EARTH AND MOON ARE INDISTINGUISHABLE IN Δ^{17}O TO SEVERAL PARTS PER MILLION

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Introduction: Recently Herwartz et al [1] suggested that a 12 ppm difference in Δ'^{17}O exists between the bulk silicate Earth (BSE) and the bulk silicate moon (BSM). While Herwartz et al [1] employed a statistical approach, averaging large numbers of laser fluorination analyses for both BSE (n=70) and BSM (n=20), only three different lunar rock fragments were analyzed. Although these samples came from three Apollo sites including Apollo 16, none represented the ancient, anorthositic highland crust. We have analyzed a broader spectrum of lunar rocks and minerals with a greater range in ^{18}O/^{16}O (δ^{18}O). This range in δ^{18}O allows us to characterize the mass-dependent fractionation effects on Δ'^{17}O at the ppm level. Controlling for mass fractionation is required when working at this level of precision. Our results indicate that there is no distinction between Earth and Moon in Δ'^{17}O at the 2 ppm (1σ) level.

A crucial concept when comparing the oxygen isotopic compositions of planetary bodies is the possibility for a range in mass fractionation laws [2,3]. A range in δ'^{18}O for relevant terrestrial and lunar samples provides constraints on the effects of different mass fractionation laws. Our approach is to measure a variety of lunar samples in an effort to achieve a range in δ'^{18}O values spanning at least 1‰. While both high and low- Ti basalts comprise most of our data, we also obtained analyses of a highland anorthositic troctolite. The goal of this approach is to define a fractionation line or envelope for the Moon.

Δ'^{17}O Reference Frame: All data are reported in a San Carlos olivine (SC Ol) reference frame where the Δ'^{17}O of SC Ol is set to zero. We retain the convention of using SMOW (VSMOW) as the reference for δ'^{18}O. Our use of SC olivine (representing Earth's mantle) as the reference for Δ'^{17}O at fixed δ'^{18}O removes any ambiguity surrounding calibrating rock measurements against water.

Different labs advocate for different mass spectrometer calibration schemes when performing high precision oxygen isotope measurements. While the adopted standards are in principle arbitrary, there are practical advantages to using a rock-based reference frame. Using Earth's mantle bypasses the intermediate step of calibrating against SMOW (a water standard measured by entirely different procedures); calibration to SMOW offers no value when comparing Earth to Moon; Earth and Moon are thought to have similar, if not identical, mantle oxygen isotopic compositions [4], very different in Δ'^{17}O from SMOW [5,6]. Also, we do not use the exponent (slope) 0.5305, corresponding to the high-temperature upper limit [1,5]. Instead, we use 0.528 because it is more typical of measurements of high-T systems (although it is recognized that in many cases these are nothing more than mixing lines). In any case, we consider the full theoretical range in exponents from 0.5305 to 0.5000 as characterizing mass fractionation, with a more limited range of 0.528 to 0.514 corresponding to measured values. It should be noted that high temperature rocks seem to always produce slopes shallower than 0.5305; most, including those from [1,4,5,6], plot between 0.529 and 0.525.

Results: Data collected in any reference frame or calibration scheme can be converted easily into any other as long as the scheme is known and the measured delta values are available (Figure 1).
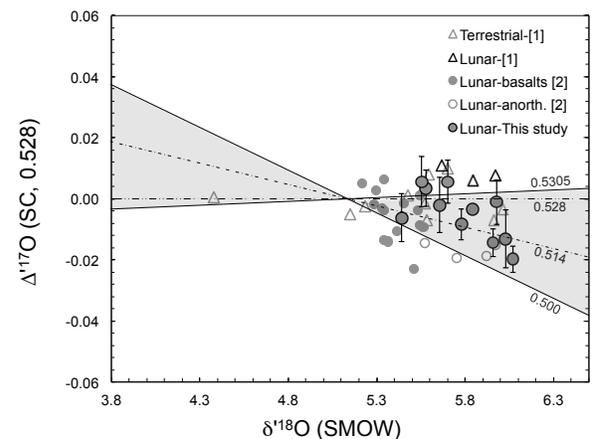

Figure 1: Comparison with literature data using the SC Ol reference frame. Lunar sample data from this study, [1] and [4]. Error bars are 1σ SEM.

Comparing the the lunar data for individual rocks from this study and those from the previous studies, we find general agreement in the range of Δ'^{17}O values (Figure 1) with the three Herwartz et al. data falling in the high end of the total range, though not outside the range defined by their terrestrial data (Figure 1).

