Mass-independent fractionation of oxygen isotopes during thermal decomposition of carbonates

Martin F. Miller[*,†], Ian A. Franchi[*], Mark H. Thiemens[‡], Teresa L. Jackson[‡], André Brack[§], Gero Kurat[¶], and Colin T. Pillinger[*]

[*]Planetary and Space Sciences Research Institute, The Open University, Walton Hall, Milton Keynes MK7 6AA, United Kingdom; [‡]Department of Chemistry, University of California at San Diego, La Jolla, CA 92093-0356; [§]Centre de Biophysique Moléculaire, Centre National de la Recherche Scientifique, Rue Charles Sadron, 45071 Orléans Cedex 2, France; and [¶]Naturhistorisches Museum, Postfach 417, A-1014 Wien, Austria

Communicated by Rudolph A. Marcus, California Institute of Technology, Pasadena, CA, June 25, 2002 (received for review March 28, 2002)

Nearly all chemical processes fractionate ^{17}O and ^{18}O in a mass-dependent way relative to ^{16}O, a major exception being the formation of ozone from diatomic oxygen in the presence of UV radiation or electrical discharge. Investigation of oxygen three-isotope behavior during thermal decomposition of naturally occurring carbonates of calcium and magnesium *in vacuo* has revealed that, surprisingly, anomalous isotopic compositions are also generated during this process. High-precision measurements of the attendant three-isotope fractionation line, and consequently the magnitude of the isotopic anomaly (Δ^{17}O), demonstrate that the slope of the line is independent of the nature of the carbonate but is controlled by empirical factors relating to the decomposition procedure. For a slope identical to that describing terrestrial silicates and waters (0.5247 ± 0.0007 at the 95% confidence level), solid oxides formed during carbonate pyrolysis fit a parallel line offset by −0.241 ± 0.042‰. The corresponding CO_2 is characterized by a positive offset of half this magnitude, confirming the mass-independent nature of the fractionation. Slow, protracted thermolysis produces a fractionation line of shallower slope (0.5198 ± 0.0007). These findings of a ^{17}O anomaly being generated from a solid, and solely by thermal means, provide a further challenge to current understanding of the nature of mass-independent isotopic fractionation.

Measurements have been conducted of the oxygen triple-isotope composition of calcium oxide, magnesium oxide, and mixed calcium–magnesium oxides formed by thermal decomposition of naturally occurring terrestrial carbonates under high vacuum conditions. The rationale was originally to devise a rapid and simplified procedure, compared with existing methods (1, 2), for high-precision measurements of oxygen isotopic anomalies in meteoritic carbonates. Carbonates were pyrolyzed by using infrared laser heating, with continuous pumping to ensure the removal of CO_2 as produced. Because calcium oxide readily hydrates and also reacts with CO_2, it was important that samples remained isolated from atmosphere after pyrolysis. For this purpose, 3–5 mg of carbonate (consisting of one or two individual grains, except in the case of fine-grained international reference materials) was thermally decomposed in the same vacuum chamber as used for subsequent fluorination of the residual solid oxide. A 25-W infrared laser, with attenuated beam, provided the heat source. For carbonate decomposition, the temperature was increased gradually from ambient, in a carefully controlled manner, ensuring that the pressure as monitored in the reaction cell did not exceed $\approx 10^{-4}$ mbar at any stage, until evolution of gas ceased and the residual solid was incandescent. It is difficult to estimate the final temperature, but it is likely to have exceeded 1,000°C. Released volatiles were continually removed during pyrolysis, to minimize the extent of back-reaction between the respective decomposition products. Oxygen triple-isotope analysis of the residual solid oxides was then performed according to established procedures for silicate rocks and minerals (3), involving infrared laser-assisted reaction with BrF_5 as the first step. After purification of the released O_2, both cryogenically at −196°C and by transfer to a 13× molecular sieve, δ^{17}O and δ^{18}O measurements[‖] were made by using a Micromass (Manchester, U.K.) PRISM III mass spectrometer.

Terrestrial carbonates, like almost all terrestrial rocks and minerals [the sole reported exceptions to date being sulfate deposits believed to have been derived by atmospheric oxidation of sulfur-bearing volatiles (4–7)], are characterized by δ^{18}O and δ^{17}O values that are in accord with mass-dependent fractionation from an isotopically homogeneous oxygen reservoir, with the associated fractionation line describing a linear relationship between the ^{17}O/^{16}O and ^{18}O/^{16}O ratios. Departures from this terrestrial fractionation line are quantified in terms of Δ^{17}O, which otherwise takes the value of zero. Such anomalies are present in many constituents of the Earth's atmosphere (8, 9), although these are generally inherited from stratospheric ozone (10) by reaction sequences involving either this component directly or via O(^{1}D), an ozone photolysis product.

