**A calibration of the triple oxygen isotope fractionation in the
SiO₂ - H₂O system and applications to natural samples**

Z. D. Sharp^{a,b,*}, J.A. Gibbons^a, O. Maltsev^a, V. Atudorei^{a,b}, A. Pack^c, S. Sengupta^c, E.L.
Shock^{d,e}, L.P. Knauth^d

^aDepartment of Earth and Planetary Sciences, University of New Mexico, 200 Yale Blvd,
Albuquerque, NM, 87131, USA

^bCenter for Stable Isotopes, University of New Mexico, 200 Yale Blvd, Albuquerque, NM,
87131, USA

^cGeowissenschaftliches Zentrum, Georg-August-Universität, Goldschmidtstraße 1, D-37073
Göttingen, Germany

^dSchool of Earth and Space Exploration and ^eSchool of Molecular Sciences, Arizona State
University, PO Box 871404, Tempe, AZ 85287-1404, USA

*Corresponding author. Tel. 001 505 277 0742
E-mail address: zsharp@unm.edu

23 Abstract

24 It is now recognized that variations in the $\Delta^{17}\text{O}$ of terrestrial materials resulting from
25 purely mass dependent fractionations, though small, have geological significance. In this study,
26 the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of selected low temperature quartz and silica samples were measured in
27 order to derive the quartz-water fractionation - temperature relationship for the three oxygen
28 isotope system. A $^{18}\text{O}/^{16}\text{O}$ quartz-water fractionation equation valid for all temperatures was
29 generated from published high temperature exchange experiments and low temperature empirical
30 estimates and is given by $1000\ln\alpha_{qz-H_2O}^{^{18}\text{O}/^{16}\text{O}} = \frac{4.20(0.11) \times 10^6}{T^2} - \frac{3.3(0.2) \times 1000}{T}$ (T in Kelvins). The
31 equilibrium $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ relationship is given by the equation $\ln\alpha^{^{17}\text{O}/^{16}\text{O}} = \theta \ln\alpha^{^{18}\text{O}/^{16}\text{O}}$. The
32 variation of θ with temperature for the quartz-water system was determined empirically using
33 low temperature marine diatoms, microcrystalline quartz and a modern sinter sample. A best fit
34 to the data give the equation $\theta_{\text{SiO}_2-\text{H}_2\text{O}} = -\frac{(1.85 \pm 0.04)}{T} + 0.5305$, indistinguishable from an
35 earlier theoretical estimate.

36 Application of the quartz-water triple isotope system to low temperature samples
37 provides constraints on both temperature and composition of the water with which the silica last
38 equilibrated. Authigenic quartz crystallization temperatures cluster around 50°C , which are lower
39 than many previous estimates. The combined $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of samples considered to be
40 in equilibrium with ocean or meteoric waters can be used to estimate both formation
41 temperatures and the $\delta^{18}\text{O}$ value of the meteoric water. Unlike other multiple isotopes systems,
42 such as combined H and O isotopes in cherts, the oxygen source and diagenetic potential for both
43 $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios are identical, simplifying interpretations from ancient samples.

1. INTRODUCTION

The foundations of stable isotope geochemistry can be traced to the pioneering work by Harold Urey almost 70 years ago (Urey, 1947). There, he laid out the theory of stable isotope fractionation as it pertains to natural systems and within several years, his team published its first estimate of paleo-ocean temperatures using the oxygen isotope ratio of ancient carbonates (Urey et al., 1951). Urey's paleotemperature equation is based on the temperature dependence of the stable oxygen isotope ($^{18}\text{O}/^{16}\text{O}$) fractionation between calcite and water. In the case of ancient samples, the oxygen isotope composition of the water is inferred. Urey recognized this problem, stating "Throughout our discussion we have neglected the possibility and even probability of some variation of the isotopic composition of the waters..." so that "these temperatures are regarded as preliminary" (Urey et al., 1951). Almost 3/4 of a century later, knowledge of the $\delta^{18}\text{O}$ value of ancient waters remains elusive. A number of approaches have been used to address the problem: multiple isotope systems have been combined to constrain the ocean composition (e.g., Knauth, 1973; Hren et al., 2009) and clumped isotope thermometers have been used to eliminate the uncertainties in estimating the $\delta^{18}\text{O}$ value of water (Eiler, 2007).

In this work we add the rare ^{17}O stable isotope as a further constraint on mineral-water fractionation and paleotemperature reconstruction. The early practitioners recognized that $\delta^{17}\text{O} \approx \frac{1}{2} \delta^{18}\text{O}$, (where $\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$, and R is the ratio of the heavy to light isotope) so that measuring the $\delta^{17}\text{O}$ value of a substance provided no additional information to $\delta^{18}\text{O}$ alone (Bigeleisen, 1952; Craig, 1957). In detail, the equilibrium fractionation of ^{17}O relative to ^{16}O between any two phases A and B is given by

$$\alpha^{17}O_{A-B} = (\alpha^{18}O_{A-B})^{\theta} \quad 1)$$

where

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad 2)$$

and R is the $^{17}\text{O}/^{16}\text{O}$ or $^{18}\text{O}/^{16}\text{O}$ ratio of the phase. Because of the near constancy of $\theta \approx 0.5$ for both equilibrium and kinetic reactions (Craig, 1957), a plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ values of Earth-derived materials gives a near-linear relationship, termed the terrestrial fractionation line or TFL (Clayton, 2003; Rumble et al., 2007). When recast in a linearized format where $\delta' =$

$$1000 \ln \left(\frac{\delta}{1000} + 1 \right) \text{ (Miller, 2002), } \delta'_A - \delta'_B = 1000 \ln(\alpha_{A-B}), \text{ and } \theta \text{ is given by}$$

$$\theta_{A-B} = \frac{\delta'^{17}O_A - \delta'^{17}O_B}{\delta'^{18}O_A - \delta'^{18}O_B} \quad 3).$$

The general terrestrial fractionation line using linearized delta values is given as $\delta'^{17}\text{O} = \lambda \times \delta'^{18}\text{O} + \gamma$. Here, λ is the empirical slope of the best fit line and γ is the y-intercept, which is often assumed to be equal to 0.

Departures from the terrestrial fractionation line, (which can be very large for extraterrestrial materials and byproducts of stratospheric photochemical reactions, e.g., McKeegan and Leshin, 2001; Thiemens et al., 2012), are expressed in $\Delta'^{17}\text{O}$ notation. $\Delta'^{17}\text{O}$ is illustrated in Fig. 1 and given by

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \times \delta^{18}\text{O} + \gamma \quad 4).$$

The $\Delta^{17}\text{O}$ notation was introduced to display small deviations from an otherwise tight correlation between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ for terrestrial materials, which is considered as the reference line (RL), with a slope of λ_{RL} and y intercept of γ . In the case of equilibrium fractionation between two phases *A* and *B*, λ is replaced by the more specific term θ (equation 1). The intercept γ of the RL is chosen as zero in this work in order to obtain a $\Delta^{17}\text{O} = 0$ for VSMOW. Various slopes (λ) have been suggested for the reference line. Barkan and Luz (2012) and Schoenemann et al. (2013) proposed using the VSMOW and SLAP (Standard Light Antarctic Precipitate) points for the definition of a suitable reference line. The advantage of this procedure is that non-linearity issues (for $\delta^{18}\text{O}$, but also for $\delta^{17}\text{O}$) of the mass spectrometer are eliminated. Under such standardization, the λ value is 0.528. We follow this procedure in this communication, where SMOW has $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values $\equiv 0\text{‰}$, SLAP has $\delta^{18}\text{O}$ value $\equiv -55.5\text{‰}$ and a $\delta^{17}\text{O}$ value of -29.699‰ . Normalized to a reference line with $\lambda_{\text{RL}} = 0.528$ gives a $\Delta^{17}\text{O}$ value of 0‰ for both SMOW and SLAP (Schoenemann et al., 2013).

If the λ parameter in equation 4 were constant under all conditions and all terrestrial materials evolved from a single uniform reservoir, then all samples on Earth would lie on a single curve in $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ space (straight line in $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space) and the $\delta^{17}\text{O}$ value would provide no additional information to the $\delta^{18}\text{O}$ value alone. Bindeman *et al.* (2014) demonstrate the near linear relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values for a single locality in Karelia, Russia, with a total spread of $\delta^{18}\text{O}$ values of 30‰ and a λ value of 0.5274 ($r^2 = 0.9999$).

