

The Chlorine Isotope Composition of the Moon and Implications for an Anhydrous Mantle

Z. D. Sharp,^{1*} C. K. Shearer,^{1,2} K. D. McKeegan,³ J. D. Barnes,⁴ Y. Q. Wang⁵

¹Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87122, USA. ²Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87122, USA. ³Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095, USA. ⁴Department of Geological Sciences, University of Texas, Austin, TX 78712, USA. ⁵Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

*To whom correspondence should be addressed. E-mail: zsharp@unm.edu

Arguably, the most dramatic geochemical distinction between the Earth and Moon has been the virtual lack of water (hydrogen) in the latter. This conclusion was recently challenged on the basis of geochemical data for lunar materials that suggest that the water content of the Moon might be far higher than previously believed. We have measured the Cl isotope composition of Apollo basalts and find that the range of isotopic values (from -1 to $+24\%$ vs. SMOC) is 25 times greater than for Earth. The huge isotopic spread is explained by volatilization of metal halides during basalt eruption, a process that could only occur if the Moon had H concentration $\sim 10^4$ to 10^5 lower than Earth, implicating that the lunar interior is essentially anhydrous.

The origin of the Moon is constrained by geophysical models of angular momentum, density and mass, and geochemical arguments based on chemical and isotopic similarities and differences between the Earth and Moon. It is now generally accepted that the Moon was formed from the impact of a Mars-sized body sometime after formation of Earth's core (1, 2), although a number of observations have not been adequately explained. Geodynamic models indicate that the impactor came from a different region of our solar system and that the bulk of the Moon originated from the impactor rather than Earth (3). This result is at odds with geochemical data, particularly with the fact that Earth and Moon have identical oxygen and chromium isotope ratios (4, 5). If the two bodies came from different regions of our solar system, it is expected that they would have different isotope ratios (6). Turbulent mixing between the molten Earth and Moon immediately following impact has been proposed as a means of homogenization (6), but such intense mixing would also tend to homogenize volatiles between the two bodies. The recognition that the Moon is strongly depleted in volatile elements and is effectively anhydrous was established soon after the return of Apollo samples (7, 8). The absence of

hydrogen in the Moon may be explained by having an anhydrous impactor (9), by exclusion of water in the Moon due to low water solubility in molten silicate at high temperature and low $p(\text{H}_2\text{O})$ (10), or if both the Earth and Moon were anhydrous during formation, and volatiles were delivered to the Earth at a later date (11).

Recently, it has been proposed that the water content of the Moon may be far higher than previously recognized. Saal *et al.* (12) measured water contents of lunar glass beads and concluded that the water content of the Moon may be equivalent to typical terrestrial Mid Ocean Ridge Basalts (MORBs). Similar high water contents of lunar basalts have been estimated from H-contents of apatite grains (13–15). Here we present Cl isotope data from lunar basalts, volcanic glasses and apatite grains to assess the water content of the Moon. Cl is extremely hydrophilic, tracking closely with water on Earth (16). It is also incompatible in nearly all silicates and extremely volatile. If the Moon were anhydrous, unique degassing and partition behavior of Cl should lead to significant Cl isotope fractionations that are distinct from those observed on Earth.

We determined Cl isotope ratios and concentrations of water-soluble leachates and silicate residues from lunar basalts and glasses using gas source mass spectrometry. A wide range of sample types were chosen to allow us to assess the effects of chemical composition/mineralogy and surface processing. In situ analyses were made on apatite grains using the Cameca 1270 ion microprobe at U.C.L.A. In order to assess the potential effect of solar wind on the Cl isotope ratio of the lunar regolith and soils, a thin film of NaCl was irradiated with a 100 keV proton beam at the Ion Beam Materials Laboratory, Los Alamos National Laboratory. The irradiated sample was analyzed for its Cl isotope composition. Detailed analytical methods and sample descriptions are given in Supp. Materials.

The Cl isotope compositions of typical terrestrial materials and meteorites are clustered around 0‰ (17) or -1.6% (18)

with a spread of $\pm 0.5\%$ (Fig. 1). Large variations in $\delta^{37}\text{Cl}$ values are seen only in the specific case where HCl gas is evolved from volcanic fumaroles (16). The enrichment of ^{37}Cl in the vapor is due to the large isotopic fractionation between the solvated Cl^- ion in an aqueous solution and HCl gas.