In rigorous terms, $\Delta^{17}O = 10^3\{[1 + (\delta^{17}O/10^3)] - [1 + (\delta^{18}O/10^3)]^\lambda\}$ per mil, where $\lambda \approx 0.52$. For δ^{17}O and δ^{18}O values within a few per mil of zero, the widely used approximation $\Delta^{17}O = \delta^{17}O - 0.52\,\delta^{18}O$ is generally valid and the magnitude of the isotopic anomaly is illustrated by a plot of δ^{17}O versus δ^{18}O. As our samples span a δ^{18}O range approaching 30 per mil, we use here a nonapproximated form of the relationship between δ^{17}O and δ^{18}O and define $\Delta^{17}O = 10^3 \ln[1 + (\delta^{17}O/10^3)] - \lambda\, 10^3 \ln[1 + (\delta^{18}O/10^3)]$. The advantages conferred by this approach (11) are that the scale of the corresponding three-isotope plot is essentially unchanged from that of a δ^{17}O versus δ^{18}O array, yet linearity is preserved over the entire range of δ values and, furthermore, λ is represented accurately by the slope of the linear regression line. Using carbonates from natural sources, including international isotopic reference materials NBS-18 (carbonatite) and NBS-19 (calcite), together with examples of dolomite, magnesite, and present-day marine mollusk shells, the unusual result was obtained that thermal decomposition of these materials under high vacuum conditions, thereby minimizing the potential for back-reaction between the residual solid oxides and the released CO_2, generates oxides that do not conform to terrestrial mass-dependent oxygen isotopic composition. Furthermore, despite the variation in origin and chemical composition of the carbonates investigated, all thermally decomposed to yield solid oxides characterized by essentially the same Δ^{17}O value (Fig. 1), which is almost an order of magnitude greater than the attendant 1σ external reproducibility (0.027‰) obtained from comparable replicate (n = 31) analyses of an obsidian (silicate) in-house reference, by using the same experimental facility (3). Some variation of δ^{18}O (and δ^{17}O) occurred between replicates: measurements on calcium oxide generated from pyrolysis of NBS-18 and NBS-19 were characterized by

---

Abbreviation: SMOW, Standard Mean Ocean Water.

[†] To whom reprint requests should be addressed. E-mail: m.f.miller@open.ac.uk.

[‖] $\delta^xO = [\{(^xO/^{16}O)_{sample}/(^xO/^{16}O)_{SMOW}\} - 1] \times 10^3$ per mil (‰), where ^{x}O represents ^{17}O or ^{18}O and SMOW is the Standard Mean Ocean Water international reference material.

www.pnas.org/cgi/doi/10.1073/pnas.172378499

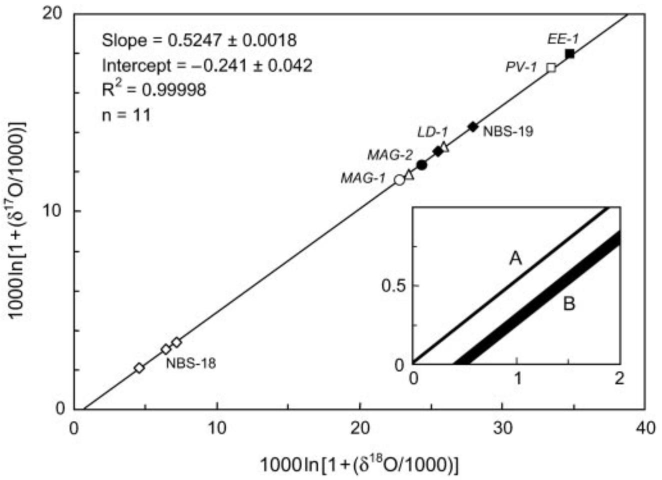

Fig. 1. Oxygen triple-isotope data from CaO, MgO, and mixed CaO + MgO formed by laser-promoted thermal decomposition of carbonates *in vacuo*, showing the fractionation line defined by the data set. Errors reported for the slope and intercept values are the respective 95% confidence limits. The offset between the attendant fractionation line (B) and that measured for the bulk silicate Earth (A) using the same experimental facility is shown (*Inset*) with the respective line widths representing 95% confidence limits on the slope values.

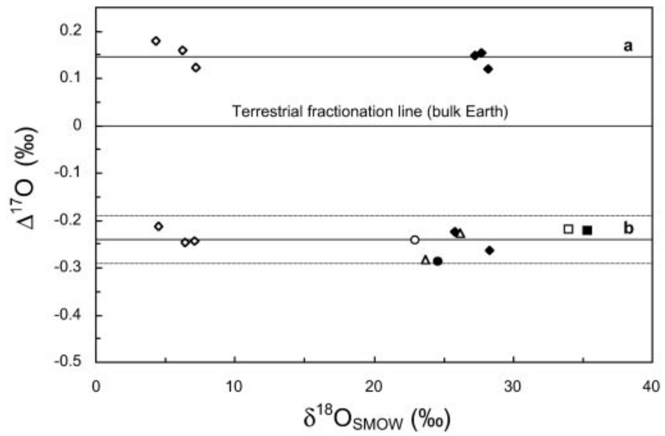

Fig. 2. Comparison between $\Delta^{17}O$ results obtained from the data shown in Fig. 1, on the one hand, and $\Delta^{17}O$ of CO_2 obtained by pyrolysis of additional grains of NBS-18 and NBS-19 under nominally identical conditions. The stippled lines indicate 2σ errors (0.050) of the mean $\Delta^{17}O$ value **b** (−0.242‰) for the solid oxides. Line **a** represents the mean $\Delta^{17}O$ value (+0.147‰) obtained from the CO_2 data; the corresponding 2σ error is 0.047. Symbols corresponding to sample identification are as designated in Fig. 1.

