close to the initial temperatures of crystallization from a silicate melt. On earth, large differences in isotopic temperatures are found between fine-grained, rapidly quenched volcanic rocks and their coarse-grained plutonic equivalents (*5*, *6*). This has been interpreted as resulting from post-crystallization retrograde isotopic exchange, on a scale comparable to the grain size, during the slow cooling of the plutonic rocks. No terrestrial rock as coarse-grained as the Apollo 11 type B samples has been found with a high isotopic temperature corresponding to its initial crystallization. Apparently the cooling conditions of the lunar samples were such as to prevent significant subsolidus exchange. The absence of water may have been an important factor.

The indistinguishability between types A and B rocks in terms of isotopic compositions or isotopic fractionations suggests that they were derived from magmas of the same isotopic composition, and that in both types the initial isotopic distribution at the time of crystallization has been quenched in, and has subsequently remained unchanged.

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Water, Hydrogen, Deuterium, Carbon, Carbon-13, and Oxygen-18 Content of Selected Lunar Material

Abstract. *The water content of the breccia is 150 to 455 ppm, with a* δD *from* -580 *to* -870 *per mil. Hydrogen gas content is 40 to 53 ppm with a* δD *of* -830 *to* -970 *per mil. The* CO_2 *is 290 to 418 ppm with* $\delta^{13}C = +2.3$ *to* $+5.1$ *per mil and* $\delta^{18}O = 14.2$ *to 19.1 per mil. Non-*CO_2 *carbon is 22 to 100 ppm,* $\delta^{13}C = -6.4$ *to* -23.2 *per mil. Lunar dust is 810 ppm* H_2O *(*$D = 80$ *ppm) and 188 ppm total carbon (*$\delta^{13}C = -17.6$ *per mil). The* ^{18}O *analyses of whole rocks range from 5.8 to 6.2 per mil. The temperature of crystallization of type B rocks is 1100° to 1300°C, based on the oxygen isotope fractionation between coexisting plagioclase and ilmenite.*

During the past 20 years a large amount of information on the relative abundance of the stable isotopes of hydrogen, carbon, oxygen, and sulfur in terrestrial and meteoritic materials has been accumulated. Consequently, it was of interest to investigate the relative abundance of these isotopes in lunar materials. In addition, determination of the water and hydrogen contents in lunar samples is important because a knowledge of these contents leads to a better understanding of the development and history of the earth's hydrosphere.

For the deuterium, the water, and some of the carbon analyses, the weighed samples were placed in a platinum crucible and the crucible was then inserted into a vacuum system. The crucible was heated, step by step, to 1350°C and H_2, He, H_2O, CO_2, and SO_2 were collected, separated, and measured, and the isotopic abundances were determined on isotope-ratio mass spectrometers. After melting, the sample was then mixed with approximately half its weight of previously combusted CuO, and the resulting mixture was combusted at 950°C in oxygen at 1 atm pressure. The collected H_2O was analyzed for D/H and the CO_2 for $^{13}C/^{12}C$ and $^{18}O/^{16}O$.

The results of the deuterium analyses are expressed as atomic ratios of deuterium to hydrogen, $D/H \times 10^6$, and also as δD per mil SMOW. The $^{13}C/^{12}C$ analyses are given as $\delta^{13}C$ per mil PDB, whereas the $^{18}O/^{16}O$ ratios are expressed as $\delta^{18}O$ per mil SMOW.

A 9.3-g sample of lunar dust (10084) and 2.7-g piece of breccia (10060-11), which had been sealed in an aluminum vacuum container in Houston until opened for processing in our laboratory, were combusted directly without being melted in vacuum. Another 3.7-g piece of the vacuum-sealed 10060-11 was processed by heating in a vacuum, as described above, to compare results with those for breccia samples 10046-21 and 10046-22 that had been exposed to laboratory atmosphere for several months.

Geoatmospheric contamination was removed by heating the samples to 50°C in vacuum, after which the temperature was raised and the volatiles were collected. No volatiles were emitted from the samples until a temperature of approximately 300°C was reached. Samples were heated at 550°C for several hours and the volatiles processed. Most of the hydrogen, some helium, more than half the H_2O, and a little CO_2 were released at this stage. The temperature was then raised to 950°C and maintained there for several hours, during which time practically all the remaining H_2O, CO_2, and SO_2 and some He were evolved. Finally the crucible was heated to 1350° to 1400°C for 15 minutes to release the remainder of the SO_2, CO_2, and He. The final combustion of the melted sample in oxygen yielded CO_2 and a negligible amount of H_2O. Results of the analysis are given in Table 1.

