

Stable Isotopes, Rare Gases, Solar Wind, and Spallation Products

$^{18}\text{O}/^{16}\text{O}$, $^{30}\text{Si}/^{28}\text{Si}$, D/H, and $^{13}\text{C}/^{12}\text{C}$ Studies of Lunar Rocks and Minerals

Abstract. The $\delta^{18}\text{O}$ of minerals from lunar gabbros and basalts are: plagioclases (+6.06 to +6.33), pyroxenes (+5.70 to +5.95), and ilmenites (+3.85 to +4.12). The uniformity of these results indicates isotopic equilibrium in the mineral assemblages. Estimated plagioclase-ilmenite temperatures range from 1150°C to 1340°C. The bulk $^{18}\text{O}/^{16}\text{O}$ and $^{30}\text{Si}/^{28}\text{Si}$ ratios of these lunar rocks are identical with ratios of terrestrial basalts, but the lunar glass, breccia, and dust are slightly enriched in the heavier isotopes. The lunar hydrogen (formed from solar wind) has a $\delta \text{D/H}$ of less than -873 per mil and the value may be even lower, as it is probably contaminated with terrestrial hydrogen. The $\delta^{13}\text{C}$ of lunar dust and breccia is unusually high relative to reduced carbon in meteorites or on earth.

The $\delta^{18}\text{O}$ values of several Apollo 11 lunar samples are given in Fig. 1. Oxygen isotope analyses were obtained by reacting the samples with fluorine gas at 600°C, following procedures outlined by Taylor and Epstein (1). The analyses presented in Fig. 1 can be supplemented by material-balance calculations of whole-rock $\delta^{18}\text{O}$ values. The total range of $^{18}\text{O}/^{16}\text{O}$ in the calculated and measured whole-rock samples from the moon is very small, from $\delta = +5.7$ to +6.3.

Essentially pure mineral separates of plagioclase and pyroxene were analyzed in each case, but the cristobalite was only 80 percent pure, and the ilmenite concentrates typically varied in purity from 70 to 90 percent. The $\delta^{18}\text{O}$ values of these impure ilmenites were very accurately corrected for the presence of the impurity (primarily pyroxene), because the volume of SiF_4 gas obtained from each sample was measured. Typically, the corrections for the ilmenite analyses were 0.2 to 0.6 per mil, but the ilmenite concentrate from 10057 was very impure and required a correction of 1.25 per mil. The utility of the SiF_4 correction procedure is illustrated by the fact that, even though the corrections are occasionally large, the final $\delta^{18}\text{O}$ values of the ilmenites range only from

+3.85 to +4.12 for five different specimens.

All the minerals show a striking uniformity in $\delta^{18}\text{O}$. The clinopyroxenes ($\delta = +5.70$ to +5.95) and plagioclases ($\delta = +6.06$ to +6.33) are practically identical, within experimental error of ± 0.1 per mil. This uniformity and the constancy of the oxygen isotopic fractionations among minerals (given as $1000 \ln \alpha$, where α is the ratio of $^{18}\text{O}/^{16}\text{O}$ in mineral A to that in min-

eral B) suggest that oxygen isotope equilibrium was essentially attained during the crystallization of these mineral assemblages. This is noteworthy in the light of the pronounced chemical zoning in the minerals, particularly the pyroxenes.

In a given rock, the order of enrichment of minerals in ^{18}O (ilmenite, pyroxene, plagioclase, free silica) is the same as that observed in many terrestrial igneous rocks and meteorites. However, the ^{18}O fractionations between plagioclase and ilmenite in the lunar gabbros are smaller than in terrestrial gabbros (2.0 to 2.3 versus 3.3 to 4.0). This is in part accounted for by the higher Ca content of the lunar plagioclase, but it also indicates that the $^{18}\text{O}/^{16}\text{O}$ ratios of coexisting minerals in the lunar gabbros were "frozen in" at a considerably higher temperature than in terrestrial gabbros (2, 3).

