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Oxygen three-isotope fractionation lines in terrestrial silicate minerals: An inter-laboratory comparison of hydrothermal quartz and eclogitic garnet

D. Rumble [a,*], M.F. Miller [b,c], I.A. Franchi [c], R.C. Greenwood [c]

[a] Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC, USA
[b] British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK
[c] Planetary and Space Sciences Research Institute, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

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Abstract

Geochemical—and perhaps biochemical—processes may yield tell-tale proxies in rocks and minerals on the Earth or other planetary bodies, in the form of distinctive slopes of linear fractionation arrays on the oxygen three-isotope plot. It is generally recognized that kinetic and equilibrium fractionation processes are described by different mass fractionation laws. We show that coupled laser fluorination, dual-inlet IRMS procedures for oxygen three-isotope analysis of silicates, at high precision, gave reproducible accuracy for the slope value as measured independently by two different laboratories, using replicates of the same silicate samples. As far as we are aware, this is the first such inter-laboratory comparison. Hydrothermal quartz (together with one chalk flint sample) with a range in $\delta^{18}O$ of 31‰ gave respective slope λ values of 0.5240 ± 0.0010 and 0.5242 ± 0.0010, using Prism III and MAT 253 mass spectrometers, respectively, at the Open University (OU). Errors were computed from weighted linear regression and are reported at the 95% confidence level. The comparable result obtained at the Geophysical Laboratory (GL), Carnegie Institution of Washington, was 0.5240 ± 0.0015. A MAT 252 mass spectrometer was used for the latter measurements and the oxygen extraction and purification procedures differed in detail from those used at the OU. In contrast, slopes measured for replicates of seven garnet samples, metamorphosed under high-temperature, high-pressure conditions, and spanning 20‰ in $\delta^{18}O$, gave 0.5262 ± 0.0008 at OU (Prism III analyses) and 0.5266 ± 0.0012 at GL.

1. INTRODUCTION

The terrestrial fractionation line (TFL) was originally described as the locus of points obtained when analyses of $\delta^{17}O$ are plotted vs. $\delta^{18}O$ for Earth's rocks and minerals (cf. Clayton et al., 1973; Matsuhisa et al., 1978; Clayton and Mayeda, 1983). For high precision measurements of the attendant slope, it is necessary to report the data in a more rigorous representation of the relationship between the three isotopes (Hulston and Thode, 1965; Miller, 2002; Young et al., 2002). The first report of the slope derived in such a manner for the TFL was for terrestrial waters (Li and Meijer, 1998). For the present paper, the form of the three-isotope plot as proposed by Miller (2002) will be used, as has been adopted in several recent studies, with $1000\ln(1 + 10^{-3}\delta^{17}O)$ the ordinate and $1000\ln(1 + 10^{-3}\delta^{18}O)$ the abscissa values. The factor of 10^{-3} is present because we use the original definition of δ as being in units of 'per mil', rather than being a dimensionless quantity. For convenience, we will abbreviate the ordinate and abscissa units as $\delta'^{17}O$ and $\delta'^{18}O$, respectively, in this paper.

The equation governing the equilibrium, mass-dependent fractionation of oxygen isotopes has the form of a straight line with slope λ, when plotted in $\delta'^{17}O$ and $\delta'^{18}O$ coordinates:

* Corresponding author.
E-mail address: rumble@gl.ciw.edu (D. Rumble).

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$$\delta'^{17}O = \lambda\delta'^{18}O + (\text{intercept on } \delta'^{17}O\text{-axis}) \quad (1)$$

Eq. (1) is derived, with no simplifying approximations, from the power law dependence of isotope fractionation:

$$^{17}R_a/^{17}R_b = [1 + k](^{18}R_a/^{18}R_b)^{\lambda} \quad (2)$$

where $^{17}R_a = {}^{17}O/^{16}O$ and $^{18}R_a = {}^{18}O/^{16}O$ in sample a and similarly for reference b (Miller, 2002). The parameter k is a measure of (but is not quite identical to) any ordinate axis offset of sample a from a reference fractionation line of slope λ on a plot of $\delta'^{17}O$ relative to $\delta'^{18}O$.

As shown by Matsuhisa et al. (1978, Appendix I), and by Young et al. (2002, Eq. (15), p. 1097), the value of the slope for equilibrium isotope partitioning at high temperature is given by

$$\lambda = (1/m_{16} - 1/m_{17})/(1/m_{16} - 1/m_{18}) \quad (3)$$

with m_{16}, m_{17}, and m_{18} being the respective atomic masses of the oxygen isotopes. The origin of the phrase 'mass-dependent isotope fractionation' as applied to elements with three or more stable isotopes is readily apparent in Eq. (3), because atomic masses are the only terms present. It should be noted, however, that the distinction between 'mass-dependent' and 'mass-independent' ('non-mass dependent') fractionation is not always obvious and depends to some extent on the slope value, λ, of the chosen reference fractionation line.

