

Electronic Supplementary Information

S.1. Oxygen corrections for N-TIMS analyses

An important step in the N-TIMS data reduction, is the correction for oxygen interferences. In this study, we have applied a two-step correction, where in step one a starting oxygen composition is used in order to determine the “true” oxygen isotope composition of the particular measurement. For the first step we have used the compositions as determined by Luguet et al. (2008):

$$^{17}\text{O}/^{16}\text{O}_{\text{Luguet}} = R_1 = 0.00038582 \quad (1)$$

$$^{18}\text{O}/^{16}\text{O}_{\text{Luguet}} = R_2 = 0.00203486 \quad (2)$$

The intensities obtained on a certain mass (I_x in V) were corrected for the effects of variable isobaric oxygen isotope interferences of the heavier oxygen isotopes (^{17}O and ^{18}O) following:

$$O_1 = 3 * R_1 \quad (3)$$

$$O_2 = 3 * R_1^2 + 3 * R_2 \quad (4)$$

$$O_3 = R_1^3 + 6 * R_1 * R_2 \quad (5)$$

$$O_4 = 3 * R_1^2 * R_2 + 3 * R_2^2 \quad (6)$$

$$O_5 = 3 * R_1 * R_2^2 \quad (7)$$

$$O_6 = R_2^3 \quad (8)$$

Where O_i represent the difference in mass (i in amu) between the analyte mass of interest and the lightest mass that could generate a potential oxide interference. For example, the ions collected on mass 234 (I_{234}) are predominantly representing $^{186}\text{Os}^{16}\text{O}_3^-$ (I^{186}) ions but also reflect oxygen complexes originating from ^{184}Os ($^{184}\text{Os}^{16}\text{O}^{17}\text{O}_2^-$ and $^{184}\text{Os}^{16}\text{O}_2^{18}\text{O}^-$). In this case, the mass difference is 2 amu and thus $O_i = O_2$. Using equations 3-8, the intensities of $^{186}\text{Os}^{16}\text{O}_3^-$ ions (I^i) can be determined as follows:

$$I^{184} = I_{232} \quad (9)$$

$$I^{186} = I_{234} - (I_{232} * O_2) \quad (10)$$

$$I^{187} = I_{235} - (I_{232} * O_3) - (I_{234} * O_1) \quad (11)$$

$$I^{188} = I_{236} - (I_{232} * O_4) - (I_{234} * O_2) - (I_{235} * O_1) \quad (12)$$

$$I^{189} = I_{237} - (I_{232} * O_5) - (I_{234} * O_3) - (I_{235} * O_2) - (I_{236} * O_1) \quad (13)$$

$$I^{190} = I_{238} - (I_{232} * O_6) - (I_{234} * O_4) - (I_{235} * O_3) - (I_{236} * O_2) - (I_{237} * O_1) \quad (14)$$

$$I^{192} = I_{240} - (I_{234} * O_6) - (I_{235} * O_5) - (I_{236} * O_4) - (I_{237} * O_3) - (I_{238} * O_2) \quad (15)$$

By obtaining the intensities on the various $^{186}\text{Os}^{16}\text{O}_3^-$ ions, masses 241 ($^{192}\text{Os}^{16}\text{O}_2^{17}\text{O}^- = I^{192}17$) and 242 ($^{192}\text{Os}^{16}\text{O}_2^{18}\text{O}^- = I^{192}18$) can be stripped from minor tri-oxide interferences as well, following:

$$I^{192}17 = I_{241} - (I_{235} * O_6) - (I_{236} * O_5) - (I_{237} * O_4) - (I_{238} * O_3) \quad (16)$$

$$I^{192}18 = I_{242} - (I_{236} * O_6) - (I_{237} * O_5) - (I_{238} * O_4) \quad (17)$$

Subsequently, these intensities were used to determine the “true” oxygen isotope compositions ($^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$) of the individual cycle:

$$^{17}\text{O}/^{16}\text{O}_{\text{true}} = R'_1 = (I^{192}17 / I^{192}) / 3 \quad (18)$$

$$^{18}\text{O}/^{16}\text{O}_{\text{true}} = R'_2 = (I^{192}18 / I^{192}) / 3 \quad (19)$$

These oxygen compositions were then used to perform the “stripping” again (equations 3-15), now with the “true” oxygen composition. This means that R_1 and R_2 in equations 3-8 are replaced by R'_1 and R'_2 .