In contrast to terrestrial basalts, lunar samples show a range of $\delta^{37}\text{Cl}$ values from -1 to $+24\%$ (Fig. 1). The large spread is indicative of conditions that do not exist on Earth. We consider three possible explanations for the large spread: 1) initial heterogeneities retained from the Moon-forming event; 2) isotopic fractionation associated with solar wind and micrometeorite bombardment; and 3) devolatilization and isotopic fractionation specific to the anhydrous character of lunar basalts.

The first of these possibilities is unlikely. Volatilization and fractionation could certainly occur during accretion of the Moon with preferential loss of the light isotope during volatile escape to space. However, maintaining such large isotopic variations in a system that was certainly molten and went through a magma ocean stage (19) would not be expected and has not been observed for other volatile elements, such as K (20).

The second scenario is similarly unlikely. Because micrometeorite bombardment and solar wind sputtering can preferentially remove the light isotopes of volatile elements, we chose samples that have experienced both minimum and maximum degrees of surface processing (Table 1) to test for a correlation between the extent of surface exposure (soil maturity) and $\delta^{37}\text{Cl}$ values. Lunar soil 64501,232, with a high maturity index and the highest $\delta^{34}\text{S}$ value ($+11.7\%$) of any of our samples, has an intermediate $\delta^{37}\text{Cl}$ value, similar to that of immature soil 61220 (21), arguing against preferential ^{35}Cl loss due to formation and removal of light HCl (g) to space. In addition, the $\delta^{37}\text{Cl}$ value of the surface volatile chlorides are always lower than the rock-bound Cl in the same sample, in some cases as much as 10%. If the surface chlorides interacted with solar wind, they should be enriched in ^{37}Cl , not depleted. Apatite grains in KREEP basalt 72275,491 were almost certainly shielded from solar wind, and yet this sample has the highest $\delta^{37}\text{Cl}$ value of all measured samples. As a final test, a thin film of NaCl was found to be isotopically unfractionated after bombarded by a 5×10^{17} ions/cm² proton source (Table 1). Preferential formation of H^{35}Cl during proton bombardment should raise the $\delta^{37}\text{Cl}$ values of the residual salt, a trend which is not seen.

The third possibility, that devolatilization of anhydrous lunar basalts caused the range of $\delta^{37}\text{Cl}$ values is supported by several trends. First, the lowest measured $\delta^{37}\text{Cl}$ values of all samples overlap the range for both terrestrial and meteorite samples. This is consistent with the idea of a well-mixed Cl isotope ratio for the inner solar system. All higher $\delta^{37}\text{Cl}$ values, as discussed below, are explained by fractionation

during degassing. Second, the $\delta^{37}\text{Cl}$ values of the leached material, representing vapor deposition of the volatile chloride species, are always lower than the coexisting silicate. These data strongly support the idea that the light isotope of Cl is lost during devolatilization.

In terrestrial magmas and lavas there is always an excess of H relative to Cl, and the dominant volatile chloride species is HCl gas. The fractionation between HCl gas and a basalt melt must be close to 0‰, because the $\delta^{37}\text{Cl}$ values of terrestrial basalts have very little variation, despite varying Cl contents. There are two factors which control Cl isotope fractionation during volatilization on Earth. The first is the preferential loss of ^{35}Cl to the vapor phase due to its higher translational velocities and vapor pressure relative to ^{37}Cl , and the second is the preferential incorporation of ^{37}Cl into HCl (gas) due to the covalent character of the bond (16, 22). The two factors tend to cancel one another, resulting in near-zero fractionation between melt and vapor. In a water-free melt, the volatile chloride species are metal chlorides (23, 24). Under such conditions, the bonding of Cl in the vapor and melt phase are similar, so that the preferential kinetic loss of the light isotope is not cancelled out by a different bonding energies of the melt and vapor phase. Vapor loss should increase the $\delta^{37}\text{Cl}$ value of the residual magma, which explains the extraordinary isotopic range of lunar samples. Na, Zn, Fe and other metal chlorides have been observed as surface coatings on lunar volcanic materials (25, 26), consistent with deposition of metal chloride vapor phases. Thermodynamic calculations also support metal halide vapor as the dominant Cl species when the Cl/H ratio is substantially greater than 1 (8).