The TFL plays different roles in different types of studies in stable isotope chemistry. For cosmochemists, the TFL is of particular interest as a reference for assessing the magnitude by which meteorites depart from the three-isotope distribution of Earth's oxygen reservoir. Distinct oxygen isotope fractionation lines lying parallel to the TFL, but displaced from it, are characteristic (and are often unique identifiers) of the parent planetary bodies. Examples include Mars, as represented by the SNC meteorites (Franchi et al., 1999) and the asteroid 4 Vesta as represented by the HED meteorites (Wiechert et al., 2004; Greenwood et al., 2005). A contrasting example is that of the Moon, whose fractionation array is coincident with a portion of Earth's (Wiechert et al., 2001; Spicuzza et al., 2007). For atmospheric chemists, the TFL serves as a reference for the quantification of oxygen isotope anomalies derived from stratospheric ozone and inherited by other oxygen-bearing constituents of the atmosphere (Mauersberger et al., 2005; Thiemens, 2006 and references therein).

Geochemists certainly value the TFL as an isotopic benchmark, but the existence of outright departures from it on Earth have been recognized during recent years. A deficiency of ^{17}O in molecular O_2 of the atmosphere in relation to most rocks, minerals, and waters, first predicted by M. Thiemens (as quoted by Bender et al., 1994), was validated by the measurements of Luz et al. (1999). And large excesses of ^{17}O, derived ultimately from isotopically anomalous ozone produced by ultraviolet photolysis of oxygen, have been discovered in deposits of sulfate, perchlorate, and nitrate minerals in arid regions and in atmospheric aerosol particles (Bao et al., 2000; Michalski et al., 2003; see also review by Thiemens, 2006). It must be concluded that not all terrestrial materials can be regarded as valid candidates for defining a TFL.

The possibility must also be admitted of multiple fractionation lines, each arising from a specific equilibrium or kinetically limited reaction mechanism. In Eq. (3) above, the slope of the TFL is stated to be $\lambda = (1/m_{16} - 1/m_{17})/(1/m_{16} - 1/m_{18})$ where the m_i are atomic masses. But the formula for λ in Eq. (3) is valid for high-temperature, equilibrium isotopic fractionation alone. In kinetic processes, the correct form of the slope is

$$\lambda = \ln(m_{16}/m_{17})/\ln(m_{16}/m_{18}) \quad (4)$$

where the m_i may be, for example, the reduced masses of vibrating diatomic molecules rather than atomic masses [Young et al., 2002, Eq. (21), p. 1097; Eq. (25), p. 1098]. A kinetically dominated process would typically give a lower slope for mass-dependent partitioning than equilibrium isotopic fractionation, but it would still be correct to refer to it as 'mass-dependent'. The possible existence of multiple mass-dependent fractionation lines may seem an inconvenience in view of the desire for a unique, fiducial line. Furthermore, an additional complication to this 'equilibrium versus kinetic' analysis of potential fractionation pathways in the case of silicates is the hypothesis that chemical composition or metamorphic history might also be an additional factor, of as yet unknown magnitude. But it is potentially far more beneficial to consider the uses of different fractionation lines as new and powerful tracers in biogeochemical cycles (Farquhar et al., 2003; Angert et al., 2004; Luz and Barkan, 2005; Johnston et al., 2005; Landais et al., 2006; Ono et al., 2006), subject to the proviso that there is strong justification for choosing a particular line as the reference.

New discoveries and new experiments in terrestrial oxygen triple-isotope geochemistry bring with them a challenge to all stable isotope geochemists: Can the isotopic composition of natural samples be measured in laboratories worldwide with sufficient accuracy and precision to exploit new research opportunities? Measurements of fractionation lines derived from linearization of $\delta^{17}O$ and $\delta^{18}O$ values and representative of kinetic or equilibrium mass-dependent processes must be robust with respect to the ultimate test provided by inter-laboratory analyses of aliquots of the same samples. Conventional wisdom states that laboratory errors of measurement are 'mass-dependent' and must 'cancel' when slopes are calculated by linear regression. Errors on measured $\Delta^{17}O$, where this term equates to the parameter k in Eq. (2) and is a measure of the offset from a reference regression line, should be lower than errors on measured values of $\delta^{17}O$ and $\delta^{18}O$, according to this idea. We sought to test conventional wisdom and to advance the study of oxygen triple-isotope geochemistry by performing an inter-laboratory comparison study on two sample populations, one of quartz and one of garnets, previously analyzed in our respective laboratories using local methodological protocols.