What is more, we find no significant positive offset from BSE in $\Delta'^{17}O$ space. All measured values for both Earth and Moon lie within a fractionation envelope defined by San Carlos olivine (Earth's mantle) $\Delta'^{17}O =$ 0.000 +/- 0.001 as the starting point. Despite representing the lower limit for mass fractionation with an exponent of 0.500, it is clear (Figure 2) that a more realistic lower limit slope of 0.514 can be used to define the fractionation envelope.
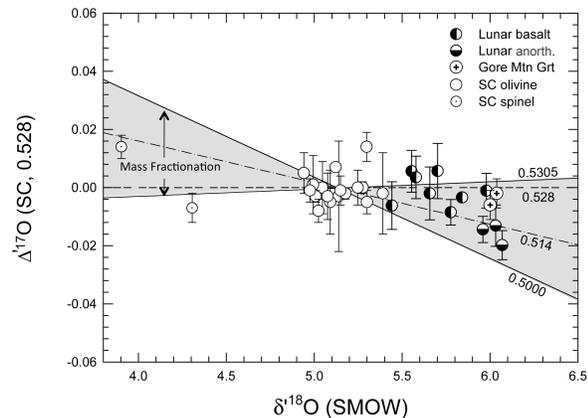

Figure 2: $\Delta'^{17}O$ vs $\delta'^{18}O$ plot for Earth and Moon. All data from this study. Error bars a 1σ SEM.

We find that lunar basalts have very little scatter about our defined reference line where San Carlos olivine has a $\Delta'^{17}O$ of 0 along a 0.528 slope (Figure 3). The average $\Delta'^{17}O$ value for these lunar basalts is -0.0008 +/- 0.002‰ (SC, 0.528), making these basalts indistinguishable from BSE at the 2 ppm level. When the anorthositic highland rock analyses are evaluated separately, the mean $\Delta'^{17}O$ is -0.016 +/- 0.002. The more negative $\Delta'^{17}O$ values (SC, 0.528), in concert with elevated $\delta^{18}O$ in the anorthositic rock, can be explained by mass fractionation considering the higher $\delta'^{18}O$ values of $\approx$ 6 ‰. These negative $\Delta'^{17}O$ values for anorthostic troctolite are similar to values obtained for highland rocks by Wiechert et al. [4]. Note that these highland values for $\Delta'^{17}O$ are lower than terrestrial Gore Mountain Garnet at comparable $\delta^{18}O$ values (Figure 2).

Measurement Conciderations: Samples were dried in an oven for 36-72 hours at 60 °C, then subsequently heated to 70°C with a IR lamp while pumping on our vacuum line to a pressure of 8.5×10^{-7} mbar. This combined oven drying followed by vacuum drying procedure is how we achieved a precision of several ppm. We believe that the main source of contamina-

tion in LF measurements is adsorbed terrestrial water. Thus for single crystals (i.e. most reference materials) and other low surface area-to-volume materials adsorbed water is less of a problem. However, for samples stored as powders at room temperature, the opposite extreme, terrestrial water can have a quantitative impact the measured values.

Ubiquitous trace amounts of NF_3 cause $^{17}O^{16}O$ interferences (at mass/charge = 33) due to NF produced in the source of the mass spectrometer. Trace NF_3 was removed by distilling the oxygen from the 13X molecular sieve at -130 °C to a second molecular sieve at -196 °C for 25 minutes. An experiment run in triplicate verified that a double distillation (re-freezing and re-distillation) of the produced O_2, while decreasing the very small residual NF_2 peak height by an additional order of magnitude had no impact on the measured values for either of the minor isotopes. As a result, we have ruled out NF contamination as a potential bias in our data. On this basis, we must look to other potential reasons for the difference between our study and that of Herwartz et al [1]. It is possible that had more samples been measured in the latter, the difference between BSM and BSE may not have persisted.
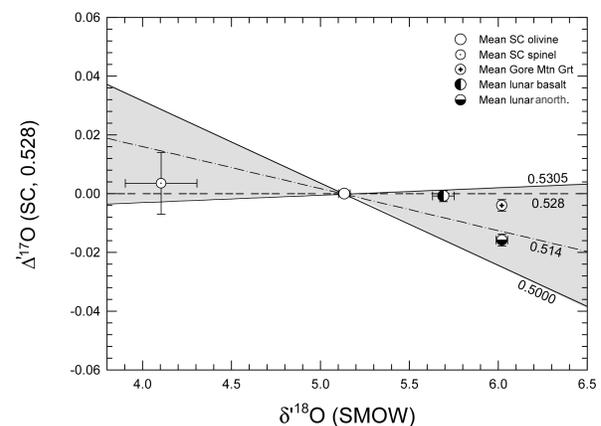

Figure 3: $\Delta'^{17}O$ vs $\delta^{18}O$ plot of averages for terrestrial reference materials and lunar samples. Error bars are 1σ SEM.

References: [1] D. Herwartz, A. Pack, B. Friedrichs, A. Bischoff (2014) *Science,* 344, p.1146. [2] E.D. Young, A. Galy, H. Nagahara. (2002). *GCA*, 66(6), p.1095. [3] X. Cao, Y. Liu. (2011). *GCA*, 75, p.7435. [4] U. Wiechert, A. N. Halliday, D.-C. Lee, G. A. Snyder, L. A. Taylor, D. Rumble. (2001) *Science*, 294, p.345. [5] A. Pack and D. Herwartz. (2014) *EPSL*, 390, p.138. [6] R. Tanaka and E. Nakamura. (2013) RCMS, 27(2), p.285.