as obtained from the other divalent metal oxides, it nevertheless demonstrates that the mechanism suggested by Buchachenko (2013) cannot be the correct explanation for the $^{17}\text{O}$ depletion in the metal oxides (and associated $^{17}\text{O}$ enrichment in CO$_2$ formed during thermal decomposition of divalent metal carbonates. This was acknowledged in that same paper, with the isotope effect being described as ‘extremely enigmatic.’ In subsequent papers (Buchachenko and Lawler, 2017; Buchachenko, 2018; Buchachenko et al., 2020) however, the same mechanism was offered as an explanation for the unusual oxygen triple-isotope fractionation during carbonate thermal decomposition, but without reference to the result of CuCO$_3$ decomposition. We infer that, in those later papers, the Buchachenko (2013) mechanism was still considered to be a valid explanation of the thermal decomposition findings reported by Miller et al. (2002) for calcium and magnesium carbonates. The implication is that thermal decomposition of CuCO$_3$ proceeds via a modification of the published hypothesis. In Section 5.6, we re-evaluate the Buchachenko (2013) mechanism in detail.

We cannot exclude the possibility that, compared to the heating of other divalent metal carbonates, the much shorter duration of the CuCO$_3$ thermal decomposition procedure, as necessitated by the need to collect the released CO$_2$, contributed to the $\Delta^{17}\text{O}$ value of the resulting CuO being slightly closer to zero than would
otherwise have been the case. During the peak release of CO₂ from CuCO₃ (at ~390°C), the gas pressure in the extraction line was, for a brief period, an order of magnitude greater than during the more protracted thermal decompositions of the natural mineral samples. The higher pressure might have resulted in greater oxygen isotopic exchange between the released CO₂ and the residual solid phase at elevated temperatures; we were not able to quantify to what extent (if any) such exchange actually occurred.

4.2. δ¹⁸O measurements, thermal stability and purity of the natural carbonates

The δ¹⁸O values of the carbonate minerals, as determined by the McCrea (1950) method during this investigation, are presented in Appendix A, Table A.1. Because several of the specimens (especially siderite) were not phase pure, as discussed below, there is some uncertainty about the accuracy of the data obtained by application of published carbonate-H₃PO₄ equilibration fractionation factors for the individual minerals. We have included these data, nevertheless, as an indication of the respective δ¹⁸O changes associated with carbonate thermolysis. A comparison of the CO₂ thermal release profiles as determined from TGA/EGA measurements is presented in Fig. 3 and illustrates the wide range of thermal stabilities of the natural carbonate mineral specimens. The results of electron probe microanalysis and X-ray powder diffraction measurements are presented in Appendix B (online supplementary data). Only the aragonite and cerussite specimens were found to be essentially free of other phases. The calcite was of slightly lower purity (>99.5 %); smithsonite and witherite specimens were ~98 % pure. In contrast, ~5 % CaCO₃ was detected in the strontianite, whereas the rhodochrosite was found to contain ~9 % FeCO₃ together with ~0.7 % MgCO₃. The siderite example contained the greatest quantity of a secondary mineral, ~23 % MgCO₃ together with ~0.2 % MnCO₃. For the present investigation, the presence of minor or trace quantities of impurities was not critical to establishing whether mass-independent fractionation of oxygen isotopes occurred during the thermal decomposition process.

Thermal decomposition of the natural divalent carbonate specimens resulted in a range of δ¹⁸O shifts in the solid phase, including significant differences between replicates. The latter variations are most probably attributable, at least in part, to variations in the respective protracted heating profiles. Because pairs of grains were subjected to the same thermal profile during the decomposition experiments, it is unsurprising that the
\( \delta^{18}O \) shifts tend to cluster in pairs. Fig. 4 illustrates this, together with the respective peak temperatures of CO\(_2\) release as determined by TGA/EGA. In the case of cerussite, the most labile of the carbonates investigated (and of high purity), pairs of grains heated in two separate experiments produced similar and negative \( \delta^{18}O \) shifts, of \(-7.6 \pm 0.3 \) \( \% \) during the transition from carbonate to solid oxide. Rhodochrosite decomposition was also characterised by a negative shift in \( \delta^{18}O \) during the formation of MnO, although of smaller magnitude \((-2.0 \pm 0.2 \) \%). In contrast, MgO formation from magnesite was accompanied by positive \( \delta^{18}O \) shifts of up to 2 \( \% \), whereas decomposition of the same specimen reported previously (Miller et al., 2002) was accompanied by negative shifts of similar magnitude. Data also reported in the same study showed that thermal decomposition of the carbonatite (calcite) reference material NBS 18 could – surprisingly – proceed with essentially no change in \( \delta^{18}O \); the resulting solid oxide being within 0.1 \( \% \) of the accepted value of 7.20 \( \% \) for NBS 18 (Coplen et al., 1983), yet the corresponding \( \delta^{17}O \) value was anomalously low, relative to mass-dependent composition. Similarly, CO\(_2\) released from NBS 18 could also be characterised by negligible shift from the \( \delta^{18}O \) value of the precursor carbonate, whereas the associated \( \delta^{17}O \) value was anomalously high. Larger shifts of \( \delta^{18}O \) (~\(-2.8 \) \%) in both decomposition products from NBS 18 were also noted, from replicates, yet without significant variation of the corresponding \( \Delta^{17}O \) value.

Uniquely among the carbonates investigated here, thermal decomposition of witherite is characterised by a bimodal CO\(_2\) release, as revealed by TGA/EGA. For the temperature ramp rate used (0.5 \(^\circ\)C min\(^{-1}\)), CO\(_2\) evolution initially occurred from 320 to 980 \(^\circ\)C, with a maximum at \(-950 \) \(^\circ\)C. As the temperature was increased further, a second release of CO\(_2\) commenced, resulting in maximum gas evolution at 1047 \(^\circ\)C and the completion of decomposition by 1060 \(^\circ\)C. For investigation of oxygen triple-isotope changes accompanying the carbonate to solid oxide transition, duplicate grains of witherite heated together to a maximum of \(-940 \) \(^\circ\)C resulted in \( \delta^{18}O \) shifts of \(-9.1 \) and \(-16.0 \) \( \% \) respectively. This is a considerably greater difference between duplicates than occurred during thermal decomposition of any of the other divalent carbonate specimens. Despite this, however, the \( \Delta^{17}O \) values of the resulting BaO differed by only 0.007 \( \% \),
which is at the experimental precision limit\(^2\). Although the vacuum line was at baseline pressure after the final (overnight) heating step of \(\sim 940\) °C, it is probable, on the basis of the TGA/EGA findings, that decomposition of the witherite was incomplete. We therefore include the BaCO\(_3\) thermal decomposition results with this proviso, which may affect the accuracy of the \(\Delta^{17}\)O measurements in this particular case, although it is evident nevertheless that thermal decomposition was accompanied by mass-independent fractionation.

5. Discussion

5.1. Relationship between \(\Delta^{17}\)O of the metal oxides and crystallographic structure of the parent carbonate

Despite the variability between replicate \(\Delta^{17}\)O measurements of individual metal oxides, there appears to be an association between the respective mean \(\Delta^{17}\)O values and whether the parent carbonate has a rhombohedral, orthorhombic or monoclinic structure (at room temperature). This is illustrated in Fig. 5, with cation radius data from Shannon (1976). The carbonate structural type, which controls the cation coordination number, is determined by the cation radius. A rhombohedral structure is adopted when the cation radius is \(\sim 70\) to 100 pm, whereas the orthorhombic form occurs when the cation radius is larger. Calcium carbonate, uniquely, adopts both structural forms, as calcite (rhombohedral) and aragonite (orthorhombic). The cation radius in CuCO\(_3\), which is monoclinic, is only 65 pm. It is noteworthy that, if a \(\Delta^{17}\)O value of close to \(-0.40\) ‰ for FeO is most appropriate for comparison with the other metal oxide examples produced using the same experimental facility and procedure (as discussed in Section 4.1.1), this implies that siderite does not fit the pattern for rhombohedral carbonates as shown in Fig. 5. Unsurprisingly, there is no apparent relationship between the magnitude of \(\Delta^{17}\)O in the solid oxides and the corresponding \(\delta^{18}\)O value. For completeness, this is shown in Fig. 6.