For any two minerals in equilibrium, we substitute θ for λ , indicating a mass-dependent fractionation. From theoretical consideration, θ is not constant (Matsuhisa et al., 1978; Young et

al., 2002; Cao and Liu, 2011), so that slight variations in $\Delta^{17}\text{O}$ occur. For oxygen, θ varies between 0.5 and 0.5305 (at $T=\infty$). (Matsuhisa et al., 1978; Young et al., 2002). From theory, Cao and Lui (2011) calculated the temperature dependence of θ for various oxides and determined that θ decreases with decreasing T . Only a few empirical estimates for equilibrium θ values have been reported. Liquid water and water vapor have $\theta = 0.529$ (Meijer and Li, 1998; Barkan and Luz, 2005), whereas CO_2 - water has a $\theta = 0.523$ (Barkan and Luz, 2012; Hofmann et al., 2012). For the pair biogenic apatite – water, Pack et al. (2013) determined a θ value at $37^\circ\text{C} = 0.523$. High- T (600 – 1150°C) empirical mineral - mineral equilibria for a granite and mantle peridotite give θ values of 0.528 – 0.529 (Pack and Herwartz, 2014). Generally low θ values are observed for fractionation processes dominated by kinetics (e.g., Luz et al., 1999; Landais et al., 2006). Meteoritic waters scatter around a trend with a slope of 0.528 suggesting fractionation controlled by liquid – vapor equilibrium and a small kinetic component with $\theta < 0.529$ (Meijer and Li, 1998; Luz and Barkan, 2010). The overall significance of the variable θ is that materials which may have evolved from a single homogenized reservoir by different processes and temperatures do not end up falling on a single $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ curve. Subtle, but resolvable departures from a single curve provide information about the formation history of the minerals (e.g., Levin et al., 2014; Passey et al., 2014).

Here, we focus on the quartz/silica – water equilibrium. For the purposes of this paper, we assume that the fractionation between quartz-water and amorphous silica - water are the same (see discussion in section 5.1). Cao and Liu (2011) calculated $\theta_{\text{qz-water}}$ as a function of temperature ranging from 0.5242 at 0°C to 0.5255 at 100°C . Pack and Herwartz (2014) made an empirical estimate of the quartz-water fractionation using modern sponge spicules. Their θ estimate was 0.5212 at $\sim 8^\circ\text{C}$. The $\delta^{18}\text{O}$ values of the sponge spicules, however, are lower than

expected for the equilibrium silica – water fractionation at 8°C, likely because they did not remove the light hydration water by stepwise fluorination (Matheney and Knauth, 1989; Dodd and Sharp, 2010). We present data from new samples in order to empirically constrain the temperature dependence of θ for silica-water.

2. METHODS

2.1 Analytical procedure

All samples were analyzed by fluorination using BrF_5 . Evolved O_2 gas was passed through a 5Å mol sieve GC column in order to remove traces of NF_3 that would otherwise cause an isobaric interference at mass 33. We have found that this method provides more complete purification than the more commonly employed cryogenic purification technique (Clayton and Mayeda, 1983). Quartz (and silica) were fluorinated using the conventional laser extraction technique (Sharp, 1990) and water was fluorinated in 1/4" nickel tubes heated to ~300°C for four minutes (O'Neil and Epstein, 1966). Sample size was between 1 and 2 mg for solids and water. In order to achieve high precision $\Delta^{17}\text{O}$ analyses, counting times were long, consisting of 3 to 4 repetitions of 20-30 cycles between reference gas and sample gas in dual inlet. Sample and standard voltages were balanced before each analysis block. Analysis of diatom sample 1094-4073 was made at the University of Göttingen, Germany using a ThermoFinnigan MAT 253 mass spectrometer with amplifier resistors matched for O_2 analysis (300 MΩ resistor, mass 32, 300 GΩ resistor, mass 33, 100 GΩ resistor, mass 34). All other samples were measured at the Center for Stable Isotopes, University of New Mexico using either a ThermoFinnigan MAT 253 or Delta XL Plus mass spectrometer with the same combination of amplifier resistors as above. No differences were observed between data collected on the Delta or MAT 253 mass

spectrometers.

Diatoms contain 'structural water' which needs to be removed before analysis. We followed the procedure of Dodd *et al.* (2010) for our amorphous silica analysis. Samples were reacted with F₂ gas for 30 - 60 minutes to remove non-tetrahedral oxygen (H₂O or OH⁻). Samples were then fluorinated using BrF₅. In cases where prefluorination was insufficient to remove all non-tetrahedral oxygen, $\delta^{18}\text{O}$ values were lower than for samples that were completely dehydrated. The $\delta^{18}\text{O}$ values of successive analyses of a single sample reach a 'plateau' value after all water was removed. Nevertheless, even with incomplete water removal, the calculated θ values are essentially constant (Fig. A1). The validity of our methodology is demonstrated in a round-robin comparative study by Chaplignin *et al.* (2011).

2.2 Standardization

Standardization is critical when comparing the triple oxygen isotope values of rocks with water. The water community has adopted a two-point calibration based on the standards VSMOW and SLAP. VSMOW, by definition has $\delta^{17}\text{O} = \delta^{18}\text{O} \equiv 0\text{‰}$ (and $\Delta^{17}\text{O} \equiv 0\text{‰}$). SLAP has a $\delta^{18}\text{O}$ value of -55.5‰ (Hut, 1987; Coplen, 1994) and a $\Delta^{17}\text{O} = 0\text{‰}$ relative to VSMOW for $\theta = 0.528$, such that the $\delta^{17}\text{O}$ value of SLAP is -29.699 (Schoenemann *et al.*, 2013). Data should be normalized to this scale taking into account possible 'compression' ($\Delta^{18}\text{O}_{\text{VSMOW-SLAP}} < 55.5\text{‰}$) using standard protocols (e.g., Sharp, 2007, Appendix B).

The 'rock' triple-isotope community is generally only peripherally tied to the VSMOW-SLAP scale. This is because very few laboratories routinely measure the triple oxygen isotope compositions of both water and minerals. There are only two published studies in which VSMOW, SLAP and mantle olivine were measured using fluorination (Kusakabe and Matsuhisa, 2008; Tanaka and Nakamura, 2013). Our and previous measurements of VSMOW, SLAP and

mantle olivine are given in Table A1 (Appendix A). Data are normalized to VSMOW = 0‰ for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$. The average $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of SLAP are -55.4‰ and -0.009‰, obviating the need for any stretching correction. The correction for all samples is made by subtracting the difference between the $\delta^{\text{x}}\text{O}_{\text{measured-SMOW}} - \delta^{\text{x}}\text{O}_{\text{SMOW}}$ from the measured $\delta^{\text{x}}\text{O}$ value of the sample. $\delta^{\text{x}}\text{O}$ is the linearized value of the sample, $\delta^{\text{x}}\text{O}_{\text{measured-SMOW}}$ is the linearized value of the measured SMOW relative to reference gas and $\delta^{\text{x}}\text{O}_{\text{SMOW}}$ is the accepted value of SMOW (=0‰). Uncertainties for SMOW and San Carlos olivine are 0.1‰ for $\delta^{18}\text{O}$ and 0.05‰ for $\delta^{17}\text{O}$ (1 σ). Because $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ errors track with each other, the uncertainties for $\Delta^{17}\text{O}$ are less than 0.009‰. Errors for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ for SLAP are greater than for VSMOW and San Carlos olivine, due to the light nature of the water sample and potential memory effects associated with analyzing a material with such an anomalously low $\delta^{18}\text{O}$ value. The precision of $\Delta^{17}\text{O}$ values are as good as for the other materials, demonstrating again the coupled uncertainties of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$.

The $\delta^{18}\text{O}$ values of San Carlos olivine are higher than the generally assumed value of ~5.3‰ (e.g., Eiler et al., 1995; Ahn et al., 2012; Pack and Herwartz, 2014). It is not clear why there is a discrepancy. Nevertheless, the $\Delta^{17}\text{O}$ value of -0.054 ± 0.008 ‰ is robust because this value does not vary with the $\delta^{18}\text{O}$ value. All silicate analyses in this work are normalized to a $\delta^{18}\text{O}$ value for San Carlos Olivine of 5.3‰ and a $\Delta^{17}\text{O}$ value of -0.054.

3. SAMPLES

Samples analyzed in this study are either silica or quartz that formed at low temperatures. Diatoms from ocean drill cores, microcrystalline quartz from a dredge sample, authigenic quartz crystals from limestone, a water-filled quartz-lined concretion (geode), and modern sinter sample

and its formation waters represent our data set. Sample descriptions are given in Appendix B and isotope data are presented in Table 1. For the calibration of the θ – T relationship for SiO_2 - H_2O , five well-characterized samples were used: diatoms from three high latitude ODP cores in the Southern Ocean, a microcrystalline quartz (MCQ) sample from the Horizon Guyot in the North Central Pacific Ocean and a modern sinter sample from Yellowstone National Park, WY. For the modern sinter, the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ value of the sinter and coexisting water were measured and the water temperature was recorded during sample collection. For the marine samples, $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of 0‰ were assumed. The calibration based on these samples was applied to the other less-well constrained samples to estimate formation conditions.

