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OXYGEN ISOTOPE ABUNDANCE MEASUREMENTS IN FINE SIZE FRACTIONS OF LUNA 16 AND 20 SOIL

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CONTENTS

Determination of $\delta^{18}O$ values in fine size fractions of Luna 16 and 20 soil appears to indicate that a simple monotonic increase in ^{18}O abundance with decreasing grain size does not exist. The weighted average $\delta^{18}O$ values for Luna 16 and 20 soil are approximately +6.33‰ and 6.65‰ relative to the s.m.o.w. standard. These averages (within errors of about ±0.2‰) fall inside the range of $\delta^{18}O$ values found by other workers for lunar soils. Three possible interpretations of the patterns of ^{18}O-enrichment with grain size are suggested. (1) The generally accepted explanation is that the heavy isotope enrichments reflect fractional evaporation and/or fractional condensation processes resulting from bombardment of the lunar soil by nuclear particles in the solar wind and/or micrometorites. Thus the fines at each locality could be a mixture of fractions with a specific range of grain sizes each with a different exposure history. The grain size fractions could each have been derived from impact events at specific distances from the Luna sample localities. (2) The low $\delta^{18}O$ values (*ca.* +5.1‰, s.m.o.w.) obtained for two fractions are difficult to explain, but could indicate concentrations of minerals with low ^{18}O abundances, such as ilmenite or olivine, in these grain sizes. Similarly the relatively enriched values obtained for other fractions could indicate concentrations of phases enriched in ^{18}O and/or susceptible to ^{18}O-enrichment in these grain sizes. (3) At least some of the results obtained could be artefacts resulting from the exposure of the samples to the atmosphere of various laboratories.

Introduction

Studies by American and French scientists have shown that the surfaces of the fine grains in most, but not all, samples of lunar soil are remarkably enriched in ^{18}O and ^{30}Si relative to crystalline lunar rocks (Epstein & Taylor 1970, 1971, 1972, 1973*a*, *b*; Taylor & Epstein 1970*a*, *b*, 1973*a*, *b*; Clayton, Onuma & Mayeda 1971; Clayton, Hurd & Mayeda 1972, 1973; Clayton 1972, 1973; Javoy, Marette & Pineau 1973; Javoy & Fourcade 1974; Onuma, Clayton & Mayeda 1970; O'Neil & Adami 1970). The range of $\delta^{18}O$ values (the terms are defined later) reported for crystalline lunar rocks is very small, from about +5.4‰ to +6.8‰ (s.m.o.w.), whereas ^{18}O enrichments up to $\delta^{18}O$ values of +55‰ (s.m.o.w.) are reported for grain surface coatings in the lunar soil. These isotopic enrichments are thought to result from isotope fractionation during the condensation of material on to the grain surfaces or vaporization of material from the grain surfaces. Both these processes may operate together. The vaporization of material on the lunar surface is thought to be due to bombardment by micrometeorites and/or particles from the solar wind or solar flares and/or cosmic rays. Some ^{16}O and ^{28}Si must escape the Moon's gravitational field, and if vaporization occurs some condensation must occur at a range of distances from the impact site. The bulk of the hydrogen in the lunar soil appears to be of solar wind origin and it is likely that the observed enrichments in ^{13}C are due to the addition of carbon from the solar wind and/or meteorites (Epstein & Taylor 1972; Kaplan, Smith & Ruth 1970; Kaplan & Petrowski 1971; Kerridge, Kaplan, Petrowski & Chang 1975; Chang *et al.* 1974). The isotopic chemistry of the light elements hydrogen, carbon, oxygen and silicon in the lunar soil is thus an integrated history of the interaction of the surface of the Moon with extra-lunar processes.