$\delta^{18}O$ values shifted, in a uniformly negative direction, by <0.1 to nearly 3‰ relative to the accepted values (7.20 and 28.65‰, respectively) for the corresponding carbonates. This finding is attributed, at least in part, to the possibility of incomplete reaction during laser-assisted fluorination of the oxide, with concomitant kinetic isotopic fractionation. Temperatures attained during the fluorination process are typically higher than the melting points of fluorination reaction products CaF_2 (1,418°C) and MgF_2 (1,263°C); in practice, a small, but variable, proportion of the solid oxides may therefore be shielded from reaction with BrF_5, by the presence of a fluoride melt. The corresponding $\Delta^{17}O$ data are seen to be invariant, however, within the limits of experimental precision. Thus, whereas incomplete extraction of molecular oxygen from the alkaline earth oxides causes kinetic isotopic fractionation (mass dependent), which serves simply to shift the data points along the associated three-isotope fractionation line, the attendant $\Delta^{17}O$ values are unaffected.

Although the data set is relatively small, the wide range of $\delta^{18}O$ values is advantageous to high-precision characterization of the attendant fractionation line. This is particularly important for the accurate determination of small (<1‰) isotopic anomalies, as in the present case, because the corresponding $\Delta^{17}O$ values are very sensitive to the assigned slope of the line (11). As shown in Fig. 1, a well-constrained ($R^2 = 0.99998$) linear array on a modified version of the three-isotope plot (11) may be derived from the complete data set. Furthermore, its slope (λ) is statistically indistinguishable from that of 0.5247 ± 0.0007 (95% confidence level) obtained from measurements of a large number of terrestrial silicates (11) by using the same experimental facility (3). However, the silicate line intercepts the *y* axis at 0.008 ± 0.009‰, whereas the parallel fractionation line defined by the solid residual oxides from carbonate pyrolysis is characterized by an offset of −0.241 ± 0.042‰ (95% confidence level errors) on the same axis.

To confirm that the carbonates contained no ^{17}O anomaly before thermal decomposition, direct fluorination of dolomite sample *LD-1* was performed, by using the laser to provide a temperature (≈400°C) sufficiently low to prevent thermal decomposition, but high enough to minimize CO_2 formation, which occurs during low temperature reaction with the bromine pentafluoride fluorinating agent (12). The molecular oxygen so formed exhibited a $\Delta^{17}O$ value of −0.020, which is indistinguishable from zero within the limits of experimental precision. Thus, we conclude that thermal decomposition of the carbonate is indeed responsible for generating the anomalous ^{17}O depletion found in the resulting oxide phase.

By implication, CO_2 released during the same carbonate pyrolysis procedure should be anomalously enriched in ^{17}O relative to the terrestrial fractionation line, with a $\Delta^{17}O$ value of close to +0.12‰. To investigate this, at the required level of precision, is considerably more challenging than the corresponding characterization of the solid oxides. CO_2 aliquots (≈25 μmol) released during laser-promoted thermal decomposition of NBS-18 and NBS-19 at the Open University were collected in borosilicate glass tubes, subsequently flame-sealed, and sent to the University of California, San Diego, for fluorination and analysis of the resulting O_2 for triple-isotope composition. Fluorination of the CO_2 was conducted in a Ni tube by reaction for 45 h at 800°C with an excess (1,000-fold) of BrF_5, for quantitative conversion of the CO_2 to O_2 and CF_4. The BrF_5 was purified immediately before use, by pumping at −90°C for 10 min. CF_4 was removed by a U-trap filled with 13× molecular sieve (60/80 mesh) and maintained at −122.5°C. Isotopic measurements ($\delta^{17}O$ and $\delta^{18}O$) of the purified O_2 were conducted by using a Finnigan-MAT (Bremen, Germany) 251 mass spectrometer. Before the fluorination step, gas chromatographic purification of the CO_2 was performed, by using an 8-ft Hayesep Q column. The contribution of blank for the fluorination procedure was in the range 0.1 to 0.2 μmol O_2; associated analytical uncertainties are indicated by 5–18 μmol samples ($n = 3$) of CO_2 prepared from NBS-18 by temperature-controlled phosphoric acid equilibration giving $\delta^{18}O$ of 6.8 ± 0.4‰, $\delta^{17}O$ of 3.6 ± 0.2‰ (2).

Replicate analyses confirmed that a positive ^{17}O anomaly was indeed present (Fig. 2), of magnitude +0.147 ± 0.047 (2σ), which substantiates the conclusion that the observed phenomenon is indeed a mass-independent fractionation effect. The fine-grained nature of NBS-18 and NBS-19 resulted in the loss of some grains, possibly partially decarbonated, by ejection from the sample well during laser-mediated pyrolysis. This is postulated as the most probable reason for the variation of δ values of the CO_2 replicates (Fig. 2), with $\delta^{18}O$ shifts of <0.1 to nearly 3‰

(negative) relative to the accepted values of the respective carbonates.

