

DEFINING THE TERRESTRIAL OXYGEN ISOTOPE FRACTIONATION LINE AND OBSERVED OXYGEN ISOTOPIC HETEROGENEITY WITHIN THE ALLENDE METEORITE A. Pack*¹, B. Horvath¹, M. Hofmann¹, A. Goldmann^{1,2}, N. Albrecht¹, M. Gellissen³, J. Zipfel⁴ and H. Palme⁴, ¹Georg-August-Universität, Geowissenschaftliches Zentrum, Abteilung Isotopengeologie, Goldschmidtstraße 1, D-37077 Göttingen, Germany; ²Universität Hannover, Institut für Mineralogie; ³Universität Kiel, Institut für Geowissenschaften; ⁴Senckenberg, Frankfurt, *apack@uni-goettingen.de.

Introduction: Since the discovery of mass-independent ¹⁶O enrichment in meteorites and their components [1], oxygen isotope analyses have become an important tool in meteorite classification [2-6], but also for better understanding processes in the Earth's atmo- [7, 8], bio- [9] and hydrosphere [10-13]. Comparison of datasets from different groups, however, is often complicated, because of ambiguity in the definition of the $\Delta^{17}\text{O}$ values.

We present a brief review of the nomenclature, a description of our analytical protocol, new data on the terrestrial fractionation line (TFL) and data from the Allende (CV3) carbonaceous chondrite.

Nomenclature: Oxygen isotopes are usually reported in the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ notation with SMOW as standard:

$$\delta^{17}\text{O}_{\text{SMOW}}^{\text{sample}} = 1000 \left(\alpha_{\text{sample-SMOW}}^{2/1} - 1 \right) \text{ and}$$

$$\delta^{18}\text{O}_{\text{SMOW}}^{\text{sample}} = 1000 \left(\alpha_{\text{sample-SMOW}}^{3/1} - 1 \right).$$

The α -values are the ratios of ¹⁷O/¹⁶O (2/1) to ¹⁸O/¹⁶O (3/1) of sample and SMOW, respectively. For mass-dependent processes, the relation between the fractionation factors α is given by:

$$\ln \alpha_{\text{sample-SMOW}}^{2/1} = \beta \ln \alpha_{\text{sample-SMOW}}^{3/1}.$$

Materials that formed by a given fractionation process (characterized by α and β ; both are, in general, a function of T), fall on a line in the 3 isotope diagram only if $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ is plotted, but not if $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ is plotted. The δ -prime notations are defined as:

$$\delta'^{17}\text{O}_{\text{SMOW}}^{\text{sample}} = 1000 \ln \alpha_{\text{sample-SMOW}}^{2/1} \text{ and}$$

$$\delta'^{18}\text{O}_{\text{SMOW}}^{\text{sample}} = 1000 \ln \alpha_{\text{sample-SMOW}}^{3/1}.$$

For mass-dependent oxygen isotope fractionation processes, β can vary between 0.500 and 0.529 [14]. The lower limit is defined by diffusion of a component, in which O is bound to a component with infinite mass. The upper limit is the high-T approximation for equilibrium isotope fractionation. The β value has, so far, only been experimentally determined for two isotope equilibria: a) water-vapor equilibrium: $\beta = 0.529 \pm 0.001$ (285 K < T < 315 K) [11] and b) for the CO₂-CeO₂ equilibrium: $\beta = 0.524 \pm 0.001$ (T = 958 K) [15]. Theoretical calculations by [16] suggest $0.5151 \leq \beta \leq 0.5233$ (298 K \leq T \leq 1000 K) for the CO₂ to water equilibrium.