4. RESULTS

The $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values, their linearized equivalents and the $\Delta^{17}\text{O}$ values are presented in Table 1. Expected geologic temperatures and those calculated from the $1000\ln\alpha_{\text{SiO}_2\text{-H}_2\text{O}}^{18\text{O}/16\text{O}} - T$ relationship are also presented in Table 1.

5. DISCUSSION

The goal of this work is to determine the relationship between $\alpha_{\text{qz-H}_2\text{O}}$ and temperature for both $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$. The ratio of these two, namely $\ln\alpha_{\text{qz-H}_2\text{O}}^{18\text{O}} / \ln\alpha_{\text{qz-H}_2\text{O}}^{17\text{O}}$ is equal to θ . If we measure the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of silica and water for a sample equilibrated at a known temperature, then we can calculate the θ value at that temperature. A best fit of the data passing through $\theta = 0.5305$ at $T = \infty$ gives the θ – T relationship.

5.1 The $^{18}\text{O}/^{16}\text{O}$ quartz-water temperature dependence

In order to expand the $\alpha_{\text{qz-water}} - T$ relationship to $^{17}\text{O}/^{16}\text{O}$, it is first necessary to define a temperature dependent fractionation equation for $\alpha^{18}\text{O}_{\text{qz-water}}$. A large number of quartz-water fractionation equations have been published. Here we synthesize published data to obtain an equation that is valid over a full range of temperatures. The quartz-water fractionation has been determined experimentally (O'Neil and Clayton, 1964; Clayton et al., 1972; Matsuhisa et al., 1978; Matsuhisa et al., 1979; Matthews and Beckinsale, 1979; Matthews et al., 1983; Hu and Clayton, 2003), theoretically (Shiro and Sakai, 1972; Becker and Clayton, 1976; Kawabe, 1978; Clayton and Kieffer, 1991; Zheng, 1991), empirically (Blattner, 1975; Sharp and Kirschner, 1994), or using a hybrid approach, combining theory and experiments (Bottinga and Javoy, 1973). Temperature of experimental quartz-water fractionation experiments are all above 250°C. Amorphous biogenic and abiogenic silica-water fractionations have also been determined experimentally or empirically (Knauth and Epstein, 1976; Kita et al., 1985; Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992; Brandriss et al., 1998; Dodd, 2011). The literature data used for our quartz-water oxygen isotope fractionation equation are given in Table 2. We include the results of exchange experiments above 250°C, inorganic silica precipitation in geothermal waters at intermediate temperatures, and cold-water diatom samples from ocean cores. Where multiple experiments were made at a particular temperature, only the average value of that study was used for our fit. The data of Clayton *et al.* (1972) were corrected to an $\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1.0412$ (O'Neil et al., 1975) in place of 1.0407 used in the original study. This puts the $\delta^{18}\text{O}$ value of water (measured as CO_2 equilibrated with water) on the same scale as the other experimental studies.

The fractionation $\ln\alpha$ is proportional to T^{-2} at high temperatures and T^{-1} at low

temperatures (e.g., Criss, 1991). There is no theoretical basis for any one 'correct' mineral-water fractionation equation. High temperature mineral-water fractionation data have been fit to equations of the form

$$1000\ln\alpha = \frac{a \times 10^6}{T^2} + \frac{b \times 1000}{T} \quad 5)$$

or

$$1000\ln\alpha = \frac{a \times 10^6}{T^2} + c, \quad 6)$$

or a hybrid of these two

$$1000\ln\alpha = \frac{a \times 10^6}{T^2} + \frac{b \times 1000}{T} + c \quad 7).$$

The constants b and c are related to the high normal modes of vibration for the water molecule (Bottinga and Javoy, 1973). At infinite temperatures, $1000\ln\alpha = 0$, so that equations 6 and 7 break down at some temperature above 1000°C.

A best fit to the high temperature data is shown in Fig. 2a. The data can be fit equally well to equations 5 or 7. The best fit to equation 5 over the temperature interval 250-800°C is given by

$$1000\ln\alpha_{qz-H_2O}^{18O/16O} = \frac{4.20(0.11) \times 10^6}{T^2} - \frac{3.3(0.2) \times 1000}{T} \quad R^2 = 0.9977 \quad 8),$$

where numbers in parentheses represent standard error of each temperature coefficient. We prefer the form of equation 5 because it satisfies the necessary condition that $\alpha = 1$ at infinite temperature. It does suggest, however, that there is a crossover at 1000°C with $1000\ln\alpha_{qz-H_2O}$ becoming negative above this temperature. Such crossovers are well known in some mineral-

water systems (e.g., O'Neil and Taylor, 1969; Saccocia et al., 2009) and are not unexpected. The difference between the measured fractionation and the best fit data are shown by the red points in Fig. 3. All measured and calculated data agree to within 0.4‰ and generally better than 0.3‰.

A best fit over the entire temperature range, including the low temperature inorganic samples (Kita et al., 1985) and diatom data (Leclerc and Labeyrie, 1987; Schmidt et al., 2001, present study) gives the equation

$$1000\ln\alpha_{qz-H_2O}^{18O/16O} = \frac{4.28(0.07) \times 10^6}{T^2} - \frac{3.5(0.2) \times 1000}{T} \quad R^2 = 0.9978 \quad 9)$$

shown in Fig. 2b. The best fit for the entire data range is almost identical to the high temperature fit alone (black vs. red curve, Fig. 2a). Equation 9 gives very similar results to that of Zheng (1993), using a semi-theoretical approach.

The differences between measured and calculated $1000\ln\alpha$ values over the entire temperature range are shown as the black points in Fig. 3. The low temperature diatom data have an overall spread of almost 4‰. Shemesh *et al.* (1992) argued that only diatom data from high latitude sites should be included in a temperature-fractionation calibration to avoid the effects of local upwelling in the more tropical sites. Of equal importance is the possibility that glacial melt water lowered the $\delta^{18}O$ value of the seawater so that the assumption that the $\delta^{18}O$ value of the water = 0‰ is not correct. The highest $1000\ln\alpha_{\text{diatom-H}_2\text{O}}$ values from Antarctic cores are 44 to 44.5‰ (Shemesh et al., 1995). Our best fit calibration curve passes through 44.6‰ at 0°C, demonstrating that our calibration is applicable to low temperature amorphous silica (diatoms).

A final concern is whether amorphous silica and quartz have the same fractionation. Stolper and Epstein (1991) and Matthews *et al.* (1994) measured the CO_2 - amorphous SiO_2 fractionation from 550-950°C. They compared their measured fractionations to the CO_2 - quartz fractionation obtained from a combination of reduced partition function ratios of quartz (Clayton

et al., 1989) and CO₂ (Chacko et al., 1991). There was a systematic offset of ~0.3‰, although no difference was seen between measured albite-CO₂ and albitic glass - CO₂ fractionations. Given the uncertainty in the reduced partition functions for quartz, a conclusion regarding the isotopic effect of amorphization of quartz is ambiguous. The lack of fractionation between albite and albite glass in these sample studies (Stolper and Epstein, 1991; Matthews et al., 1994) suggests that amorphization has a negligible effect. We would argue that because the quartz-water and diatom-water data agree so well with each other, that any non-zero fractionation between amorphous silica and quartz can safely be ignored for the purpose of this study. The excellent agreement of the semi-theoretical quartz-water calibration of Zheng (1993) with our diatom-based calibration further validates the assumption that the quartz-water and amorphous silica - water fractionations are very nearly the same.

5.2 Triple oxygen isotope analyses

5.2.1 θ -T relationship

Our empirical calibration of $\theta_{\text{qz-water}}$ is based on five samples: two diatom samples from the Antarctic Zone of the Southern Ocean where the ocean temperature and water isotope composition are well constrained, a microcrystalline quartz sample from the Central Pacific in equilibrium with ocean water and a modern sinter with coexisting water and a measured formation temperature. Diatoms were analyzed following the method of Dodd *et al.* (2010). Multiple aliquots of the same sample were loaded into a sample holder and prefluorinated to remove hydroxyl and H₂O oxygen. Nevertheless, we found that the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of the two diatom samples increased with each successive analysis (Table 1), indicating that not all of the water was removed during prefluorination in the early analyses. The last-analyzed samples

should be closest to the true values and indeed give formation temperatures closer to those expected for growth in Antarctic waters. These were used for our calibration. Regardless of the measured $\delta^{18}\text{O}$ values, the θ values determined for each successive analysis are identical within ± 0.0002 (Fig. A1), a finding also observed by Rumble *et al.* (2007). Therefore, although there may be some uncertainty in the true $\delta^{18}\text{O}$ value of the diatoms, the calculated θ values are robust.