If CO_2 released during laser-promoted carbonate pyrolysis is not immediately removed from contact with the heated, residual solid oxide, the possibility of back reaction, with concomitant exchange of oxygen isotopes, will serve to reduce and eventually eliminate the isotopic anomaly. This was confirmed by performing pyrolysis of dolomite *LD-1* in an evacuated, closed system, with no pumping or cryogenic trapping of volatiles. After a period of 30 min with the residual solid heated to incandescence (to prevent carbonate formation) and in contact with evolved CO_2, the volatile phase was removed and the residual solid oxide was analyzed for oxygen isotopic composition. No ^{17}O anomaly was detectable, within the limits of experimental precision. Thus, although extensive kinetic studies would be required to characterize the parameters controlling the rate at which the isotopic anomaly is removed, it is apparent at this stage that the magnitude of the observed anomaly will largely depend on the experimental details of the pyrolysis procedure.

To eliminate the possibility that generation of the isotopic anomaly was an artifact associated with the use of infrared laser radiation to promote thermal dissociation of the carbonates, grains of the same examples of calcite, magnesite, and dolomite were (separately) subjected to extended heating by a tube furnace, under high vacuum and with continuous pumping. Single grains (3–5 mg) were loaded into quartz glass tubes (6 mm external diameter) that formed an integral part of a high vacuum system. After outgassing for several hours at 100°C, until the vacuum was $<10^{-6}$ mbar, samples were gradually heated, with constant pumping, to a temperature just below that at which major onset of thermal decomposition occurred. CO_2 pressure in the system at this point was about 10^{-3} mbar. The temperature was then maintained for a period in excess of 12 h, until CO_2 evolution essentially ceased. The incremental heating procedure was then repeated, while ensuring that the gas pressure did not exceed about 10^{-3} mbar. Subsequent heating of the sample to >900°C released no further CO_2. The quartz tubes were then flame-sealed under high vacuum, and the resulting ampoules were transferred to a glove box and flushed by dried, high-purity nitrogen, which conformed to the cleanliness requirements for a class 10,000 facility. The ampoules were opened in this environment and the individual oxide grains (none of which had disintegrated during heating) were loaded into the cell used for fluorination. Subsequently, the cell was sealed, still containing dry nitrogen, removed from the glove box, and coupled to the vacuum system used for laser-assisted fluorination. Such a procedure allowed the oxide grains to be characterized for oxygen triple-isotopic composition without being exposed to the atmosphere. The results of the analyses (Fig. 3) confirmed that generation of an isotopic anomaly derives from carbonate thermal dissociation and is not related to whether or not infrared laser radiation is used for heating. Also apparent is that prolonged thermal decomposition under high vacuum conditions produces isotopic data that fit an attendant fractionation line of notably shallower slope than was obtained by the laser-promoted pyrolysis. This is evidence for control of the fractionation line slope, for the decarbonation reaction, by a change of empirical factors. Theoretical considerations indicate that the fractionation line slope for kinetically controlled processes is usually of smaller magnitude than that obtained under equilibrium conditions (13, 14); fractionation of oxygen isotopes during aerobic respiration appears to provide empirical confirmation of this effect (11, 14). However, whereas it is probable that kinetic effects played a more significant role during the prolonged thermal decomposition regime than was the case during the laser-assisted pyrolysis procedure, there is unlikely to be a direct analogy with the simple, gaseous diffusion case on which current models of kinetic effects on the fractionation line slope are based.

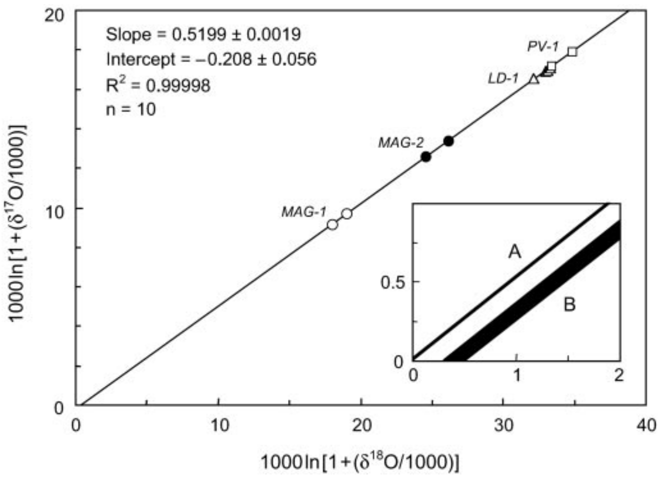

Fig. 3. Oxygen triple-isotope data from CaO, MgO, and mixed CaO + MgO formed by prolonged, slow thermal decomposition of carbonates *in vacuo*, in the absence of laser irradiation, showing the fractionation line defined by the data set. As for Fig. 1, errors reported for the slope and intercept values are the respective 95% confidence limits. The offset between the attendant fractionation line (B) and that measured for the bulk silicate Earth (A) using the same experimental facility is shown (*Inset*), with the respective line widths representing 95% confidence limits on the slope values.