The $\Delta^{17}\text{O}$ value is a measure for the magnitude of mass-independent isotope effects, but can also be result of differences in β for kinetic and equilibrium processes. The $\Delta^{17}\text{O}_{\text{RL}}$ value of a sample is defined by:

$$\Delta^{17}\text{O}_{\text{RL}}^{\text{sample}} = \delta'^{17}\text{O}_{\text{SMOW}}^{\text{sample}} - \beta_{\text{RL}} \delta'^{18}\text{O}_{\text{SMOW}}^{\text{sample}} - \gamma_{\text{RL}}.$$

The reference line RL is defined by the slope (β_{RL}) and the intercept (γ_{RL}).

Traditionally, terrestrial rocks and minerals were analyzed to define the RL (TFL). It is commonly assumed that the slope of the TFL is 0.52 and the intercept at zero, i.e. SMOW falls on the TFL. Recent high-accuracy and -precision analyses of rocks and minerals gave $\beta_{\text{TFL}} = 0.524$ [17, 18]. The intercept of the TFL is commonly assumed to be zero.

The importance of a precise definition of $\Delta^{17}\text{O}$ is demonstrated in the following example. Hydrous matrix of the CM2 chondrite Murchison has a $\delta^{18}\text{O}_{\text{SMOW}} \approx +11\text{‰}$ [19]. The difference in $\Delta^{17}\text{O}$ for $\beta = 0.520$ and $\beta = 0.524$ is 0.044‰. This is in the same range as the uncertainty that is currently obtained with fluorination techniques.

Analytical protocol: We analyzed a large number of terrestrial and extraterrestrial rocks and minerals by means of laser fluorination [20]. Between 0.05 and 2 mg sample (silicates, oxides) are loaded into a Ni sample holder. The samples are fluorinated by means of a 50 W CO₂ laser in an atmosphere of ~20 mbar purified F₂. The sample gas was purified with NaCl for removal of F₂ and a cold trap (-196°C) for removal of Cl₂. The sample O₂ was collected in a 5Å molecular sieve trap (-196°C). The sample gas was then transported with He to a second 5Å molecular sieve trap, from where it was released at 92°C using an automated trap. The sample O₂ entered the source of the THERMO MAT253 multicollector gas mass spectrometer in continuous flow mode after passing through a 5Å molecular sieve GC column of a THERMO GasBench. The GC was used in order to remove NF₃ from the sample gas. The NF fragment interferes with ¹⁷O¹⁶O and leads to erroneous high $\Delta^{17}\text{O}$ [18]. Reference O₂ was injected using the open split valve of the GasBench. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of the reference gas was analyzed by the Jerusalem group (Luz and Barkan) relative to SMOW.

The external reproducibility in $\Delta^{17}\text{O}$ was between ± 0.04 and $\pm 0.05\text{‰}$ (1 σ , SD). The uncertainty in $\Delta^{17}\text{O}$

was limited by the mass spectrometric measurements in continuous flow mode.

The TFL: We have analyzed 703 terrestrial rocks that span $\delta^{18}\text{O}_{\text{SMOW}}$ between -6 and $+24\%$. The samples include a variety of felsic and mafic rocks and NBS-28 quartz. The rocks and minerals define a TFL with (1σ uncertainties):

$$\delta^{17}\text{O}_{\text{SMOW}}^{\text{sample}} = 0.5251 \pm 0.007 \delta^{18}\text{O}_{\text{SMOW}}^{\text{sample}} - 0.014 \pm 0.008.$$

Note that the TFL has an intercept of $\gamma_{\text{TFL}} = -0.014\%$. This implies that SMOW does *not* fall on the rocks- and minerals-defined TFL.