Temperature estimates for the diatoms depend on the corresponding $\delta^{18}\text{O}$ value of the ocean. Assuming modern $\delta^{18}\text{O}$ values for seawater, temperature estimates range from 4°C (sample 1094) to 17°C (1093 and Horizon Guyot). Both diatom samples are from glacial periods when increased continental ice should increase the $\delta^{18}\text{O}$ value of the ocean. Schrag *et al.* (2002) measured the $\delta^{18}\text{O}$ value of pore waters from Leg 177, Hole 1093 and calculated $\delta^{18}\text{O}$ values of seawater during the Last Glacial Maximum to be 1‰ higher than the modern. Assuming a similar increase during Marine Isotope Stage 10 for sample 1093, temperature estimates for both diatom samples are increased by 3°C. These temperatures are clearly too high and suggest that either the quartz-water calibration is incorrect, a fraction of H_2O remained in the diatom during fluorination, or sample purification was not 100%. The Horizon Guyot MCC sample could be as old as mid-Eocene, with $\delta^{18}\text{O}_{\text{ocean water}}$ of $\sim -0.6\text{‰}$. If it equilibrated with this lighter water, the temperature estimate decreases by 2°C. The error introduced by the uncertainties in the $\delta^{18}\text{O}_{\text{water}}$ value is a factor of 6 less than the error of the best fit.

A final consideration is the corresponding change in $\delta^{17}\text{O}$ value of the ocean during transfer of ice to the continents during glacial periods. We assume that the $\delta^{18}\text{O}$ value of continental ice is -30‰ . Removing $\sim 3\%$ of the ocean to continental ice with a $\delta^{18}\text{O}$ value of -30‰ and corresponding $\delta^{17}\text{O}$ value of -15.973‰ (Luz and Barkan, 2010) will change the

calculated θ value by only 0.0002. The transfer of a few percent of water to the continents has a trivial effect on our θ determinations.

A best fit of θ vs temperature using the low temperature diatom, microcrystalline quartz and sinter data (Fig. 4), as well as a $\theta = 0.5305$ at $T = \infty$, gives the following equation for qz-H₂O:

$$\theta_T = -\frac{(1.85 \pm 0.04)}{T} + 0.5305, R^2 = 0.9998 \quad 10).$$

The temperature for each sample was estimated using the measured $1000 \ln \alpha_{\text{SiO}_2\text{-H}_2\text{O}}$ value and equation 9. If instead we use the assumed temperatures of formation for these samples (*e.g.*, near-zero for Antarctic diatoms), the constant in equation 10 changes from 1.85 to 1.81. This difference corresponds to change in θ at 0°C of only 0.0002.

The θ values for mineral-mineral pairs in a granite and peridotite are also shown in Fig. 4. These values are based on the fractionation between coexisting silicates (Pack and Herwartz, 2014) and have moderately large uncertainties. Nevertheless they plot precisely on our θ - T curve even though they are for anhydrous mineral fractionation. This result suggests that mineral-mineral and mineral-water θ values converge at temperatures above 600°C. What is clear is that the effect of temperature on θ is most dramatic at low temperatures (Fig. 5). The $d\theta/dT$ value at 700°C is an order of magnitude less than at 0°C. All igneous and high-grade metamorphic rocks should fractionate with a θ value between 0.528 and 0.529.

The theoretical quartz-water data from Cao and Liu (2011) are also shown in Fig. 4. They are identical to our results within analytical uncertainty. The Cao and Liu data show that the θ - T relationship is a function of $1/T$ and $1/T^2$. Given the limited temperature range of our calibration,

we are able to fit our data equally well with only a $1/T$ term, although a second-order term may be required when data from intermediate temperature (250-500°C) samples are acquired.

5.2.2. Application to natural samples

Combining equations 9 and 10 gives the fractionation for $^{17}\text{O}/^{16}\text{O}$ as a function of temperature. From the relationship $\ln \alpha^{17\text{O}/^{16}\text{O}} = \theta \ln \alpha^{18\text{O}/^{16}\text{O}}$, the quartz-water $^{17}\text{O}/^{16}\text{O}$ fractionation is given by

$$1000 \ln \alpha_{qz-H_2O}^{17\text{O}/^{16}\text{O}} = \left(\frac{4.28 \times 10^6}{T^2} - \frac{3500}{T} \right) \left(0.5305 - \frac{1.85}{T} \right) \quad (11),$$

and

$$\Delta^{17}\text{O} = \left(\frac{4.28 \times 10^6}{T^2} - \frac{3500}{T} \right) \left(0.5305 - \frac{1.85}{T} - \lambda_{RL} \right) \quad (12),$$

where λ_{RL} is the chosen slope of the RL. A number of different λ_{RL} values have been used in the literature. There is no 'correct' λ_{RL} value, and presently no agreement on a 'standard' λ_{RL} value.

We wish to point out that in fact, all interpretations and conclusions are completely independent of assumed λ_{RL} . It is simply a bookkeeping tool for illustrating small differences in the measured and expected $\delta^{17}\text{O}$ values (*e.g.*, Pack and Herwartz, 2014). Appendix C illustrates this concept.

We adopt a value of $\lambda=0.528$ in keeping with the hydrology literature and because it is close to the high temperature limit seen in natural materials.

Our data for samples equilibrated with ocean water can be plotted as $1000 \ln \alpha_{qz-H_2O}^{18\text{O}/^{16}\text{O}}$ vs. $\Delta^{17}\text{O}$ (Fig. 6), where each point on the curve gives the equilibrium values for a particular

373 temperature. (Note that $1000\ln\alpha_{x-y} = \delta'_x - \delta'_y = \Delta'_{x-y}$, where the ' indicates a linearized δ value).

374 In this plot, T is removed as a variable, which allows for the $\Delta^{17}\text{O}$ value to be computed as a

375 function of $\ln\alpha_{qz-H_2O}^{18\text{O}/16\text{O}}$ for all temperatures. (See Appendix D for derivation.). The utility of the

376 three-isotope system is clear. With the $\delta^{18}\text{O}$ value alone, it is impossible to ascertain whether a

377 sample was in equilibrium with ocean water or underwent later diagenesis with a meteoric

378 component. When plotted in $\Delta^{17}\text{O} - \delta^{18}\text{O}$ space, additional information is gained. If a particular

379 sample does not lie on the curve in Fig. 6, it cannot have been in equilibrium with ocean water at

380 any temperature.

381 A second example of the utility of the three isotope system is in an application to

382 authigenic quartz crystals from an 'unaltered' Triassic limestone from Romania. The $\delta^{13}\text{C}$ and

383 $\delta^{18}\text{O}$ values of the limestone are consistent with formation from ocean water at $\sim 20\text{--}22^\circ\text{C}$ with

384 minimal diagenesis (Appendix B). Conodonts, agglutinated foraminifera and mm-size doubly-

385 terminated authigenic quartz crystals are found as trace phases in the limestone. The $\delta^{18}\text{O}$ values

386 of quartz crystals are only 1‰ higher than the calcite, clearly indicating that the two phases are

387 not in equilibrium (Sharp and Kirschner, 1994). The source of the diagenetic fluid responsible

388 for the authigenic quartz crystals is indeterminate from the $\delta^{18}\text{O}_{qz}$ values alone. When taken

389 together, however, the $\delta^{18}\text{O} - \delta^{17}\text{O}$ values of the quartz plot precisely in equilibrium with

390 seawater at $\sim 50^\circ\text{C}$ (Fig. 6). These results suggest that the quartz formed by dissolution of

391 metastable sponge spicules (e.g., Williams et al., 1985) and re-precipitation as quartz at 50°C in

392 non-lithified, bioturbated sediments with porewaters that had a seawater isotopic composition.

393 The 50°C recrystallization value is in good agreement with independent estimates for opal-A to

394 opal -CT transition temperatures (Keller and Isaacs, 1985), but considerably below an estimate

of 80°C for the opal-CT to quartz transition (Murata et al., 1977). Interestingly, the calcite has not isotopically re-equilibrated at 50°C presumably because the calcite was in chemical equilibrium with the porewater and therefore did not undergo any recrystallization during heating (*e.g.*, O'Neil., 1977).

The curve in Fig. 6 can be 'flipped' so that it represents the $\Delta^{17}\text{O} - \delta^{18}\text{O}$ values of water in equilibrium with quartz of a particular composition. In Fig. 7, the average oxygen isotope composition of sinter sample 120722SN and corresponding water are plotted along with the global meteoric water line (Luz and Barkan, 2010; Li et al., 2015). Also shown is the range of $\delta^{18}\text{O}$ values for Yellowstone cold and hot waters (Kharaka et al., 2002). The sinter and coexisting thermal water plot in $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ equilibrium with each other at ~42°C, in excellent agreement with the measured temperature of 47°C. The water is at the high end of the $\delta^{18}\text{O}$ values for thermal waters for Yellowstone and suggests that boiling has modified the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ water values from the primary meteoric value.