Although the precision of the slope shown in Fig. 3 appears to be similar to the corresponding value associated with laser-induced pyrolysis (Fig. 1), presentation of the same data in a different format (Fig. 4) indicates clearly that it is the calcium-bearing phases that are primarily responsible for the magnitude of the observed degree of scatter. In contrast, the magnesite to MgO conversion gives excellent reproducibility of the associated slope and hence $\Delta^{17}O$ value. This finding is in accord with the much slower rate of back-reaction between MgO and CO_2 during magnesite decarbonation, compared with the time scale of $CaO + CO_2$ recombination under similar conditions (15). Considering only the four data points corresponding to the two duplicated MgO samples, the associated R^2 linear regression coefficient is 0.9999998, the slope of the fractionation line is 0.5198 ± 0.0007, and the intercept equates to -0.203 ± 0.015

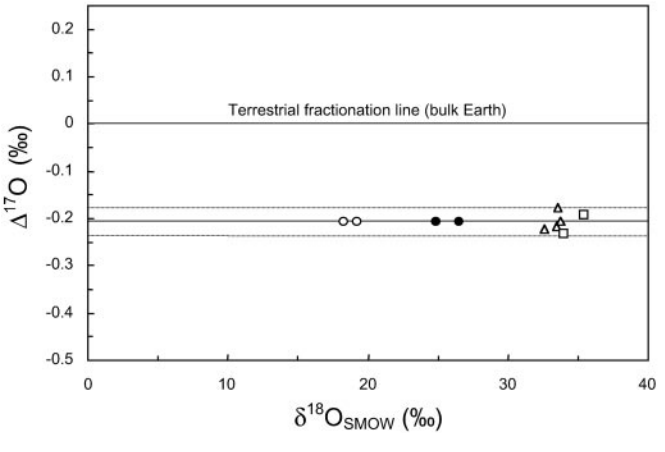

Fig. 4. $\Delta^{17}O$ results obtained from the information illustrated in Fig. 3 and highlighting the very low scatter of MgO data. The stippled lines indicate 2σ errors (0.030) of the mean $\Delta^{17}O$ value of −0.207‰. Symbols corresponding to sample identification are as designated in Fig. 1.

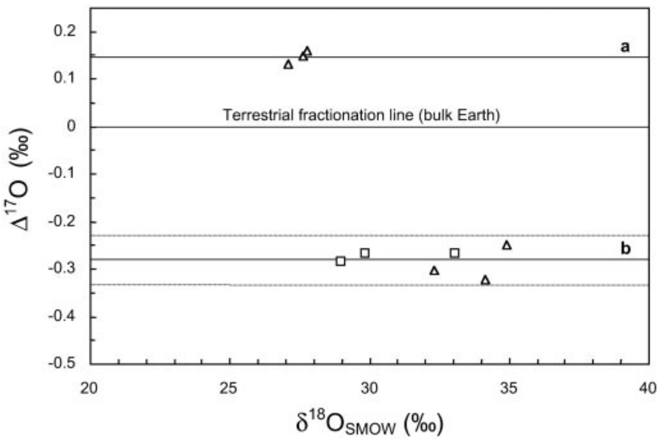

Fig. 5. $\Delta^{17}O$ of mixed calcium and magnesium oxides, together with corresponding CO_2, obtained from laser-promoted pyrolysis of three replicates of dolomite *LD-1* by using an experimental facility (University of California, San Diego) different from that used to generate the data shown in Fig. 1. $\Delta^{17}O$ replicates of the residual solid oxide similarly generated from marine mollusk *PV-1* are also shown. The stippled lines indicate 2σ errors (0.053) of the mean $\Delta^{17}O$ value **b** (−0.281‰) for the six measurements. Line **a** represents the mean CO_2 $\Delta^{17}O$ value (+0.146‰) obtained from three replicates of dolomite *LD-1*. Symbols corresponding to sample identification are as designated in Fig. 1. Because the slope of the attendant fractionation line may not be precisely determined from these results, a value was assigned (0.5233) for the calculation of $\Delta^{17}O$ values from the corresponding δ values, such that the magnitude of the mean $\Delta^{17}O$ of the solid phase is exactly twice that of the CO_2 (but opposite in sign).

(95% confidence level). Calculation of the MgO $\Delta^{17}O$ values on the basis of a slope of 0.5198, in conjunction with the measured δ values, shows a range of only ±0.001 about the mean value of −0.203‰.

The finding of a mass-independent isotopic anomaly associated with thermal decomposition of carbonates was further substantiated by replication at the University of California, San Diego, of experiments conducted at the Open University and involving laser-promoted pyrolysis of fragments of the same dolomite rock *LD-1* and marine mollusk shell *PV-1*. A procedure nominally identical to that reported above was used, although details of the experimental arrangement (such as the volume of the chamber used for pyrolysis and the associated pumping rate) differed. In one case (*LD-1* replicates), oxygen triple-isotope data of both the residual solid oxide and CO_2 generated during the same pyrolysis experiment were obtained. For calculation of the corresponding $\Delta^{17}O$ values, it was initially assumed that the fractionation line slope value as obtained by using laser-promoted pyrolysis at the Open University (0.5247, Fig. 1) would be applicable. However, the resulting $\Delta^{17}O$ for the solid oxides is $-0.326 \pm 0.054‰$ (2σ), with the CO_2 being $+0.108 \pm 0.025‰$. On the basis that the $\Delta^{17}O$ value of the solid phase should equate to twice that (but opposite in sign) of the released CO_2, as indeed was found to be the case earlier (Fig. 2), it is clear that a different slope value must apply. For solid oxide and CO_2 $\Delta^{17}O$ values to be in the correct ratio, the corresponding slope value is 0.5233, which evidently lies between the possibly limiting values of 0.5247 and 0.5198 as given by the respective experimental arrangements described above. Assigning a slope value of 0.5233 allows the results depicted in Fig. 5 to be obtained. The measured δ values, together with all others presented in this study, are shown in Table 1.