The hydrogen gas emitted by the samples may have been present as molecular hydrogen trapped in the solid material. Alternately, it may have been generated during heating by the reactions of water with carbon, metallic iron, or ferrous iron present in the silicates. The fact that all the hydrogen was liberated below 550°C, whereas appreciable amounts of water continued to be released above that temperature, would tend to rule out reactions with the reduced forms of iron or with carbon. The possibility still exists that the hydrogen equilibrated isotopically with the water vapor. At 550°C the equilibrium constant of the reaction $H_2O + HD \rightleftarrows HDO + H_2$ is 1.3 (*1*). The hydrogen evolved at 550°C is depleted in deuterium by a factor of 2 to 4 compared with the water evolved at the same temperature—far in excess of the amount to be expected under equilibrium conditions at the temperature of our experiments.

The isotopic compositions of the hydrogen and water are those to be expected for isotopic equilibrium at temperatures from 0° to 200°C, which is well within the lunar temperature range. It is possible that the hydrogen orig-

Table 1. Results of heating and combustion of selected Apollo 11 material. Concentrations are ±20 percent of amount present; D/H × 10^6 = ±20 percent; $\delta^{13}C$ = ±0.2 percent; $\delta^{18}O$ = ±0.2 percent; and δD = ±10 percent. The $\delta^{13}C$ values are per mil deviations from PDB; $\delta^{18}O$ values are per mil deviations from SMOW; δD values are per mil deviations from SMOW. The D/H × 10^6 was calculated from the δD SMOW values, using the relation D/H × 10^6 = .158 (1000 + δD per mil).

Sample No.	Sample type	Weight (g)	Vacuum heating											Oxygen combustion					Total				
			He		H_2			H_2O			CO_2			H_2O			CO_2		H_2, $H_2 + H_2O$			Carbon	
			cm³/g	$^4He/^3He$	ppm	D/H × 10^6	δD (‰)	ppm	D/H × 10^6	δD (‰)	ppm C	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	ppm	D/H × 10^6	δD (‰)	ppm C	$\delta^{13}C$ (‰)	ppm	D/H × 10^6	δD (‰)	ppm	$\delta^{13}C$ (‰)
10046-21	Breccia	1.704	0.15	4000 ± 300	50	27	−830	455	38	−760	79	+2.3	+19.1	5			102	−23.2	100	33	−790	181	−12.0
10046-22	Breccia	3.574	0.13	4000 ± 200	60	~5	−970	372	66	−580	140	+5.1	+18.8	37			78	−22.7	105	~28	~−820	218	−4.8
10060-11	Breccia	3.712	0.8	2000 ± 200	66	~22	−860	152	21	−870	79*	+3.0	+14.2	10			22	−25.7	83	~46	~−710	>101	−3.2
10060-11	Breccia	2.766	←										→	720	51	−680	113	−10.6	80	51	~−680	113	−10.6
10017-16	Crystal-line	2.028			~1			~25						27			69	−20.0	>6			>69	−20.0
10084-43†	Dust	9.311	←										→	810	80	−490	188	−17.6				188	−17.6

* A small amount of CO_2 released between 550° and 950° C was lost from this sample.

† Mineral separation on the lunar dust sample (10084) using heavy liquids and a magnetic separator was unsuccessfully attempted. The separated fractions were then recombined, washed in pure acetone, dried, and combusted as described.

