

OXYGEN, SILICON, CARBON, AND HYDROGEN ISOTOPE FRACTIONATION PROCESSES IN LUNAR SURFACE MATERIALS, by S. Epstein and H. P. Taylor, Jr., Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91109 -- Contr. No. 2445.

The sources of hydrogen so far definitely identified in lunar materials are the solar wind, cosmic-ray spallation, and terrestrial H_2O contamination. At the present time our data do not permit us to identify other possible sources of hydrogen, such as meteorites, comets, or primary lunar H_2O . The major source of H_2 gas is clearly the solar wind, as shown by the fact that the H_2 in lunar soils and soil-breccias is almost completely devoid of deuterium. Spallation hydrogen is very deuterium-rich and has been observed in small quantities in the gas extracted from lunar surface rocks during fusion. New evidence for the presence of spallation deuterium is given by a δD value of $+43\%$ for an aliquot of gas from 14310 basalt. The deuterium concentration in the lunar H_2O is similar to terrestrial water vapor from temperate climatic areas, but more importantly there is a relationship between the δD of the water in lunar soils and the $\text{H}_2\text{O}/\text{H}_2$ ratio as shown in Fig. 1. This relationship is caused by cross-contamination of this water with oxidized solar wind hydrogen during its extraction from lunar materials. When the $\text{H}_2\text{O}/\text{H}_2$ ratio is > 1 , this cross-contamination is sufficiently small so that the δD of the water acquires its maximum value and remains roughly independent of the $\text{H}_2\text{O}/\text{H}_2$ ratio. This "plateau" in the δD value lies at about -120% . We know that the bulk of this H_2O lies on the grain-surfaces in the lunar soils, because of its ease of extraction, and because its presence is identified by abnormally low δO^{18} values in the oxygen stripped from the grain surfaces during partial fluorination experiments. However, it is still possible that some of this H_2O is of true lunar origin. "Rusty rock" breccia 66095 is an important sample in this regard, because it contains possible lunar goethite, abnormally large amounts of H_2O , and is almost devoid of extractable H_2 gas. The ratio of $\text{H}_2\text{O}/\text{H}_2 \gg 1$. The average δD value of H_2O extracted at room

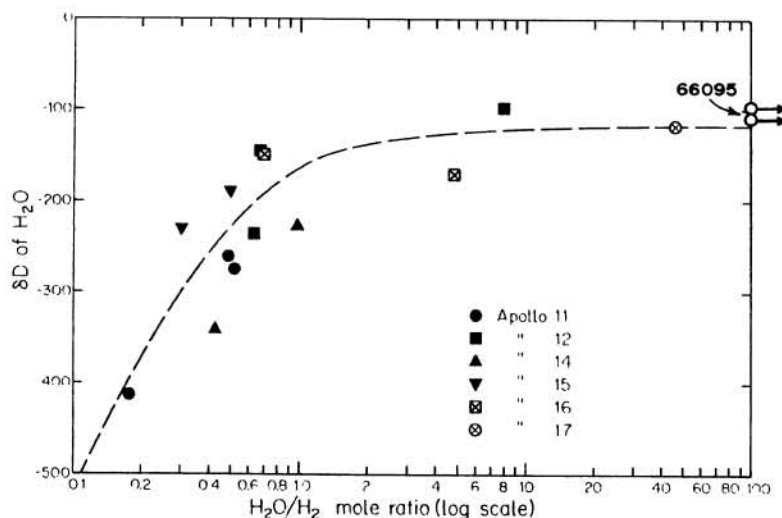


FIGURE 1.

temperature by pumping in vacuum is -110 (7.5μ moles $\text{H}_2\text{O}/\text{g}$) and the average δD value of H_2O extracted from 25° to 600° is almost the same, -97 (30μ moles/g). This water was extracted in about 15 successive increments, with the largest portion driven off at $\sim 50^\circ$ – 400°C . This detailed extraction procedure was used in order to be able to detect any water of highly unusual isotopic composition,