Although no established $\delta^{17}O$ data exist for the NBS-18 and NBS-19 reference materials, calculation on the basis of the respective $\delta^{18}O$ values (16) in conjunction with a high-precision, nonapproximated version of the three-isotope fractionation line for terrestrial silicates and waters (11) gives 3.77‰ for NBS-18 and 14.93‰ for NBS-19. From the information given in Table 1, it is seen that preservation of the NBS-18 $\delta^{18}O$ value to within 0.1‰ was achieved in one case during carbonate pyrolysis and subsequent fluorination of the resulting solid oxide, whereas the corresponding $\delta^{17}O$ value changed by −0.29‰. Moreover, although some reduction in $\delta^{18}O$ from the respective NBS-18 and NBS-19 documented values occurred during replication of the pyrolysis and fluorination procedure for both reference carbonates, the magnitude of the shifts was less than 3‰ in all cases. The importance of this observation is that it demonstrates the improbability of the anomalous isotopic compositions of the solid oxides being attributable to mass-dependent fractionation processes for which the attendant slope values differ substantially from that characteristic of terrestrial silicates and waters. Such a mechanism does account for a significant proportion of the isotopic anomaly of tropospheric O_2, for example (11, 14), on the basis of the fractionation line associated with aerobic respiration being of notably lower slope than that describing terrestrial waters. However, respiration is associated with a strong discrimination against ^{18}O relative to ^{16}O, resulting in an attendant $\delta^{18}O$ shift of 18‰ (dark respiration) to 25–30‰ in cyanide-resistant respiration (17). Isotopic fractionation of comparable magnitude clearly did not occur in the experiments with NBS-18 and NBS-19 as presented in this article.

The purpose of including examples of dolomite, magnesite, and marine mollusk shells in the investigation, in addition to the NBS-18 and NBS-19 references, was twofold. Apart from establishing whether the unusual isotope effect is apparently universal to such carbonates, the objective was to provide a wide range of $\delta^{18}O$ values, thereby allowing accurate and precise characterization of the slope of the three-isotope fractionation line associated with carbonate thermal decomposition. It is suggested that accurate, independent characterization of the respective $\delta^{18}O$ values of these additional carbonates, while enlarging the data set, would not contribute important new information, as it is clearly $\Delta^{17}O$ (as determined) that is the critical parameter. The carbonate $\delta^{18}O$ value of the dolomite sample (*LD-1*) was established, however, on the basis of temperature-controlled reaction (50°C) with phosphoric acid (18) followed by isotopic measurements on the released CO_2. A result of 30.26‰ was obtained, with calculation of the corresponding $\delta^{17}O$ value giving 15.76‰. The extent of isotopic homogeneity of the dolomite, which contains traces of silica, is not known. What is noteworthy, however, is that thermal decomposition of the dolomite, with subsequent fluorination of the residual solid oxide assemblage, resulted in a shift of $\delta^{18}O$ value in either a positive or negative direction, depending on the experimental protocol adopted. Table 1 shows that the experiments involving laser-assisted pyrolysis at the Open University facility produced a $\delta^{18}O$ reduction of magnitude in the region of −4 to −7‰, whereas adopting a similar procedure on a comparable system at the University of California, San Diego, resulted in a smaller and less variable $\delta^{18}O$ shift, which occurred in a positive direction. The most reproducible $\delta^{18}O$ data, however, were obtained after protracted pyrolysis of the dolomite with a tube furnace; furthermore, these results were in reasonably close agreement to those generated during the University of California laser-assisted thermal decomposition experiments. In all cases, however, it is evident that the residual solid oxides were characterized by anomalous depletion of ^{17}O.

The discovery that carbonate pyrolysis causes mass-independent fractionation of oxygen isotopes, together with the quantification of its magnitude, has significant implications. Specifically, it has been shown that a ^{17}O anomaly was generated from a solid reagent. Furthermore, unlike most documented sources of mass-independent isotopic fractionation, as distinct from chemical reactions that simply transfer an existing isotopic

Table 1. Carbonate samples investigated in this study, with measurements of the oxygen isotopic compositions of the corresponding oxides formed by thermal decomposition *in vacuo*