\(^2\) The smaller \(\delta^{18}\)O shift coincided with the lack of melt formed during laser-assisted fluorination of the solid oxide. A similar finding was observed during fluorination of one of the strontium oxide grains.
A puzzling feature of the relationship illustrated in Fig. 5 is that, for several of the carbonate minerals, it has been documented that the crystallographic form changes at elevated temperature. Aragonite undergoes transformation to the calcite structure at ~ 480–500 °C (Rao et al., 1975; Yoshioka and Kitano, 1985; Okumura et al., 2018), with the actual temperature varying with the nature and amount of impurities present. The presence of small amounts of Sr stabilises the aragonite phase, whereas biogenic examples usually transform to calcite at lower temperatures (Yoshioka and Kitano, 1985). The phase transition occurs at lower temperatures than required for the commencement of thermal decomposition, so it is feasible that the aragonite specimen heated in our investigation may have fully transformed to calcite before any release of CO₂ occurred. However, during TGA/EGA analysis, maximum CO₂ release was at 652 °C, lower than the 687 °C observed for the calcite example at the same heating rate. Furthermore, the Δ¹⁷O values of the resulting CaO were different.

The two most thermally stable carbonates included in this investigation, BaCO₃ and SrCO₃, are also known to transform at high temperature to rhombohedral structures. The respective transitions (for the pure compounds) have been reported as occurring at 803 °C (Okumura et al., 2018; Arvanitidis et al., 1996) or 806 °C (Lander, 1949) in BaCO₃ and at 912–924 °C (Rao et al., 1975; Lander, 1951) in SrCO₃. These transformations have been attributed to the onset of rotational disorder in the CO₃²⁻ ions (Lander, 1951). BaCO₃ additionally undergoes a higher temperature transformation, at 964–976 °C (Okumura et al., 2018; Arvanitidis et al., 1996; Lander, 1951), to a cubic (halite) structure, cation coordination number 8.

Conversely, quantum chemical modelling of the thermal decomposition of magnesite have shown that a structural phase transition from the rhombohedral form to a chiral orthorhombic structure occurs during the thermal decomposition process (Zhao et al., 2015).

For the aragonite group carbonates, the mean C–O distance and O–C–O bond angle increase linearly with unit cell volume, whereas the aplanarity of the CO₃²⁻ group (defined by the distance of the C atom from the plane formed by the three O atoms) decreases (Antao and Hassan, 2009). The CO₃²⁻ group thus becomes more symmetrical (C–O distances nearly equal) and less aplanar as the cation radius increases, i.e. in the progression Ca < Sr < Pb < Ba (aragonite to witherite). Thus, the aragonite structure is the most distorted,
whereas that of witherite is the least distorted, in terms of the geometry of the CO$_3^{2-}$ group (Antao and Hassan, 2009). Furthermore, the symmetry of a carbonate anion containing either one $^{17}$O or $^{18}$O atom differs from that containing only the major isotope, $^{16}$O.

Of the nine elements represented as cations in the various carbonate specimens used for this investigation, we note that only one is monoisotopic ($^{55}$Mn). Furthermore, the nucleus has non-zero spin (5/2). The two stable isotopes of copper, $^{63}$Cu and $^{65}$Cu, also have spin-active nuclei (3/2). All the other cations have more than two stable isotopes; furthermore, spin-active nuclei are present at only minor or trace abundances, as shown in Appendix A, Table A.2, compiled from literature data. The relatively large difference between the $\Delta^{17}$O values of MnO and CuO formed from thermal decomposition of the respective carbonates (as shown in Fig. 5) indicates that the abundance of spin-active nuclei in the metal cation is not influential in determining the $\Delta^{17}$O value of the metal oxide.

5.2. Non-photochemical processes associated with anomalous $\Delta^{17}$O values

Only a small number of non-photochemical processes that generate mass-independent oxygen isotopic distributions have been reported. Thermal dissociation of ozone at 110 °C (Wen and Thiemens, 1991) is one example, with the $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios changing by an equal amount. Perhaps the most surprising finding is that reported by Sun and Bao (2011a, 2011b), who showed that the diffusion, at low pressure, of molecular O$_2$ gas in a closed volume defies mass-dependent isotopic distributions when a thermal gradient is applied. It was postulated (Sun and Bao, 2011b) that a – usually negligible – nuclear spin effect on the gas diffusion coefficient may be largely responsible, amplified by the temperature gradient. As noted by those authors, such an effect had been predicted from theoretical considerations some 35 years earlier (Zel’dovich and Maksimov, 1976). We are unconvinced, however, by the suggestion (Sun and Bao, 2011a; 2011b) that their finding may be relevant to explaining the isotopic anomaly generated by thermal decomposition of calcium and magnesium carbonates. In the carbonate decomposition experiments, the gaseous product CO$_2$ was continuously removed by vacuum pumping, or by cryogenic trapping to effect complete and quantitative gas transfer.
5.3. The thermal decomposition mechanism – overview

Whereas there have been numerous investigations of the thermal decomposition of divalent metal carbonates (especially of calcite) over many decades, details of the mechanism remain largely conjectural. Recent quantum chemical modelling of the thermal decomposition of calcite (Zhao et al., 2013) and magnesite (Zhao et al., 2015), involving detailed potential energy surface calculations, have explored the relative feasibility of different reaction pathways. These theoretical studies provide valuable information towards elucidating the decomposition mechanism at the molecular level. By comparing activation energy barriers and rate constants with experimental results, the energetically most favourable route was identified in both cases. When combined with relevant kinetic studies (Wang et al., 2017), the decomposition was shown to be consistent with a multi-step process and the identity of intermediate and metastable phases suggested. Much remains to be understood, however. The occurrence of a ‘mass independent’ oxygen isotopic fractionation during the thermal decomposition process provides further clues to establishing the details of the process.

In crystalline solids, it is excitations of low energy phonons across the Brillouin zone that determine the thermal free energies and thus isotopic fractionation factors. *Ab initio* calculations require that the three-dimensional potential energy surface and vibrational frequencies be defined, and at sufficiently high resolution to discriminate between different isotopes. This is impractical, as the associated computational and experimental requirements are too demanding. Furthermore, even if such a task was achievable, it has been shown that dissociation pathways do not always proceed via the ‘saddle point’ transition state on the potential energy surface. The first such report was on formaldehyde decomposition (Townsend et al., 2004), where a second trajectory was identified: this involved one H atom nearly detaching via the (energetically favourable) H + HCO channel, but lacking sufficient energy for complete dissociation. The H atom ‘roamed’ far from the main reaction path on the potential energy surface until it abstracted the other hydrogen atom, yielding vibrationally excited H\textsubscript{2} and rotationally ‘cold’ CO. Since that seminal discovery, numerous other examples of ‘roaming’ reactions have been identified. In a recent review (Suits, 2020), it was noted that the phenomenon has become recognised as being quite common, especially in unimolecular dissociations.
Typically, the process involves near-dissociation of a quasi-bound system to radical fragments, followed by reorientation at long range and intramolecular abstraction. This can lead to the formation of unexpected reaction products, amongst other characteristics. We are not aware, however, that ‘roaming’ during the decomposition of any crystalline solid has been investigated, to date.

Three processes which might be implicated in the unusual fractionation of oxygen triple-isotopes during carbonate thermal decomposition are:

- A particular combination of mass-dependent processes, or a kinetic process involving an unusual θ value (although explicable by established theory);
- Fermi resonance occurring during carbonate vibrational modes at the temperature of incipient decomposition and coincidentally leading to enhancement of the abundance of $^{17}$O in the released CO$_2$;
- A mechanism based on the magnetic isotope effect, but differing from that proposed by Buchachenko (2013).

We now consider these possibilities, in turn.

5.4. Could the $^{17}$O anomaly result from one or more mass-dependent processes?

It has been recognised for many years, from δ$^{18}$O measurements, that thermal decomposition of carbonates is associated with a kinetic isotope effect (Sharma and Clayton, 1965). Cartigny et al. (2012) suggested that the oxygen isotope anomaly reported by Miller et al. (2002) might be the result of a fortuitous combination of equilibrium exchange and kinetic fractionation processes, characterised by mass-dependent fractionation laws with different θ values, such that the combined effect is to mimic a mass-independent fractionation process across a wide range of isotopic compositions. The idea was illustrated schematically by Cartigny et al. (2012). Such a combination does seem implausible, however, as was subsequently acknowledged (Eiler et al., 2013). More recently, Yeung and Hayles (2021) argued, from a consideration of transition state theory, that $\theta_{A\rightarrow B}$ values associated with kinetic fractionation of oxygen triple-isotopes in chemical processes (reactant A → products B) are actually not bounded by any limits, in principle, and therefore may exceed the 0.5305 maximum that applies to equilibrium exchange. The authors noted that the
range of reported values, both measured and calculated, is therefore surprising; the absence of ‘anomalous’ kinetic $\theta_{A-B}$ values suggests that bounds on its value are ‘imposed by chemical and not mathematical’ limits. Yeung and Hayles (2021) suggested that the lower zero-point energy of isotopically substituted reactants may mitigate against the expression of anomalous reduced partition function ratios of the transition state values as anomalous kinetic isotope effects.