For samples that are thought to have formed in equilibrium with meteoric water, the triple oxygen isotope composition of a single mineral can be used to estimate both the temperature and $\delta^{18}\text{O}$ value of the meteoric water. The concept is illustrated for two crystalline quartz-filled nodules (geodes) and the famous doubly-terminated Herkimer Diamond quartz samples (New York, USA) in Fig. 8. The first sample is a 'stalagtitic' quartz geode (Fig. 9) from Morocco (precise locality unknown). The optical-grade quartz is oriented as parallel crystalline 'stalagmites' or fingers, each with a central microcrystalline core. It appears that the crystal fingers formed from water migrating through the core (tube?), leading to crystallizing at the tip of the growing finger. The second is a Keokuk geode from Hancock County, Illinois. This geode contained

liquid water, so that we were able to measure the isotopic composition of both the water and quartz. We recognize that there is a reasonable possibility that the water may postdate the formation of the quartz. Nevertheless, the combined isotope data allow us to assess possible equilibrium and temperature of formation.

The equilibrium water curve for the Moroccan sample crosses the field of meteoric water at $\sim 50^\circ\text{C}$ and a $\delta^{18}\text{O}$ value of meteoric water between -7.5 to -4.0‰ (green point, heavy black curve in Fig. 8). By assuming only that the mineralizing fluid was meteoric water, we are able to determine both the formation temperature and local meteoric water value of this sample. Our estimate for the $\delta^{18}\text{O}$ value of meteoric water is precisely in the range of modern meteoric water in Morocco (Winckel et al., 2002; Ettayfi et al., 2012). The 50°C temperature is the same as the authigenic quartz crystals from the Triassic limestone.

The Keokuk geode and the water filling the cavity appear to be in near-equilibrium with each other. The $\Delta^{18}\text{O}_{\text{qz-H}_2\text{O}}$ value alone would be ambiguous, but the near perfect fit of the geode and water for both isotope systems (red curve in Fig. 8) suggests that the water *could* be formation water, or at least has the same isotopic composition of formation water. The Herkimer diamond sample also appears to be in equilibrium with meteoric water at 50°C (curve not shown). In all, the Romanian authigenic quartz, the Keokuk geode, the Moroccan 'stalagtite' and the Herkimer diamond all have a near 50°C formation temperature, suggesting that in general, amorphous silica may transform to quartz at $\sim 50^\circ\text{C}$.

6. CONCLUSIONS

Adding $^{17}\text{O}/^{16}\text{O}$ ratios to the oxygen isotope mix takes the oxygen isotope system from a one dimensional line to a curve in a two dimensional plane. The $\delta^{18}\text{O}$ values of solid samples

have long been used to estimate the temperature by assuming a formation water value, but obviously, there is an unavoidable ambiguity in the temperature estimate because the actual $\delta^{18}\text{O}_{\text{water}}$ value is not known. A $\delta^{18}\text{O}_{\text{silica}}$ value of 35‰ could be in equilibrium with ocean water at 30°C, but it could also be in equilibrium with a lighter meteoric water at a lower temperature -- there simply is no unique solution. In the three-isotope system, a measured $\delta^{18}\text{O}$ value requires a specific corresponding $\delta^{17}\text{O}$ value to be in equilibrium with water of a specific composition. For a measured $\delta^{18}\text{O}_{\text{silica}}$ value of exactly 30‰, the $\delta^{17}\text{O}$ value must be 15.63‰ to satisfy the condition that it could have been in equilibrium with ocean water. Any other $\delta^{17}\text{O}$ value would conclusively demonstrate that this silica sample was not in equilibrium with ocean water under any temperature conditions. Similarly, if a sample is thought to have equilibrated with meteoric water, then the intersection of the $\delta^{18}\text{O} - \Delta^{17}\text{O}$ curve with the meteoric water field (as in Fig. 8) provides both the $\delta^{18}\text{O}_{\text{water}}$ values and formation temperature. We recognize that the $\delta^{18}\text{O} - \Delta^{17}\text{O}$ meteoric water line is actually a band and not a discrete line, but as more data are obtained regionally, the meteoric water line will become further constrained for a given geographic location and time period (Li et al., 2015).

Multiple isotope systems have been used to constrain temperature and/or meteoric water values of authigenic minerals. For example, researchers have combined H and O isotopes from cherts to place further constraints on formation conditions (e.g., Knauth and Epstein, 1976; Hren et al., 2009). This approach has a number of complicating factors. Are both isotope systems in equilibrium with the formation waters? Were both isotope systems inherited from the same source at the same time? Has one or both undergone later diagenesis? The 'diagenetic potential' of these two elements could be vastly different. For example, hydrogen may be more easily

exchanged than oxygen. For $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, the diagenetic potential as well as source are identical. None of the abovementioned problems exist in the triple oxygen isotope system.

Most laboratories that have laser fluorination systems for traditional oxygen isotope analysis can relatively easily modify their system for simultaneous analysis of $^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{17}\text{O}$, and $^{16}\text{O}^{18}\text{O}$. As more data are collected, the picture for nascent triple oxygen isotope system will become clearer and better defined.

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708 **Figure captions:**

709 Fig. 1. Illustration of the mathematical significance of $\Delta^{17}\text{O}$. The $\delta^{18}\text{O} - \delta^{17}\text{O}$ values define a
710 line with a slope λ_{RL} and y intercept of γ . The difference in the measured $\delta^{17}\text{O}$ value and the
711 $\delta^{17}\text{O}$ value calculated from $\delta^{18}\text{O} \times \lambda + \gamma$ is given by the $\Delta^{17}\text{O}$.

712 Fig. 2. Best fit for temperature ($1/T^2$) vs. $1000\ln\alpha_{\text{qz-H}_2\text{O}}$ from published fractionation data (Table
713 2). Fig. 2a: Best fit to the experimental data above 250°C. The best fit is given by the red curve
714 (equation 8). Fig. 2b: Best fit to the experimental high- T data and the low temperature empirical
715 data (from geothermal sinters and ocean diatom samples) over the entire temperature range
716 (equation 9, black curve).

717 Fig. 3. Difference in the measured $1000\ln\alpha_{\text{SiO}_2\text{-H}_2\text{O}}$ values and those calculated using equations 8
718 (red circles) and 9 (black circles). The 3‰ scatter at the low temperature end is due to the
719 variability of published $\delta^{18}\text{O}_{\text{diatom}}$ data. The best-fit curve over the entire temperature range
720 (equation 9) gives a $1000\ln\alpha$ value of 44.6 ‰ at 0°C, which is within 1‰ of the highest $\delta^{18}\text{O}$
721 values measured for Antarctic diatoms (Shemesh et al., 1995).

722 Fig. 4. Temperature - θ plot for low-temperature samples. Our data (Table 1 and shown as blue
723 circles) are fit with a curve passing through the high temperature theoretical limit ($\theta = 0.5305$,
724 shown by blue star) with a slope of $-1.85/T$ (T in K). The published theoretical values for quartz-
725 water are from Cao and Liu (2011, grey triangles) and their best fit (curved line). Error in θ
726 estimate for the diatom samples is ± 0.0001 , smaller than the size of the symbols. Also shown are
727 the empirical θ estimates for silicate mineral fractionations from a granite (assumed $T=620^\circ\text{C}$)
728 and mantle xenolith (assumed $T = 1050^\circ\text{C}$) from Pack and Herwartz (2014).

729 Fig. 5. Plot of θ vs. T ($^\circ\text{C}$) showing the dramatic effect of changing θ at low temperatures. Above
730 600°C , the θ value is nearly constant at 0.528 to 0.529 (grey rectangle). Data as in Fig. 4.

731 Fig. 6. $\Delta^{17}\text{O} - \delta^{18}\text{O}$ plot of quartz or amorphous silica in equilibrium with ocean water. The
732 curved line is the equilibrium quartz values as a function of temperature. Any sample that does
733 not plot on the line cannot be in equilibrium with ocean water. The position of a sample on the
734 curve provides the equilibrium temperature. Note: the samples plotted in this figure were used to
735 generate the curve. Oval shapes illustrate 1σ errors in $\Delta^{17}\text{O}$ values. Errors in $\delta^{18}\text{O}$ values are
736 less than the thickness of each point.

737 Fig. 7. $\Delta^{17}\text{O} - \delta^{18}\text{O}$ plot of water in equilibrium with quartz/silica. This plot is similar to that
738 shown in Fig. 6 except that the origin is now the mineral, and the curve represents the $\Delta^{17}\text{O} -$
739 $\delta^{18}\text{O}$ values of water in equilibrium with a specific quartz/silica sample. Sample 120722SN is a
740 modern sinter sample. The curve originating at the silica $\Delta^{17}\text{O} - \delta^{18}\text{O}$ values passes through the
741 measured $\delta^{18}\text{O} - \delta^{17}\text{O}$ water values at 42°C , in good agreement with the measured temperature
742 in the spring of 47°C . The curve also shows published $\delta^{18}\text{O} - \delta^{17}\text{O}$ values for meteoric water

(Luz and Barkan, 2010; Li et al., 2015) and the range of hot (red) and cold (blue) $\delta^{18}\text{O}$ values for Yellowstone waters (Kharaka et al., 2002). The large uncertainties in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values for sinter probably reflect sample heterogeneity due to variable isotopic composition of water and temperature.