1.1. Previous TFL measurements

Previously-published measurements of the slope of the TFL for rocks, minerals, and meteoric waters are shown in Fig. 1, where the raw data have been converted into

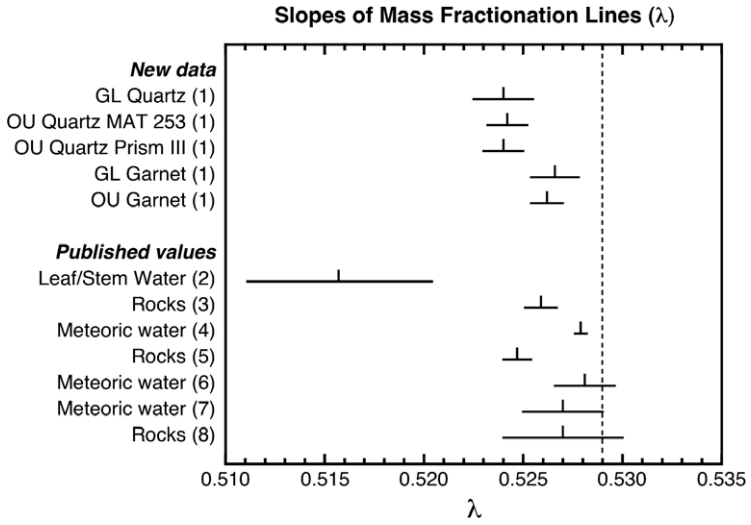

Fig. 1. Published values of λ compared to the results of this study. Literature $\delta^{17}O$ and $\delta^{18}O$ data were converted to linearized δ' for purposes of computing λ. Mean values are marked by vertical ticks; horizontal bars indicate the corresponding 95% confidence intervals [except see (6)]. The vertical dashed line marks $\lambda = 0.529$, the equilibrium value for water vapor–liquid fractionation (Barkan and Luz, 2005). (1) GL Quartz, Geophysical Lab measurements for quartz and chalk flint; GL Garnet, Geophysical Lab measurements for garnet; OU, Open University, see Table 3; (2) Landais et al. (2006); (3) Spicuzza et al. (2007); (4) Barkan and Luz (2005); (5) Miller et al. (1999); (6) Li and Meijer (1998), with horizontal bar indicating standard error; (7) Jabeen and Kusakabe (1997); (8) Robert et al. (1992).

$\delta'^{17}O$ and $\delta'^{18}O$ to enable valid comparison. Analytical methods included externally heated fluorination of rocks with BrF_5 (Robert et al., 1992); fluorination of water with BrF_5 (Jabeen and Kusakabe, 1997); electrolysis of water with $CuSO_4$ as electrolyte (Li and Meijer, 1998); laser-heated fluorination of minerals with BrF_5 (Miller et al., 1999; Spicuzza et al., 2007), and fluorination of water with CoF_3 (Barkan and Luz, 2005). The precision on the slope measurements may approach or even exceed 0.001 at the 95% confidence level, on a laboratory-by-laboratory basis. Despite differences in both samples and methods of analysis, the disagreement in measured slopes for meteoric water between different laboratories is no worse than 0.0011. The inter-laboratory investigations of water samples demonstrate that the slope of the TFL for meteoric waters can be measured reliably to high precision. But none of the published data sets makes a comparison between the measurements of different laboratories on aliquots of the same mineral samples.

1.2. Analytical methods

A description of analytical methods at the Planetary and Space Sciences Research Institute (PSSRI) of the Open University (OU) is provided by Miller et al. (1999). Geophysical Laboratory (GL) analytical procedures are given in Rumble and Hoering (1994). In both laboratories, oxygen extraction from silicate minerals for $\delta^{17}O$ and $\delta^{18}O$ analyses is performed using purified BrF_5 while heating with a Synrad 25 W CO_2 laser (wavelength 10.6 microns). Differences between analytical practices at the two laboratories do not appear to exert a strong control on the results. Samples are loaded into the reaction chamber, evacuated, and then fluorinated overnight at GL, followed by measurements of blank. At the OU, samples are evacuated overnight and then blanks are measured. The reaction chamber at GL is that described by Sharp (1990). Laser fluorination at GL is conducted under a pressure of 30 torr of BrF_5, whereas approximately 210 torr is used at the OU. Another difference is that, at the OU, O_2 gas is transferred using molecular sieve 13X cooled with liquid nitrogen, whereas molecular sieve 5A is used at GL. Mass spectrometric analyses of O_2 at the OU are usually performed with a Micromass Prism III mass spectrometer, but for the purpose of the present exercise the O_2 extracted from the quartz samples was 'split' and also analyzed using a newly-commissioned Thermo-Fisher MAT 253. Analysis at GL made use of a Thermo-Fisher MAT 252 mass spectrometer. All these three instruments are of similarly high mass resolution and abundance sensitivity.

Analytical difficulties were encountered by both laboratories in attempting to analyze fine-grained aliquots of quartz and chalk flint samples. Under a CO_2 laser beam, fine-grained mineral grains tend to jump out of the sample holder. Individual grains may ignite in fluorinating reagent and blaze an incandescent trail across the reaction chamber. The result of these difficulties is decreased yields of oxygen in relation to the amount of mineral sample loaded and, typically, $\delta^{18}O$ values lower than would have been obtained using resistance-heated fluorination procedures (cf. Clayton and Mayeda, 1963). These effects have been observed elsewhere and remedies such as use of a low power, defocused laser beam have been recommended (Valley et al., 1995). In addition, gentle melting, under vacuum, of mineral grains with a low power, defocused laser prior to fluorination, to form a more massive, less easily disturbed aggregate (as is routinely employed at both laboratories) was attempted. Despite best efforts, the resulting $\delta^{18}O$ values measured at

