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## Isotopic fractionation and the quantification of $^{17}\text{O}$ anomalies in the oxygen three-isotope system: an appraisal and geochemical significance

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**Abstract**—The oxygen three-isotope plot provides valuable insights to geochemical and cosmochemical processes in which the relationship of  $^{17}\text{O}/^{16}\text{O}$  relative to  $^{18}\text{O}/^{16}\text{O}$  is of interest. It is generally recognised, however, that the usual format of this diagram, illustrating the variation of  $\delta^{17}\text{O}$  with  $\delta^{18}\text{O}$ , is based on the approximation of a power law function to linear format. In contrast, the relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for entity  $a$  measured with respect to reference  $b$  is accurately represented by the linear function:

$$1000\ln\left(1 + \frac{\delta^{17}\text{O}}{1000}\right) = \lambda 1000\ln\left(1 + \frac{\delta^{18}\text{O}}{1000}\right) + 1000\ln[1 + k_{a,b}]$$

where  $k_{a,b}$  is a measure of the offset (if any) of  $a$  from the mass-dependent fractionation line, of slope  $\lambda$ , on which  $b$  lies. The respective ordinate and abscissa scales are essentially unchanged from those of the corresponding  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  plot yet, unlike the latter, the slope of the fractionation line is invariant to both the magnitude of the  $\delta$  values and to the isotopic composition of the reference.

Application to high precision measurements which encompass a wide range of  $\delta$  values reveals that slope differences (or indeed similarities) between comparable data sets may be disguised by the limitations of the  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  diagram, with adverse consequences for the accurate quantification of  $\Delta^{17}\text{O}$  values. This may be addressed by re-defining  $\Delta^{17}\text{O}$ , the offset from a reference fractionation line, as  $1000k_{a,b}$ . In turn, this is very closely approximated by  $1000\ln[1 + k_{a,b}]$ , the intercept on the ordinate axis of a  $1000\ln[1 + (\delta^{17}\text{O}/1000)]$  versus  $1000\ln[1 + (\delta^{18}\text{O}/1000)]$  plot, for values of  $1000k_{a,b}$  not exceeding  $\sim 5$ . The same analysis shows that the fractionation factor  $\alpha_{17/16}$  for a given system is related to the corresponding  $\alpha_{18/16}$  value by:

$$\alpha_{17/16} = [1 + k_{a,b}](\alpha_{18/16})^\lambda$$

These findings are equally applicable to the reporting of data from other three-isotope systems, such as magnesium. Copyright © 2002 Elsevier Science Inc.

### 1. INTRODUCTION

Oxygen, the most abundant element in the Earth's crust, has two minor isotopes,  $^{17}\text{O}$  and  $^{18}\text{O}$ , with respective natural abundances of approximately 0.038% and 0.20%. The oxygen three-isotope plot, illustrating the variation of  $\delta^{17}\text{O}$  as a function of  $\delta^{18}\text{O}$ , is a well established representation of the relationship between the respective abundances of the two minor isotopes, with all but very few terrestrial materials appearing to fit a linear function of slope  $\sim 0.52$  (Matsuhisa et al., 1978), where  $\delta^x\text{O} = [\{({}^x\text{O}/^{16}\text{O})_{\text{sample}}/({}^x\text{O}/^{16}\text{O})_{\text{reference}}\} - 1] \times 1000$  per mil (‰). The slope of this 'terrestrial fractionation line' is in accord with the fractionation of  $^{17}\text{O}/^{16}\text{O}$  relative to  $^{18}\text{O}/^{16}\text{O}$  being exclusively a function of the mass of the respective isotopomers. Departures from the terrestrial line have long been recognised in most meteorites (Clayton et al., 1973; Clayton et al., 1976; Clayton 1993), and probably reflect the preservation of primordial oxygen isotopic heterogeneity from the early solar system.

The discovery by Thiemens and Heidenreich (1983) that ozone formation from molecular oxygen does not conform to mass-dependent isotopic behaviour presented a considerable challenge to the theoretical framework that describes the prin-

ciples of stable isotope distributions, with a satisfactory explanation having been proposed only recently (Gao and Marcus, 2001). Mass-independent oxygen isotopic compositions have now been identified in many components of the Earth's atmosphere (as reviewed by Thiemens, 1999; Weston, 1999); in such cases, the isotopic anomalies generally appear to be linked to reactions involving stratospheric ozone. The recent discovery of terrestrial sulphate-bearing rocks which contain  $^{17}\text{O}$  anomalies (Bao et al., 2000a, 2000b; Bao et al., 2001) extends these observations to the terrestrial rock record, although it is probable that the anomalous isotopic compositions are associated with an atmospheric origin.

In tandem with these findings has been the development of experimental procedures which, together with advances in mass spectrometry technology, have led to significantly improved precision of oxygen triple-isotope measurements of waters (Li and Meijer, 1998); dissolved  $\text{O}_2$  (Luz et al. 1999); and silicates (Miller et al., 1999a). The identification and discrimination of  $^{17}\text{O}$  anomalies at the level of tens per meg (Luz et al., 1999; Luz and Barkan, 2000), where one per meg equates to  $10^{-3}$  per mil, highlights the need for an accurate and consistent system of reporting, as it is widely recognised (e.g., Matsuhisa et al., 1978; Clayton and Mayeda, 1996) that the oxygen three-isotope plot originally devised for the classification of meteorites (Clayton et al., 1976), whilst useful for data sets that do not

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incorporate a wide range of  $\delta$  values, is based on a simplification of the relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ .

## 2. THEORY

### 2.1. The Mass-Dependent Fractionation Line: Slope and $\Delta^{17}\text{O}$ Definitions

It was postulated by Craig (1957), from the established theoretical basis of the quantitative effects of isotopic substitution under equilibrium (Urey, 1947; Bigeleisen and Mayer, 1947) and kinetic (Bigeleisen, 1949) conditions, that fractionation of the three oxygen isotopes between entities  $a$  and  $b$  during chemical or physical fractionation should be described by  $(^{17}R_a/^{17}R_b) = (^{18}R_a/^{18}R_b)^{0.5}$ , where  $^{17}R_a$  and  $^{18}R_a$  refer to the respective  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios in  $a$ ;  $b$  is a reference material. On this basis,  $\alpha_{17/16} = (\alpha_{18/16})^{0.5}$  from the definition of the respective fractionation factors. The value of the exponent term was refined by Matsuhisa et al. (1978), who calculated the logarithmic reduced partition function ratios  $\ln(Q_{17}/Q_{16})/\ln(Q_{18}/Q_{16})$ , equivalent to the isotopic fractionation factor ratios, for a number of oxygen compounds and exchange reactions. A range of 0.520 to 0.528 was reported for equilibrium conditions, whereas calculations for diffusion processes indicated greater variation, from 0.500 to 0.523. A value of 0.520 was chosen (for the quartz-water system) as a compromise between theory and experimental measurements on terrestrial rocks and waters. This is the origin of the proportionality factor in the well-known identity  $\delta^{17}\text{O} = 0.52\delta^{18}\text{O}$ . However, it is generally recognised (e.g., Clayton and Mayeda, 1996) that this linear relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  is an approximation derived from the power law:

$$\alpha_{17/16} = (\alpha_{18/16})^{0.52}.$$

Li and Meijer (1998) used high precision measurements of the oxygen three-isotope distribution in natural waters to establish that the respective fractionation factors do follow a power law relationship:

$$\frac{^{17}R_a}{^{17}R_b} = \left(\frac{^{18}R_a}{^{18}R_b}\right)^\lambda \quad (1)$$

where  $\lambda$  was determined empirically to be  $0.5281 \pm 0.0015$ . For the present paper, Eqn. 1 is adopted as a starting point for oxygen three-isotope mass-dependent fractionation in terrestrial systems, but without assigning any specific value to the exponent  $\lambda$ . In the case of oxygen from extraterrestrial reservoirs, where mass-dependent fractionation lines may be offset parallel to that of the bulk silicate Earth, a further term is required, to quantify the offset:

$$\frac{^{17}R_a}{^{17}R_b} = [1 + k_{a,b}] \left(\frac{^{18}R_a}{^{18}R_b}\right)^\lambda \quad (2)$$

In this case,  $b$  refers specifically to a material which lies on the terrestrial fractionation line, whilst  $k_{a,b}$  is a measure of the offset of  $a$  from that line. For example, the offset between the terrestrial line and that associated with the SNC meteorites (the parent body of which is most probably Mars) has been accurately characterised by Franchi et al. (1999), although not in this format. Equation 2 is also applicable to the identification of

terrestrial oxygen reservoirs which lie off the bulk Earth fractionation line; tropospheric  $\text{O}_2$  is an example. Such an offset may be indicative of a mass-independently fractionated component, or the result of a specific fractionation process characterised by a  $\lambda$  value which is distinct from that which describes the oxygen three-isotope distribution in terrestrial rocks (with the exception of the anomalous sulphates referred to above) and waters. In terms of  $\delta$  values, as generally measured rather than absolute ratios, (2) becomes:

$$1 + \frac{\delta^{17}\text{O}}{1000} = [1 + k_{a,b}] \left(1 + \frac{\delta^{18}\text{O}}{1000}\right)^\lambda \quad (3)$$

It is noted that some authors (e.g., Li and Meijer, 1998) regard the definition of  $\delta$  as including a factor of 1000, so that any  $\delta^{17}\text{O}/1000$  and  $\delta^{18}\text{O}/1000$  terms should be written as  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  respectively. That convention is not widely adopted and is thus avoided here, to minimise confusion. Taking natural logarithms of the equalities in (3) and scaling up by a factor of  $10^3$  gives:

$$1000\ln\left(1 + \frac{\delta^{17}\text{O}}{1000}\right) = \lambda 1000\ln\left(1 + \frac{\delta^{18}\text{O}}{1000}\right) + 1000\ln[1 + k_{a,b}] \quad (4)$$

Thus, a plot of  $10^3\ln(1+10^{-3}\delta^{17}\text{O})$  against  $10^3\ln(1+10^{-3}\delta^{18}\text{O})$  should produce a straight line of slope  $\lambda$  and intercept corresponding to  $10^3\ln[1+k_{a,b}]$ . The respective ordinate and abscissa axis scales are essentially unchanged from those of a corresponding  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  plot; also, any offset on the ordinate axis will be of similar magnitude to that given by the established definition of  $\Delta^{17}\text{O}$ , i.e.,  $\delta^{17}\text{O} - 0.52\delta^{18}\text{O}$  (after Clayton and Mayeda, 1988), if  $\lambda \sim 0.52$ . Hulston and Thode (1965) reported the use of a similar equation to (4), for the accurate determination of linear fractionation slopes in the sulphur multiple isotope system, over a wide range of  $\delta$  values. If  $\Delta^{17}\text{O}$  is now defined as  $1000k_{a,b}$ , the following applies:

$$\begin{aligned} \Delta^{17}\text{O} &= 1000k_{a,b} \cong 1000\ln[1 + k_{a,b}] \\ &= 1000\ln\left(1 + \frac{\delta^{17}\text{O}}{1000}\right) - \lambda 1000\ln\left(1 + \frac{\delta^{18}\text{O}}{1000}\right) \end{aligned} \quad (5)$$

Using the well-known identity that

$$\ln(1 + x) = x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots \cong x \quad \text{where } x \ll 1, \quad (6)$$

it is readily apparent that the right-hand terms of (5) may be approximated to give:

$$\Delta^{17}\text{O} \cong \delta^{17}\text{O} - \lambda'\delta^{18}\text{O} \quad (7)$$