ISOTOPE FRACTIONATION PROCESSES

S. Epstein, and H. P. Taylor, Jr.

such as water formed from oxidation of solar wind H_2 . No such unusual water was detected. Except for the final 4%, the range in δD values of the various aliquots was only -75 to -145‰ . The highest temperature fraction of water had a δD of -196 . Because of the high H_2O/H_2 ratio the data for 66095 plot off to the right of Fig. 1, as shown by the arrows (upper = average δD of high-T H_2O ; lower = low-T H_2O). Note that both δD values are identical to the δD "plateau" established for other lunar samples. Inasmuch as the low-T H_2O from 66095, as well as the bulk of the H_2O in lunar soils, seem to us to be due to terrestrial contamination, this suggests a similar origin for the high-T H_2O in 66095.

Lunar basalts apparently contain about 10 to 40 ppm carbon with $\delta C^{13} \approx -20$ to -30 (Friedman et al., 1972; Kaplan et al., 1970). Some of the higher concentrations may be attributable to slight contamination, because the most probable terrestrial contamination also has $\delta C^{13} = -20$ to -30 . Two new analyses of large, carefully handled aliquots of 14310 basalt by us give 17 and 14 ppm and $\delta C^{13} = -25.3$ and -21.9 , respectively. Thus, measurements from several laboratories indicate that, in spite of the coincidence in δC^{13} between the basalts and contaminant carbon, most lunar basalts should have about 10 to 20 ppm of indigenous primary carbon. A much greater amount of carbon is present in lunar soils and breccias; this must have been added from the solar wind, from carbonaceous meteorites or comets, or from some unknown source elsewhere on the moon. An approximate linear relationship exists between solar wind H_2 content and carbon content; this can be interpreted qualitatively as possible evidence for a solar wind origin for much of the carbon, although a meteoritic origin cannot be excluded as the total amount of meteoritic debris in the soil should also be a function of exposure time at the lunar surface. A knowledge of the isotopic composition of the carbon is critical as abundance measurements alone cannot distinguish between these various possibilities. The total range of δC^{13} and concentration of lunar carbon is shown on Fig. 2 by the stippled pattern; the δC^{13} has an apparent bimodal distribution. The only two lunar samples we have found that seem to be clearly anomalous are 61221 and 74220 (orange soil), as these samples plot in the "gap" shown on Fig. 2. The orange soil sample, composed of tiny glass spherules, is anomalous because it probably lost most of its carbon at the time of its formation (it now has only 3.5 ppm carbon, the lowest value yet analyzed for a lunar sample). Sample 61221 is probably anomalous because

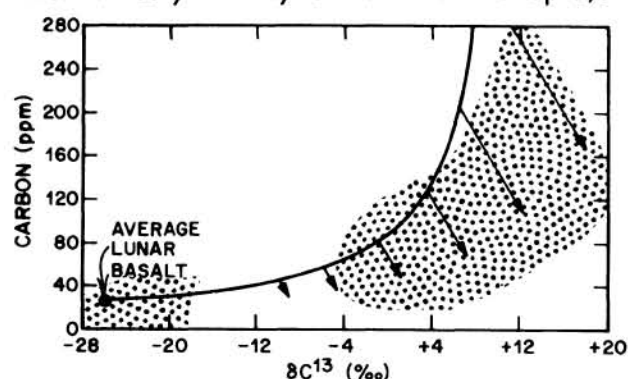


FIGURE 2.

it contains a major meteoritic (or cometary) component; this would explain why its high carbon content (97 ppm) is accompanied by a very low δC^{13} value (-13.9‰) and low solar wind H_2 content. Carbonaceous chondrites have similar δC^{13} values (Boato, 1954). Fig. 2 shows a hypothetical mixing model that might explain most of the lunar carbon isotopic and concentration data. The hypothetical curve represents mixing of the lunar basalts with an "exotic" component having $\delta C^{13} \approx +10$ (i.e. possible solar wind

ISOTOPE FRACTIONATION PROCESSES

S. Epstein and H. P. Taylor, Jr.

value?). The diagonal arrows indicate how the δC^{13} and concentration of carbon in such a two-component mixture would be changed during the fractional volatilization of carbon that might accompany particle bombardment. This model, or analogous models using different δC^{13} values for the "exotic" component(s), seem adequate to explain most of the lunar carbon data.