Allende: Allende is a coarse grained agglomerate of chondrules, matrix, Ca- and Al-rich inclusions (CAIs), amoeboid olivine aggregates (AOA) and dark inclusions (DI). A single Allende slice with a total area of 22.5 cm^2 and a thickness of 0.4 cm was cut into 39 rectangular pieces with an average mass of 619 mg each. We analyzed 32 of the 39 $0.3 - 1.1 \text{ g}$ pieces ($\Sigma = 19.2 \text{ g}$). Our data spread along the Allende mixing line (AML), that is defined by data from [19] to:

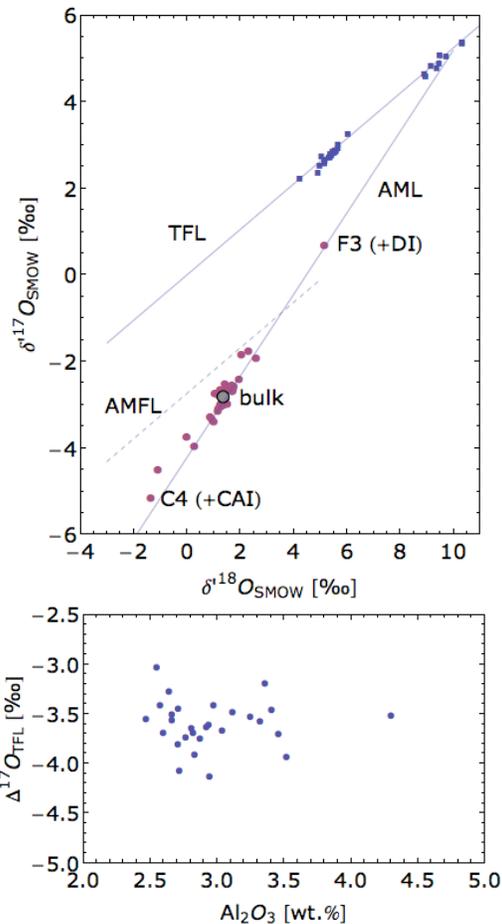
$$\delta^{17}\text{O}_{\text{SMOW}} = 0.938 \delta^{18}\text{O}_{\text{SMOW}} - 4.229\%.$$

The aliquot with the lowest $\Delta^{17}\text{O}$ (C4) contains a large CAI, whereas the sample with the highest $\Delta^{17}\text{O}$ (F3) hosts a DI. The weighted averages for $\delta^{17}\text{O}_{\text{SMOW}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ are $-2.77 \pm 0.17\%$ and $+1.39 \pm 0.19\%$ (1σ SE). The weighted average of $\Delta^{17}\text{O}_{\text{TFL}}$ is $-3.58 \pm 0.07\%$ (1σ , SE). Clayton and Mayeda [21] reported $\delta^{17}\text{O}_{\text{SMOW}} = -2.56\%$ and $\delta^{18}\text{O}_{\text{SMOW}} = +1.64\%$. Both, our weighted mean and the datum from [21] fall on the Allende mixing line (see Fig.).

Excluding two extreme cases (C4, F3), no correlation between the chemical composition (e.g., Al_2O_3 , see Fig.) and $\Delta^{17}\text{O}_{\text{TFL}}$ is observed, although $\Delta^{17}\text{O}_{\text{TFL}}$ spans a range of 1% .

No data fall on the Allende mass fractionation line (AMFL) [22].

Conclusions: i) The $\Delta^{17}\text{O}$ value should be calculated using the δ -prime instead of the δ -notation. ii) The rocks- and minerals-defined TFL has a slope of 0.5251 ± 0.007 and an intercept of $-0.014 \pm 0.008\%$. The β_{TFL} is likely the result of equilibrium fractionation between minerals, melts and fluids. Experimental data [15] show that equilibrium β can be < 0.529 . iii) When reporting $\Delta^{17}\text{O}$ values, one should always give β_{RL} and γ_{RL} of the reference line used. iv) Allende is isotopically heterogeneous on the scale of $< 1 \text{ g}$. The absence of a correlation between $\Delta^{17}\text{O}_{\text{TFL}}$ and chemical composition indicates that variations in $\Delta^{17}\text{O}_{\text{TFL}}$ are not related to heterogeneous distribution of ^{16}O -rich refractory components. v) Specimens with masses $> 1 \text{ g}$ are representative for the Allende bulk composition.



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