The change in the $\delta^{37}\text{Cl}$ value of the melt during vapor loss of a metal chloride can be modeled assuming Rayleigh distillation, where $\delta_{\text{final}} = \delta_{\text{initial}} + (1000 + \delta_{\text{initial}})(F^{\alpha-1} - 1)$, F is the fraction of Cl remaining in the silicate melt and α is the fractionation between vapor and melt given by $\alpha = (1000 + \delta_{\text{vapor}})/(1000 + \delta_{\text{silicate melt}})$. For volatilization of a liquid into a vacuum $\alpha = \sqrt{m_1/m_2}$, where m_1 and m_2 are the masses of the light and heavy isotopologue of the vaporizing species (27). For common chloride species NaCl, FeCl₂ and ZnCl₂, α is 0.983, 0.992, and 0.993, respectively. These fractionations are similar to the measured $\Delta^{37}\text{Cl}$ (silicate-vapor) value from samples 64501,232 ($\alpha = 0.990$) and 61220,39 ($\alpha = 0.992$). Actual fractionations less than those computed from relative mass differences have been observed experimentally (28) and are expected when diffusion rates are insufficient to maintain isotopic homogeneity in the melt. Nevertheless, the lighter isotope diffuses faster through the melt, so that fractionation during volatilization will still occur. Volatilization can only increase the $\delta^{37}\text{Cl}$ value of the residual Cl in the melt. The lowest value of all samples is -0.7% , measured on leachates

of a fire-fountain glass (74002). This value is similar to bulk Earth and meteorite samples (17) and may be slightly lighter than bulk Moon because it is a vapor condensate sample and is likely the product of some fractionation. This sample is also anomalously volatile rich and is the only sample that has significant hydrogen {Saal, 2008 #13}. As a result, the volatile Cl species could have been HCl, and little fractionation during degassing would be expected. Mare basalt 12040,214 has both $\delta^{37}\text{Cl}$ and $\delta^{34}\text{S}$ values of 0‰, suggesting minor fractionation during degassing. We conclude that the undifferentiated Moon appears to have a $\delta^{37}\text{Cl}$ value close to 0‰, similar to Earth.

Initial Cl contents were calculated assuming Rayleigh distillation and an initial $\delta^{37}\text{Cl}$ value of 0‰ (see Suppl. Material). The amount of Cl vapor loss necessary to reach a ^{37}Cl enrichment equivalent to a $\delta^{37}\text{Cl}$ value of +20‰ ranges from 63% to 98% for an assumed initial $\delta^{37}\text{Cl}$ value of 0‰ and α between 0.983 and 0.992, respectively (Fig. 2). These are minimum degrees of degassing because diffusion-limited exchange will cause a reduction in the fractionation between melt and vapor. The calculated Cl contents of the undegassed basalts (and apatite grains for the ion microprobe analyses) have a positive correlation with the $\delta^{37}\text{Cl}$ values (Table 1). It is reasonable that samples with high initial Cl contents would lose proportionally more Cl than Cl-poor ones, and therefore evolve to higher $\delta^{37}\text{Cl}$ values.

The H contents of lunar magmas must have been substantially lower than their Cl contents, or else HCl (g) rather than metal chlorides would have been the volatilizing species, and no isotopic fractionation would have occurred. Excepting one pigeonite basalt sample, the calculated initial Cl concentrations of three undifferentiated lunar basalts are all close to 40 ppm (Table 1). Cl volatilization is only expected to have occurred after 90–95% crystallization has taken place (14), concentrating Cl in the remaining liquid. Primitive melts therefore had Cl concentrations at least ten times less, approximately 4 ppm. Finally, primitive melts generated in the mantle should be concentrated in incompatible elements relative to bulk lunar mantle by a factor ~ 10 (29), so that the lunar mantle should have a Cl concentration of ~ 400 ppb, with H contents around 10 ppb (given that the a.m.u. ratio Cl/H = 35.45/1.01), compared to the bulk Earth of ~ 260 ppm (30). (See Suppl. Materials for details).