Although an isotopic temperature calibration curve involving ilmenite has not yet been determined, an estimate of the quartz-ilmenite and plagioclase-ilmenite geothermometer curves can be made on the basis of (i) the plagioclase-magnetite curve used by Taylor (3) in estimating "isotopic temperatures" of various igneous rocks; (ii) the plagioclase- H_2O calibration curves of O'Neil and Taylor (4); (iii) the quartz- H_2O curve of Clayton *et al.* (5); and (iv) the observation that in natural mineral assemblages, $1000 \ln \alpha$ for quartz-ilmenite is equal to $0.92 \times 1000 \ln \alpha$ for quartz-magnetite (6). The constructed curves are:

$$1000 \ln \alpha_{\text{Q-I}} = 1.35 + 4.56 (10^6 T^{-2})$$

$$1000 \ln \alpha_{\text{P-I}} = 0.72 + 3.22 (10^6 T^{-2})$$

where Q-I is quartz-ilmenite and P-I is plagioclase (An_{90})-ilmenite.

The plagioclase-ilmenite temperatures calculated for lunar samples are as follows: 10058, 1243°C; 10044, 1202°C; 10017, 1154°C; 10003, 1338°C; and 10057, 1212°C. When the quartz-ilmen-

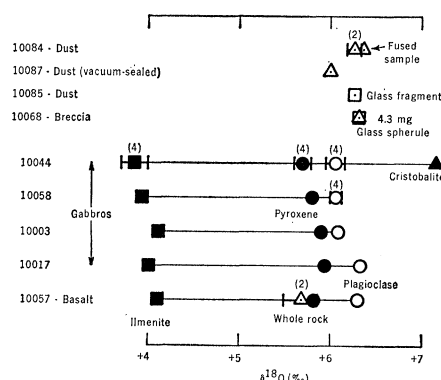


Fig. 1. $\delta^{18}\text{O}$ measurements (relative to standard mean ocean water) of lunar rocks and minerals from the Sea of Tranquillity. The numbers in parentheses indicate number of separate analyses, and the error bars represent the average deviation. All other analyses are single determinations.

ite curve is used, 10044 gives a cristobalite-ilmenite temperature of 1260°C, almost concordant with the 1202°C plagioclase-ilmenite temperature of this rock. The above temperatures can be compared with temperatures of 920°C for a Skaergaard gabbro and 820°C for a Kiglapait gabbro, both of which are compatible with estimates made on these rocks based on the independent Fe-Ti oxide geothermometer of Buddington and Lindsley (7). The inference can be drawn that the lunar gabbros crystallized and cooled very rapidly under relatively "drier" conditions than many terrestrial gabbros; if P_{H_2O} had been high, we should expect to observe more evidence of post-crystallization oxygen isotopic exchange.

The bulk $^{18}O/^{16}O$ ratios of the lunar rocks and minerals are indistinguishable from those of terrestrial basalts, the best average δ value for pristine unaltered basalt being +5.9 per mil (3). Pyroxenes from most stony meteorites (ordinary chondrites, enstatite chondrites, and

achondrites) also have $\delta^{18}O$ values identical with the lunar pyroxenes. However, notable exceptions are the basaltic achondrites, hypersthene achondrites, and mesosiderites, which have $\delta^{18}O$ of +3.7 to +4.4. If the $^{18}O/^{16}O$ ratios of the Sea of Tranquillity samples are characteristic of the rest of the moon, the moon would appear to be more closely related to the chondrites and the earth than to the basaltic achondrites.

The SiF_4 released during reaction of samples with fluorine was collected and analyzed for $^{30}Si/^{28}Si$ in a specially designed, double-collecting mass spectrometer for 9-inch radius, having an all-metal sample introduction system (except for the magnetic switching valves). The data are plotted in Fig. 2, along with data for a few meteorites, tektites, and terrestrial igneous rocks. To a first approximation, the lunar gabbros are very similar to terrestrial samples in $\delta^{30}Si$. Plagioclase is invariably enriched in ^{30}Si relative to coexisting pyroxene, but within experimental error of ± 0.08 per

mil the plagioclases from all the gabbros are essentially identical, as are the pyroxenes. Data on terrestrial rocks and meteorites are not sufficient to support any firm conclusions about the $\delta^{30}Si$ variations, but the hypersthene and enstatite achondrite pyroxenes appear to be distinctly lower in ^{30}Si than the lunar pyroxenes, and they are clearly more depleted than the lunar dust, glass, and breccia.