The only other report we are aware of in which oxygen triple-isotope fractionation during mineral thermal decomposition was investigated is that by Clayton and Mayeda (2009). In their study, the magnesian minerals brucite and serpentine, $\text{Mg(OH)}_2$ and $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ respectively, were thermally dehydrated in vacuum. Following brucite dehydration, conducted at 300°C, the $\delta^{18}\text{O}$ value of the released water was found to be about 15 ‰ lower than the brucite, whereas the MgO (periclase) also formed was correspondingly enriched in $^{18}\text{O}$. The brucite, periclase and released water fitted a fractionation line of slope 0.503 on a $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ plot\(^3\). For serpentine dehydration, conducted in steps from 100 to 600°C, a slope of 0.507 was obtained. These values are within the range for (mass-dependent) kinetic fractionation processes in the triple-isotope system as described by Young et al. (2002). We note that brucite dehydration essentially involves proton transfer between OH groups; it has been shown (Liu et al., 2018) to fit a first-order single reaction model for the main step (300–400 °C), whereas the diffusion of water molecules dominates at higher temperatures. This is accordingly quite different from the thermal decomposition of carbonates. Furthermore, unless the transition state in the carbonate thermal decomposition mechanism can be shown to cause such very different triple-isotope fractionation behaviour from that of the Young et al. (2002) kinetic model, leading to predicted kinetic $\theta_{A-B}$ values of ~0.60 or greater, it seems unlikely that our findings can be explained by such a possibility.

5.5. Fermi resonance

\(^3\) A noted by Clayton and Mayeda (2009), their correction for the significant ‘tailing’ of the $m/e$ 32 ion beam into the $m/e$ 33 collector may have been an underestimate, in which case the true values of the reported slopes would have been slightly greater.
Fermi resonance occurs when two different vibrational modes ($\nu_a$, $\nu_b$) of a molecule but belonging to the same symmetry species coincidentally overlap in their wavenumber values. In this case, the vibrational wavefunctions become hybridized, resulting in mixed vibrational states and excitations with new cm$^{-1}$ positions that lie slightly above and below the initially expected values. The higher frequency component is typically the fundamental vibration of the molecule, whereas the second is often an overtone or combination band. The case was classically described for molecular CO$_2$, where the symmetric stretching ($\nu_1$) vibration with an unperturbed frequency estimated as 1337 cm$^{-1}$ is nearly twice that of $\nu_2$ (667 cm$^{-1}$). Because both have the same symmetry, they couple to give new frequencies slightly above or below these initial values, depending on the pressure and temperature conditions and whether the molecules are in a gaseous or condensed state. Because these vibrational frequency changes – although small – affect the thermal free energy of the molecules, they also influence the isotopic fractionation factors for reactions that involve them. Different Fermi resonance situations are exhibited by solid carbonates. In a Raman and infrared spectroscopic study of aragonite-strontianite (Ca$_{x}$Sr$_{1-x}$CO$_3$) solid solutions (Alía et al., 1997), it was suggested that infrared spectral data were consistent with an overtone 2$\nu_4$ band being in Fermi resonance with the corresponding $\nu_3$ fundamental.

In calcite, $\nu_3$ occurs at 1432 cm$^{-1}$, which is very close to twice the $\nu_4$ frequency of 714 cm$^{-1}$. Similarly, in strontianite, twice the frequency of the $\nu_4$ line at 704 cm$^{-1}$ is close to the $\nu_3$ line at 1400 cm$^{-1}$. In cerussite, the corresponding values are 685 cm$^{-1}$ and 1369 cm$^{-1}$. The positions of the infrared and Raman bands for a free carbonate group, together with those for calcite and the orthorhombic carbonates aragonite, strontianite, witherite and cerussite, are illustrated in Fig. 31 of Speer (1983). These correspond to the observed rather than the uncoupled values that would be predicted before the occurrence of any Fermi resonance. It has already been demonstrated that changes in the vibrational frequencies of the internal and external modes of calcite associated with oxygen isotopic substitution occur and are likely to persist to high temperature, with effects on isotopic fractionation factors (Gillet et al., 1993; Gillet et al., 1996). It is therefore plausible that Fermi resonance effects occurring during vibrational excitation at the thermal decomposition temperatures of
metal carbonates could influence the oxygen triple-isotope compositions of the decomposition products. This possibility remains to be tested experimentally (see Section 5.9).

5.6. The Magnetic Isotope Effect and evaluation of the Buchachenko (2013) hypothesis

The occurrence of the magnetic isotope effect was postulated by Lawler and Evans (1971), although initially its magnitude was considered to be negligible. It involves the formation of an ion-radical pair, the lifetime of which is sufficient for hyperfine coupling between spin-active nuclei and unpaired electrons to influence interconversion between the electronic singlet and triplet states of the pair. Such spin-state mixing changes the proportion of reactive intermediates that can participate in spin-selective reactions. Empirical findings compatible with such a mechanism were described by Buchachenko et al. (1976). During the following four decades, numerous other examples have been documented, involving spin-active nuclei of various elements (Buchachenko and Lawler, 2017). Salikhov (1996) gives a comprehensive introduction to the concept and theory. Unlike the nuclear field shift effect, which acts both at equilibrium and in kinetically hindered reactions (by changing activation energies in the latter case), magnetic isotope effects are purely kinetic, affecting the rates of formation and branching ratios of possible reaction products (Dauphas and Schauble, 2016). In support of a magnetic isotope effect mechanism being responsible for the experimental findings we report here, we note that Miller et al. (2002) showed that when the thermal decomposition products of NBS 18 calcite were characterised by a δ^{18}O value almost identical (within 0.1‰) to that of the parent carbonate, the corresponding δ^{17}O values of the CaO and CO\textsubscript{2} differed from each other by 0.40 ‰. This indicates that the mechanism responsible must involve a specific characteristic of {^{17}O} that is not associated with {^{18}O}. The non-zero nuclear spin of {^{17}O} (value 5/2) is such a characteristic.

Whereas most investigations of the magnetic isotope effect have involved radical pair reactions in the liquid phase (notably in solution) and have established a strong viscosity dependence that mediates the lifetimes of the cage radicals, solid state examples have been documented. For example, Turro et al. (1985) showed that partial photolysis of solid dibenzyl ketone adsorbed on porous silica generates anomalous enrichment of {^{17}O} and {^{13}C} in the residual ketone. Silicon oxidation by oxygen (Koplak et al., 2013) provides another example, with {^{29}Si} (nuclear spin 1/2, nuclear magnetic moment 0.555) being oxidised twice as
rapidly as $^{28}$Si and $^{30}$Si. It is worth also highlighting that magnetic field effects, which also share essentially the same mechanism of spin-state mixing in spin-correlated radical pairs and spin-selective reaction, are numerous and have been well studied in many solid state reactions. In such cases, electrons and ‘holes’ migrate, rather than the radicals themselves, and are often referred to as bipolaron pairs.

The Buchachenko (2013) hypothesis to explain the $^{17}$O anomaly associated with thermal decomposition of divalent metal carbonates is based on carbonate decomposition proceeding via thermal generation of a short-lived ion-radical pair in the singlet spin-state, with the metal ion being reduced to univalency. With calcium as the cation, for example,

$$\text{Ca}^{2+}\text{CO}_3^{2-} \rightarrow (\text{Ca}^{+}\text{CO}_3^{-})^S$$ (8)

In the case of $^{17}$O, this singlet born radical pair can undergo coherent singlet-triplet spin-state mixing to generate the triplet radical pair, driven by the hyperfine coupling to the $^{17}$O nucleus (while this does not occur in zero applied magnetic field in the case of $^{16}$O or $^{18}$O, as those nuclei have zero spin).

$$(\text{Ca}^{+}^{17}\text{OCO}_2^{-})^S \leftrightarrow (\text{Ca}^{+}^{17}\text{OCO}_2^{-})^T$$ (9)

Back electron transfer to regenerate the carbonate is spin-selective, taking place only from the singlet state radical pair:

$$(\text{Ca}^{+}\text{CO}_3^{-})^S \rightarrow \text{Ca}^{2+}\text{CO}_3^{2-}$$ (10)

$$\text{Ca}^{+}\text{CO}_3^{-})^T \rightarrow \text{Ca}^{2+}\text{CO}_3^{2-}$$ (11)

Buchachenko considers the forward reaction of triplet pairs in which the CO$_3$– anion-radical undergoes fast β-scission of a C–O bond as follows:

$$(\text{Ca}^{+}^{17}\text{OCO}_2^{-})^T \rightarrow ^{17}\text{OCO} + (\text{Ca}^{+}^{\cdot})^T$$ (12)

Back electron transfer in the Ca$^+^{\cdot}$ generates the oxide product. Buchachenko implies that all singlet radical pairs will re-combine and all triplet radical pairs will produce the oxide product. A more detailed presentation would also include the fact that the product can be formed from the singlet state radical pair and that this reaction also competes with back electron transfer:

$$(\text{Ca}^{+}^{17}\text{OCO}_2^{-})^S \rightarrow ^{17}\text{OCO} + (\text{Ca}^{+}^{\cdot})^S$$ (13)
However, this subtlety only qualitatively reduces the size of the effect and is not problematic for the mechanism. Nevertheless, it is important to recognise that, in this proposed mechanism, reaction (13) represents the only decomposition channel for those carbonate anion radicals which contain no $^{17}$O. It is the spin-selective back electron transfer to the carbonate that is important in determining the differing reactivity of singlet and triplet radical pairs.