Table 1
Results of isotopic analysis of hydrothermal quartz and a chalk flint sample, analyzed at the Open University and at the Geophysical Laboratory of the Carnegie Institution Washington

Sample	Open University Prism III		Open University MAT 253		Geophysical Laboratory MAT 252	
	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
CFS	17.701	33.995	17.722	34.029	17.037	32.829
	17.677	34.001	17.682	33.929	17.600	33.794
					16.885	32.473
					16.186	31.236
					17.188	33.060
CQ1	1.384	2.639	1.465	2.719	0.873	1.769
	1.350	2.551	1.394	2.601	0.382	0.646
					1.123	2.063
					0.171	0.335
CQ4	12.183	23.376	12.246	23.415	12.070	23.096
	12.420	23.781	12.447	23.799	11.891	22.864
					11.586	22.209
					11.626	22.207
					12.293	23.523
LQS	5.784	11.002	5.809	11.117	5.579	10.653
	5.800	11.030	5.821	11.105	5.316	10.412
					5.451	10.368
					4.891	9.488
					5.501	10.531
DQC	10.231	19.532	10.275	19.587	9.504	18.232
	10.198	19.477	10.328	19.732	9.779	18.731
					9.756	18.566
CQ2	4.319	8.222	4.414	8.304	3.884	7.413
	4.350	8.251			3.711	7.081
					4.035	7.682
AQC	7.453	14.279	7.468	14.241	7.072	13.560
	7.486	14.320	7.531	14.376	7.090	13.572
					6.417	12.231
					6.889	13.177

Each reported datum represents an independent analysis of an aliquot of a given sample. These data, after linearization, were analyzed by error-weighted, linear least squares regression. Results are reported to three decimal places, as in the mass spectrometer print-out, to minimize rounding errors in regression for λ. Earlier measurements of the same samples were included in the study by Miller et al. (1999).

GL on the OU samples approach (from the low side), but do not equal, OU $\delta^{18}O$ values (Table 1).

We recalculated our "δ" values, measured in relation to mass spectrometer working reference gases, as $\delta'^{(17\text{ or }18)}O = 1000\ln(1 + \delta^{(17\text{ or }18)}O/1000)$. An error-weighted linear regression of the linearized data was performed with ISOPLOT 3.0, taking into account error correlations, to obtain the slopes and intercepts of our data sets (York, 1969; Ludwig, 2003).

2. SAMPLES

Six samples of terrestrial quartz, together with a chalk flint, all of which were used in previous oxygen isotope investigations at the OU (Miller et al., 1999; Miller, 2002) were used in this study. The samples were from a variety of geological environments, but were all of hydrothermal, near-surface origin. Localities included hydrothermal mineralization associated with the Yanshanian granites (Gangxhou, China), a glass sand from Loch Aline, Scotland, and chalk flint from Brandon (Norfolk, England). The $\delta^{18}O_{VSMOW}$ values ranged from +2.5‰ to +34.0‰ (Table 1).

The garnet samples (Table 2) used for this study were obtained by standard methods of mineral separation from hand specimens of coesite-eclogite facies eclogites and garnet peridotites from Dabieshan and Sulu, China, and from diamond-eclogite facies eclogites from Kokchetav, Kazakhstan (Rumble and Yui, 1998; Masago et al., 2003; Zhang et al., 2005).

3. RESULTS

Measured slopes (λ) for quartz samples are the same for the OU's Prism III and GL's MAT 252 mass spectrometers and differ by 0.0002 for OU's MAT 253 and GL's MAT 252 (Fig. 1 and Table 3). Values of the slope for garnet samples differ by only 0.0004 (Fig. 1 and Table 3). These results confirm that the measurement of a TFL for silicate minerals by laser fluorination may be conducted at the same high standard of accuracy and precision as that for meteoric waters (cf. Fig. 1).

Table 2
Analytical data for garnets

Sample	Open University Prism III		Geophysical Laboratory MAT 252	
	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
A12[a]	5.708	10.912	5.541	10.479
	5.635	10.782	5.409	10.258
A15[a]	4.305	8.204	4.114	7.728
	4.212	8.089	4.067	7.760
F430[a]	−0.073	−0.074	−0.092	−0.206
	−0.148	−0.210	−0.147	−0.345
95-YS-1[b]	−2.732	−5.142	−2.611	−5.017
	−2.774	−5.205	−2.655	−5.116
			−2.676	−5.089
			−2.602	−5.093
			−2.541	−4.959
			−2.746	−5.377
			−2.793	−5.399
			−2.503	−4.994
			−2.525	−4.967
			−2.675	−5.128
			−2.662	−5.127
			−2.569	−5.002
			−2.580	−4.996
			−2.557	−4.949
			−2.564	−4.932
			−2.526	−4.916
95-QL-2H[b]	−5.607	−10.598	−5.520	−10.515
	−5.569	−10.521	−5.587	−10.642
			−5.420	−10.461
			−5.452	−10.432
			−5.490	−10.523
			−5.476	−10.543
			−5.481	−10.572
			−5.466	−10.600
			−5.539	−10.601
			−5.419	−10.330
			−5.367	−10.257
GMTNcrs	3.015	5.820	3.077	5.716
	3.087	5.925	3.243	6.040
			3.080	5.785
			3.199	5.989
			3.233	5.898
			3.303	6.051
			3.184	5.846
			3.144	5.921
			3.288	6.014
			3.197	5.897
			3.222	5.901
			3.094	5.728
			3.108	5.750
			3.075	5.699
			3.213	5.969
			3.112	5.817
			3.076	5.795
			3.210	5.893
			3.266	6.161
			3.143	5.886
			3.266	6.094
			3.261	6.105
			3.176	5.927
			3.116	5.852

