Oxygen Isotope Fractionation between Minerals and an Estimate of the Temperature of Formation

Abstract. *Oxygen isotopic compositions of separated minerals from three type A and four type B rocks are very uniform. The* $\delta^{18}O$ *values are: plagioclase, 6.20; clinopyroxene, 5.75; ilmenite, 4.45 (parts per thousand relative to Standard Mean Ocean Water). The isotopic distribution corresponds to equilibrium at 1120°C. The isotopic composition of lunar pyroxenes falls within the range for pyroxenes of terrestrial mafic and ultramafic rocks, ordinary chondrites, enstatite chondrites, and enstatite achondrites, but above the range for basaltic achondrites, hypersthene achondrites, and mesosiderites. Glass isolated from the lunar soil has a* $\delta^{18}O$ *value of 6.2, significantly richer in* ^{18}O *than the crystalline rock fragments in the soil.*

Oxygen isotope analyses have been done on the separated major mineral phases of seven lunar rocks of types A and B, on whole rock samples of types C and D, and on glass spherules and rock fragments separated from type D.

One-gram samples of the crystalline rocks were crushed in a steel mortar, ground in an agate mortar under acetone, and sieved through stainless steel sieves. For the coarser grained type B rocks, the size fraction between 325- and 500-mesh (25 to 43 μm) was used for mineral separation. For the finer grained type A rocks the fraction passing through the 500-mesh sieve (<25 μm) was used. Mineral separation was accomplished in a few cases by handpicking grains from the coarser fractions, but usually by centrifugation in heavy liquids (bromoform, methylene iodide, and Clerici solutions). Densities of the liquids used are given for each sample in Table 1. Mineral purity was evaluated by x-ray diffraction and optical microscopy, and was >95 percent in all samples, and usually >98 percent.

Oxygen was extracted from 10-mg portions of the separated minerals by the bromine pentafluoride procedure (*1*). Manometric measurement of the oxygen yield gave the quantitative determinations of oxygen content (Tables 1 and 2). Experimental error is estimated as ±1 percent of the amount present. Oxygen was converted to carbon dioxide and the oxygen isotope ratio was measured with a 60°, 15-cm, double-collecting mass spectrometer. Oxygen extraction was carried out in duplicate for all samples, and each gas sample was further analyzed in duplicate. Results of isotope analyses are given in Tables 1 and 2. Standard error of the mean of the duplicate measurements is estimated to be ± .07 per mil.

Oxygen contents of all phases analyzed are in agreement with values calculated from the estimated major-element compositions. No evidence of nonstoichiometry with respect to oxygen has been seen.

The uniformity of isotopic composition from rock to rock, for a given mineral, is very striking. Of the type A and type B rocks, only sample 58(35) shows any systematic departure from the mean, each of its minerals having an ^{18}O content 0.2 per mil lower than the means of the other rocks.

The soil and microbreccia have ^{18}O contents similar to one another, and about 0.5 per mil greater than that of the crystalline rocks. From the approximate modal compositions of the crystalline rocks given in the preliminary reports, their whole-rock $\delta^{18}O$ is estimated to 5.7 ± 0.1 per mil. Fragments of type A and type B rocks were handpicked from the 50- to 100-mesh (150 to 300 μm) fraction of the lunar soil and were found to have isotopic compositions in this range (Table 2). Irregular brown glass fragments (refractive index 1.68) were found to have almost the same composition, and may have been derived by fusion of crystalline rocks.

Glassy spherules, mean diameter 300 μm, were also separated from the soil, and have an ^{18}O content significantly greater than that of the rock fragments, implying addition of an isotopically heavier component or an isotopic fractionation in the process of formation of the spherules. An addition to the soil of 2 percent carbonaceous chondrite-like

Table 1. Oxygen contents and isotopic compositions of minerals from type A and type B rocks. Cr, cristobalite; Pc, plagioclase; Cpx, clinopyroxene; Ol, olivine; Il, ilmenite.