Note that the ‘forbidden’ route of back electron transfer from the triplet state radical pair in step (12), which would re-generate CaCO$_3$, means that the overall lifetime of the radical pair is increased. Under conditions of continuous radical pair formation (as we have here), the concentration of radical pairs at any given time increases, leading to an increased production rate of C$^{17}$CO + CO$^{17}$O and Ca$^{17}$O. The presence of $^{17}$O ‘switches on’ coherent S-T mixing, which reduces regeneration of the original CaCO$_3$ from back electron transfer. Thus, the overall decomposition is faster than for the $^{18}$O-containing isotopomer. In the latter, some pairs now become triplet; these are more likely to react rather than re-generate CaCO$_3$.

Finally, Buchachenko concludes that reaction (12) will cause the CO$_2$ to become anomalously enriched in $^{17}$O whereas the Ca$^{2+}$O$_2^-$ becomes correspondingly depleted. At first sight, this mechanism seems plausible. However, more careful inspection reveals that it is actually incapable of explaining our experimental observations. The problem lies in step (12) and is an artefact of ordering the symbols in a particular way, implying that somehow in the triplet reaction channel, $^{17}$O will only be present in the carbon dioxide formed, not in the metal oxide. Step (12) actually represents three different possibilities:

$$ (\text{Ca}^+\text{OC}^{17}\text{OO}^-)^T \rightarrow \text{OC}^{17}\text{O} + (\text{Ca}^+\text{O}^-)^T \quad (14) $$

$$ (\text{Ca}^+\text{OC}^{17}\text{O}^-)^T \rightarrow \text{OC}^{17}\text{O} + (\text{Ca}^+\text{O}^-)^T \quad (15) $$

$$ (\text{Ca}^+\text{OC}^{17}\text{O}^-)^T \rightarrow \text{OC}^{17}\text{O} + (\text{Ca}^+^{17}\text{O}^-)^T \quad (16) $$

All three radical pairs are identical and so would undergo singlet-triplet state mixing at the same rate. The mechanism does not propose that these subsequent reactions show any difference in rate (i.e., they are not spin-selective steps) and therefore the proposed mechanism does not lead to any $^{17}$O enrichment in the CO$_2$ or depletion in the Ca$^{2+}$O$_2^-$. The triplets in reactions (14) to (16) could all be replaced by the corresponding
singlet states, and all occurrences of $^{17}\text{O}$ replaced by $^{18}\text{O}$, yet these three reactions would still take place at the same rate (neglecting any kinetic isotope effect), as this is a two-electron spin-independent process.

Does the Buchachenko mechanism still predict a MIE? The answer is ‘yes’, it predicts that singlet-triplet state mixing takes place in the $^{17}\text{O}$-containing carbonate isotopomer, but not in the other isotopomers. This implies that, during thermal decomposition, carbonate containing $^{17}\text{O}$ will decompose faster than carbonate which does not contain $^{17}\text{O}$. The effect of this would be that, after partial decomposition, the resulting metal oxide and carbon dioxide would both be relatively enriched in $^{17}\text{O}$, whereas the residual carbonate would be correspondingly depleted in $^{17}\text{O}$. However, if carbonate decomposition proceeds to completion (as in our experiments), neither of the decomposition products would contain a $^{17}\text{O}$ anomaly, regardless of whether or not singlet-triplet mixing had taken place (i.e., there would be no evidence of MIE involvement). The mechanism proposed by Buchachenko (2013) therefore cannot be a correct description of the thermal decomposition of any of the carbonates we investigated, as its ‘true’ outcome is not in accord with our experimental findings.

5.7. A new MIE-based hypothesis to explain the $^{17}\text{O}$ anomaly

What is clear from the problem with the Buchachenko mechanism is that, in order to have a radical pair-based mechanism that causes the observed oxygen triple-isotope distributions in the two reaction products, the spin-state mixing rate must differ between radical pairs that can selectively generate these two products. Additionally, there are two further key features that any plausible mechanism must possess. The first is that the mechanism must generate a difference in yield of products in which the $^{17}\text{O}$ appears (the metal oxide or the carbon dioxide), rather than just a difference in their rates of production. The second is that the mechanism must also be able to explain how the radicals in the pair become sufficiently separated such that the electron exchange interaction becomes similar to – or negligible – relative to the size of the hyperfine coupling. This condition is necessary to observe coherent radical pair spin effects. We propose a new radical pair-based mechanism that fulfils these criteria and predicts $^{17}\text{O}$ enrichment in the carbon dioxide and depletion in the metal oxide, consistent with the experimental findings and the magnetic properties of the proposed intermediate radicals. We then consider the plausibility of this mechanism, based on other studies.
of the mechanism of carbonate decomposition and the results of magnetic field effect measurements. Finally, we propose a diagnostic test.

The first important postulate of the mechanism is that, when strongly heated, the carbonate ions are vibrationally excited and capable of undergoing vibrational dissociation (into O \(^{-}\) and CO\(_2\) \(^{-}\)). For this to have any consequence, however, there must be somewhere in the lattice structure for one of the resulting fragments to move to, otherwise the energy is distributed and the bond reforms. Thus, the first step of the mechanism is to consider the diffusion of defect sites in the crystalline lattice to a position adjacent to the dissociating carbonate ion. With a lattice vacancy available, we propose that the carbonate ion undergoes homolytic cleavage of one of the C–O bonds, generating a radical pair which consists of O \(^{-}\) and CO\(_2\) \(^{-}\), with the latter having occupied the vacancy, causing a separation of the two radicals. As the carbonate ion remains in the singlet ground electronic state (the temperature is not high enough for significant electronic excitation), the spatially separated radical pair is generated in the singlet state:

\[
\text{CO}_3^{2-} + \text{‘vacancy site’} \rightarrow (\text{O}^{-}\text{CO}_2^{-})^S
\]  

If neither member of the radical pair contains \(^{17}\text{O}\) (or \(^{13}\text{C}\)), no hyperfine coupling is possible and so, in zero field, no coherent spin-state mixing to the triplet state of the radical pair can occur. The fate of such radical pairs is either to re-form the carbonate ion, or for electron transfer to take place from the CO\(_2\) \(^{-}\) to O \(^{-}\), generating the metal oxide and carbon dioxide. The CO\(_2\) then diffuses through the lattice and escapes once it reaches the surface. However, if the carbonate ion contains \(^{17}\text{O}\), there are now three possible arrangements, leading to two different radical pairs by reaction (17):

\[
\begin{align*}
^{17}\text{OCOO}^2- & \rightarrow (^{17}\text{O}^{-}\text{COO}^-)^S \\
\text{OC}^{17}\text{OO}^2- & \rightarrow (\text{O}^{-}\text{C}^{17}\text{OO}^-)^S \\
\text{OCO}^{17}\text{O}^2- & \rightarrow (\text{O}^{-}\text{CO}^{17}\text{O}^-)^S
\end{align*}
\]

The radical pairs produced by reactions (19) and (20) are identical. As above, both radical pairs can undergo bond reformation from the singlet state only, to regenerate the original carbonate:

\[
\begin{align*}
(\text{O}^{-}\text{CO}_2^-)^S & \rightarrow ^{17}\text{OCOO}^2^- \\
(\text{O}^{-}\text{C}^{17}\text{OO}^-)^S & \rightarrow \text{OC}^{17}\text{OO}^2-
\end{align*}
\]
which can dissociate again via any of reactions (18) – (20). This step is critical, as it allows interconversion between the two types of radical pair, which is necessary for a yield effect rather than solely a kinetic effect. Also, as above, electron transfer (which is also spin-selective, occurring only from the singlet state) can generate the reaction products:

\[(^{17}\text{O}^-\cdot\text{CO}_2^-)^S \rightarrow ^{17}\text{O}^+ + \text{CO}_2\]  \hspace{1cm} (23)

\[(O^-\cdot\text{C}^{17}\text{OO}^-)^S \rightarrow O^+ + \text{C}^{17}\text{OO}\]  \hspace{1cm} (24)