In this study, we observed that the $^{17}\text{O}/^{16}\text{O}$ composition imposes a significant inaccuracy on the stable Os isotope composition when total Os signal intensities dropped below 1 V. Therefore, instead of accomplishing equations (16) and (18), the $^{17}\text{O}/^{16}\text{O}$ composition was based on the “true or measured” $^{18}\text{O}/^{16}\text{O}$ composition as determined in equation (19). In order to calculate the $^{17}\text{O}/^{16}\text{O}$ from the measured $^{18}\text{O}/^{16}\text{O}$ the relationship between the stable oxygen isotopes needs to be considered. In this study, we assume that the oxygen isotopic compositions vary as a result of equilibrium mass-dependent isotopic fractionation. The relationship among the three stable oxygen isotopes is exponential and can be written as:

$$\delta^{17}\text{O} + 1 = (\delta^{18}\text{O} + 1)^\lambda \quad (20)$$

, where λ defines the slope of the line. By taking a logarithm, equation (20) can be linearized (Miller, 2002¹):

$$10^3 * \ln(\delta^{17}\text{O}/10^3 + 1) = \lambda * (10^3 * \ln(\delta^{18}\text{O}/10^3 + 1)) \quad (21)$$

To calculate the $^{17}\text{O}/^{16}\text{O}$ composition, equation (21) can be re-written:

$$\delta^{17}\text{O} = e^{\lambda * (\ln((\delta^{18}\text{O}/10^3) + 1))} * 10^3 \quad (22)$$

with,

$$^{17}\text{O}/^{16}\text{O}_{\text{true}} = (\delta^{17}\text{O}/10^3 + 1) * ^{17}\text{O}/^{16}\text{O}_{\text{VSMOW}} \quad (23)$$

, where λ is 0.526, as we assume that the fractionation occurs along the “Terrestrial Fractionation Line” (TFL²) for which the average literature values is 0.526 e.g. 3-5. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ use the VSMOW (Vienna Standard Mean Ocean Water) as reference values. Generally, the $^{18}\text{O}/^{16}\text{O}$ ratio of VSMOW is accepted to be 0.0020052⁶ whereas there is more debate about the $^{17}\text{O}/^{16}\text{O}$ ratio, with values ranging between 0.000380⁷ and 0.000384⁸. Using data of this study we obtain an intercept with zero at a value of 0.000382 which is within the range previously observed and, therefore, used in this study (Fig. S.1). To determine this intercept we used analyses that were obtained at a beam intensity of >2 mV on mass 241. If these analyses are plotted in $10^3 \ln(1+\delta^{17}\text{O}/10^3)$ vs. $10^3 \ln(1+ \delta^{18}\text{O}/10^3)$ space, following the approach of Miller (2002)¹, a regression coefficient (λ) of 0.488±0.072 (95 c.i.) is obtained (Fig. S.1). Isoplot 4 was used to calculate the slope as well as the error on the slope. When the selected analyses are considered in $^{17}\text{O}/^{16}\text{O}$ vs. $^{18}\text{O}/^{16}\text{O}$ space an approximate linear relationship with a slope of 0.092 ± 0.014 (95 c.i.) and an intercept of 0.000197 ± 0.000027 (95 c.i.) is obtained. This is within error of the values obtained when assuming a slope of 0.526 over the $^{18}\text{O}/^{16}\text{O}$ interval of 0.002007 to 0.002055 (the range in $^{18}\text{O}/^{16}\text{O}$ observed in this study); 0.0994 x + 0.000183, where x is $^{18}\text{O}/^{16}\text{O}$.

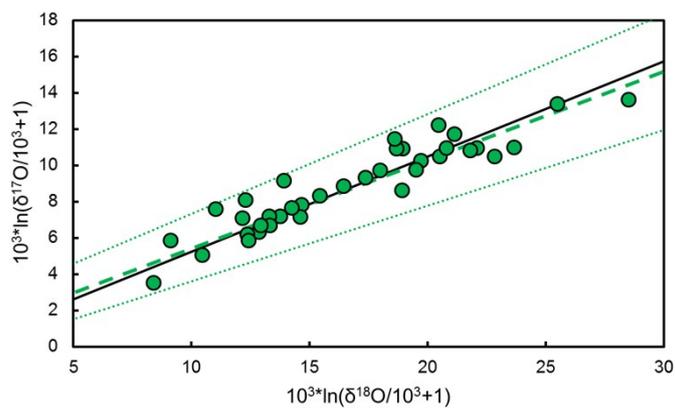


Figure S.1 Measured $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ compositions of analyses with a beam intensity of >2 mV on mass 241 plotted as delta values in logarithmic form. The regression line (dashed line) is within error (dotted lines) of the terrestrial fractionation line with a slope of 0.526 (solid line).

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