Fig. 8. Triple isotope values of three authigenic quartz samples. Waters in equilibrium with the Moroccan geode (shown in Fig. 9) are defined by the thick black curve. They cross the meteoric water band in the range -7 to -4‰ at 40 to 50°C. This is in good agreement with the $\delta^{18}\text{O}$ values of modern Moroccan meteoric water (grey band, Winckel et al., 2002; Ettayfi et al., 2012). The Keokuk geode and included water plot in near equilibrium at ~40°C (red curve). The Herkimer diamond samples could be in equilibrium with meteoric water at ~50°C, or could be a mixture of meteoric waters and pore waters at at higher temperature ~80°C (curves not shown).

Fig. 9. Moroccan geode showing stalagmitic 'fingers' of quartz. The appearance suggests that the quartz precipitated from drip waters that migrated through the open tubes in the center of each finger. Red oval highlights a cut section showing the microcrystalline core of the 'fingers'. Width of geode is 13 cm.

Fig. A1. $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ plot of multiple analyses of diatom sample 1094-4073. Each successive analysis gave a higher $\delta^{18}\text{O}$ value due to more complete removal of structural 'water'. Nevertheless, all samples plot on a curve passing through the origin with a resultant θ value of 0.5236 ± 0.0004 , illustrating the covariance of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$.

Fig. C1. Graphical illustration of θ . Figs a and b are the same data with different θ_{ref} values. Fig. c is the result of Fig. a sheared upward on the right side. The curves in Fig. b and c are identical. Data points are not representative of any sample, but illustrate how sample data scale proportionally with equilibrium curves regardless of assumed λ .

Table 1. Triple oxygen isotope data for selected materials. The bold samples were used for the best fit of θ vs. T. Calculated temperatures from quartz-water fractionations. All data relative to VSMOW. Sample 1094-4073 was analyzed at the U. of Goettingen; all other analyses were made at the UNM.

Sample	material	T(°C) Calc./ assumed	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$ $\theta=0.528$	θ
1094-4073-1	diatom	9/0	21.877	42.208	21.641	41.342	-0.187	0.5235
-2		7/0	22.233	42.921	21.989	42.025	-0.200	0.5232
-3		4/0	22.823	44.010	22.566	43.069	-0.174	0.5240
1093_leg 177-1	diatom	6/4	22.416	43.170	22.168	42.264	-0.147	0.5245
-2		8/4	22.031	42.502	21.792	41.623	-0.186	0.5235
-3		7/4	22.208	42.854	21.965	41.961	-0.190	0.5235
PS1772-1	diatom	5/0	22.546	43.465	22.296	42.547	-0.169	0.5240
-2		6/0	22.267	42.936	22.023	42.040	-0.174	0.5239
-3		5/0	22.437	43.271	22.189	42.361	-0.178	0.5237
Horizon Guyot	chert	17	20.537	39.573 39.4*	20.329	38.810	-0.161	0.5238
1207225N	sinter		10.678	20.518	10.621	20.311	-0.103	
			9.299	17.797	9.256	17.640	-0.058	
			10.953	20.988	10.893	20.771	-0.074	
			9.719	18.578	9.672	18.408	-0.047	
	average		10.162	19.470	10.111	19.283	-0.047	
120722SN	water		-6.49	-12.29	-6.51	-12.36	0.02	
			-6.93	-13.20	-6.95	-13.29	0.06	
			-6.57	-12.51	-6.59	-12.59	0.06	
	average		-6.663	-12.667	-6.683	-12.747	0.047	
120722SN 1000ln(qz-H ₂ O)		42/47			16.794	32.030	-0.117	0.5243
Herkimer diamond	euhedral quartz		12.433	23.838 23.8**	12.357	23.558	-0.081	
			12.648	24.209	12.569	23.921	-0.061	
	average		12.541	24.023	12.463	23.739	-0.071	
Triassic DC609	euhedral quartz		15.575	29.886	15.455	29.448	-0.094	
DC9044	euhedral quartz		15.390	29.591	15.272	29.161	-0.124	
Dover	chert		13.323	25.465	13.235	25.146	-0.042	
Morocco stalagmite	euhedral quartz		13.636	26.113	13.544	25.787	-0.071	
Keokuk Geode	euhedral quartz		14.481	27.716	14.377	27.339	-0.057	
	water		-2.57	-4.96	-2.57	-4.97	0.05	

* Measurement from Knauth (1973), corrected to VSMOW.

** Measurement from Clayton and Epstein (1958).

773 Table 2 Published oxygen isotope data for quartz (silica) - water fractionation. Diatom samples
774 ($n = 17$, not listed) are from Leclerc and Labeyrie (1987).

$1000\ln \alpha$	T (°C)	reference	notes
9.03	250	(Matsuhisa et al., 1978)	
0.64	800	(Matsuhisa et al., 1979)	Average of 2 experiments
1.05	700	(Matsuhisa et al., 1979)	Average of 9 experiments
1.49	600	(Matsuhisa et al., 1979)	Average of 7 experiments
2.31	500	(Matsuhisa et al., 1979)	Average of 6 experiments
4.11	400	(Matsuhisa et al., 1979)	Average of 6 experiments
6.64	300	(Matsuhisa et al., 1979)	1 experimental pair
8.6	265	(Matthews and Beckinsale, 1979)	Synthesis experiments from silicic acid
5.3	360	(Matthews and Beckinsale, 1979)	Synthesis experiments from silicic acid
3.6	465	(Matthews and Beckinsale, 1979)	Synthesis experiments from silicic acid
0.91	750	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412. Used only 100% exchanged results
1.48	650	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
2.04	580	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
2.28	550	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
2.8	490	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
1.14	750	(Hu and Clayton, 2003)	Reacted at 1.5 GPa
1.84	600	(Hu and Clayton, 2003)	Reacted at 1.5 GPa
2.73	500	(Hu and Clayton, 2003)	Reacted at 1.5 GPa
1.43±0.18	600	(Matthews et al., 1983)	Run at multiple pressures. Only partial exchange.
3.99	400	(Matthews et al., 1983)	Run at multiple pressures. Only partial exchange
9.12	250	(Matthews et al., 1983)	One experiment only
20.65	92.7	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
22.84	87	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
24.99	80	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
28.20	58	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
32.56	34	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters

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APPENDIX A. STANDARDIZATION

Data for standards VSMOW, SLAP and San Carlos olivine are shown in Table A1. Data are normalized to VSMOW, such that the $\delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values are all 0‰. All other data are corrected by subtracting the $\delta^x\text{O}_{\text{ref gas}} - \delta^x\text{O}_{\text{VSMOW}}$ (or $\Delta^{17}\text{O}_{\text{ref gas}} - \Delta^{17}\text{O}_{\text{VSMOW}}$) from each analysis. $\delta^x\text{O}_{\text{ref gas}}$ is the linearized measured $\delta^x\text{O}$ (or calculated $\Delta^{17}\text{O}_{\text{ref gas}}$) of VSMOW and $\delta^x\text{O}_{\text{VSMOW}}$ (and $\Delta^{17}\text{O}_{\text{VSMOW}}$) are the accepted values of VSMOW $\equiv 0$ ‰. Uncertainties for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ analyses are ± 0.05 and ± 0.1 ‰ (1σ). Uncertainties for $\Delta^{17}\text{O}$ are less than 0.01‰ (1σ). The higher precision for $\Delta^{17}\text{O}$ is due to the covariance of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ such that the $\Delta^{17}\text{O}$ remains constant regardless of small variations in the measured $\delta^{18}\text{O}$ value.

Fig. A1 plots the measured $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of three analyses of diatom sample 1094-4073. The $\delta^{18}\text{O}$ values increase with increasing degrees of prefluorination, but all samples lie on the same line passing through the ocean water value (assumed $\delta^{17}\text{O} = \delta^{18}\text{O} = 0$ ‰). The slope of the line is θ and is the same for all three analyses.

792 Table A1. Measured oxygen isotope compositions for water and olivine
793 standards with corrected reference to give VSMOW = 0‰. $\Delta^{17}\text{O}'$ values
794 are for the equation $\Delta^{17}\text{O}' = \delta^{17}\text{O}' - 0.528 \times \delta^{18}\text{O}'$. Also shown are
795 published values for SLAP and olivine.