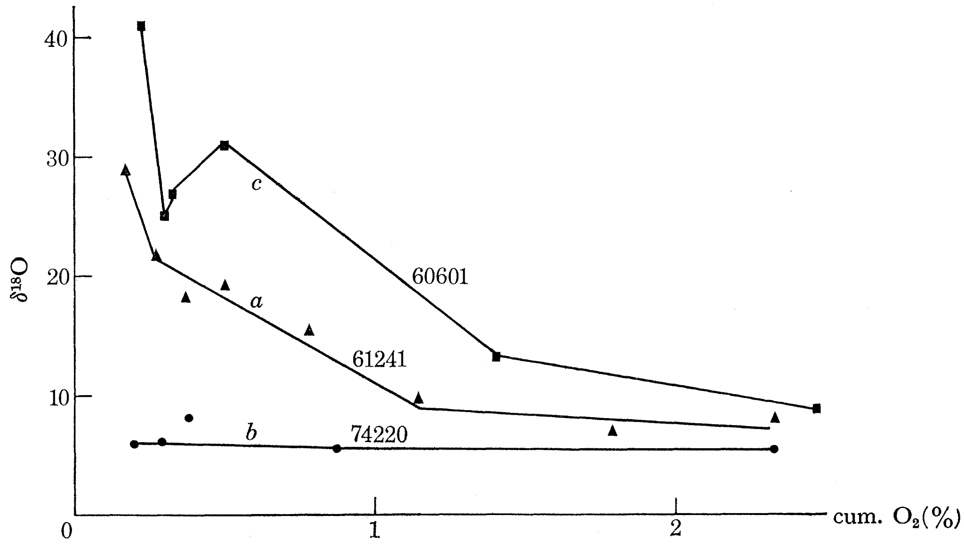

FIGURE 1. $\delta^{18}O$ values plotted against cumulative percentage of oxygen released in fluorine stripping experiments on three lunar soils (from Taylor & Epstein 1973*a*). The lines are schematic and have not been fitted to the data points. Note that in detail all three soils yield curves of similar shape.

The oxygen and silicon data from which the conclusions outlined above have been drawn have been obtained mainly from so called 'fluorine stripping' experiments in which bulk samples are fluorinated at progressively higher temperatures releasing the oxygen for analysis in time/temperature steps. A typical set of results is illustrated in figure 1, curve *a*. The $\delta^{18}O$ and $\delta^{30}Si$ curves normally correlate closely. The heavy isotope enrichments are accompanied by a decreasing O_2/Si ratio indicating that the material lost during the vaporization process has an O_2/Si ratio > 2 (Epstein & Taylor 1973*a*). The Apollo 17 orange soil figure 1, curve *b*) shows no such surface enrichment (Taylor & Epstein 1973*a*) and must therefore have been exposed at the lunar surface very recently. However certain soils notably from the Apollo 16 (Taylor & Epstein 1973*a*) and Apollo 17 (Epstein & Taylor 1973*a*, *b*) landing sites show dips and humps in the oxygen curves obtained from fluorine stripping experiments (figure 1, curve *c*). At present it is not certain whether these irregularities in the normal simple monotonic decrease in δ^{18}O with progressive fluorination are correlated with similar effects in δ^{30} Si because few silicon analyses have been made over the critical region. Taylor & Epstein (1973*a*) attributed these irregularities in the oxygen curve to the adsorption of ^{18}O-depleted 'lunar water'. Adsorbed water would provide an explanation for the apparent (but not conclusive) lack of correlation between the oxygen and silicon curves for these samples which was noted above. Whether this adsorbed water is really lunar water (i.e. water indigenous to the Moon) or terrestrial water contaminating the samples and introduced either while the astronauts were on the moon or subsequently during the handling of the samples is controversial (Friedman, Hardcastle & Gleason 1974; Epstein & Taylor 1973*b*).

Because the experimental technique of fluorine stripping must to some extent mask any possible relation between grain size and ^{18}O-enrichment we have determined δ^{18}O values in sieved size fractions of the < 48 µm fractions of Luna 16 and 20 soils. The < 48 µm fraction represents about 30 % of the bulk soil sample, although this percentage is necessarily approximate because dry sieving does not achieve a perfect separation.

TABLE 1. ^{18}O VALUES RELATIVE TO S.M.O.W. FOR SIEVED SIZE FRACTIONS OF LUNA 16 AND 20 SOILS

size fraction ...	< 25 µm	25–40 µm	40–48 µm	weighted average
sample				
Luna 16	+6.73 ‰	+8.40 ‰	+5.10 ‰	+6.33 ‰
Luna 20	+7.16 ‰	+5.04 ‰	+7.19 ‰	+6.65 ‰

EXPERIMENTAL DETAILS

Aliquots of the < 48 µm grain size fractions were wet sieved by means of stainless steel sieves into three size fractions, 40–48 µm, 25–40 µm and 25 µm. Carbon tetrachloride was chosen as the sieving medium because it is oxygen free; also in the event of carrying over into the reaction vessels adsorbed on the samples it was thought unlikely that this would yield isobaric interferences. Note $m/e = 47$ (e.g. C–O–F$^+$) is not collected with $m/e = 46$ in our mass spectrometer. Aliquots of the grain size fractions weighing between about 0.5 and 4.0 mg were placed in a dry nitrogen atmosphere for 24 h, loaded into nickel bombs, evacuated, and fluorinated using bromine pentafluoride at about 550 °C for 12 h, essentially as described by Clayton & Mayeda (1963). The oxygen released was converted to carbon dioxide by reaction with graphite at dull red heat over a platinum catalyst. The resulting carbon dioxide was analysed in a high precision double collecting mass spectrometer (Beckinsale *et al.* 1973) and the isotopic composition of the oxygen derived from that of the carbon dioxide as described by Craig (1957). The data are presented in table 1 in standard delta notation in per mil (‰), where

$$\delta = \left(\frac{^{18}\mathrm{O}/^{16}\mathrm{O}_{\mathrm{standard}} - {}^{18}\mathrm{O}/^{16}\mathrm{O}_{\mathrm{sample}}}{^{18}\mathrm{O}/^{16}\mathrm{O}_{\mathrm{standard}}} \times 10^3\right).$$