Carbonate sample	Pyrolysis procedure	Pyrolysis product analyzed	δ^{18}O, ‰	δ^{17}O, ‰	Assigned slope, λ	Δ^{17}O, ‰
NBS-18	a	CaO	7.11	3.48	0.5247	−0.243
Replicate			4.52	2.16		−0.213
Replicate			6.39	3.10		−0.247
NBS-19	a	CaO	25.78	13.22	0.5247	−0.223
Replicate			28.26	14.47		−0.262
LD-1	a	CaO + MgO	26.20	13.43	0.5247	−0.226
Replicate			23.65	12.05		−0.282
EE-1	a	CaO	35.32	18.15	0.5247	−0.221
PV-1	a	CaO	33.93	17.44	0.5247	−0.219
MAG-1	a	MgO	22.95	11.73	0.5247	−0.239
MAG-2	a	MgO	24.58	12.53	0.5247	−0.286
NBS-18	a	CO_2	6.20	3.41	0.5247	0.161
Replicate			7.15	3.87		0.122
Replicate			4.32	2.45		0.181
NBS-19	a	CO_2	27.27	14.37	0.5247	0.149
Replicate			28.19	14.82		0.119
Replicate			27.71	14.60		0.153
LD-1	b	CaO + MgO	32.58	16.58	0.5198	−0.219
Replicate			33.44	17.03		−0.212
Replicate			33.58	17.14		−0.174
Replicate			33.76	17.19		−0.202
PV-1	b	CaO	35.40	18.05	0.5198	−0.188
Replicate			33.95	17.27		−0.227
MAG-1	b	MgO	18.20	9.22	0.5198	−0.204
Replicate			19.20	9.73		−0.202
MAG-2	b	MgO	24.86	12.64	0.5198	−0.203
Replicate			26.43	13.45		−0.203
LD-1	c	CaO + MgO	34.90	17.86	0.5233	−0.250
Replicate			32.33	16.48		−0.303
Replicate			34.15	17.40		−0.321
LD-1	c	CO_2	27.63	14.51	0.5233	0.148
Replicate			27.11	14.23		0.132
Replicate			27.77	14.60		0.159
PV-1	c	CaO	28.98	14.78	0.5233	−0.282
Replicate			29.84	15.24		−0.265
Replicate			33.06	16.90		−0.266

Note that, as discussed in the text, the reported δ values may be shifted—by several per mil in some cases—from the corresponding true values, although Δ^{17}O results are not significantly affected. Pyrolysis procedures were as follows: (a) Laser-promoted thermal decomposition, performed at the Open University. Fluorination and isotopic analysis of CO_2 were undertaken at the University of California, San Diego. (b) Slow, protracted decomposition of carbonates at the respective, incipient decomposition temperature in the absence of laser irradiation. This was conducted at the Open University. (c) Laser-promoted pyrolysis, undertaken at the University of California, San Diego. For replicates of *LD-1* in this case, isotopic measurements were conducted on the solid oxides and CO_2 released during the same pyrolysis experiments, in the order listed. Although all δ values are reported (relative to SMOW) to two decimal places, the raw data (three decimal places) were used in calculating the corresponding Δ^{17}O results. *LD-1* is a fine-grained dolomite from the base of Mount Lagazuoi, Belluno, Italy. *EE-1* and *PV-1* are shell fragments from modern marine mollusks *Ensis ensis* and *Patella vulgata*, respectively. *MAG-1* and *MAG-2* are both magnesites from Styria, Austria: *MAG-1* is of hydrothermal origin and from Oberdorf an der Laming, whereas *MAG-2* is from Kraubath and is a product of serpentinization of an ultramafic rock.

anomaly, no excitation by photochemical or electrical discharge processes is required to generate the effect. A satisfactory theoretical explanation of mass-independent isotope effects, including the prediction of their magnitude, has proved remarkably elusive ever since this phenomenon was first reported (19), with significant progress having been achieved only recently (20, 21). Complementary experimental investigations (9, 22) hitherto have generally (and necessarily) involved gaseous reactants in electronically excited states, which introduces additional complexity and uncertainties to the system. The thermal decomposition of ozone (23, 24) is an exception, involving only ground-state molecular and atomic species. Sensitivity to catalysis by impurities and surfaces, however, is a significant impediment to further investigation of that reaction.

Since the initial discovery of mass-independent isotopic fractionation (19), the role of molecular symmetry in the formation of such anomalies has been the subject of much debate (8, 9), culminating in the quantum-level model of Gao and Marcus (21) for ozone formation. We note here that there are qualitative, geometrical similarities between the respective thermal decompositions of ozone and carbonates. The basic configuration of the carbonate ion as a planar, structural unit is remarkably uniform in nature, with little variation of bond lengths or angles (25). In calcite and its isotypes, the carbonate ion contains oxygen in an equilateral triangular arrangement; this configuration is very closely approximated in other carbonates (25). Microwave spectral analysis of ozone (26) indicates that the bond angle is slightly less than that of O—C—O in the carbonate ion. Furthermore, the respective decomposition products, carbon dioxide and molecular oxygen, share $D_{\infty h}$ point group symmetry.

Calcite and dolomite account for more than 90% of carbonates in the Earth's crust (25) and thermal decarbonation of these occurs on a large scale at subduction zones and during high grade metamorphism. Under such conditions, however, which usually involve a hydrous fluid phase, oxygen isotopic exchange is facilitated. It is therefore unlikely that any mass independently fractionated oxygen component is preserved in oxide-bearing rocks or minerals derived from carbonate pyrolysis in nature. Similarly, volcanogenic CO_2 derived from carbonate thermal decomposition will rapidly lose any anomalous oxygen isotopic characteristics, through exchange reactions with water (27, 28), as is the case with stratospheric CO_2 influx (29). In a cosmochemical context, the recent detection of calcite and dolomite in dust shells around evolved stars (30) suggests that thermal processing of such material may provide a hitherto unrecognized mechanism for the mass-independent fractionation of oxygen isotopes in protoplanetary systems. The main focus of interest in the present findings, however, is in the context of the fundamental physical chemistry of solids: how they are bound and dissociate. It is salutary to note that 18 years elapsed between the initial discovery of mass-independent fractionation and the publication of a quantum-level model that satisfactorily explained the mechanism of the empirical findings. Furthermore, unlike that original case, which involved a relatively simple, gas-phase reaction, the findings reported here involve a system of significantly greater complexity. A satisfactory explanation of the mechanism therefore poses new challenges to established theories of isotopic fractionation.