However, in the $^{17}\text{O}$ case, these radical pairs can both undergo coherent spin-state mixing to the triplet state, due to the hyperfine coupling to the $^{17}\text{O}$:

\[(^{17}\text{O}^-\cdot\text{CO}_2^-)^S \leftrightarrow (^{17}\text{O}^-\cdot\text{CO}_2^-)^T\]  \hspace{1cm} (25)

\[(O^-\cdot\text{C}^{17}\text{OO}^-)^S \leftrightarrow (O^-\cdot\text{C}^{17}\text{OO}^-)^T\]  \hspace{1cm} (26)

While it may be possible from the triplet state of these radical pairs for the CO$_2^-$ to revert back to its original oxide partner and become trapped there if the vacancy escapes (and ultimately to regenerate the carbonate ion after spin relaxation), the electron transfer (i.e. the forward reaction) is spin-forbidden. As a result, the triplet radical pair cannot generate the decomposition products. Fig. 7 shows the overall kinetic scheme with no isotope distinction, whereas Fig. 8 provides an exhaustive representation in the case of $^{17}\text{O}$, to highlight the two different possible radical pairs.

The critical steps, then, are the singlet-triplet mixing reactions (25) and (26) and the spin selective forward electron transfer reactions (23) and (24). The latter occur at the same rate, so the MIE arises due to a difference in the efficiency of the coherent spin-state mixing in reactions (25) and (26). If (25) is more efficient than (26), then the ($^{17}\text{O}^-\cdot\text{CO}_2^-$) radical pair will be more likely to undergo spin-state mixing and less likely to proceed to products than the (O$^-\cdot$ C$^{17}$OO$^-$) pair. This would lead to the carbon dioxide being enriched in $^{17}$O and the metal oxide being depleted. If (26) is faster than (25), then the opposite is true, and the carbon dioxide will be depleted in $^{17}$O, whereas the metal oxide will be enriched.

Based on the experimental findings (i.e. that the carbon dioxide is unusually enriched in $^{17}$O whereas the metal oxide is correspondingly depleted in $^{17}$O, not vice versa) then, for this mechanism to be correct, the spin-state mixing in the ($^{17}\text{O}^-\cdot\text{CO}_2^-$) radical pair should be faster than in the (O$^-\cdot$ C$^{17}$OO$^-$) pair (and not
vice-versa), which suggests that the hyperfine coupling to $^{17}\text{O}$ in the $^{17}\text{O}^-$ radical ion should be greater than the hyperfine coupling in the $^{17}\text{OO}^-$ radical. It might be anticipated that this would be true, given that, in the $^{17}\text{OO}^-$ radical, the electron is delocalised and thus has less spin density on the $^{17}\text{O}$ atom than in $^{17}\text{O}^-$, although the ‘s’ character of the orbitals involved is also very important. In practice, this can be confirmed by existing measurements and calculations to determine the $^{17}\text{O}$ hyperfine coupling in these two species.

Blondel et al. (2001) determined the hyperfine structure of the $^{17}\text{O}^-$ radical ion, using photodetachment microscopy, as 151 MHz (5.4 mT), whereas Chiesa and Giamello (2007) measured the $^{17}\text{O}$ hyperfine coupling in the $^{17}\text{OO}^-$ radical to be 102.2 MHz (3.7 mT), from EPR spectra of this radical on the surface of MgO. The correct relative magnitudes, together with the fact that both proposed radical species have been observed experimentally, provides credible support for our proposed mechanism.

Further support for such a mechanism is provided by its compatibility with recent studies of the thermal decomposition of calcite (Zhao et al., 2013; Wang et al., 2017; Li et al., 2018) and magnesite (Zhao et al., 2015). In these investigations, the decomposition mechanism was found to proceed via the reaction sequence (using MgCO$_3$ as the example; Zhao et al., 2015):

$$\text{MgCO}_3 \rightarrow (\text{MgO})\text{CO}_2 \rightarrow \text{MgO} + \text{CO}_2$$ (27)

Quantum chemical calculations were used to examine the energies of the different possible intermediate geometries after cleavage of the one of the carbonate C–O bonds, to generate the intermediate indicated in reaction (27). Their findings are consistent with the formation of a radical pair via homolytic cleavage, as we propose. As discussed in those papers, the decomposition of calcite and magnesite (and, by extension, the other metal carbonates under consideration) proceeds via a complex mechanism which involves chemical bond breaking, lattice destruction and formation and absorption, desorption and diffusion of gaseous

---

4 Hyperfine coupling constants are reported in the literature as a frequency (usually in MHz) or magnetic flux density (usually in milliTesla or Gauss, where 1 mT = 10 G). Conversion between MHz and mT values is given by the Larmor precession relationship:

$$f = 10^{-9} \frac{\mu_B g}{h} B$$

where $\mu_B$ is the Bohr magneton, $g$ is the free electron g-value and $h$ is Planck’s constant.

Substitution of numerical values gives, for a magnetic flux density of 1 mT, a frequency of: $(10^{-9} \times 2.00232 \times 9.27401 \times 10^{-24})/(6.62607 \times 10^{-34}) = 28.025$ MHz.
products, among other complications (Zsakó, 1968). Our proposed mechanism represents a simple overview of the chemical reaction occurring and, while relying on the generation or movement of lattice vacancies, does not address the detailed mechanism of how the lattice changes or how the carbon dioxide moves through and escapes from it. However, if our proposed MIE mechanism is indeed the correct explanation of our experimental measurements, then it carries some broad implications for the decomposition mechanism.

5.7.1. Time and length scales for radical pair reactions

In order to manifest magnetic field and isotope effects, radical pair reactions must meet two key requirements. The first is that the individual radicals comprising the pair must separate to sufficient distances to allow hyperfine coupling-driven coherent spin-state mixing before spin-selective reaction. The second is that they must remain at these separations long enough for the spin-state mixing process to have a measurable effect. The former is because the electron exchange interaction, which drops very rapidly with the separation of the members, completely overwhelms the hyperfine coupling and stops coherent spin-state mixing when the radicals are close together. Typically, radical pair constituents need to be at least 5-8 Å apart for appreciable spin-state mixing to be possible (and even further apart for optimal mixing). In the case of the latter, based on publications mentioned above, the difference in hyperfine coupling of the two radicals is of the order of 50 MHz (1.8 mT) which, given that the nuclear spin of $^{17}$O is 5/2, requires the radical pair lifetime to be of the order of nanoseconds to tens of nanoseconds, in order to produce an appreciable difference between the pairs. Both these facts are accounted for by the need for lattice vacancies to allow the C–O bond dissociation to take place completely and generate a separated radical pair, allowing spatial configurations where the spin-state mixing is possible and where back electron transfer to form products is still sufficiently rapid. One can imagine other variants of this general mechanism, which cannot easily be distinguished on the basis of an isotope effect alone. For example, the process might be restricted to being a surface effect, with bond-breaking occurring on the lattice surface rather than in an embedded vacancy. Such intricacies are beyond the scope of this initial mechanistic proposal. What is important is that the radical pair can only undergo coherent spin-state evolution at appropriate spatial separation of the individual radicals.
In order to confirm that the mechanism highlighted in Fig. 8 can produce the observed isotope effect, simple kinetic simulations were performed in which spin-state mixing was treated approximately as a simple, first-order rate process, with a rate coefficient equal to the hyperfine coupling (in frequency units). These simulations – using code written in MATLAB™ – were performed by expressing the reaction scheme in Fig. 8 as a series of first order linear differential equations in matrix form and using matrix exponentiation to obtain the time propagator. The time dependence of the principal species was then determined, using a time step of 1 ns. The simulations produced a clear yield effect on the reaction, resulting in $^{17}\text{O}$ enrichment in the CO$_2$, consistent with the experimental findings. Fig. 9 shows an example simulation for a particular set of kinetic parameters. Depending on the various rate coefficients, the magnitude of the enrichment can be controlled and the overall rate matched to the actual decomposition timescale. Most combinations of parameters will produce much smaller effects than the example provided here. Furthermore, in conventional MIEs, the effect can be large as the magnetic isotope ‘switches on’ spin-state mixing in the pair relative to other nuclei where no spin-state mixing takes place. In this mechanism, the effect arises due to the reactions of two different radical pairs which both contain $^{17}\text{O}$ and which both undergo coherent spin state mixing. The effect arises only due to differences in the efficiency of the mixing in otherwise very similar radical pairs (based on the small difference in their hyperfine coupling), leading to much smaller effects than in conventional kinetic MIEs.

