

THREE ISOTOPES OF OXYGEN IN LUNAR SAMPLES – THE SAME AS EARTH OR DIFFERENT?

C. T. Pillinger¹, R. C. Greenwood¹, D. Johnson¹, E. K. Gibson^{1,2}, M. F. Miller^{1,3} and I. A. Franchi¹, ¹Planetary and Space Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK. ²Mail Code K, NASA Johnson Space Center, Houston, TX 77058. U.S.A. ³British Antarctic Survey, High Cross, Madingley Rd, Cambridge CB3 0ET [For correspondence email to c.t.pillinger@open.ac.uk]

Introduction: One of the most important measurements that can be made for any extraterrestrial sample is determination of the relative abundance of ¹⁶O, ¹⁷O and ¹⁸O. To make the comparison, investigators report their results as delta (δ) values compared to terrestrial reference materials. Another way of presenting the data is to plot $\delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ for a suite of specimens because for any given reservoir, i.e. a planetary parent body such as the Earth or Mars, the numbers should define a line of gradient approximately one half. Different bodies should be identified from their $\Delta^{17}\text{O}$ which has traditionally been defined by the equation $\Delta^{17}\text{O} = \delta^{17}\text{O} - (a \text{ constant, ca. } 0.52) \times \delta^{18}\text{O}$.

Early oxygen isotope studies on lunar (and terrestrial) samples were carried out by heating rock or soil samples with fluorine-containing reagents in bombs. The resulting blanks were high and the amounts of material reacted quite large, with a consequence that the minor ¹⁷O isotope abundances were neglected. In more recent times, a number of groups have developed techniques utilising focused lasers as heat sources and the three isotope measurements have become more precise.

Three modern O isotope studies [1–3] have reported that lunar rocks are indistinguishable (within errors) from terrestrial sources (Figure).

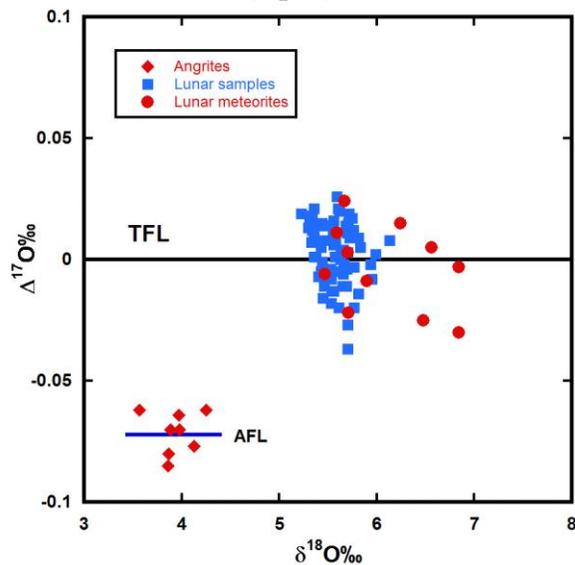


Figure. Lunar samples [1,2,3] compared to lunar meteorites (source Meteoritical Bulletin Database). TFL = Terrestrial Fractionation Line; AFL = Angrite (a basaltic rock meteorite type) Fractionation Line.

In addition, more and more results from other multi-isotope element systems (H, Mg, Si, K, Ti, Cr, Fe and W) similarly show identical compositions for lunar and terrestrial isotope ratios. These results are difficult to reconcile with the classic giant impact model of lunar formation [4]. In this scenario the Moon was formed 4.53 billion years ago as the result of an impact between the proto-Earth and a Mars-sized impactor. However, the present angular momentum of the Earth-Moon system was taken as a primary constraint and as a result the impact would have been of relatively low energy, with the Moon forming predominantly from impactor-derived material.

More recent formulations of the giant impact model [5,6] have proposed that the angular momentum of the Earth-Moon system was initially much higher than present day values and was subsequently reduced through an orbital resonance between the Moon and Sun. As a consequence much higher energy impacts are permissible resulting in much greater levels of homogenization between the proto-Earth and impactor [5,6].

convened to review the consequences of these new impact scenarios and the implications of recent isotope and geochemical studies for models of lunar formation [7]. It was pointed out by Halliday, Stephenson and Melosh, *inter alia*, that the dynamics of any such giant impact, as established by computer models and simulations, may still require the Moon to be created predominantly from the impactor. In which case the impactor has to be, fortuitously or coincidentally, similar to the proto-Earth in isotopic composition. Although the more recent giant impact models [5,6] postulate nearly complete homogenisation of the impactor and proto-Earth, these are for the moment essentially untestable propositions. As a result of the present uncertainty we are left in the somewhat embarrassing situation that, forty-five years after Apollo 11, we have yet to establish satisfactorily the origin of the Moon.

Specific problems: (i) Perhaps rather surprisingly the basis of the Earth – Moon comparison, the slope of the so-called terrestrial fractionation line (TFL) is not a fixed parameter and varies slightly depending on the samples used to define it. This results in different groups using different TFLs (i.e. different values for the approximately 0.52 constant) when comparing the results from the two bodies. (ii) There is no lunar equivalent of the TFL for the Moon. Instead of a lunar

fractionation line (LFL), lunar isotope data are compared to an assigned TFL. A range of specimens likely to have different $\delta^{18}\text{O}$ values (e.g. mineral separates) have not been studied for their $\delta^{17}\text{O}$ values by laser techniques. (iii) Contributions to the lunar regolith from extra-lunar sources such as micrometeorites, the solar wind and the isotopic fractionation effects accompanying these interferences to the isotopic systematics of the Moon have not been investigated.