We acknowledge, with appreciation, thoughtful and detailed comments by the two anonymous reviewers. The findings reported herein derived originally from an investigation conducted for an autonomous component (STONE), led by André Brack, of the Foton-12 mission of the European Space Agency's Microgravity program. M.F.M. acknowledges funding from the United Kingdom Particle Physics and Astronomy Research Council and thanks (as does M.H.T.) Huiming Bao for useful discussions and contributions toward the experimental investigations conducted at the University of California, San Diego.

1. Bhattacharya, S. K. & Thiemens, M. H. (1989) *Z. Naturforsch. A.* **44,** 435–444.
2. Farquhar, J., Thiemens, M. H. & Jackson, T. (1998) *Science* **280,** 1580–1582.
3. Miller, M. F., Franchi, I. A., Sexton, A. S. & Pillinger, C. T. (1999) *Rapid Commun. Mass Spectrom.* **13,** 1211–1217.
4. Bao, H., Thiemens, M. H., Farquhar, J., Campbell, D. A., Lee, C. C.-W., Heine, K. & Loope, D. B. (2000) *Nature (London)* **406,** 176–178.
5. Bao, H., Campbell, D. A., Bockheim, J. G. & Thiemans, M. H. (2000) *Nature (London)* **407,** 499–502.
6. Bao, H., Michalski, G. M. & Thiemens, M. H. (2001) *Geochim. Cosmochim. Acta* **65,** 2029–2036.
7. Thiemens, M. H., Savarino, J., Farquhar, J. & Bao, H. (2001) *Acc. Chem. Res.* **34,** 645–652.
8. Thiemens, M. H. (1999) *Science* **283,** 341–345.
9. Weston, R. E. (1999) *Chem. Rev.* **99,** 2115–2136.
10. Lyons, J. R. (2001) *Geophys. Res. Lett.* **28**, 3231–3234.
11. Miller, M. F. (2002) *Geochim. Cosmochim. Acta* **11**, 1881–1889.
12. Sharma, T. & Clayton, R. N. (1965) *Geochim. Cosmochim. Acta* **29**, 1347–1353.
13. Matsuhisa, Y., Goldsmith, J. R. & Clayton, R. N. (1978) *Geochim. Cosmochim. Acta* **42**, 173–182.
14. Young, E. D., Galy, A. & Nagahara, H. (2002) *Geochim. Cosmochim. Acta* **66**, 1095–1104.
15. Agrinier, P., Deutsch, A., Schärer, U. & Martinez, I. (2001) *Geochim. Cosmochim. Acta* **65,** 2615–2632.
16. Coplen, T. B., Kendall, C. & Hopple, J. (1983) *Nature (London)* **302**, 236–238.
17. Angert, A. & Luz, B. (2001) *Geochim. Cosmochim. Acta* **65,** 1695–1701.
18. Rosenbaum, J. & Shepherd, S. M. F. (1986) *Geochim. Cosmochim. Acta* **50,** 1147–1150.
19. Thiemens, M. H. & Heidenreich, J. E., III (1983) *Science* **219,** 1073–1075.
20. Hathorn, B. C. & Marcus, R. A. (1999) *J. Chem. Phys.* **111,** 4087–4100.
21. Gao, Y. Q. & Marcus, R. A. (2001) *Science* **293,** 259–263.
22. Bhattacharya, S. K., Savarino, J. & Thiemens, M. H. (2000) *Geophys. Res. Lett.* **27**, 1459–1462.
23. Wen, J. & Thiemens, M. H. (1990) *Chem. Phys. Lett.* **172,** 416–420.
24. Wen, J. & Thiemens, M. H. (1991) *J. Geophys. Res.* **96,** 10911–10921.
25. Reeder, R. J. (1983) in *Reviews in Mineralogy*, ed. Ribbe, P. H. (Mineral. Soc. Am., Washington, DC), Vol. 11, pp. 1, 4–6.
26. Horváth, M., Bilitzky, L. & Hüttner, J. (1985) in *Ozone*. *Topics in Inorganic and General Chemistry*, ed. Clark, R. J. H. (Elsevier, New York), Monograph 20, pp. 13–14.
27. Zeebe, R. E., Wolf-Gladrow, D. A. & Jansen, H. (1999) *Marine Chem.* **65,** 135–153.
28. Chiodini, G., Allard, P., Caliro, S. & Parello, F. (2000) *Geochim. Cosmochim. Acta* **64,** 2479–2488.
29. Luz, B., Barkan, E., Bender, M. L., Thiemens, M. H. & Boering, K. A. (1999) *Nature (London)* **400,** 547–550.
30. Kemper, F., Jager, C., Waters, L., Henning, T., Molster, F. J., Barlow, M. J., Lim, T. & de Koter, A. (2002) *Nature (London)* **415,** 295–297.