	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}'$	$\delta^{18}\text{O}'$	$\Delta^{17}\text{O}'$
VSMOW	-0.113	-0.210	-0.113	-0.210	-0.002
	0.038	0.088	0.038	0.088	-0.008
	0.052	0.100	0.052	0.100	-0.001
	0.022	0.021	0.022	0.021	0.011
	-0.018	-0.046	-0.018	-0.046	0.007
	-0.015	-0.052	-0.015	-0.052	0.013
	0.003	0.018	0.003	0.018	-0.007
	0.030	0.079	0.030	0.079	-0.012
Average	0.000	0.000	0.000	0.000	0.000
Stdev	0.052	0.103	0.052	0.103	0.009
SLAP	-29.488	-55.080	-29.932	-56.655	-0.018
	-29.213	-54.580	-29.648	-56.126	-0.014
	-29.758	-55.589	-30.210	-57.194	-0.012
	-29.915	-55.896	-30.372	-57.519	-0.002
	-29.875	-55.823	-30.331	-57.442	-0.001
average	-29.650	-55.394	-30.099	-56.987	-0.009
Stdev	0.296	0.556	0.305	0.588	0.007
SLAP ¹	-29.21	-54.65	-29.645	-56.200	0.029
SLAP ²	-29.44	-55.02	-29.882	-56.592	-0.002
SCO	2.835	5.493	2.831	5.478	-0.061
	2.850	5.488	2.846	5.473	-0.043
	2.819	5.455	2.815	5.440	-0.057
	2.922	5.656	2.918	5.640	-0.060
	2.907	5.604	2.903	5.588	-0.047
	2.907	5.646	2.903	5.630	-0.069
	2.913	5.633	2.909	5.618	-0.057
	2.943	5.687	2.939	5.670	-0.055
	2.956	5.689	2.952	5.672	-0.043
	2.883	5.553	2.879	5.538	-0.045
	2.900	5.610	2.896	5.595	-0.058
	2.798	5.409	2.794	5.394	-0.054
Average	2.886	5.577	2.882	5.561	-0.054
Stdev	0.050	0.095	0.050	0.094	0.008
SCO ¹	2.89	5.26	2.886	5.246	0.116
Olivine ²	2.70	5.28	2.696	5.266	-0.084

¹ (Kusakabe and Matsuhisa, 2008), ² (Tanaka and Nakamura, 2013)

APPENDIX B. DESCRIPTION OF SELECTED SAMPLES

1093-Leg 177 - A-23-H-4-W - From ODP Leg 177, Hole 1093. Located farther to the north than Hole 1094 at the present day polar front zone, with $\delta^{18}\text{O}$ values of carbonate ~0.5 to 1‰ heavier than sample 1094 (Hodell et al., 2003). Sample from 109.0 to 111.0 meters composite depth (mcd). Age: ~400ka, MIS 10.

1094-4073 - From ODP Leg 177. Hole 1094 drilled at 53°S. Water depth - 2807 m. Location is in the present ice-free Antarctic Zone, but was covered by sea ice during last glaciation (Gersonde et al., 1999). The $\delta^{18}\text{O}_{\text{calcite}}$ for this core range from 3.5 to 4.5 ‰ (Hodell et al., 2003) relative to PDB, consistent with a 0°C temperature and $\delta^{18}\text{O}_{\text{ocean}}$ of -1 to 0‰. From 21.77 metres depth ~111k.a MIS 5d. Donated by Aldo Shemesh. Measured in Goettingen. All other samples measured at UNM.

120722SN: Hot Spring Sinter and Water – Sampled in 22 July 2012 from a mid-range temperature spring (44°41'58.43"N, 110°46'1.94"W) at Sylvan Springs in Yellowstone National Park as part of a long-term project to quantify connections between the geochemical compositions of hot springs and the microbial communities they support. Additional data from an earlier sample of this spring are reported by Windman et al. (2007) (sample 040718U).

Chert from Horizon Guyot - Dredged during an investigation of Horizon Guyot, Pacific Ocean. 168°52.3'W, 10°28.0' N, 1700 m water depth. Transmitted to Paul Knauth by Harmon Craig. Greater than 98% granular microcrystalline quartz. $\delta^{18}\text{O} = 38.85\text{‰}$ by Knauth (1973).

DC 609, 9044 - Early-Middle Triassic transition marine pelagic limestone from North Dobrogea, Romania (Atudorei, 1999). Trace phases include minor conodonts, agglutinated foraminifera and mm-sized doubly-terminated euhedral quartz crystals. These samples do not contain sponge spicules, although they are found in equivalent lithologies elsewhere. The lithologies are strongly bioturbated. Carbonate isotope values: DC 9044; $\delta^{13}\text{C}=4.53$ and $\delta^{18}\text{O}=-2.35$ ‰ PDB. DC 9045; $\delta^{13}\text{C}=4.40$ and $\delta^{18}\text{O}=-2.48$ ‰ PDB. $\delta^{18}\text{O}_{\text{calcite}}$ values correspond to a temperature of 20-22°C for a $\delta^{18}\text{O}_{\text{ocean}} = -1\text{‰}$ (vs. SMOW).

Herkimer diamond - Cambro-Ordovician silicified dolomite hosted quartz crystals. Optically pure doubly terminated glassy crystals.

Keokuk geode - Keokuk geode from the lower Warsaw formation, Hancock County, Illinois. Sample contained liquid water which was extracted by drilling through the geode wall.

Moroccan stalagtitic geode - sample of unknown origin. Purchased in Morocco by K. Zielger. The geode is filled with parallel coarsely crystalline quartz fingers forming in an open cavity (Fig. 9). Each finger has a tube-like central shaft which presumably acted as a conduit for water migration to the growing tip of each stalagtitic finger. The outer layers of the stalagmites are composed of optically pure quartz crystals, whereas the interior shaft is microcrystalline. We analyzed the coarse optically pure material.

843
844 ***PSI772-8***: Diatom-rich section of a sediment core from the Southern Ocean (Lat: -55.4583,
845 Long: 1.1633 (Gersonde and Hempel, 1990). The sample was deposited in Marine Isotope Stage
846 5. The purified diatom sample is 99.49% silica (Chapligin et al., 2011) with a $\delta^{18}\text{O}$ value from a
847 laboratory intercomparison of 42.8‰. Our value of 43.5‰ is identical to our previous analysis
848 (UNM: $43.5 \pm 0.1\text{‰}$, $n = 10$) of this sample (Chapligin et al., 2011).
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APPENDIX C. THE (LACK OF) SIGNIFICANCE OF λ_{RL}

A triple isotope reference line (RL), whether it be considered as a Terrestrial Fractionation Line (Clayton, 2003; Kusakabe and Matsuhisa, 2008), a meteoric water line (Luz and Barkan, 2010) or a more generic format, is used to illustrate small displacements of a particular sample from that reference line (Fig. 1). The choice of the reference line does not have any mathematical or geological significance in and of itself. Temperatures, etc. are all based on equations 1-5 and 8-13. The reference λ is not in the mathematics. This is illustrated in Fig. C1, where the same data are plotted in $\Delta^{17}\text{O} - \delta^{18}\text{O}$ space for three different λ values. The points are

Fig. C1. Graphical illustration of λ . Figs. C1a and C1b are the same data with different λ_{RL} values. Fig. C1c is the result of Fig. a sheared upward on the right side. The curves in Fig. C1b and C1c are identical. Data points are not representative of any sample, but illustrate how sample data scale proportionally with equilibrium curves regardless of assumed λ .

arbitrary values. The red spot is a typical mantle composition, the green and blue points are low temperature samples. The curved line is the quartz-water equilibrium curve and the straight blue line is an extension of the MWL to positive $\delta^{18}\text{O}$ values. Although Fig. C1a ($\lambda=0.5305$) and Fig. C1b ($\lambda = 0.525$) appear very different, they actually convey identical information. Fig. C1c is generated by taking Fig. C1a and skewing the right edge upward. The lines and points in Fig. C1c exactly match those in curve C1b.

Appendix D. DERIVATION OF THE $\Delta^{17}\text{O} - \delta^{18}\text{O}$ CURVE.