This is the usual representation of  $\Delta^{17}\text{O}$ , with  $\lambda'$  set to 0.52. A distinction is made here between  $\lambda$  and  $\lambda'$ , for two reasons: firstly, as is widely appreciated,  $\lambda'$  is not independent of the range of sample  $\delta$  values. In fact, it increasingly diverges from  $\lambda$  as the sample data set includes points of greater  $|\delta^{17}\text{O}|$  and  $|\delta^{18}\text{O}|$ . Secondly, an important—though not widely recognized—consequence of simplifying the logarithmic terms in (5) by application of (6) is that, whereas  $\lambda$  is independent of the isotopic composition of the reference material,  $\lambda'$  is not. This is of particular significance when sample isotopic data are reported with respect to a reference material which does not fit on

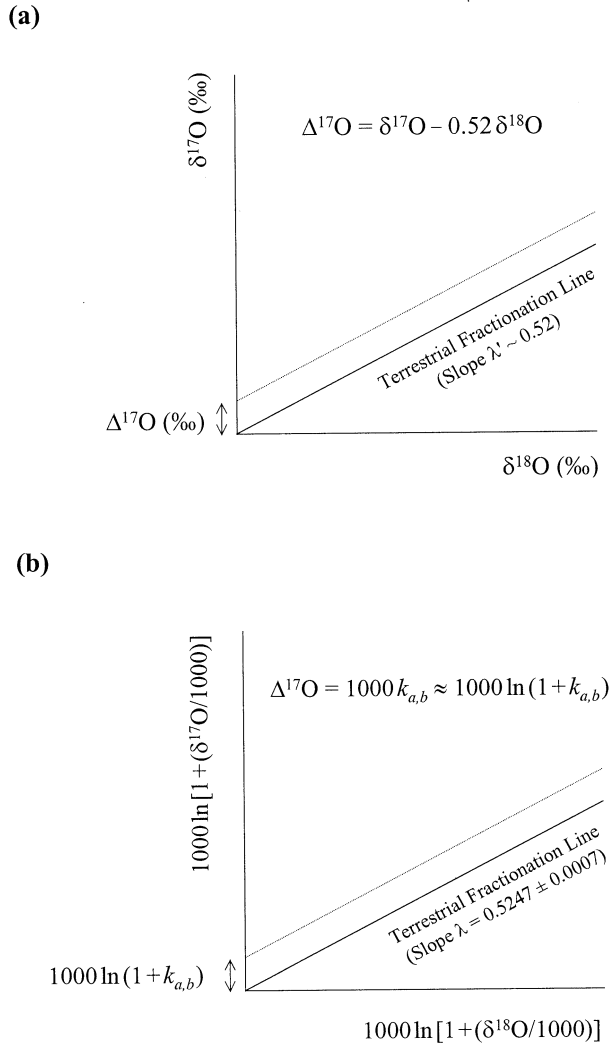


Fig. 1. Comparative, schematic representation of oxygen three-isotope plots, illustrating mass-dependent fractionation of a reservoir anomalously enriched in  $^{17}\text{O}$  relative to the bulk Earth. (a). ‘Conventional’ representation. (b). Format proposed in the present work, with slope value as discussed in Section 3.1. The respective axis scales are numerically similar to those in (a).

the same mass-dependent fractionation line, or where the isotopic composition of the reference material is not well characterised. It should be noted, however, that the value of  $\Delta^{17}\text{O}$  as given by either (5) or (7) is dependent on the isotopic composition of the reference material, relative to which the  $\delta$  values are reported. A schematic comparison of the alternative three-isotope fractionation plots, as derived from (7) and (5) respectively, is shown in Figure 1. The slope value shown in part (b) is derived from measurements on a wide range of terrestrial silicate rocks reported by Miller et al. (1999a).

## 2.2. Comparison of Alternative Definitions of $\Delta^{17}\text{O}$

For samples of isotopic composition within a few per mil of that of the reference material, the difference between  $\Delta^{17}\text{O}$  values calculated on the basis of (7) and with a  $\lambda'$  value of 0.52,

rather than using  $10^3 k_{a,b}$  in conjunction with a highly accurate value of  $\lambda$  (5) is generally negligible, i.e., within the analytical error of measurement, if  $\lambda$  and  $\lambda'$  are of similar value. Another alternative definition of  $\Delta^{17}\text{O}$  (Farquhar et al., 1999) is based on the power law relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  (3), without conversion to linear format. Thus:

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 10^3 \left[ \left( 1 + \frac{\delta^{18}\text{O}}{1000} \right)^\lambda - 1 \right] \quad (8)$$

which may also be expressed as

$$\Delta^{17}\text{O} = 10^3 \left[ \left( 1 + \frac{\delta^{17}\text{O}}{1000} \right) - \left( 1 + \frac{\delta^{18}\text{O}}{1000} \right)^\lambda \right] \quad (9)$$