Mineral	Type B rocks			Type A rocks			
	20 (24)	22 (36)	71 (22)	17 (21)	44 (22)	47 (15)	58 (35)
				*Specific gravity**			
Cr	5.74						>2.38
Pc	5.14	2.71–2.81	2.71–2.82	2.70–2.77	2.69–2.77	2.70–2.75	2.71–2.82
Cpx	4.41	3.36–3.44	3.36–3.47	3.33–3.56	hand-pick	hand-pick	3.36–3.52
Ol							
Il	6.19	>4.2	>4.2	>4.3	>4.2	>4.3	>4.2
				Oxygen content (wt. %)			
Cr							53.4
Pc	45.8	46.3	47.2	47.3	46.4	46.5	46.7
Cpx	42.0	42.6	42.1	42.9	42.5	42.0	42.6
Ol	40.5						
Il	33.7	33.9	33.1	33.3	32.0	31.9	32.4
				$\delta^{18}O$†			
Cr	2.70–2.82						7.09
Pc	3.36–3.46	6.31	6.17	6.16	6.18	6.20	6.00
Cpx	3.54–3.65	5.71	5.72	5.81	5.77	5.76	5.53
Ol	>4.2						
Il		4.55	4.47	4.51	4.35	4.29	4.24
				$\Delta^{18}O$‡			
Pc-Cpx	0.45	0.60	0.45	0.35	0.41	0.44	0.47
Cpx-Il	1.32	1.15	1.24	1.29	1.41	1.46	1.28
Pc-Il	1.77	1.75	1.69	1.64	1.82	1.90	1.75

* Values quoted are specific gravities of liquids that bracket the value for the separated mineral. † ^{18}O content in per mil terminology: deviation of $^{18}O/^{16}O$ ratio in parts per thousand from ratio in standard mean ocean water (SMOW). ‡ Oxygen isotope fractionism, $\Delta^{18}O$, defined as 1000 ln α, where α is a fractionation factor for two phases, for example, $^{18}O/^{16}O$ in plagioclase divided by $^{18}O/^{16}O$ in ilmenite.

meteorites, as suggested (*2*), would cause an ^{18}O enrichment of about 0.2 per mil. Addition of other known types of meteoritic material would have a negligible effect because of the similarity of their isotopic composition to that of the soil (*3*). Enrichment of ^{18}O in glass resulting from a loss of volatiles in very high-temperature fusion has been shown experimentally (*4*), and may play some part on the moon.

The mean value of the $^{18}O/^{16}O$ ratio in objects of the solar system may be determined in part by the region in the early solar nebula within which the solid particles accreted. There may have been gradients in isotopic composition which are reflected today in differences among the planets, their satellites, and the meteorites and asteroids. Such differences have been observed for various classes of meteorites (*3*). Lacking data for the average oxygen-isotope composition of the moon, perhaps the best we can do at this stage is to compare the isotopic composition of a particular major mineral with that of similar minerals in terrestrial rocks and meteorites. The ^{18}O content of the Apollo 11 pyroxenes is identical with that of pyroxenes from some mantle-derived rocks: garnet peridotites and pyroxenites from kimberlite pipes (*5*). The lunar pyroxenes lie at the high end of the distribution for oceanic basalts and andesites (*5, 6*).

The lunar pyroxenes fall into group II (*3*), which contains the ordinary chondrites, enstatite chondrites, and enstatite achondrites. They are distinctly richer in ^{18}O than the pyroxenes of group I meteorites: basaltic achondrites, hypersthene achondrites, and mesosiderites.

If we speculate that oxygen isotope gradients in the early solar system were in the direction of decreasing ^{18}O outward, as suggested by the data on meteorites, then the oxygen isotope results on Apollo 11 rocks indicate an initial condensation either at the same position as terrestrial material, or somewhat nearer the sun.

Isotopic fractionations between pairs of minerals can be used to determine the temperature of last equilibration of the minerals. In favorable cases, this may simply be the temperature of their initial crystallization. Isotopic fractionations between pairs of major phases are shown in Table 1. For a given mineral pair the observed fractionations are identical, within experimental error, for all seven rocks analyzed: plagioclase-clinopyroxene, 0.45 ± 0.04; clinopyroxene-ilmenite, 1.31 ± 0.08; plagioclase-ilmenite, 1.76 ± 0.06.

Table 2. Oxygen contents and isotopic compositions of various fractions of type C and type D rocks. The $\delta^{18}O$ values are relative to standard mean ocean water.

Sample	Description	O content (wt. %)	$\delta^{18}O$
	Type C		
60 (12)	Whole rock	41.3	6.03
	Type D		
84 (46)	Whole rock	42.6	6.18
84 (46)	Glass spherules	42.2	6.22
84 (46)	Glass fragments	42.3	5.88
84 (46)	Type A fragments	41.7	5.74
84 (46)	Type B fragments	40.6	5.64
84 (46)	"Anorthosite" fragments	44.8	5.89