5.7.2. Experiments to test a MIE-based mechanism and their consequences for this new mechanism

As discussed above, we conducted two specific tests of the Buchachenko MIE mechanism. The first was the oxygen isotopic measurements on copper (II) carbonate thermal decomposition products. In the Buchachenko mechanism, one radical pair member is the metal cation in univalent state. In the case of Cu$^+$, this has no unpaired electron and thus the Buchachenko mechanism predicts that the MIE should not occur in this particular example. In the new mechanism, however, no univalent metal ion is formed and the metal cations are not generally involved directly in the steps of the decomposition reaction. On this basis, there is no reason to suggest that the anomalous isotope effect would be different in the case of copper (II) carbonate...
thermal decomposition, which is consistent with the experimental findings. The potential influence of the divalent metal ion in our proposed mechanism is discussed below.

The second test was to investigate the effect of an applied magnetic field of ~0.25 T during the thermal decomposition reaction, using siderite as the carbonate example. Applying the magnetic field produced no effect on the oxygen triple-isotope ratios in the resulting FeO. However, this does not exclude the possibility that different values of magnetic flux density might have an effect. It is also worth noting that, in all the other experiments conducted for this investigation (with no magnetic field applied), samples would still have experienced a local (and small) magnetic field, generated by the electrical current flowing through the helical heating coil of the surrounding tube furnace. The upper limit of the magnitude of this magnetic field is estimated to have been about 3 mT, at the highest temperatures.

We note that some of the experiments discussed in the initial report (Miller et al., 2002) were performed using an infrared (10.6 μm) laser instead of a heating coil for the carbonate heating process; this would have been associated with a magnetic field much closer to zero. In those experiments, which involved carbonates of Ca and Mg only, anomalous $^{17}$O depletion occurred in the resulting metal oxides, but to a lesser extent than when using a tube furnace as the heat source. The observed difference may or may not be significant in the present context. An additional complication is that the laser heating was conducted over a much shorter period (1–2 hours, rather than several days as when heating by tube furnace), which was probably influential. In summary, a $^{17}$O anomaly was produced in all the carbonate thermal decomposition experiments, regardless of whether the heating was conducted in (almost) zero magnetic field, or in fields of a few mT, or ~250 mT.

In the case of the new hypothesis as proposed here, there are three different mechanisms that may be important to consider, for magnetic fields in the range of 0 to 0.25 T. The first is the electron Zeeman effect. It can be considered – to a first approximation – that an applied magnetic field would serve to reduce the spin-state mixing efficiency by two-thirds in the radical pairs. In zero field, the singlet state can mix with all three triplet states, whereas in high field, two of the triplet states are energetically inaccessible due to the electron Zeeman effect. Unlike ‘conventional’ MIEs, which would see a magnetic field effect increase /
decrease and then saturate at high field, in our proposed mechanism it is the relative response of the two radical pairs which is important. This means that changes due to an applied field should be manifest when the two pairs behave most differently. This corresponds to the field region where the gradient of the conventional field effect is maximum – i.e. above zero field and less than field strengths at which the Zeeman effect is saturated. Secondly, there might be an opposite effect of increasing the spin-state mixing efficiency at weaker fields, due to the so-called low field effect (LFE), as discussed by Woodward (2002) and by Timmel and Henbest (2004). This will be manifest at fields strengths of a few mT or less. A third possible effect that might be manifest is due to an increase in spin-state mixing resulting from more rapid mixing between the S and T₀ states due to a difference in g-values of the two radicals comprising the pair. The difference in g-values will be identical for the two different radical pairs and so will give an equal increase in the S–T₀ mixing rate for both radical pairs; this could also influence the size of the observed MIE. Typical g-values for oxygen-centred radicals are somewhat larger than for typical carbon-centered radicals and, if large enough, this might influence the size of the MIE at magnetic fields of 250mT and more. It is clear from the complexity and overlapping nature of these mechanisms that, without an appropriate simulation, it is difficult to predict how an applied magnetic field might influence the magnitude of the MIE. In addition, as explained, the effect arises from the way in which a magnetic field affects the two ¹⁷O-containing radical pairs differently, which also makes simple estimation difficult.

In order to properly investigate the effect of an applied magnetic field on the magnitude of ¹⁷O enrichment (or depletion), detailed spin-dynamic simulations have been conducted for this study, based on the kinetic model shown in Fig. 9. The details of these simulations are beyond the scope of this article and will be presented elsewhere. Early results, however, suggest that an applied magnetic field in the range of a few tens of mT would increase the magnitude of the ¹⁷O anomaly and therefore making such a measurement would be a good diagnostic test for this new magnetic isotope effect-based mechanism. The reason that the magnetic field effect is not manifest at 250 mT in this case may be due to saturation of the Zeeman effect and the fact that both radical pairs have had their singlet-triplet mixing efficiency reduced by the same ratio. At weaker fields, however, the magnetic field affects the two radical pairs differently for the same magnetic
field value, leading to a magnetic field effect in the field range of mT to tens of mT, as preliminary simulations suggest.

Some of the metal cations (Cu$^{2+}$, Mn$^{2+}$, Fe$^{2+}$) have non-zero spin electronic ground states. This begs the question of whether this would influence the magnitude of the enrichment. Whereas paramagnetic ions may induce incoherent spin relaxation in the adjacent radical pairs through modulation of the dipolar interaction, the effect at zero field is not well understood. In addition, the magnitude of any influence will depend on the detailed kinetic parameters of the reaction and may be negligible. Therefore, without much more detailed information, it is difficult to make any reasonable prediction about the extent to which it might affect the proposed mechanism.

With regard to the potential effect of the crystallographic structure on the magnitude of the effect, this may influence the availability and separation of vacancies which could potentially influence the size of the observed effect, but any clear correlation would require a much more detailed picture of vacancy behaviour in these materials as decomposition takes place.

5.8. Cosmochemical implications

Thermal decarbonation of carbonates in nature, despite occurring on a large scale at subduction zones and during high grade metamorphism in the Earth’s crust, invariably proceeds under conditions which facilitate oxygen isotope exchange with hydrous fluids or melts. Therefore, any anomalous $^{17}$O depletion in the condensed phase would be transient. However, our findings may be of relevance in a cosmochemical context. The reported detection of calcite associated with amorphous silicates in two planetary nebulae (Kemper et al., 2002) and protostars (Ceccarelli et al., 2002; Chiavassa et al., 2005) devoid of planetary bodies, together with the experimental demonstration that carbonates can be formed with amorphous silicates during the non-equilibrium condensation of a silicate gas in a H$_2$O-CO$_2$-rich vapour (Toppani et al., 2005), suggests that thermal processing of such material may provide a mechanism for the mass-independent fractionation of oxygen isotopes in protoplanetary systems. We note that the magnitude of the change in $\Delta''^{17}$O associated with the transition from carbonate to divalent metal oxide, as reported above, is of the order of the $\Delta''^{17}$O difference between bulk silicate Earth and Mars; the latter is characterised by a $\Delta''^{17}$O value of
0.305 ± 0.004 ‰, standard error (Franchi et al., 1999), if reported using the definition of $\Delta^{17}O$ ($\lambda_{RL} = 0.524$ and $\gamma_{RL} = 0$ in Eq. (6)) as adopted throughout this paper. For comparison, carbonate extracted from meteorite ALH84001, believed to be of Martian origin, is characterised by a $\Delta^{17}O$ value of 0.74 ± 0.05 ‰ (recalculated from Farquhar et al., 1998).

In contrast to thermal processing of carbonates and with hyperfine coupling of $^{17}O$ postulated, Haberkorn et al. (1977) suggested that hyperfine modulated radical recombination may occur in a cosmochemical context on interstellar grain surfaces, leading to isotopic enrichment of spin-active isotopes such as $^{17}O$ in the molecules formed.

5.9. Suggestions for further investigation

For further investigation of the unusual isotope effect, reducing the $\Delta^{17}O$ variations between replicate decompositions of the same carbonate mineral is a principal requirement. Use of a constant heating rate for all specimens, whilst continuing to minimise the potential for oxygen isotope exchange between the thermal decomposition products, could improve data consistency and comparability. Thermal decomposition at constant heating rate in a helium flow (Sharp et al., 2003), with trapping of the evolved CO$_2$, may be an effective alternative to heating in vacuo. Such refinements, leading to more precisely defined $\Delta^{17}O$ values, would strengthen – or refute – the apparent relationship between carbonate crystallographic structure and the magnitude of $\Delta^{17}O$ in the thermal decomposition products. In addition, testing whether the magnitude of the isotopic anomaly in individual examples exhibits a magnetic field dependence when the flux density is a few tens of mT provides a means of validating (or refuting) the MIE-based hypothesis presented in this paper.