Table 2 (*continued*)

Sample	Open University Prism III		Geophysical Laboratory MAT 252	
	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
95-M-1A[b]	0.119	0.284	0.287	0.423
	0.175	0.404	0.431	0.657
			0.369	0.584
			0.051	0.086
			0.080	0.101
			0.162	0.294
			0.211	0.280
			0.029	−0.040
			0.082	−0.033
			−0.113	−0.338
			0.167	0.214
			0.180	0.174
			0.179	0.205
			0.154	0.237
			0.165	0.237
			0.162	0.175
			−0.068	−0.143
			0.005	−0.135
			0.041	0.032
			0.074	−0.048
			0.060	−0.041
			0.150	0.184
			0.187	0.162
			0.189	0.264
C25-141-60[c]	2.860	5.496	2.874	5.355
	2.700	5.165	2.780	5.099

Each reported datum represents an independent analysis of an aliquot of a given sample. These data, after linearization, were analyzed by error-weighted, linear least squares regression. Results are reported to three decimal places, as in the mass spectrometer print-out, to minimize rounding errors in regression for λ. Geophysical Laboratory data were obtained by W. G. Ernst, H. Masago, D. Rumble and Z. Zhang (Rumble and Yui, 1998; Rumble et al., 2002; Masago et al., 2003; Zhang et al., 2005).

[a] Masago et al. (2003).

[b] Rumble and Yui (1998).

[c] Zhang et al. (2005).

Table 3
Comparison of TFL slopes measured at the Open University (PSSRI) with those at the Geophysical Laboratory (GL)

Silicate mineral	PSSRI slope (λ)		GL slope (λ)
	Prism III	MAT 253	MAT 252
Silica (quartz or flint)	0.5240 ± 0.0010 $n = 14$	0.5242 ± 0.0010 $n = 13$	0.5240 ± 0.0015 $n = 29$
Garnet	0.5262 ± 0.0008 $n = 16$		0.5266 ± 0.0012 $n = 83$

Values of λ were obtained by error-weighted, linear least squares regression with correlated errors (York, 1969; Ludwig, 2003) of data presented in Tables 1 and 2. Precision refers to the 95% confidence level.

The difficulties encountered in analyzing fine-grained quartz and flint samples described above provided an unexpected data set for testing the impact of analytical errors in $\delta^{17}O$ and $\delta^{18}O$ on λ and $\Delta^{17}O$ values. The values of $\delta^{17}O$ and $\delta^{18}O$ for fine-grained quartz and chalk flint measured at GL are fractionated in relation to those analyzed at OU. Despite worst-case differences in $\delta^{18}O$ values of up to 3‰ (Table 1), values of λ differed by only 0.0002 between the two laboratories (Table 3). A plot of $\delta'^{18}O$ vs. $\Delta^{17}O$ shows no systematic relationship between the two variables (Fig. 2). Values of $\Delta^{17}O$ average 0.01‰ (±0.04) for the GL quartz data, calculated with $\lambda = 0.524$ as obtained by error-weighted linear regression of GL data (Fig. 2). We have confirmed the conventional wisdom that laboratory errors of measurement on δ-values are 'mass-dependent' and must 'cancel' when slopes are calculated by linear regression.

The surprising result of our work is the difference in linearized $\delta'^{17}O$ vs. $\delta'^{18}O$ slopes between the quartz and garnet samples (Fig. 1 and Table 3). The measured slopes of the two mineral groups overlap slightly at the 95% confidence level (GL data only), but the observation that both laboratories agree on the magnitude and sign of the differences in slope, as measured on two different mass spectrometers, suggests that the difference may be significant. We tested the significance of the differences in λ between quartz and garnet analyses by performing (1) ordinary least squares (OLS) regression without error weighting, as found in Microsoft's EXCEL spreadsheet; and (2) error-weighted linear regression of York (1969) as implemented by Ludwig (2003), on the same data sets. The results for both OLS and