A similar equation to (8) was used by Farquhar et al. (2000b) for quantifying  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  anomalies in SNC meteorites. (8) and (9) give a very similar result (identical when  $\delta^{18}\text{O} = 0$ ) to the parameter  $10^3 k_{a,b}$  proposed in (5), if exactly the same value of  $\lambda$  is used. However, they have the disadvantage that  $\lambda$  needs to be determined independently, whereas use of the  $10^3 \ln(1 + 10^{-3} \delta^{17}\text{O})$  versus  $10^3 \ln(1 + 10^{-3} \delta^{18}\text{O})$  plot allows both  $\lambda$  and  $\Delta^{17}\text{O}$  to be readily determined, simultaneously, from high precision data sets that span a wide range of  $\delta$  values. It should be noted, however, that  $\Delta^{17}\text{O}$  is very sensitive to the precise value of the exponent  $\lambda$  used in (8) and (9); this is also true of (5). Farquhar et al. (1998, 1999) and Farquhar et al. (2000a) adopted  $\lambda = 0.52$ . However, if this differs from the ‘true’ value by as little as 1%, the resulting  $\Delta^{17}\text{O}$  may be seriously in error, depending on the  $\delta$  values of the samples under consideration. An example of this is illustrated in Figure 2, which was derived as follows: For samples fitting a mass-dependent fractionation line parallel to that which describes terrestrial silicates (slope  $\lambda = 0.5247$  on the ‘revised’ three isotope plot, see Figure 1b), with an offset of  $-0.25$  ‰, (5) may be used to obtain the  $\delta^{17}\text{O}$  values for corresponding  $\delta^{18}\text{O}$  data. Although  $\Delta^{17}\text{O}$  defined by (5) is invariant to the  $\delta$  values, as illustrated by line (a) in Figure 2, substitution of the same  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  data set into (8) or (9), with an exponent  $\lambda$  of 0.52, gives a linear relationship between  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , but of non-zero slope (line (b)). Changing the exponent term to 0.5247 causes rotation of line (b) about the point  $\delta^{18}\text{O} = 0$ , to essentially eliminate the slope and give close coincidence between lines (a) and (b). Alternatively, calculation of  $\Delta^{17}\text{O}$  values by  $\delta^{17}\text{O} - 0.52\delta^{18}\text{O}$ , i.e., based on (7) with  $\lambda' = 0.52$ , shows that the results form a parabolic curve (c) in Figure 2. Only at point  $\delta^{18}\text{O} = 0$  do all three lines coincide. It is interesting to note that, for all positive values of  $\delta^{18}\text{O}$  shown in Figure 2, the  $\Delta^{17}\text{O}$  values calculated by the widely-used  $\delta^{17}\text{O} - 0.52\delta^{18}\text{O}$  formulation are actually closer to the ‘true’ value than is obtained by the use of (8) or (9) if a slightly inaccurate value is used for the exponent term.

## 2.3. Relationship between Fractionation Factors $\alpha_{17/16}$ and $\alpha_{18/16}$

By definition,  $\alpha_{17/16} = {}^{17}R_d/{}^{17}R_b$  and  $\alpha_{18/16} = {}^{18}R_d/{}^{18}R_b$ , with the standard notation, as defined above. As shown in (2), the power law which appears to describe mass-dependent fractionation of oxygen isotopes is:

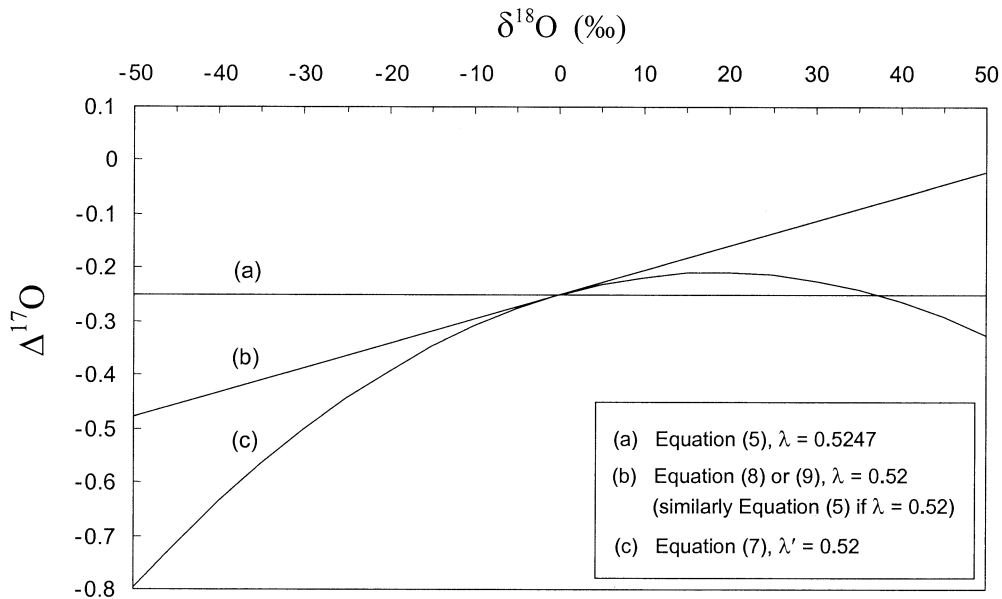


Fig. 2. An example of the effect of different definitions of  $\Delta^{17}\text{O}$  on the magnitude of this parameter. For samples fitting a mass-dependent fractionation line parallel to that of the bulk Earth ( $\lambda = 0.5247$ ) but offset by  $1000k_{a,b} = -0.25$  (line *a*), line *b* represents  $\Delta^{17}\text{O}$  values calculated with (8) or (9) and with  $\lambda = 0.52$  (after Farquhar et al., 1999). Line *c* gives the corresponding  $\Delta^{17}\text{O}$  values obtained from (7) and with  $\lambda' = 0.52$ , which is the most widely used representation of  $\Delta^{17}\text{O}$  (after Clayton and Mayeda, 1988).

$${}^{17}R_d/{}^{17}R_b = [1 + k_{a,b}]({}^{18}R_d/{}^{18}R_b)^\lambda$$

from which it follows that:

$$\alpha_{17/16} = [1 + k_{a,b}](\alpha_{18/16})^\lambda \quad (10)$$

Where *a* and *b* lie on the same mass-dependent fractionation line, then  $k_{a,b} = 0$  and the  $\alpha$  values are related simply by:

$$\alpha_{17/16} = (\alpha_{18/16})^\lambda \quad (11)$$

#### 2.4. Comparison of $\lambda$ and $\lambda'$ Using Model Data

To assess the extent of the  $\delta^{18}\text{O}$  range over which (7) is a satisfactory approximation to (5), and to examine the relationship between  $\lambda$  and  $\lambda'$ , the following procedure was adopted:

For  $\delta^{18}\text{O}$  values from  $-50$  to  $-5$  ‰ and from  $+5$  to  $+50$  ‰ at 5 ‰ intervals, and for  $\lambda$  values of precisely 0.510, 0.515, 0.520 and 0.525, the corresponding  $\lambda 10^3 \ln(1 + 10^{-3} \delta^{18}\text{O})$  values were calculated. These are equivalent to  $10^3 \ln(1 + 10^{-3} \delta^{17}\text{O})$ , from which the respective  $\delta^{17}\text{O}$  values may be obtained. (Note that, for simplicity, the case where no anomalous  ${}^{17}\text{O}$  component is present, i.e.,  $\Delta^{17}\text{O} = 0$ , is considered here.) By performing least-squares linear regression of the resulting  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  data, direct comparison may be made between  $\lambda$  and the corresponding  $\lambda'$  values for this particular data set (Fig. 3).  $\delta^{18}\text{O}$  ranges of  $+5$  to  $+50$  ‰ and  $-5$  to  $-50$  ‰ have been considered separately for two reasons: Firstly, experimental data sets do not usually encompass a much larger  $\delta^{18}\text{O}$  range; secondly, it is apparent that whether the sample isotopic data are either more positive than the reference material, or more negative, influences whether  $\lambda' < \lambda$  or  $\lambda' > \lambda$ . Finally, it is interesting to note that, whereas there is general recognition that a  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  array results in a

greater degree of curvature for increasing values of  $|\delta^{17}\text{O}|$  and  $|\delta^{18}\text{O}|$ , least squares regression of the isotopic data produces a surprisingly good linear fit to the curve, even for an extended range of  $\delta$  values. For example, for the above data set encompassing  $\delta^{18}\text{O}$  values of  $+5$  to  $+50$  ‰, and for  $\lambda'$  values incrementing by 0.005 from 0.510 to 0.525, the corresponding linear regression coefficients ( $R^2$ ) all exceed 0.99999. A consequence of the regression is that a small offset is introduced to the ordinate axis intercept (67 per meg, in the examples cited). In the case of 'real' data, the degree of scatter inherent with even high precision measurements may occasionally give rise to the situation whereby least squares linear regression of  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  actually gives a marginally better degree of fit than does similar regression of  $10^3 \ln(1 + 10^{-3} \delta^{17}\text{O})$  versus  $10^3 \ln(1 + 10^{-3} \delta^{18}\text{O})$ . An example of this is presented in Section 3.3.

### 3. APPLICATIONS

#### 3.1. High Precision Characterisation of the Mass-Dependent Fractionation Line for the Bulk Earth

Matsuhisa et al. (1978) reported that empirical measurements of  $\lambda'$  for 35 terrestrial rock and water samples yielded a slope of  $0.5164 \pm 0.0033$  (std. error), which forms the basis of the widely-used  $\lambda'$  value of 0.52 in (7). As the experimental data were not published, however, it has not been possible to derive the corresponding value of  $\lambda$ . A comparative study by Robert et al. (1992) in which  $\lambda'$  was measured for Precambrian cherts, modern cherts and mantle-derived lavas, found that the oxygen isotopic compositions were all consistent with mass-dependent fractionation from a single reservoir. Based on the data presented by Robert et al. (1992),  $\lambda$  values of  $0.5280 \pm 0.0073$  and

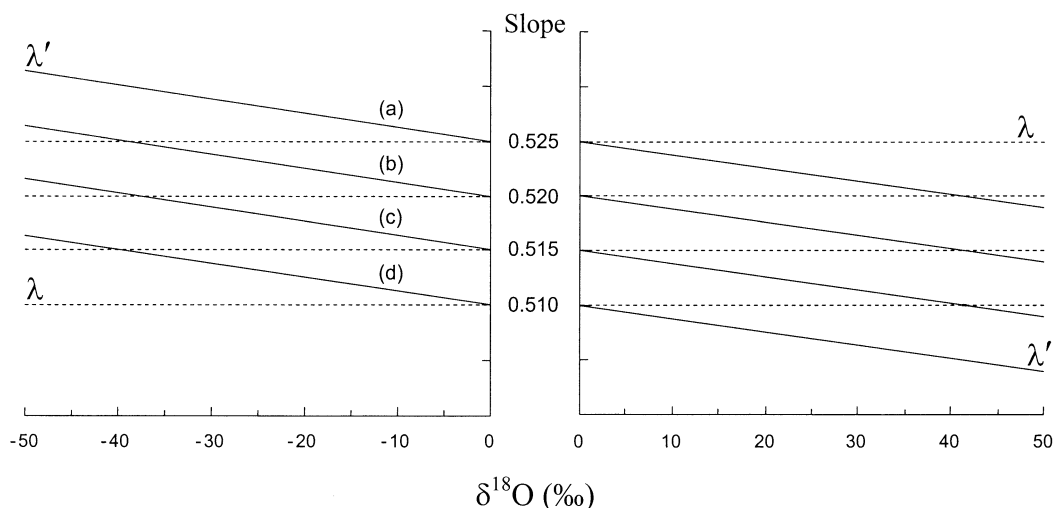


Fig. 3. The variation of  $\lambda'$  as a function of the  $\delta^{18}\text{O}$  values of individual data points, for oxygen three-isotope data sets characterised by respective  $\lambda$  values of (a) 0.525, (b) 0.520, (c) 0.515, (d) 0.510. Note that for a given  $\lambda$ ,  $\lambda'$  attains the same value only for  $\delta^{18}\text{O} = 0$  and that the distribution of individual  $\delta$  values will determine the magnitude of  $\lambda'$  for the data set. For example, for  $\lambda = 0.525$  and with 10 data points evenly distributed between  $\delta^{18}\text{O}$  values of  $-5$  and  $-50$  ‰, regression of the  $\delta^{17}\text{O}$  data against corresponding  $\delta^{18}\text{O}$  values gives  $\lambda' = 0.5320$ ,  $R^2 = 0.999990$  and the intercept on the ordinate axis is 71 per meg. If the same number of data points are evenly distributed between  $\delta^{18}\text{O}$  values of  $+5$  and  $+50$  ‰, the corresponding  $\lambda'$  is 0.5183,  $R^2 = 0.999991$ , and the ordinate axis intercept is 67 per meg.

$0.5273 \pm 0.0064$  (95% confidence level) may be determined for the Precambrian and modern cherts, respectively. These data are in accord with the experimental investigation by Li and Meijer (1998) of the oxygen three-isotope relationship in terrestrial waters of meteoric or oceanic origin.