Detection of electron paramagnetic resonance (EPR) signals from a carbonate sample undergoing thermal decomposition would provide definitive evidence for the presence of radicals. Conversely, however, the absence of EPR signals would not unambiguously demonstrate that radicals are not being produced; the short lifetimes ($10^{-9}$ to $10^{-7}$ s) of the radicals would make them difficult to detect by either continuous wave EPR with field modulation or by pulsed EPR. Under quasi ‘steady state’ conditions of carbonate thermal decomposition, the number of radicals present would not be expected to be large.
Future investigations might also include other divalent carbonate mineral examples, such as otavite (CdCO$_3$) and spherocobaltite (CoCO$_3$), both of which are rhombohedral; possibly laboratory reagent examples of other divalent metal carbonates too – for which it would be prudent to conduct oxygen triple-isotope measurements of the released CO$_2$ in addition to those of the metal oxide. This is in case oxidation by air O$_2$ (which is characterised by $\Delta^{17}$O $\sim$ –0.36 ‰, relative to the reference line used in our investigation) was involved at any stage of the synthesis. Furthermore, although the cation is monovalent, Ag$_2$CO$_3$ decomposes readily to form the metal oxide and CO$_2$, at a lower temperature than divalent carbonate examples. Because Ag$_2$CO$_3$ is monoclinic, the oxygen triple-isotope fractionation pattern associated with its thermal could therefore be usefully compared with that of CuCO$_3$ decomposition, under identical experimental conditions. The $\Delta^{17}$O value of the resulting Ag$_2$O should be similar to that reported herein for CuO, if the $\Delta^{17}$O relationship with cation coordination number is as suggested from our findings.

Whether or not Fermi resonance occurs in the vibrational spectra of any of the carbonates included in our investigation, at the temperatures associated with thermal decomposition, is – as far as we are aware – unresolved. If it does occur, Fermi resonance might be expected to influence the oxygen triple-isotope compositions of the thermal decomposition products. The correct assignment of spectral features can be challenging, however, in experiments and simulations when double peaks are present, because such peaks can have different origins. Fermi dyads are a common class of such doublets, stemming from resonance of the fundamental excitation of a mode with the overtone of another. A new approach to unambiguously characterising Fermi resonances in density functional theory (DFT) based simulations of condensed phase systems (Basire et al., 2017) suggests that spectral features can be confidently assigned and the two resonating modes identified. The application of such an approach to analysing the infrared and Raman spectra of carbonates at elevated temperatures, in conjunction with isotopic substitution modelling, offers a promising way forward to explore what role, if any, Fermi resonance has on the magnitude of $\Delta^{17}$O present in carbonate thermal decomposition products.

6. Conclusions
We have demonstrated that anomalous fractionation of $^{17}$O/$^{16}$O relative to $^{18}$O/$^{16}$O occurs during the thermal decomposition of all (eleven) divalent metal carbonate examples investigated, regardless of the cation identity. The magnitude of the anomaly, quantified as $\Delta^{17}$O, ranged from $-0.20$ $\%$ to $-0.43$ $\%$ in individual samples of solid oxide, when $\lambda_{RL}$ is assigned as 0.524 and when a protracted, controlled heating protocol was utilised. The exact magnitude of the anomaly is dependent on the experimental details. For thermal decomposition conducted under similar conditions, there appears to be a correlation between the magnitude of $\Delta^{17}$O in the solid oxide and the cation coordination number (at room temperature) in the parent carbonate. An explanation consistent with the empirical findings, and based on a mechanism involving the magnetic isotope effect, is proposed. This has strong similarities to recent quantum chemical calculations of calcite and magnesite thermal decompositions. Further work is required to validate the proposed pathway, which we emphasise is a theoretical model based on the postulate that radicals are generated as transient intermediates in the carbonate decomposition process. Finally, we cannot exclude the possibility that Fermi resonance might be contributing to the isotopic anomaly, in at least some of the examples investigated.

**Declaration of Competing Interest**

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.

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**Appendix B. Supplementary data**

The results of electron probe and powder X-Ray diffraction measurements of the natural carbonate minerals used in this investigation are available online at:


**Appendix A.**

**Table A.1 Results of $\delta^{18}$O measurements of the natural carbonate specimens**

Carbonates were reacted with concentrated H$_3$PO$_4$ under temperature-controlled conditions (McCrea, 1950) and the evolved CO$_2$ analysed for $\delta^{13}$C and $\delta^{18}$O. The various fractionation factors ($\alpha$) used to determine the $\delta^{18}$O values of the carbonates from the isotopic measurements of CO$_2$ are listed, together with the corresponding literature reference. Samples were in the form of either small grains (sg) or powders (p). The $\delta^{18}$O value of the dolomite has been reported previously (Miller et al., 2002) as 30.26 ‰ relative to VSMOW.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mass (mg)</th>
<th>Reaction T (°C)</th>
<th>CO$<em>2$ $\delta^{18}$O$</em>{VPDB}$ (‰)</th>
<th>$\alpha$</th>
<th>Ref.</th>
<th>Carbonate $\delta^{18}$O$_{VPDB}$ (%)</th>
<th>Carbonate $\delta^{18}$O$_{VSMOW}$ (%)</th>
<th>Carbonate $\delta^{18}$O$_{VSMOW}$ mean (%)</th>
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Table A.2 Stable isotopes of cation elements in the carbonate specimens

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<th>Isotope</th>
<th>Atomic mass (Da)</th>
<th>Natural abundance (atom %)</th>
<th>Nuclear spin (I)</th>
<th>Magnetic moment (μ/μN)</th>
<th>Electronic structure (gas, ground state)</th>
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<tr>
<td></td>
<td>130 Ba</td>
<td></td>
<td>132 Ba</td>
<td></td>
<td>134 Ba</td>
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<td>0.937365</td>
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Data source: www.webelements.com

References


Internatnl. Symp. Isotopomers (ISI 2012), Washington DC, p. 61 (abstr.).

https://www.yumpu.com/en/document/read/21466085/sixth-international-symposium-on-isotopomers-
geophysical-


Table 1 Sample details. Apart from the magnesite and dolomite, which were used in the previous investigation (Miller et al., 2002), all natural carbonate mineral specimens were provided from the mineralogy collection of the Natural History Museum, London.

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<thead>
<tr>
<th>Sample</th>
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<th>Origin</th>
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<td>Rhombohedral carbonates</td>
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<td>Magnesite</td>
<td>MgCO₃ SC654 (NHM Wien)</td>
<td>Hydrothermal origin, Oberdorf an der Laming, Styria, Austria</td>
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<td>Calcite</td>
<td>CaCO₃ BM.1973,514</td>
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<td>MnCO₃ BM.1907,640</td>
<td>Lake County, Colorado, U.S.A.</td>
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<td>Siderite</td>
<td>FeCO₃ BM.1905,147</td>
<td>Allevard, Isère, France</td>
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<td>Smithsonite</td>
<td>ZnCO₃ BM.1929,1754</td>
<td>Kabwe (‘Broken Hill’) mine, Kabwe, Central Province, Zambia</td>
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<td>Dolomite</td>
<td>Ca,Mg(CO₃)₂</td>
<td>Fine-grained sample from base of Mt. Lagazuoi, Belluno, Italy</td>
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<td>Orthorhombic carbonates</td>
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<td>SrCO₃ BM.1907,638</td>
<td>Drensteinfurt, Munster, North Rhine-Westphalia, Germany</td>
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Table 2 Oxygen triple-isotope compositions of the solid oxides formed from carbonate thermal decomposition, together with the corresponding data from CO₂ released during CuCO₃ thermolysis.

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<th>δ¹⁸O ‰</th>
<th>SE</th>
<th>δ¹⁸O shift ‰</th>
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### Orthorhombic structure

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### Monoclinic structure

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<td>7.604</td>
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<td>* (#2) 9.798</td>
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<td>7.604 ± 0.018</td>
<td>7.708 ± 0.015</td>
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#### Isotopic composition of the CuCO₃, inferred from the CuO and CO₂ data:

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#### Notes:
- Data in italics are reproduced from Miller et al. (2002). ‘SE’ refers to standard error of the mean.
- Data in parentheses are derived from the inferred δ¹⁷O and δ¹⁸O values of the synthesised CuCO₃.
- § Pyrolysis conducted in the presence of an applied static magnetic field of flux density ~250 mT.
- * Pyrolysis conducted using a new extraction line and different heating duration (see text).