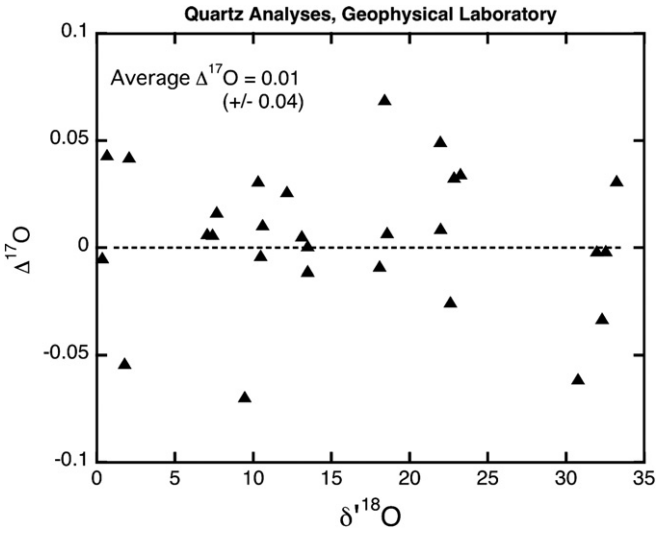

Fig. 2. Plot of $\Delta^{17}O$ vs. $\delta'^{18}O$ for quartz and chalk flint analyses. There is no systematic relationship between $\Delta^{17}O$ and errors in measuring $\delta'^{18}O$.

error-weighted linear regression are in good agreement on λ values. The precision of λ values estimated with the aid of OLS is comparable to that derived from error-weighted linear regression. We report the York regression errors in Fig. 1 and Table 3. Differences in λ between quartz and garnet are 0.0022 as measured at OU (Prism III), compared to 0.0026 at GL, with 2σ errors of 0.0010–0.0015 (quartz) and 0.0008–0.0012 (garnet), respectively (Fig. 1 and Table 3). We conclude that the measured differences in λ lie just at the edge of our capability to distinguish them.

4. DISCUSSION

We have demonstrated the resolution of differences in λ for ^{16}O–^{17}O–^{18}O fractionation at a level of 0.001–0.002 for silicate minerals. Others have shown that even finer distinctions of 0.0001 can be made on water samples (Barkan and Luz, 2005). Can these newfound capabilities be put to good use geochemically? Consider an example afforded by recent advances in sulfur isotope geochemistry: measured differences in λ values for ^{32}S–^{33}S–^{34}S fractionation accompanying alternative biochemical pathways in the metabolism of sulfur by microbes have been used to demonstrate that disproportionation of sulfur compounds was active in organisms by 1300 million years before present (Johnston et al., 2005). Is it possible that similar studies of oxygen isotope fractionation would provide calibrated proxies for atmosphere–biosphere–hydrosphere interactions?

Variations in λ values for geochemical and biochemical reactions are controlled by a number of factors, including temperature, and reaction mechanisms. In the example of sulfur isotope fractionation cited above, it is the kinetics of specific biochemical pathways that result in measurable differences in λ. Values of λ for oxygen isotopes vary over a narrow range in the realm of crustal temperatures: for equilibrium oxygen isotope partitioning between CO_2–H_2O, values of 0.5233, 0.5235, 0.5249, and 0.5251 for temperatures of 0, 25, 227, and 727 °C have been calculated (Matsuhisa et al., 1978). Experimental determination of the λ for equilibrium fractionation between water liquid–vapor gives a constant value of 0.529 over the temperature range 11.4–41.5 °C (Barkan and Luz, 2005). The effect of pressure on λ is expected to be even smaller than that of temperature. Calculations of the effect of 10 kbar pressure in changing equilibrium $^{18}O/^{16}O$ fractionation between quartz and rutile show changes of 0.17‰ at 300 °C and 0.05‰ at 800 °C; the pressure effect on partitioning of $^{17}O/^{16}O$ would be approximately one-half of these values (Polyakov and Kharlashina, 1994). A potentially major control on λ would be exerted by fractionations changing sign or "crossing-over" (Deines, 2003), but the phenomenon has not been definitively observed during geochemical processes (Schauble, 2004).

The strongest control on λ measured to date is by reaction kinetics. A pronounced effect on λ for ^{16}O–^{17}O–^{18}O fractionation between stem and leaf water is manifested during evapo-transpiration by plants (Landais et al., 2006). Values of λ in the range from 0.5111 to 0.5204 have been measured during the transpiration of leaf water (Fig. 1). The values reflect the fractionation effects of liquid–vapor equilibrium, water vapor diffusion in air, and isotopic exchange with atmospheric moisture (Landais et al., 2006). The value of λ for equilibrium liquid–vapor oxygen isotope exchange is 0.529, so the effects of reaction kinetics are notable (Fig. 1; Barkan and Luz, 2005; Landais et al., 2006).

We do not have a preferred explanation for the difference in slope measured between quartz and garnet samples in this study. The mineral samples experienced vastly different pressure–temperature–time (P–T) histories. Rocks from which the garnets were separated were deposited near Earth's surface, subducted into the upper mantle where they were subjected to temperatures of 700 °C and pressures of 30 kbar during the Triassic, and then exhumed to the surface (Rumble and Yui, 1998) or, in the case of rocks

from Kazakhstan, subducted to greater depths, where diamond crystallized from organic carbonaceous residues (Masago et al., 2003). These rocks have been thoroughly recrystallized under extreme *P–T* conditions. Both isotopic and chemical studies suggest that chemical equilibrium was closely approached, if not fully achieved, during ultra-high pressure metamorphism (Rumble and Yui, 1998). By comparison, the quartz and flint samples crystallized under low *P–T*, near-surface conditions. The magnitude of the measured difference in λ between the quartz and garnet samples, 0.0022–0.0026, is similar to that calculated for the effect of a change in temperature of 700 °C on oxygen isotope exchange between CO_2 and H_2O (Matsuhisa et al., 1978), but the agreement may be fortuitous and not determinative.