The glass-rich dust and breccia are also clearly richer in both ^{18}O and ^{30}Si than the whole-rock gabbros and basalts. These discrepancies in $\delta^{30}Si$ and $\delta^{18}O$ must be caused by either (i) an ^{18}O - and ^{30}Si -enriched constituent in the dust and breccia that is not derived locally from the nearby gabbros and basalts, or (ii) vapor fractionation of the glass during its formation (presumably mainly by impact melting), with resulting enrichment in both ^{18}O and ^{30}Si . It has been shown experimentally by Walter and Clayton (8) that fractional vaporization of SiO_2 -rich glass indeed produces

Table 1. Isotopic and concentration data for hydrogen, carbon, and rare gases extracted from samples 10084, 10087, and 10061 from the Sea of Tranquillity.*

Sample fractions	Hydrogen gas			Carbon			Water			Rare gases	
	Conc. (μ mole/g)	Deuterium conc.		Conc. (ppm)	$\delta^{13}\text{C}/^{12}\text{C}$	Conc. (μ mole/g)	Deuterium conc.		Conc. (cm^3/g)	H_2 gas/ rare gases (vol. ratio)	
		δ D/H	ppm				δ D/H	ppm			
Sample 10084, No. 2 (2.40 g)											
A	None			Trace		6.05	-150	133	None		
B	8.56	-888	18	}	+ 17.8	4.09	-365	100	0.100	4.6	
C	12.93	-856	23								
D	1.45	-615	60								
Total	22.94	-853	23	155.1	+ 16.3	11.07	-483	81	0.140	0.56	
Sample 10084, No. 1 (1.85 g)											
A	None			}	+ 18.6	11.58	-275	114	0.275	2.5	
B	10.30	-849	24								
C	11.34	-828	27								
D	0.72	-609	61	58					0.140	0.56	
Total	22.36	-830	27	143		11.58	-275	114	0.515	2.4	
Sample 10061 (0.55 g), vacuum-sealed breccia											
A	None			}	+ 10.1	8.9	-412	92	0.044	5.0	
B	17.86	-882	18								
C	32.06	-868	21								
D	Trace			188	+ 10.9				Trace		
Total	49.92	-873	20	262	+ 10.8	8.9	-412	92	0.234	2.6	
Sample 10084† ‡, No. 3 (1.71 g)											
A				None			}	7.83	-329	105	
B	9.40	-850	24	Trace							
Sample 10087† (~ 2 g)											
B	4.47	-850	24								
C§	20.87	-843	25								
Total	25.34	-844	25								

*Note: δ values for hydrogen relative to standard mean ocean water (SMOW) in per mil. Deuterium concentration of SMOW assumed to be 157 ppm (10). δ values for carbon are relative to PDB standard in per mil. Fraction A gases evolved below 500°C, almost wholly water. Fraction B gases evolved between 500° and 550°C, a mixture of CO₂, CO, H₂, H₂O, and rare gases. Fraction C gases evolved between 550° and 650°C, a mixture of CO₂, CO, H₂, H₂O, and rare gases. Fraction D gases evolved between 650° and 1500°C, dominantly CO. †Hydrogen purified through palladium thimble at ~650°C. ‡Lunar dust sample heated in quartz tube to release hydrogen (to avoid contact of released H₂ and H₂O with hot platinum). §Lunar dust exposed to water of $\delta \approx -980$ per mil prior to extraction of hydrogen fraction C.

an enrichment of ^{18}O in the remaining sample. Whether an analogous process also exists for $^{30}\text{Si}/^{28}\text{Si}$ cannot be stated until some experiments are done, but it is reasonable to suppose that ^{28}Si would be preferentially boiled off during a high-temperature impact melting.

The isotopic composition and concentration of hydrogen and carbon in the lunar samples are given in Table 1. The results are for different fractions A, B, C, and D extracted from each sample at designated temperature ranges. Note that the first fraction A contains mostly H_2O and the last fraction is primarily CO , resulting probably from reaction of carbon with ilmenite. All samples except lunar dust sample 3 were loaded in an atmosphere dried with P_2O_5 .

Two procedures were used to quantitatively separate the hydrogen from the rare gases and other noncondensable gases: (i) the H_2 was converted to H_2O by reaction with hot CuO , the H_2O being isolated and converted to H_2 by reaction with hot U metal, and (ii) the H_2 gas was allowed to diffuse through a palladium thimble at 650°C . The two methods gave similar results. During the combustion of the noncondensable gases, CO_2 was formed and separated from the H_2O . The rare gases remained after all other gases were converted into condensable compounds.

Before gases were extracted from lunar material, about 1 cm^3 of deuterium-depleted H_2 ($\delta = -980$) was run through the extraction procedures. This flushing reduced the errors due to possible contamination with isotopically normal water that may have been present in the extraction line.