Fig. 1. Mass-dependent relationship between the oxygen triple-isotope compositions of the metal oxides formed from thermal decomposition of the various natural carbonate samples. Data points represent the mean of replicates; individual measurements are reported in Table 2. Error bars indicate the respective ranges obtained from replicates. For PbO, MnO and ZnO, the error bars are of similar size, or smaller than, the associated data point symbols. Tight coupling of the respective ordinate and abscissa data – as a result of the fractionation conforming to ‘mass-dependent’ norms – resulted in deviations from the least squares linear regression line being of very small magnitude: all ordinate deviations were within the range −0.044 to +0.057. Uncertainties of the slope and intercept values of the regression line are reported as standard error.

Fig. 2. Relationship between the oxygen triple-isotope compositions of CuO and CO₂ formed from thermal decomposition of replicate grains of the synthesised CuCO₃ sample, together with the inferred oxygen isotopic composition of the CuCO₃.

Fig. 3. CO₂ thermal evolution profiles of the natural carbonate specimens (crushed to a fine grain size) as a function of heating temperature (ramp rate 0.5 °C min⁻¹) in helium flow (53.8 mL min⁻¹). Individual peak temperatures are labelled in parentheses, together with the carbonate mass (mg) used. Uniquely, a bimodal release of CO₂ was observed from witherite; the initial (broad) peak maximum was at ~950 °C.
Fig. 4. Illustrating the relative thermal stabilities of the natural carbonate examples used in this investigation, as exemplified by the temperature at which maximum CO$_2$ evolution occurred during TGA/EGA, with heating at a ramp rate of 0.5 °C min$^{-1}$ in a flow of helium. Also shown are the individual replicate data points, indicating the respective shifts in $\delta^{18}$O accompanying the carbonate to solid oxide transformation.

Fig. 5. Illustrating the relationship between carbonate structural group (as determined by the cation radius) and the $\Delta^{17}$O value of the metal oxide produced by thermal decomposition of the corresponding carbonate mineral. Solid oxide $\Delta^{17}$O data produced from rhombohedral carbonates are denoted by ●, whereas orthorhombic examples are shown as ■. The sole example characterised by a monoclinic structure for the carbonate is illustrated by ◆. Cation radius data are from Shannon (1976). The mean $\Delta^{17}$O value of the metal oxides derived from thermal decomposition of the rhombohedral carbonates (calcite and isotypes) and orthorhombic carbonates (aragonite and isotypes) are denoted by ———— and ———— respectively. Similarly, shows the mean $\Delta^{17}$O value of the CuO replicates produced from the thermal decomposition of CuCO$_3$.

Fig. 6. Illustrating the lack of a systematic relationship between the $\Delta^{17}$O values of the divalent metal oxides produced by carbonate thermal decomposition and the corresponding linearised $\delta^{18}$O values. Also shown are the data from CO$_2$ released during thermal decomposition of CuCO$_3$, together with recently-reported results (Miller et al., 2020) from silicate standards San Carlos olivine and UWG-2 garnet, for comparison. Symbols are as defined for Fig. 5.

Fig. 7. Proposed simple model reaction mechanism for the thermal decomposition of metal carbonates. $k_{\text{vac}}$ is the pseudo first order rate coefficient for the arrival of vacancies at the site of a vibrationally excited carbonate ion (incorporating the concentration of vacancies). Vacancies are lost as they diffuse away from the carbonate, with rate coefficient $k_{-\text{vac}}$. The forward and back rate coefficients for the movement of the carbonate ion radical between the vacancy and original sites are designated as $k_{\text{jump}}$ and $k_{-\text{jump}}$ respectively; these coefficients are set to be equal, i.e. assuming equal probability for ‘jumping’ between the sites in either direction. $k_f$ is the rate coefficient for the forward electron transfer reaction (which is spin-state selective and takes place only from the singlet ion radical pair). $k_{\text{ST}}$ is a simple, first order rate coefficient which approximates the coherent spin-state mixing process of singlet and triplet radical pairs. $k_{\text{rel}}$ is the rate of the return of triplet state close pairs to the carbonate ion due to incoherent electron spin relaxation. Relaxation is also possible between the singlet and triplet radical pairs, but is neglected here to simplify the model. Inclusion of such relaxation would reduce the size of any magnetic isotope effect but would have negligible effect on the overall decomposition rate.

Fig. 8. Explicit representation of the scheme presented in Fig. 7 for the case of a carbonate ion containing $^{17}$O. The most abundant isotope of oxygen, $^{16}$O, is shown without the associated mass number. Two radical pairs are possible, produced in a 1:2 ratio. These undergo spin-state mixing at different rates ($k_{\text{ST1}}$ and $k_{\text{ST2}}$), resulting in a difference in the respective yields of the two products.
Numerical simulation of the kinetic scheme presented in Fig. 8. Parameters were selected to be physically reasonable and produce a substantial magnetic isotope effect, for clarity. Adjusting the parameters (over a reasonable range) can result in the magnitude of the effect being very much smaller, in accord with the experimental observations. The following values were used: $k_{\text{jump}} = 10^9$ s$^{-1}$, $k_f = 10^8$ s$^{-1}$, $k_{\text{ST1}} = 1.5 \times 10^9$ s$^{-1}$, $k_{\text{ST2}} = 1.0 \times 10^9$ s$^{-1}$, $k_{\text{rlx}} = 1.0 \times 10^6$ s$^{-1}$. The values of $k_{\text{vac}}$ and $k_{\text{vac}}$ affect the long timescale behaviour over which the decomposition occurs, but do not change the magnitude of the isotope effect. $k_{\text{vac}}$ was set to be $10^{-3}$ s$^{-1}$, to give an overall decomposition timescale of similar magnitude to the experimental data. $k_{\text{vac}}$ was arbitrarily set to $10^2$ s$^{-1}$, as it has a negligible effect on the shape of the curves when large relative to $k_{\text{vac}}$, but slow relative to all the other processes. Because the magnetic isotope effect doesn’t change the $^{18}\text{O}/^{16}\text{O}$ ratio, the thermal decomposition products will have the same $\delta^{18}\text{O}$ value as the parent carbonate. If a kinetic isotope effect occurs during the thermal decomposition, however, causing $^{18}\text{O}$ enrichment in the released CO$_2$ and consequently $^{18}\text{O}$ depletion in the metal oxide (Sharma and Clayton, 1965; see also Fig. 2 of this paper), this will be superimposed on the model results illustrated. The same process would similarly affect the distribution of $^{17}\text{O}$, in a mass-dependent manner (Eqn. (3), with $\theta = 0.51 \pm 0.05$).
$10^3 \ln(1 + \delta^{17}O)$

$y = (0.5243 \pm 0.0011)x - (0.343 \pm 0.023)$

$R^2 = 0.999966$

$n = 10$

Figure 1
Figure 2

- $\Delta^{17}O = -0.010\%$ (#2)
- $\Delta^{17}O = 0.084\%$ (#2)
- $\Delta^{17}O = -0.001\%$ (#3)
- $\Delta^{17}O = 0.111\%$ (#3)

- CuCO$_3$ composition (inferred): $\Delta^{17}O = -0.001\%$ (#3)
- CO$_2$ from CuCO$_3$ pyrolysis:
  - $\Delta^{17}O = 0.084\%$ (#2)
  - $\Delta^{17}O = 0.111\%$ (#3)

Reference line, $\lambda_{RL} = 0.524$, $\gamma_{RL} = 0$
Figure 3

CO$_2$ ion current (nA) vs. Temperature (°C)

- Cerussite: (301, 20.84)
- Siderite: (510, 9.30)
- Rhodochrosite: (498, 10.99)
- Smithsonite: (458, 10.09)
- Dolomite: (641, 8.52)
- Magnesite: (576, 8.06)
- Aragonite: (652, 8.98)
- Stronianite: (837, 11.44)
- Calcite: (687, 9.19)
- Witherite: (1043, 15.74)
Figure 4
Figure 6
Figure 7

\[
\begin{align*}
\text{CO}_3^{2-} & \xrightleftharpoons[k_{\text{vac}}]{k_{\text{vac}}} \text{CO}_3^{2-} \\
\text{CO}_3^{2-} \text{ vacancy} & \xrightarrow{k_{\text{jump}}} \{O^- \cdot CO_2^-\}_S \\
\{O^- \cdot CO_2^-\}_S & \xrightarrow{k_f} \text{O}^{2-} + \text{CO}_2 \\
\{O^- \cdot CO_2^-\}_S \text{ vacancy} & \xrightarrow{k_{\text{jump}}} \{O^- \cdot CO_2^-\}_T \\
\end{align*}
\]
Figure 9