A more recent investigation of the mass-dependent fractionation line for terrestrial silicate rocks and minerals by Miller et al. (1999a) explored whether, by utilising higher analytical precision compared to previously published studies, the degree of scatter could be significantly reduced, or whether it was indeed inherent (as suggested by Matsuhisa et al., 1978) in selecting a mixture of representative samples from a wide range of geological environments and processes. Further details of that study are currently in preparation. Meanwhile, it is noted that, as reported by Miller et al. (1999a), least squares linear regression of  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  for the complete data set indicates that terrestrial silicates of diverse origin and age do appear to conform to a single fractionation line, with very low scatter. Miller et al. (1999a) recorded a  $\lambda'$  value of  $0.5244 \pm 0.0004$  (std. error) when the isotopic data were reported relative to the laboratory 'working standard'  $\text{O}_2$ . (At the time, the latter had not been independently characterised for  $\delta^{17}\text{O}_{\text{VSMOW}}$ ; it had hitherto been assumed that the value would correspond to that obtained from (7), with  $\lambda' = 0.52$ , in conjunction with the accurately known value of  $\delta^{18}\text{O}_{\text{VSMOW}}$ .) Calibration at the Hebrew University of Jerusalem, however, showed that the 'working standard'  $\text{O}_2$  was significantly offset from the terrestrial fractionation line, which is in accord with its probable origin of fractional distillation from liquefied air. Subsequent conversion of the terrestrial silicate isotopic raw data (unpublished) from Miller et al. (1999a), to values relative to VSMOW, results in a change of  $\lambda'$  to  $0.5217 \pm 0.0007$  (95% confidence level). Using the reporting format of (4) for the

three-isotope plot, the same data set gives a slope ( $\lambda$ ) of  $0.5247 \pm 0.0007$  (95% confidence level).

Because errors in the respective measurements of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  are correlated,  $\lambda$  was also calculated on the basis of the York regression algorithm (York, 1969), using the computational procedure of Ludwig (1999), for comparison with the value obtained above. Miller et al. (1999b) reported that, on this basis, a value of  $0.5244 \pm 0.0012$  at the 95% confidence level was obtained. Unfortunately, incorrect x–y error information was incorporated into the computations. Using the proper procedure (K. Ludwig, pers. comm.) gives a  $\lambda$  value of  $0.52467 \pm 0.00076$  at the 95% confidence level (i.e., very similar to that obtained by simple, least squares linear regression), with a corresponding mean square of weighted deviates (MSWD) of 0.84. Subsequent high precision  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  measurements of natural waters, performed using an adaptation of the method developed by Baker et al. (2001), gave an identical value of  $\lambda$  (Miller et al., in preparation), within the limit of experimental precision (95% confidence level of 0.0009). It is therefore suggested that this highly precise value of  $\lambda$  appears to describe the oxygen three-isotope mass-dependent fractionation line for terrestrial silicates and waters, which forms a reference datum for the characterisation of  $^{17}\text{O}$  anomalies. This reference line is essentially representative of a bulk Earth value (which is possibly a more accurate term than 'terrestrial fractionation line'), on the basis that the total mass of (tropospheric and stratospheric) components known to deviate from it is extremely small, by comparison.

### 3.2. Fractionation Line Slopes Associated with Other Data Sets

Oxygen three-isotope data sets encompassing  $\delta^{18}\text{O}$  values of ten per mil are uncommon in the literature. One example,

however, is that reported by Savarino and Thiemens (1999), who published  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  measurements of  $\text{H}_2\text{O}_2$  from rainwater; their 32 data points spanned a  $\delta^{18}\text{O}$  range in excess of 30 ‰. From the results presented,  $\lambda'$  may be calculated as  $0.514 \pm 0.012$  (at the 95% confidence level). Regression of the same isotopic data on the basis of (4) gives  $\lambda = 0.522 \pm 0.013$ , which indicates more convincingly that the value may actually be identical to that for silicates and waters, as given in the previous Section. This raises the general question of whether other mass-dependent fractionation data sets, reported on the basis of the 'conventional' three-isotope plot, may also be in accord with the slope for silicates and waters, if the isotopic data are reported in terms of  $\lambda$  rather than  $\lambda'$ . Conversely, the use of  $\lambda'$  values in conjunction with a change of isotopic reference (such as from VSMOW to atmospheric  $\text{O}_2$ ) may disguise significant differences between the fractionation line slope and that given by terrestrial silicates or water samples. An example of this latter effect is given in Section 3.3.

### 3.3. Magnitude and Sources of the $^{17}\text{O}$ Anomaly of Atmospheric $\text{O}_2$

The possibility that tropospheric  $\text{O}_2$  might contain a mass-independently fractionated component, derived from stratospheric influx, was postulated by Thiemens (1993) (pers. comm. cited in Bender et al., 1994). That tropospheric  $\text{O}_2$  does indeed lie off the terrestrial fractionation line was confirmed by Thiemens et al. (1995) and Luz et al. (1999). The latter work reported that the  $\delta^{17}\text{O}$  value of VSMOW relative to ambient air  $\text{O}_2$  (referred to as HLA) as the reference material is  $-11.778$  ‰; thus, the  $\delta^{17}\text{O}$  value of atmospheric  $\text{O}_2$  relative to VSMOW equates to  $1000 \times [(1000/(1000 - 11.778)) - 1]$ , i.e., 11.918 ‰. The  $\delta^{18}\text{O}$  value of tropospheric  $\text{O}_2$  has long been established as 23.5 ‰ (Kroopnick and Craig, 1972). Inserting these  $\delta^{17}\text{O}_{\text{VSMOW}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values into (5) gives  $\Delta^{17}\text{O} = -0.340$  when  $\lambda$  is set to 0.5247 as suggested in Section 3.1. This is the magnitude of the  $^{17}\text{O}$  anomaly of tropospheric  $\text{O}_2$  relative to terrestrial rocks and waters.