The concentration of the H_2 is $22.7\text{ }\mu\text{mole/g}$ for dust and $50\text{ }\mu\text{mole/g}$ for the breccia. The $\delta\text{ D}$ varies from -873 per mil (20 ppm D) to -830 per mil (27 ppm D). It is almost certain that the δ values give only the maximum deuterium concentrations for lunar hydrogen, because the waters extracted from the lunar samples are depleted in deuterium relative to normal terrestrial fresh waters. The data in Table 1 indicate that during the extraction, isotopic exchange occurred between the very light lunar H_2 and the adsorbed H_2O .

We have calculated some material balances: Assuming that the lunar H_2 gas, before contamination, originally had zero deuterium content, the adsorbed water in lunar dust samples (10084) 2 and 1, breccia (10061), and lunar dust (10087) must have had δ

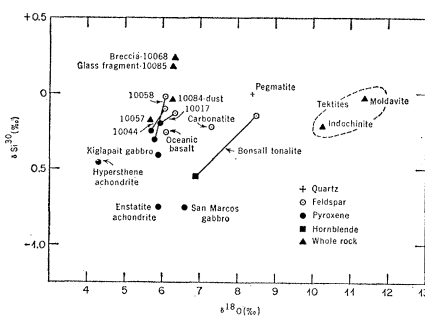


Fig. 2. Graph of $\delta^{30}\text{Si}$ (relative to a quartz standard from a pegmatite, Pala, California) versus $\delta^{18}\text{O}$ for lunar rocks and minerals. For comparison, some analyses of meteorites, tektites, and terrestrial igneous rocks are also plotted.

values of $+45$, $+57$, $+300$, and -148 , respectively. If it is assumed that the contaminating water has a δ value of -150 per mil, the original lunar hydrogen would have had δ values of -904 , -891 , -917 , and -996 , respectively. If the contaminating H_2O has a δ value of -75 per mil (a value reasonable for Houston water vapor), the lunar hydrogen would have δ values of -943 , -930 , -936 , and -1057 , respectively. The calculations for sample 10087 are least reliable, because the data in Table 1 represent an incompletely extracted H_2O fraction. If the first condition prevailed (no D in lunar H_2), the contaminating water is unusually concentrated in deuterium. This is possible if the lunar samples were contaminated with evaporated water from, for example, the astronauts' space suits. The presence of some deuterium (about 10 ppm) in the lunar H_2 gives a more reasonable δ value for the contaminating water. Hence, although some deuterium is possibly present in the lunar H_2 , we conclude that most of the H_2 is of solar wind origin and is very low in deuterium. Clearly the best procedure to determine the actual δ values for lunar hydrogen is to avoid H_2O contamination, or, if that is impossible, to use H_2O that is highly depleted in deuterium in operations where H_2O might come into contact with the lunar samples. The presence of significant deuterium in solar wind H_2 is very unlikely, considering the mean reaction time of 4 seconds for the reaction: $\text{D} + \text{H} \rightarrow {}^3\text{He}$ (9).

Another possibility is that there is present in the lunar rocks some primary water of relatively normal deuterium content in addition to the solar wind hydrogen. This possibility has not been eliminated by our experiments. Further

evidence that the lunar H_2 is of solar wind origin is that it is more loosely bound than are the rare gases themselves. The ratio of H_2 to rare gases decreases with progressive heating of the lunar samples (Table 1).

The carbon in the lunar samples appears to be heterogeneously distributed (~ 145 ppm in the dust and ~ 260 ppm in breccia), and it has a unique high $\delta^{13}\text{C}$ of about $+19$ per mil for the lunar dust and about $+11$ per mil for the breccia. These values are unlike any reduced natural carbon obtained on earth or in meteorites. There are several possibilities that can account for this carbon:

1) Solar-wind carbon is a possible source, inasmuch as there is a correlation between the amounts of carbon and hydrogen in the lunar samples (Table 1). However, if the carbon extracted from the samples is a mixture of lunar carbon and solar-wind carbon, they are both present in essentially similar chemical form. Otherwise, carbon extracted at different temperatures would be expected to have different $\delta^{13}\text{C}$ values.

2) If some process involved in the formation of lunar dust and breccia causes fractional loss of carbon, isotopic fractionations can occur; in such a case, we can say little about the ultimate origin of the carbon.

3) Since the possible terrestrial sources of carbon contaminants such as grease and rocket fuel have low δ values, it is unlikely that the $\delta^{13}\text{C}$ values of lunar dust are due to terrestrial contamination.

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