The fractionation between phases x and y is given by

$$1000 \ln \alpha_{x-y}^{18\text{O}} = \frac{a \times 10^6}{T^2} - \frac{b \times 10^3}{T} . \quad \text{D1,}$$

and

$$1000 \ln \alpha_{x-y}^{17\text{O}} = \left(\frac{a \times 10^6}{T^2} - \frac{b \times 10^3}{T} \right) \theta_{x-y} \quad \text{D2,}$$

From equation 4,

$$\Delta^{17}\text{O} = \left(\frac{a \times 10^6}{T^2} - \frac{b \times 10^3}{T} \right) \theta_{x-y} - \left(\frac{a \times 10^6}{T^2} - \frac{b \times 10^3}{T} \right) \lambda_{RL} \quad \text{D3.}$$

For

$$\theta_{x-y} = -\frac{c}{T} + 0.5305 \quad \text{D4,}$$

equation D3 can be rewritten as

$$\Delta^{17}\text{O} = \left(\frac{a \times 10^6}{T^2} - \frac{b \times 10^3}{T} \right) \left(-\frac{c}{T} + 0.5305 - \lambda_{RL} \right) \quad \text{D5.}$$

λ_{RL} is the chosen value in order to display $\Delta^{17}\text{O}$. Commonly, λ_{RL} is taken as 0.52, 0.528 or

0.5305, although the choice of λ_{RL} is discretionary and does not affect any of the results.

Equation D1 can be rearranged to solve for temperature, given by the following equation where

$$\Delta' = 1000 \ln \alpha_{x-y} = \delta^{18}\text{O}_x - \delta^{18}\text{O}_y$$

$$T(K) = \frac{500 \left(-b + \sqrt{b^2 + 4a \cdot \Delta'} \right)}{\Delta'} \quad \text{D6.}$$

Substituting the right side of equation D6 into D5 gives the solution for $\Delta^{17}\text{O}$ as a function of Δ' .

884
885 Figure 1

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Figure 9

Table 1. Triple oxygen isotope data for selected materials. The bold samples were used for the best fit of θ vs. T. Calculated temperatures from quartz-water fractionations. All data relative to VSMOW. Sample 1094-4073 was analyzed at the U. of Goettingen; all other analyses were made at the UNM.

Sample	material	T(°C) Calc./ assumed	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$ $\theta=0.528$	θ
1094-4073-1	diatom	9/0	21.877	42.208	21.641	41.342	-0.187	0.5235
-2		7/0	22.233	42.921	21.989	42.025	-0.200	0.5232
-3		4/0	22.823	44.010	22.566	43.069	-0.174	0.5240
1093_leg 177-1	diatom	6/4	22.416	43.170	22.168	42.264	-0.147	0.5245
-2		8/4	22.031	42.502	21.792	41.623	-0.186	0.5235
-3		7/4	22.208	42.854	21.965	41.961	-0.190	0.5235
PS1772-1	diatom	5/0	22.546	43.465	22.296	42.547	-0.169	0.5240
-2		6/0	22.267	42.936	22.023	42.040	-0.174	0.5239
-3		5/0	22.437	43.271	22.189	42.361	-0.178	0.5237
Horizon Guyot	chert	17	20.537	39.573 39.4*	20.329	38.810	-0.161	0.5238
1207225N	sinter		10.678	20.518	10.621	20.311	-0.103	
			9.299	17.797	9.256	17.640	-0.058	
			10.953	20.988	10.893	20.771	-0.074	
			9.719	18.578	9.672	18.408	-0.047	
	average		10.162	19.470	10.111	19.283	-0.047	
120722SN	water		-6.49	-12.29	-6.51	-12.36	0.02	
			-6.93	-13.20	-6.95	-13.29	0.06	
			-6.57	-12.51	-6.59	-12.59	0.06	
	average		-6.663	-12.667	-6.683	-12.747	0.047	
120722SN 1000ln(qz-H ₂ O)		42/47			16.794	32.030	-0.117	0.5243
Herkimer diamond	euhebral quartz		12.433	23.838 23.8**	12.357	23.558	-0.081	
			12.648	24.209	12.569	23.921	-0.061	
	average		12.541	24.023	12.463	23.739	-0.071	
Triassic DC609	euhebral quartz		15.575	29.886	15.455	29.448	-0.094	
DC9044	euhebral quartz		15.390	29.591	15.272	29.161	-0.124	
Dover	chert		13.323	25.465	13.235	25.146	-0.042	
Morocco stalagmite	euhebral quartz		13.636	26.113	13.544	25.787	-0.071	
Keokuk Geode	euhebral quartz		14.481	27.716	14.377	27.339	-0.057	
	water		-2.57	-4.96	-2.57	-4.97	0.05	

* Measurement from Knauth (1973), corrected to VSMOW.

** Measurement from Clayton and Epstein (1958).

910 Table 2 Published oxygen isotope data for quartz (silica) - water fractionation. Diatom samples
911 ($n = 17$, not listed) are from Leclerc and Labeyrie (1987).

$1000\ln \alpha$	T (°C)	reference	notes
9.03	250	(Matsuhisa et al., 1978)	
0.64	800	(Matsuhisa et al., 1979)	Average of 2 experiments
1.05	700	(Matsuhisa et al., 1979)	Average of 9 experiments
1.49	600	(Matsuhisa et al., 1979)	Average of 7 experiments
2.31	500	(Matsuhisa et al., 1979)	Average of 6 experiments
4.11	400	(Matsuhisa et al., 1979)	Average of 6 experiments
6.64	300	(Matsuhisa et al., 1979)	1 experimental pair
8.6	265	(Matthews and Beckinsale, 1979)	Synthesis experiments from silicic acid
5.3	360	(Matthews and Beckinsale, 1979)	Synthesis experiments from silicic acid
3.6	465	(Matthews and Beckinsale, 1979)	Synthesis experiments from silicic acid
0.91	750	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412. Used only 100% exchanged results
1.48	650	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
2.04	580	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
2.28	550	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
2.8	490	(Clayton et al., 1972)	Corrected $\alpha_{\text{qz-H}_2\text{O}}$ from 1.0407 to 1.0412.
1.14	750	(Hu and Clayton, 2003)	Reacted at 1.5 GPa
1.84	600	(Hu and Clayton, 2003)	Reacted at 1.5 GPa
2.73	500	(Hu and Clayton, 2003)	Reacted at 1.5 GPa
1.43±0.18	600	(Matthews et al., 1983)	Run at multiple pressures. Only partial exchange.
3.99	400	(Matthews et al., 1983)	Run at multiple pressures. Only partial exchange
9.12	250	(Matthews et al., 1983)	One experiment only
20.65	92.7	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
22.84	87	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
24.99	80	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
28.20	58	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters
32.56	34	(Kita et al., 1985)	Empirical. Silica precipitated from geothermal waters

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914 Table A1. Measured oxygen isotope compositions for water and olivine
915 standards with corrected reference to give VSMOW = 0‰. $\Delta^{17}\text{O}'$ values
916 are for the equation $\Delta^{17}\text{O}' = \delta^{17}\text{O}' - 0.528 \times \delta^{18}\text{O}'$. Also shown are
917 published values for SLAP and olivine.

	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}'$	$\delta^{18}\text{O}'$	$\Delta^{17}\text{O}'$
VSMOW	-0.113	-0.210	-0.113	-0.210	-0.002
	0.038	0.088	0.038	0.088	-0.008
	0.052	0.100	0.052	0.100	-0.001
	0.022	0.021	0.022	0.021	0.011
	-0.018	-0.046	-0.018	-0.046	0.007
	-0.015	-0.052	-0.015	-0.052	0.013
	0.003	0.018	0.003	0.018	-0.007
	0.030	0.079	0.030	0.079	-0.012
Average	0.000	0.000	0.000	0.000	0.000
Stdev	0.052	0.103	0.052	0.103	0.009
SLAP	-29.488	-55.080	-29.932	-56.655	-0.018
	-29.213	-54.580	-29.648	-56.126	-0.014
	-29.758	-55.589	-30.210	-57.194	-0.012
	-29.915	-55.896	-30.372	-57.519	-0.002
	-29.875	-55.823	-30.331	-57.442	-0.001
average	-29.650	-55.394	-30.099	-56.987	-0.009
Stdev	0.296	0.556	0.305	0.588	0.007
SLAP ¹	-29.21	-54.65	-29.645	-56.200	0.029
SLAP ²	-29.44	-55.02	-29.882	-56.592	-0.002
SCO	2.835	5.493	2.831	5.478	-0.061
	2.850	5.488	2.846	5.473	-0.043
	2.819	5.455	2.815	5.440	-0.057
	2.922	5.656	2.918	5.640	-0.060
	2.907	5.604	2.903	5.588	-0.047
	2.907	5.646	2.903	5.630	-0.069
	2.913	5.633	2.909	5.618	-0.057
	2.943	5.687	2.939	5.670	-0.055
	2.956	5.689	2.952	5.672	-0.043
	2.883	5.553	2.879	5.538	-0.045
	2.900	5.610	2.896	5.595	-0.058
	2.798	5.409	2.794	5.394	-0.054
Average	2.886	5.577	2.882	5.561	-0.054
Stdev	0.050	0.095	0.050	0.094	0.008
SCO ¹	2.89	5.26	2.886	5.246	0.116
Olivine ²	2.70	5.28	2.696	5.266	-0.084

¹ (Kusakabe and Matsuhisa, 2008), ² (Tanaka and Nakamura, 2013)