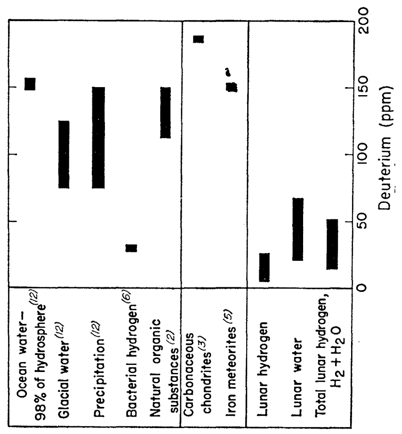

Fig. 1. The deuterium content of hydrogen containing materials from terrestrial, meteoritic, and lunar sources (*13*); D/H was calculated using a value of 158 × 10^{-6} for SMOW.

inates as solar wind protons and then slowly reaches isotopic equilibrium with the water already present in the rocks. The isotopic composition of the hydrogen therefore may not be that of the solar wind. The water may be present as liquid or gas inclusions in the solid phases or as water present in the glass structures.

Although all the samples that we analyzed have had some exposure to terrestrial water vapor, we do not believe that terrestrial water is a serious contaminant in these samples. This opinion is based on several lines of evidence.

1) The water is not evolved below about 300°C. This would tend to rule out adsorbed water.

2) All the breccia samples, both those kept open to the terrestrial environment and those sealed in vacuum, reacted similarly when heated and gave about the same amounts of hydrogen and water with about the same deuterium content.

3) The deuterium abundance of the water is far lower than that to be expected from water picked up from the terrestrial atmosphere by the glass phase present in the rocks. As determined from data on volcanic glasses containing secondary water that is derived from meteoric or atmospheric sources (*2*), the secondary water should range from about 145 ppm D (hydrated in Houston) to about 125 ppm D (hydrated in Denver).

We do not think that the lower water content of the vacuum-sealed sample indicates large-scale contamination by terrestrial water in the other samples because there appears to be great variability in water content between two pieces of the same breccia that had been exposed to the terrestrial atmosphere for several months.

Contamination with unexpended rocket fuel dumped on the lunar surface can be ruled out by the results of Flory *et al.*, which were published in the report of the Lunar Sample Preliminary Examination Team (*3*). Additions of rocket exhaust gases cannot be as easily determined as can those of organic fuel, and these gases still remain a possibility as a contaminant, particularly in the very porous, high-surface-area breccias. The CO_2 and SO_2 results discussed later, however, tend to rule out rocket exhaust contamination.

The piece of vacuum-sealed 10060-11 that was crushed in the laboratory prior to its combustion in oxygen and exposure to the laboratory air for approximately 5 minutes has approximately 70 ppm more water than the total water collected by heating the other vacuum-sealed piece in vacuum. In addition, the water from the combusted sample is slightly enriched in deuterium as compared with the water from the other sample. These differences may be due to the uptake of "heavy" (~ 150 to 200 ppm D) water from the atmosphere during sample handling, or they may represent inhomogeneity in the breccia. From our experience with the several pieces of breccia 10046, we favor the latter explanation—that of sample inhomogeneity.

Figure 1 is a plot of the deuterium abundances of terrestrial, meteoritic, and lunar material. If the analysis given here is of true lunar water, deuterium in the earth is enriched by a factor of about 3 to 5 over that in the moon. If the moon is a sample of the primitive earth, the earth will have lost at least two-thirds of its original hydrogen by escape from the exosphere to outer space.

The total carbon content of the lunar samples is reasonably constant at 150

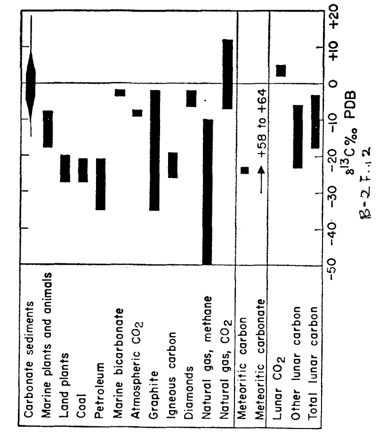

Fig. 2. The relative ^{13}C abundance of terrestrial, meteoritic, and lunar sources (*14*).

Table 2. Oxygen isotope compositions (δ ^{18}O); δ values are per mil deviations from the SMOW standard. Numbers in parentheses refer to number of analyses made.