In principle, any two of these fractionations provide two independent measures of "isotopic temperature." A minimum test of the existence of equilibrium is that these two temperatures agree. Unfortunately, laboratory calibration of isotopic thermometers involving pyroxene and ilmenite has not been done, so that this test cannot yet be carried out rigorously. It is, however, possible to compare the relative magnitudes of two isotopic fractionations with those found within the same mineral assemblage in various terrestrial rocks. This is done in Fig. 1 for the assemblage plagioclase-clinopyroxene-magnetite with analytical data for terrestrial mafic igneous rocks, both intrusive and extrusive (*5, 6*). Because of the dependence of fractionations involving plagioclase on the chemical composition of the plagioclase (*7*), all data have been normalized to a feldspar composition of An_{60}. This amounts to an effective increase in the δ value of lunar plagioclase by 0.16 per mil. Furthermore, the isotopic fractionation between ilmenite and magnetite is very small, but not negligible, at igneous temperatures, so that the ilmenite δ value has been reduced by 0.20 per mil to determine a hypothetical magnetite δ value. The resulting point, representing the average fractionation for the seven Apollo 11 samples analyzed, has been plotted on the plagioclase-pyroxene-magnetite diagram, and falls on the previously determined line through the data points for terrestrial rocks. It is virtually indistinguishable from the results for recent Hawaiian basalts. Hence the evidence for isotopic equilibrium among the major phases is fairly strong.

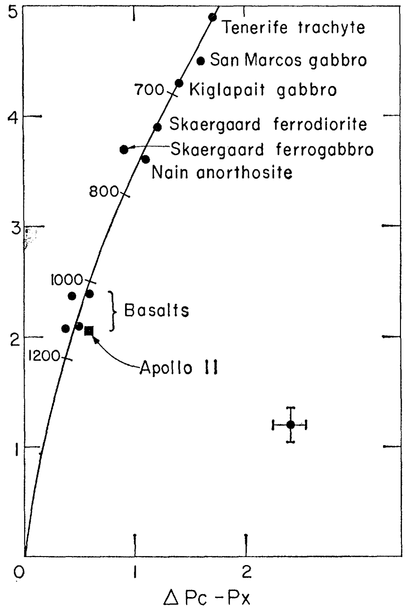

Fig. 1. Plagioclase-clinopyroxene-magnetite "concordancy diagram." Data on terrestrial rocks are from reference (*6*). Temperatures indicated along concordancy line are determined from the plagioclase-magnetite isotopic thermometer (*7, 8*). Pc, plagioclase; Px, pyroxene; Mt, magnetite. Analytical error is indicated by bars on point in lower right-hand corner.

A similar "concordancy" test for the system plagioclase-clinopyroxene-olivine indicates that the olivine of sample 20 (24) was in isotopic equilibrium with the other minerals. Data for terrestrial samples are not available to make this test for cristobalite in sample 58(35), but the magnitude of the cristobalite-plagioclase fractionation of 1.08 is within 0.1 of the value estimated by extrapolation of laboratory calibrations of the quartz-feldspar system to the isotopic temperature inferred for these rocks.

The best estimate of an isotopic temperature can be made from the fractionation between plagioclase and ilmenite. This is possible through the experimental calibration of the plagioclase-magnetite pair (*7, 8*), along with the small ilmenite-magnetite fractionation, estimated on the basis of measurements on terrestrial basalts to be about 0.20 at the temperatures involved. The resulting isotopic temperature is 1120°C, with an analytical uncertainty of ± 30°C. (Somewhat larger systematic errors may exist in the calibration of this isotopic thermometer, particularly since this temperature lies outside the range of the laboratory calibration.)

The isotopic temperature is very similar to those of terrestrial mafic extrusive rocks, which, in turn, are in good agreement with other estimates of extrusion temperatures. Hence it appears that the isotopic temperatures are very 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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References and Notes

→ R. N. Clayton and T. K. Mayeda, *Geochim. Cosmochim. Acta* **27**, 43 (1963).
2. R. R. Keays, R. Ganapathy, J. C. Laul, E. Anders, G. Herzog, P. M. Jeffery, *Science*, this issue.
3. H. P. Taylor, Jr., M. B. Duke, L. T. Silver, S. Epstein, *Geochim. Cosmochim. Acta* **29**, 489 (1965).
4. L. S. Walter and R. N. Clayton, *Science* **156**, 1357 (1967).
5. G. D. Garlick, *Earth Planet. Sci. Lett.* **1**, 361 (1966); A. T. Anderson, R. N. Clayton, T. K. Mayeda, unpublished data.
6. H. P. Taylor, Jr., *Contrib. Mineral. Petrol.* **19**, 1 (1968).
7. J. R. O'Neil and H. P. Taylor, Jr., *Amer. Mineral.* **52**, 1414 (1967).
8. J. R. O'Neil and R. N. Clayton, in *Cosmic and Isotopic Chemistry*, H. Craig, S. L. Miller, G. J. Wasserburg, Eds. (North-Holland, Amsterdam, 1964), p. 157.
9. Supported by NASA grant NAS-9-7888.

4 January 1970

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-