The high  $\delta^{18}\text{O}$  value of tropospheric  $\text{O}_2$  relative to that of ocean waters, often referred to as the Dole effect (Dole, 1935), is largely attributed to the strong discrimination against  $^{18}\text{O}$  (and, by implication,  $^{17}\text{O}$ ) during respiration (Epstein and Zeiri, 1988; Guy et al., 1989; Kiddon et al., 1993), although many details remain unclear (Bender et al., 1994; Angert and Luz, 2001). In contrast to respiration, photosynthesis, which is the primary source of atmospheric oxygen, generates  $\text{O}_2$  of essentially the same isotopic composition as the water used in this process (Guy et al., 1993; Luz and Barkan, 2000).

Luz et al. (1999) reported high precision measurements of the oxygen three-isotope fractionation line associated with respiration in a closed terrarium containing *Philodendron* plants, non-sterilised soil and natural water. Before measurements, the ambient air  $\text{O}_2$  was biologically cycled by photosynthesis and respiration to remove the  $^{17}\text{O}$  anomaly with respect to natural waters. Using ambient air  $\text{O}_2$  (HLA) as the isotopic reference material, a slope of 0.521 was obtained on the basis of the  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  plot. If the (unpublished) isotopic data are reported with respect to VSMOW, however, the slope value is significantly reduced, as shown in Figure 4 (a). Converting the same data set to the format of (4) also produces a linear array, but

with a slope that is independent of the isotopic reference (Fig. 4 (b)). Comparison of Figure 4 (a) and (b) also reveals the surprising result that the regression coefficient is marginally lower for the 'exact' plot, Figure 4 (b), despite a  $\delta^{18}\text{O}$  range in excess of 20 ‰.

If it is assumed that marine photosynthetic production is the dominant source of  $\text{O}_2$  formation globally, with attendant isotopic composition close to that of VSMOW, and that oxygen three-isotope fractionation of this reservoir by respiration (involving a positive shift of  $\delta^{18}\text{O}$  by approximately 22 ‰), is described by the results presented in Figure 4, it is apparent that a proportion of the  $^{17}\text{O}$  anomaly of atmospheric  $\text{O}_2$  may be accounted for by the difference between the respective slopes of the respiration line and that which describes the bulk Earth. This is shown schematically in Figure 5, from which it is apparent that approximately 44% of the  $^{17}\text{O}$  anomaly of tropospheric  $\text{O}_2$  relative to terrestrial rocks and waters may be accounted for on this basis. Thus, the flux of stratospheric  $\text{O}_2$  input to the troposphere (Holton et al., 1995) may contribute only 56% of the measured anomaly. This obviously has implications for atmospheric chemistry models involving stratospheric-tropospheric exchange. It is noted that a difference in fractionation line slopes between respiration and the bulk Earth was published by Young et al. (2002) as a possible mechanism for explaining the isotopic anomaly of atmospheric  $\text{O}_2$ . The actual magnitude of the respiration-derived component may, in reality, depend on complex interaction of numerous second-order factors. For example, the isotopic composition of photosynthetic oxygen derived from meteoric waters will be notably more negative than that of VSMOW (Luz and Barkan, 2000), and encompass a wide range of values on a global scale; also, local humidity will control evapo-transpiration from leaves, which is itself associated with isotopic discrimination (Dongmann, 1974).

## 4. CONCLUSIONS

Unlike the oxygen three-isotope plot based on the variation of  $\delta^{17}\text{O}$  with  $\delta^{18}\text{O}$ , the slope of the line obtained from linear regression of  $10^3 \ln(1 + 10^{-3} \delta^{17}\text{O})$  against  $10^3 \ln(1 + 10^{-3} \delta^{18}\text{O})$  is invariant to both the distribution of  $\delta^{18}\text{O}$  (and  $\delta^{17}\text{O}$ ) data and to the identity of the isotopic reference material. This provides the basis for a consistent and robust reporting format, particularly applicable to high precision data sets, even though it may not necessarily lead to an improved degree of linear fit of the experimental data. It is suggested that previous discrepancies (or, indeed, similarities) between the slopes of different, high precision data sets reported on the basis of the  $\delta^{18}\text{O}$  versus  $\delta^{17}\text{O}$  plot may need to be reassessed.

From the intercept on the ordinate axis,  $10^3 \ln(1 + k_{a,b})$ , the parameter  $10^3 k_{a,b}$  may be obtained (defined here as  $\Delta^{17}\text{O}$ ), which records the magnitude of any departure (if  $10^3 k_{a,b} \neq 0$ ) from a reference fractionation line, usually that representative of the bulk Earth. For most findings reported to date,  $10^3 k_{a,b}$  will be indistinguishable from  $10^3 \ln(1 + k_{a,b})$ . As an example, for  $10^3 k_{a,b}$  as large as 5 per mil, the error incurred by this approximation will be only 12 per meg. A corollary is the need to obtain consensus on an accurate value of the slope ( $\lambda$ ) of the bulk Earth reference line, which recent empirical measurements suggest is essentially constant. Equally important, for  $\Delta^{17}\text{O}$