The standard adopted is s.m.o.w. (standard mean ocean water). The results in table 1 differ slightly from the preliminary data presented to the Soviet-American Lunar conference in 1974. They are based directly on s.m.o.w. defined from Rose Quartz = 8.45 ‰ and Snowbird Quartz = 16.20 ‰ and on this basis our calculated results for the NBS 28 Quartz standard obtained during the course of analysis of the Luna 16 and 20 samples average + 9.7 ‰ s.m.o.w. The normal reproducibility in determining δ^{18}O values has averaged about ± 0.08 ‰ (1σ standard deviation) but for samples as small as the Luna 16 and 20 soil fractions ($<$ 20 micromoles of carbon dioxide in some cases) is it suggested that ± 0.2–0.3‰ would be a more realistic error. The blanks from the sample chemistry do not normally contribute a significant quantity of carbon dioxide to the analysed gas and are too small to enable determination of their isotopic composition. At worst the blank might amount to a few per cent of the sample analysed and thus would not significantly affect the $\delta^{18}O$ value determined unless the blank and the sample had very different isotopic compositions.

Discussion

First it is noted that the weighted average $\delta^{18}O$ values obtained for each soil are (within errors) consistent with the values obtained by American and French workers for bulk samples. The Luna 20 $\delta^{18}O$ value may be 0.1 or 0.2‰ higher than typical values but since the errors in calculating these weighted means may be somewhat larger than those associated with individual $\delta^{18}O$ values (because of possible weighing errors) this difference is probably not significant.

Secondly it appears that significant variations in $\delta^{18}O$ value occur in the grain size fractions. It is suggested that two possible interpretations of the pattern of $\delta^{18}O$-enrichment with grain size are possible. (1) If it is accepted that the heavy isotope enrichment reflects the surficial interaction with extra-lunar processes described in the introduction, then the irregular enrichments we observe indicate that each grain size fraction may have a different exposure history. It is possible to account for this by using a model in which each grain size fraction is derived from an impact event at a specific distance from the Luna sample localities. The situation envisaged is somewhat analogous to the distribution of grain sizes in pyroclastic fragments in the ash falling after a terrestrial volcanic eruption. It is suggested that the soil at each locality is made up of fractions (perhaps amounting to only a few grains) each of which reflects the increment which arrived from a specific impact event. If a fraction added to the soil at a particular locality is mature and shows the effects of extensive interaction with the solar wind and/or micrometeorites then it is possible to enhance the ^{18}O content of particular grain sizes. It is possible to explain the irregularities in the $\delta^{18}O$ (? and $\delta^{30}Si$) curves obtained by fluorine stripping on this basis.

(2) The $\delta^{18}O$ values for each grain size fraction could reflect the concentration of particular phases or chemistry in these grain sizes. However, because of the small size of the Luna samples it was necessary to fluorinate the whole of each grain size fraction and we were not able to investigate this possibility. The two relatively low $\delta^{18}O$ values of about $+5.1$‰ in table 1 are somewhat lower than typical values for lunar soils, although within the limits of error noted above these results are consistent with the values obtained for the Apollo 17 orange soil which range from about $+5.6$ to 5.8‰† (Clayton, Hurd & Mayeda 1973). It is possible that these relatively low values reflect the concentration of phases such as ilmenite or olivine, which have low ^{18}O contents, in these grain sizes. Alternatively these grain sizes could have chemical compositions favouring low $\delta^{18}O$ values, such as low silicon and high iron contents. Similarly it is possible that the relatively ^{18}O-enriched values obtained for other grain size fractions indicate concentration of phases or chemistry relatively enriched in ^{18}O (such as plagioclase) and/or phases or chemistry susceptible to ^{18}O-enrichment processes in these size ranges.

(3) A third possibility we considered was that the results have been modified by contamination by terrestrial water either introduced on the moon or in the various laboratories prior to

† Corrected to the Caltech definition of s.m.o.w. by adding 0.3‰.

analysis. However, the fact that despite the lack of elaborate handling precautions the weighted average δ^{18}O values for both Luna samples are so similar to American and French workers values leads us to suggest that terrestrial contamination is unlikely to be of significance.

All things considered, we find the first of the three interpretations of our data presented above the most satisfactory.

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