Isotopic anomalies in lunar samples have been seen in other elemental systems, but never with the extreme variations observed for the Cl isotopes. What makes Cl unique is its hydrophilic affinity and high volatility compared to all other isotopic systems studied in lunar samples. It is therefore an extremely sensitive indicator of H contents. If lunar basalts had initial H contents anywhere close to terrestrial magmas (e.g., MORB), then the extreme

fractionations observed in the lunar materials would not have occurred. We suggest that the Moon was anhydrous as initially proposed (7), and that the high H contents calculated for some lunar samples are atypical. High H contents are only found in anomalous samples with extreme volatile contents, and are likely the product of igneous processes that resulted in extreme volatile enrichment. In contrast to other samples, they have $\delta^{37}\text{Cl}$ values close to 0‰ and are inconsistent with the high and variable $\delta^{37}\text{Cl}$ values reported for the majority of lunar samples.

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33. Funding was provided by NASA Origins grant 07-SSO07-0077 to Sharp, a NASA LASER grant NNX08AY786 to Shearer and a NASA Cosmochemistry grant to McKeegan. The UCLA ion microprobe facility is partially supported by a grant from the NSF Instrumentation and Facilities Program. Thanks to Lunar curator G. Lofgren and the Lunar curation facility and staff. P. Burger provided imaging and quantitative elemental analyses of apatite.

Supporting Online Material

www.sciencemag.org/cgi/content/full/science.1192606/DC1

Materials and Methods

Table S1

References

20 May 2010; accepted 26 July 2010

Published online 5 August 2010; 10.1126/science.1192606

Include this information when citing this paper.

Fig. 1. Chlorine isotope composition of selected terrestrial materials and lunar samples (triangles – ion microprobe; diamonds, gas source mass spectrometry). Silicate and leachate samples in filled and open, respectively. Matched leachate-silicate pairs are circled. Terrestrial and meteorite data from (17, 31, 32) and references therein. Error bars are smaller than the size of symbols.

Fig. 2. Calculated trajectories of $\delta^{37}\text{Cl}$ values of basalt during loss of metal chloride volatiles. A $\delta^{37}\text{Cl}$ value of 20‰ is obtained at >70% (NaCl) to >90% (Fe,ZnCl₂) volatilization ($F < 0.3$) assuming an initial $\delta^{37}\text{Cl}$ value of 0‰. The α values of 0.983 and 0.992 are obtained from the relationship $\alpha = \sqrt{m_1/m_2}$, for NaCl and Zn,FeCl₂, respectively.

Table 1. Cl contents and $\delta^{37}\text{Cl}$ values for lunar samples and irradiated salt experiment. Initial Cl contents were calculated assuming Rayleigh distillation, an α value of 0.99 and an initial $\delta^{37}\text{Cl}$ value of 0‰.

Sample	Notes	Surface exposure	Cl concentration (ppm)	$\delta^{37}\text{Cl}$ (‰ vs. SMOC)	Calculated initial Cl content (ppm)
74220,862	Pyroclastic, glass	yes	50*	8.6, 9.3	
10017,34	Vesicular basalt; ilmenite (high K) basalt	no	24.7, † 12.3	4.7, † 2.7*	40
12040,214	Mare basalt		11*	0.0	
64501,232	Mature soil	yes	8, † 19*	15.7, † 5.6*	38
61220,39	Immature trench soil	yes	10, † 16*	14.3, † 6.1*	42
66095	'Rusty rock' w/ FeCl_2 , fumarole?, regolith breccia	yes	117*	15.6, † 14.0,* 14.1*	
12034,116	Regolith, breccia	yes		16.0 †	
12052	Pigeonite basalt	no	5	2.5 †	6
74002,36	Hand picked glass beads	yes	80	-0.7*	
15555,207	Apatite (SIMS); olivine normative MARE basalt	no	0.56 ‡	13.1 ‡	
12040,46	Apatite (SIMS) olivine basalt	no	0.83 ‡	17.2 ‡	
72275,491	Apatite (SIMS) KREEP basalt clast in fragmental breccia	minor	1.22 ‡	24.5 ‡	
Non-irradiated salt				+0.1	
Irradiated salt				-0.1	

*leachate; †non-leachable; ‡wt % in apatite.