5. CONCLUSIONS

The principal conclusions from the present work are twofold: firstly, the level of agreement obtained on inter-laboratory comparison of the oxygen triple-isotope fractionation line as measured independently by two laboratories using aliquots of the same quartz samples, or same garnet samples, provides the first validation of high precision measurements of the slope of the line for silicate minerals. Thus, design differences between high-resolution mass spectrometers of comparable performance, and small differences in laboratory procedures, are not influential factors. Secondly, there is a distinction in the slope given by eclogitic garnets, compared to that obtained from hydrothermal quartz samples. The reasons for this remain unclear, although the influence of metamorphic grade and silicate chemical composition remain two avenues for further exploration.

The good agreement between two laboratories, at a precision of 0.001 in measuring the slopes of mass-dependent oxygen triple-isotope fractionations in two mineral groups, should encourage those who wish to pursue the next level of research in multi-isotope geochemistry. Both in oxygen (Angert et al., 2004; Luz and Barkan, 2005; Landais et al., 2006) and in sulfur (Farquhar et al., 2003; Johnston et al., 2005; Ono et al., 2006) isotope geochemistry there are enticing research opportunities to distinguish between kinetically-controlled vs. equilibrium processes—and secondary factors—in a variety of terrestrial environments.

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REFERENCES

Angert A., Cappa C. D., and DePaolo D. J. (2004) Kinetic ^{17}O effects in the hydrologic cycle: indirect evidence and implications. *Geochim. Cosmochim. Acta* **68**, 3487–3495.

Bao H., Thiemens M. H., Farquhar J., Campbell D. A., Lee C. C.-W., Heine K., and Loope D. B. (2000) Anomalous ^{17}O compositions in massive sulphate deposits on the Earth. *Nature* **406**, 176–178.

Barkan E., and Luz B. (2005) High precision measurements of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios in H_2O. *Rapid Commun. Mass Spectrom.* **19**, 3737–3742.

Bender M. L., Sowers T., and Labeyrie L. (1994) The Dole effect and its variation during the last 130,000 years as measured in the Vostok ice core. *Global Biogeochem. Cycles* **8**, 363–376.

Clayton R. N., and Mayeda T. K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* **27**, 43–52.

Clayton R. N., and Mayeda T. K. (1983) Oxygen isotopes in eucrites, shergottites, nakhlites, and chassignites. *Earth Planet. Sci. Lett.* **62**, 1–6.

Clayton R. N., Grossman L., and Mayeda T. K. (1973) A component of primitive nuclear composition in carbonaceous meteorites. *Science* **182**, 485–488.

Deines P. (2003) A note on intra-elemental isotope effects and the interpretation of non-mass-dependent isotope variations. *Chem. Geol.* **199**, 179–182.

Farquhar J., Johnston D. T., Wing B. A., Habicht K. S., Canfield D. E., Airieau S., and Thiemens M. H. (2003) Multiple sulfur isotopic interpretations of biosynthetic pathways: implications for biological signatures in the sulphur isotope record. *Geobiology* **1**, 27–36.

Franchi I. A., Wright I. P., Sexton A. S., and Pillinger C. T. (1999) The oxygen-isotopic composition of Earth and Mars. *Meteoritics Planet. Sci.* **34**, 657–661.

Greenwood R. C., Franchi I. A., Jambon A., and Buchanan P. C. (2005) Widespread magma oceans on asteroidal bodies in the early Solar System. *Nature* **435**, 916–921.

Hulston J. R., and Thode H. G. (1965) Variations in the S^{33}, S^{34}, and S^{36} contents of meteorites and their relation to chemical and nuclear effects. *J. Geophys. Res.* **70**, 3475–3484.

Jabeen I., and Kusakabe M. (1997) Determination of $\delta^{17}O$ values of reference water samples VSMOW and SLAP. *Chem. Geol.* **143**, 115–119.

Johnston D. T., Wing B. A., Farquhar J., Kaufman A. J., Strauss H., Lyons T. W., Kah L. C., and Canfield D. E. (2005) Active microbial sulfur disproportionation in the mesoproterozoic. *Science* **310**, 1477–1479.

Landais A., Barkan E., Yakir D., and Luz B. (2006) The triple isotopic composition of oxygen in leaf water. *Geochim. Cosmochim. Acta* **70**, 4105–4115.

Li W. J., and Meijer H. A. J. (1998) The use of electrolysis for accurate $\delta^{17}O$ and $\delta^{18}O$ isotope measurements in water. *Isotopes Environ. Health Stud.* **34**, 349–369.

Ludwig, K. (2003) ISOPLOT 3.0, A Geochronological Toolkit for Microsoft Excel. Berkeley Geochronology Center, <http://www.bgc.org/isoplot_etc/software.html/>.