Certain lunar breccias are enriched in O^{18} relative to lunar basalts, suggesting they may in large part be derived from lunar soil; in some such examples there is independent petrographic and chemical evidence that support this hypothesis. The high δO^{18} values are accompanied by high δSi^{30} values, and it is known that these are a result of extremely large O^{18} and Si^{30} enrichments (up to +55 and +30‰, respectively) on the surfaces of grains in all the lunar fines. These O^{18} - and Si^{30} -enrichments are directly related to the amount of solar wind H_2 in the samples and are a result of bombardment by meteorites, micrometeorites, and/or nuclear particles, with preferential loss of Si^{28} and O^{16} . Some of the δO^{18} and δSi^{30} surface enrichments of lunar fines are shown in Fig. 3. These particular δO^{18} curves are atypical in that they do not show a smooth decrease in δO^{18} as the grain surfaces are "stripped off" during fluorination. Such irregular effects do not show up in the δSi^{30} curves, one possible explanation being that adsorbed low- O^{18} H_2O (or a hydrated mineral such as goethite) is present in the soils, thus complicating the δO^{18} record. A lunar soil breccia that has been heated or metamorphosed at temperatures above about 600°C will have lost most of its solar wind hydrogen and rare gases, but the grain-surface δO^{18} and δSi^{30} enrichments may be preserved. We do not yet know at how high a temperature these grain-surface isotopic effects disappear, but even if they are completely "smoothed out" by diffusion during a metamorphic event, there will still remain a significant 0.3–0.8‰ whole-rock δO^{18} enrichment and a 0.1–0.5‰ whole-rock δSi^{30} enrichment. No lunar igneous process has yet been identified which can produce as much as a 0.3‰ enrichment in O^{18} . Even the peculiar "granitic" breccia 12013 has a δO^{18} similar to lunar basalts. Therefore, it is likely that all significant δO^{18} enrichments in lunar materials are attributable to a lengthy exposure of the disaggregated material at the lunar surface. A good case can probably be made that essentially all "volatile" elements on the grain-surfaces of the lunar fines are isotopically enriched in the heavy isotope (oxygen, silicon, carbon, sulfur, potassium, etc.).

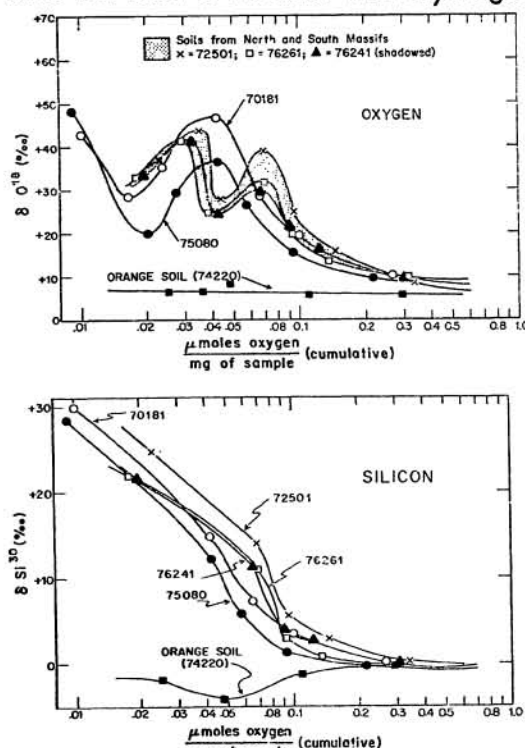


FIGURE 3.

References: Boato G. (1954) *Geoch. Cosmoch.*, 6, 209; Friedman I., et al. (1972) *Apollo 15 Lun. Samp.*, 302; Kaplan I.R., et al. (1970) *Apollo 11 Proc., Geoch. Cosmoch., Suppl. 1*, 2, 1317.