Sample	Plagioclase	Pyroxene	Ilmenite	Other	Whole rock
Fine grained					
10057-20					5.8 ± 0.1 (2)
Crystalline					
10017-16	**6.3** ± 0.1 (2)	5.7 ± 0.1 (2)	3.8 ± 0.1 (2)		5.9 ± 0.1 (2)
10050-34	**6.2** ± ? (4)	5.6 ± 0.1 (2)	4.0 ± 0.2 (2)		
Breccia					
10046-21					5.7 ± 0.2 (2)
10060-11					6.2 ± 0.2 (2)
Dust					
10084-43					
Whole rock					6.2 ± 0.1 (3)
Dark glass				6.7 (1)	
Plagioclase (>90%)	6.1 (1)				
Magnetic separate				5.6 ± 0.1 (2)	
Ilmenite (~50%)			5.4 (1)		

± 50 ppm, with a $\delta^{13}C$ of −3 to −20. This is within the range to be expected for average earth carbon (see Fig. 2). Contamination by exhaust gases is again a possibility, but the tenacity with which the CO_2 is held in the samples would tend to rule out this possibility. The CO_2 could have been formed in our laboratory by reduction of the silicates by elemental carbon, but this reaction usually does not begin at temperatures under about 1600°C. The water-gas reaction ($C + H_2O \rightarrow CO + H_2$) is also a high-temperature reaction (~ 900°C). In addition, the evolution of SO_2 is difficult to explain as an artifact of our experimental procedure or as rocket-exhaust contamination. We believe that the CO_2 is truly lunar and may be present as liquid or gaseous inclusions in the solid phases. The carbon extracted by combustion after sample heating and removal of CO_2 is probably present as either carbides or elemental carbon.

The $^{18}O/^{16}O$ ratio of the CO_2 varies from +14.2 to +19.1. These values are much heavier than the $\delta^{18}O$ in the silicates and oxides analyzed below, and this fact is another indication that the CO_2 did not form from the reduction of silicates by carbon. The heavy oxygen may be due to equilibration between the CO_2 and H_2O and the silicates and oxides. It is known that the oxygen of CO_2 in fluid inclusions exchanges with the oxygen present in the host mineral (*4*).

Boato (*5*) has analyzed carbon in both carbonaceous chondrites (−3.7 to −18.8) and ordinary chondrites (−24.5 ± 0.2). These values are in the same range as that determined by our analysis of lunar materials. Clayton (*6*) has found very heavy carbon (+58.6 to +64.4 per mil) in carbonate minerals from Orgueil, a carbonaceous chondrite. This heavy carbon exceeds the range of the carbon in the lunar samples that we have examined.

Oxygen was liberated from the samples by reaction with BrF_5 at 550°C (*7*). The oxygen was converted to CO_2 and analyzed on an isotope-ratio mass spectrometer. The $\delta^{18}O$ values are given relative to the SMOW standard in Table 2.

The lunar whole-rock analyses lie between 5.7 and 6.2 and fall in the 5.5 to 7.0 range found for most terrestrial volcanic rocks (*8*). The lunar pyroxene value of 5.7 is in the 5.3 to 6.3 range found by Taylor *et al.* (*9*) to be characteristic of chondrites and enstatite achondrites. Meteorites which contain anorthitic plagioclase and which have chemical characteristics similar to those of lunar materials (for example, basaltic achondrites and mesosiderites) have δ values for pyroxene which are 1 to 2 per mil lower and thus do not appear to be genetically related to lunar material.

Because mineral separation on the lunar fines was difficult, the analyses of these separates are not particularly meaningful. Since the whole rock is 6.2 and some separates yield lower values, there must be an isotopically heavy component, which may be cristobalite.

From the oxygen isotope fractionations between plagioclase and ilmenite and from the laboratory calibrations of the systems plagioclase-water (*10*) and magnetite-water (*11*), an estimate can be made of the temperature of crystallization of type B rocks. Oxygen yields of 106 to 114 percent (over stoichiometric $FeTiO_3$) were obtained for the ilmenite samples, and the measured δ values of 4.6 (10017) and 4.3 (10050) were corrected to the values shown in the table on the basis that the excess yields were due to pyroxene impurities. The values in the table will have to be raised slightly when the magnesium contents of the ilmenites become known. This uncertainty and the fact that only two crystalline rocks were analyzed in this study places limits on the precision of the isotopic temperature. From our data we estimate the plagioclase-ilmenite fractionation to be between 1.8 and 2.2 per mil, implying a crystallization temperature of 1100° to 1300°C for type B rocks.

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