Luz B., and Barkan E. (2005) The isotopic ratios $^{17}O/^{16}O$ and $^{18}O/^{16}O$ in molecular oxygen and their significance in biogeochemistry. *Geochim. Cosmochim. Acta* **69**, 1099–1110.

Luz B., Barkan E., Bender M. L., Thiemens M. H., and Boering K. A. (1999) Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity. *Nature* **400**, 547–550.

Masago H., Rumble D., Ernst W. G., Parkinson C. D., and Maruyama S. (2003) Low $\delta^{18}O$ eclogites from the Kokchetav massif, northern Kazakhstan. *J. Metamorphic Geol.* **21**, 579–587.

Matsuhisa Y., Goldsmith J. R., and Clayton R. N. (1978) Mechanisms of hydrothermal crystallization of quartz at 250 °C and 15 kbar. *Geochim. Cosmochim. Acta* **42**, 173–182.

Mauersberger K., Krankowsky D., Janssen C., and Schinke R. (2005) Assessment of the ozone isotope effect. *Adv. Atomic Mol. Opt. Phys.* **50**, 1–54.

Michalski G., Scott Z., Kabiling M., and Thiemens M. H. (2003) First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate. *Geophys. Res. Lett.* **30**, 1870.

Miller M. F. (2002) Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* **66**, 1881–1889.

Miller M. F., Franchi I. A., Sexton A. S., and Pillinger C. T. (1999) High precision $\delta^{17}O$ isotope measurements of oxygen from silicates and other oxides: Method and applications. *Rapid Commun. Mass Spectrom.* **13**, 1211–1217.

Ono S., Wing B. A., Johnston D., Farquhar J., and Rumble, III, D. (2006) Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. *Geochim. Cosmochim. Acta* **70**, 2238–2252.

Polyakov V. B., and Kharlashina N. N. (1994) Effect of pressure on equilibrium isotopic fractionation. *Geochim. Cosmochim. Acta* **58**, 4739–4750.

Robert F., Rejou-Michel A., and Javoy M. (1992) Oxygen isotopic homogeneity of the Earth: new evidence. *Earth Planet. Sci. Lett.* **108**, 1–9.

Rumble D., and Hoering T. C. (1994) Analysis of oxygen and sulfur isotope ratios in oxide and sulfide minerals by spot heating with a carbon dioxide laser in a fluorine atmosphere. *Acc. Chem. Res.* **27**, 237–241.

Rumble D., and Yui T. F. (1998) The Qinglongshan oxygen and hydrogen isotope anomaly near Donghai in Jiangsu province, China. *Geochim. Cosmochim. Acta* **62**, 3307–3321.

Rumble D., Giorgis D., Ireland T., Zhang Z., Xu H., Yui T. F., Yang J., Xu Z., and Liou J. G. (2002) Low $\delta^{18}O$ zircons, U-Pb dating, and the age of the Qinglongshan oxygen and hydrogen isotope anomaly near Donghai in Jiangsu Province, China. *Geochim. Cosmochim. Acta* **66**, 2299–2306.

Schauble E. A. (2004) Applying stable isotope fractionation theory to new systems. *Rev. Mineral. Geochem.* **55**.

Sharp Z. D. (1990) A laser-based microanalytical method for the in-situ determination of oxygen isotope ratios of silicates and oxides. *Geochim. Cosmochim. Acta* **54**, 1353–1357.

Spicuzza M. J., Day J. M. D., Taylor L. A., and Valley J. W. (2007) Oxygen isotope constraints on the origin and differentiation of the Moon. *Earth Planet. Sci. Lett.* **253**, 254–265.

Thiemens M. H. (2006) History and applications of mass-independent isotope effects. *Annu. Rev. Earth Planet. Sci.* **34**, 217–262.

Valley J. W., Kitchen N. E., Kohn M. J., Niendorf C. R., and Spicuzza M. J. (1995) UWG-2, a garnet standard for oxygen isotope ratios: strategies for high precision and accuracy with laser heating. *Geochim. Cosmochim. Acta* **59**, 5223–5231.

Wiechert U., Halliday A. N., Lee D.-C., Snyder G. A., Taylor L. A., and Rumble D. (2001) Oxygen isotopes and the Moon-forming giant impact. *Science* **294**, 345–348.

Wiechert U., Halliday A. N., Palme H., and Rumble D. (2004) Oxygen isotope evidence for rapid mixing of the HED meteorite parent body. *Earth Planet. Sci. Lett.* **221**, 373–382.

York D. (1969) Least-squares fitting of a straight line with correlated errors. *Earth Planet. Sci. Lett.* **5**, 320–324.

Young E. D., Galy A., and Nagahara H. (2002) Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* **66**, 1095–1104.

Zhang Z. M., Rumble, III, D., Liou J. G., Xiao Y. L., and Gao Y. J. (2005) Oxygen isotope geochemistry of rocks from the Pre-Pilot Hole of the Chinese Continental Scientific Drilling Project (CCSD-PPH1). *Am. Mineral.* **90**, 857–863.

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