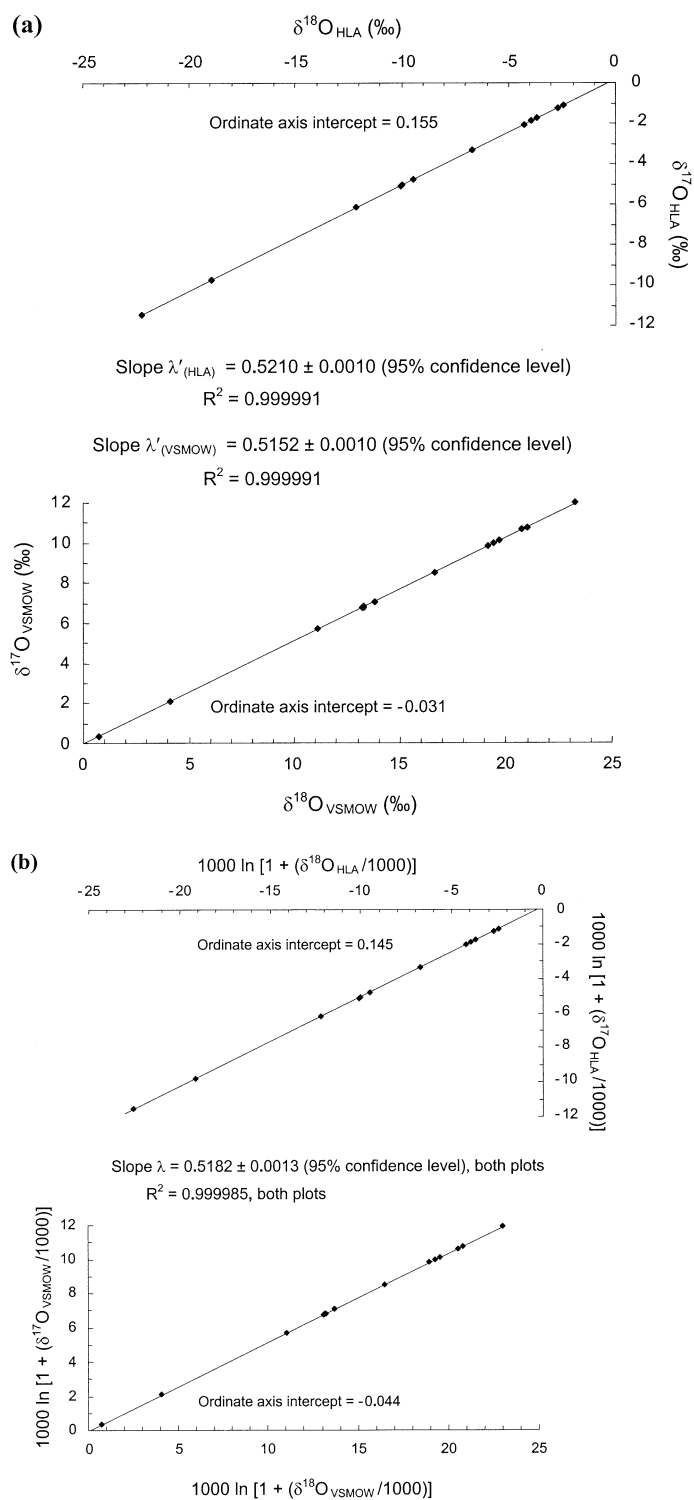


Fig. 4. An example of the effect on the fractionation line slope and  $\Delta^{17}\text{O}$  of changing the reference to which  $\delta$  values are reported, from ambient air  $\text{O}_2$  (HLA) to VSMOW. The data ( $n = 14$ ) refer to isotopic fractionation of  $\text{O}_2$  during respiration in a closed system (Luz et al., 1999), after removal of the atmospheric isotopic anomaly by biologic recycling involving respiration and photosynthesis. (a). Regression of  $\delta^{17}\text{O}$  against  $\delta^{18}\text{O}$ . Both  $\Delta^{17}\text{O}$  and the slope ( $\lambda'$ ) of the fractionation line depend on whether the isotopic data are referred to HLA or VSMOW. (b). Data plotted according to (4) of the present work. Note that the slope ( $\lambda$ ) is invariant to the isotopic composition of the reference material, although the value of  $\Delta^{17}\text{O}$  is not.

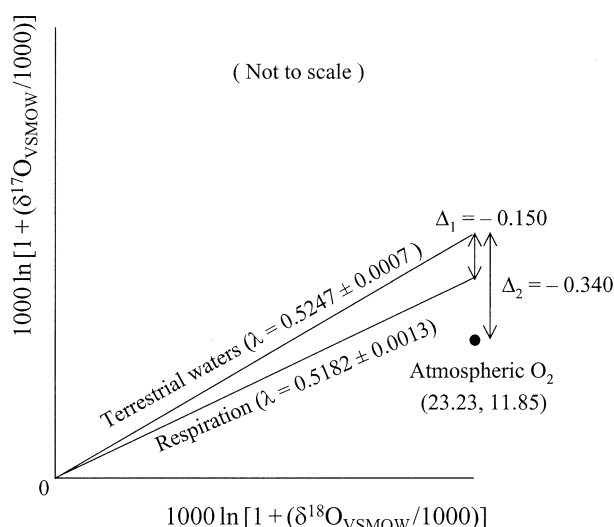


Fig. 5. Schematic representation of the contribution to the isotopic anomaly of atmospheric  $O_2$  resulting from fractionation during respiration. The reported uncertainties on the respective fractionation lines refer to the 95% confidence level.  $\Delta_1$  indicates the ordinate value of the respiration line relative to terrestrial waters (and silicates), for an abscissa value corresponding to that of atmospheric  $O_2$ .  $\Delta_2$  similarly indicates the magnitude of the  $^{17}O$  anomaly of atmospheric  $O_2$  relative to the fractionation line for the bulk Earth, calculated on the basis of (5).

comparison consistency, is to standardise on a single isotopic reference material for the reporting of  $\delta$  values. At present, VSMOW is used almost universally, although tropospheric  $O_2$  (HLA) has been preferred by at least one major research group.

An example of the application of the approach reported in this paper is that it is possible to accurately quantify the difference between the fractionation line slope associated with global geological and hydrological process, on the one hand, and respiration, on the other hand, and to show that the magnitude of the difference can provide an explanation for the origin of approximately 44% of the  $\Delta^{17}O$  value of atmospheric  $O_2$ , which has hitherto been attributed solely to stratospheric input. Although the respiration line may be a useful alternative  $\Delta^{17}O$  reference for oxygen three-isotope studies involving some biogeochemical or physiological processes, confusion will reign if it is not made very clear that any reported  $^{17}O$  anomalies are not referenced to the bulk terrestrial line.

Finally, the data treatment presented here is also directly applicable to the reporting of high precision measurements of other three-isotope systems, of which magnesium is a notable example (Galy et al., 2000; Galy et al., 2001).

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