Possible solutions: (i) Characterising fractionation lines to high levels of precision and accuracy requires that the approximation of a linear relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ be removed, by using the more mathematically correct $10^3\ln(1+\delta^{17}\text{O})$ and $10^3\ln(1+\delta^{18}\text{O})$ as the respective ordinate and abscissa parameters on for the three-isotope plot [8]. The parameter $\Delta^{17}\text{O}$ is then defined as $10^3\ln(1+\delta^{17}\text{O}) - \lambda 10^3\ln(1+\delta^{18}\text{O})$, where λ is the slope of the fractionation line obtained by measurements of a group of 'reference' samples. Depending on the samples chosen, λ may take a value between ~ 0.524 and ~ 0.527 for terrestrial silicates. Studies [2] and [3] used a nearly identical value for λ (0.5259 ± 0.0008 and 0.5262 ± 0.0008 respectively, 95% confidence level). In contrast, study [1] used the earlier definition of $\Delta^{17}\text{O}$; unfortunately, the raw isotopic data were not made available, so direct comparison with investigations [2] and [3] cannot be made.

(ii) Establishing a LFL requires the analysis of samples which have undergone fractionation. In the case of the Earth, the TFL extends over a wide range of $\delta^{18}\text{O}$ values largely because of low temperature interactions involving water. No such equivalent processing has occurred at near-equatorial locations on the Moon, which are markedly devoid of any indigenous water (with the exception of apatites associated with KREEP-rich samples). This situation could change once polar latitudes, where water ice seems to exist in permanently shaded locations, have been sampled. An attempt has been made to investigate mineral separates from lunar basalts, but the measurements were made using old-fashioned methods and whilst the results show $\delta^{18}\text{O}$ values ranging from 4.00 to 7.15‰, no $\delta^{17}\text{O}$ values have been reported [9].

A way of obtaining O isotopic data from a wider range of lunar materials may be to measure individual grains from the 1 to 2 mm fractions sieved from bulk soils. Petrologic examination of this 10% by wt fraction (A10085) separated from the Apollo 11 grab soil A10002 revealed the heterogeneity of the lunar regolith. Indeed, rock types not apparent in the A11 hand specimen collection were recognised, together with almost pure mineral grains or at least bimineralic fragments. A 1 to 2 mm lunar particle can weigh between

1.5 and 12 mg, easily adequate for sub-dividing for repeat O isotope measurements and characterisation by auxiliary methods.

We have selected a small number of individual particles from two lunar soils A10085 and A65522, the latter a highland sample, because so far oxygen three-isotope studies have concentrated on Mare locations. Analysis of these, together with standards of the same size (with appropriate blank corrections applied) show that oxygen isotope measurements of hand-picked individual lunar soil grains are entirely feasible (Table).

Table Preliminary $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of single lunar grains

	$\delta^{17}\text{O}\text{‰}$	$\delta^{18}\text{O}\text{‰}$	$\Delta^{17}\text{O}$	Des.
10085	3.254	6.222	-0.006	Agglut 1
10085	3.188	6.122	-0.019	Min A
10085	3.269	6.283	-0.023	Spherule
65522	3.355	6.414	-0.005	Agglut 2
65522	3.111	5.929	0.004	Min B
65522	3.092	5.901	0.000	Min C

(iii) A variety of investigators have shown that bulk lunar soils are slightly enriched in ^{18}O , by ca. 0.4 to 0.5‰, compared to the rocks from which they are derived. Epstein and Taylor [11] attempted to rationalise this shift by using stepped fluorination. They found that the first stages of the fluorination process liberated tiny amounts of oxygen with $\delta^{18}\text{O}$ values approaching +50‰ and concluded that either the very finest soil grains or the glass portion of glassy agglutinates underwent preferential attack. Although we have yet to characterise the particles fully, except from their external visual appearance, none of the individual hand-picked fragments investigated as part of this study showed the $\delta^{18}\text{O}$ enrichments encountered by Epstein and Taylor [11]. We have previously shown that the laser heating method reveals the small, fractions of a per mil shifts, seen for bulk soils with the heated bomb methods.

References: [1] Wiechert U. et al. (2001) *Science*, 294, 345–348. [2] Spicuzza M. J. et al. (2007), *Earth Planet. Sci. Lett.*, 253, 254–265. [3] Hallis L. J. et al. (2010), *Geochim. Cosmochim. Acta*, 74, 6885–6899. [4] Canup R. M. and Asphaug E. (2001) *Nature* 412, 708–712. [5] Cuk M. and Stewart S. T. (2012) *Science* 338, 1047–1052. [6] Canup R. M. (2012) *Science* 338, 1052–1055. [7] <http://royalsociety.org/events/2013/origin-moon/> [8] Miller M. F. (2002) *Geochim. Cosmochim. Acta*, 66, 1881–1889. [9] Clayton et al. (1971) *LPSC II*, 1417–1420. [11] Epstein S. and Taylor H. P. Jr. (1971) *LPSC II*, 1421–1441.