

Volatile components in the moon: Abundances and isotope ratios of Cl and H in lunar apatites. J. W. Boyce^{1,2}, Y. Guan¹, A.H. Treiman³, J.P. Greenwood⁴, J. M. Eiler¹, C. Ma¹ ¹Division of Geological & Planetary Sciences, Caltech, 1200 E. California Blvd., Pasadena, CA 91125; ²Department of Earth & Space Sciences, UCLA, 90095-1567; ³Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058; ⁴Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459.

Introduction: Observations of terrestrial levels of highly volatile elements in lunar apatite, including H [1-3], suggested that some lunar melts were at least “damp” if not “wet” at some point in their histories. On the other hand, the very high $\delta^{37}\text{Cl}$ values in lunar rocks and apatites (up to $\sim+30\%$ [4]) have been taken to mean that their parent magmas were essentially anhydrous, because such large Cl isotope fractionations could not occur in water-bearing systems. In the laboratory, however, fractionations up to $\delta^{37}\text{Cl} = +9\%$ have been seen in the system of $\text{HCl}_{\text{liquid}} + \text{HCl}_{\text{gas}}$ [5], so there might have been lunar conditions that permitted large fractionations of Cl isotopes in the presence of H.

Here we examine the relationship between [H] and both the concentration and isotopic composition ([Cl] and $\delta^{37}\text{Cl}$) of lunar apatites from 9 thin sections of 8 different lunar samples: 10044,12; 10044,644; 12013,148; 12039,42; 12040,211; 14305,94; 75055,55; 76535,56; & 79215,51.

Methods: All [H], [Cl], and $\delta^{37}\text{Cl}$ values reported here were measured on the Cameca 7f-GEO secondary ion mass spectrometer (SIMS) at Caltech. $\delta^{37}\text{Cl}$ analyses were performed in separate sessions from the concentration measurements, but in all cases were made on the same crystals. δD values for the first seven sample above are from [3,6], from different crystals in the same thin sections. δD values for 76535 and 79215 were taken at Caltech [7, unpublished data].

Isotopic measurements. $\delta^{37}\text{Cl}$ was measured with a ~ 0.7 nA, 10 kV focused Cs⁺ primary beam with normal-incidence electron gun charge compensation. Samples were pre-sputtered with a 25x25 μm rastering beam of ~ 2 nA for 10 minutes. $^{37}\text{Cl}^-$ and $^{35}\text{Cl}^-$ were collected with an electron multiplier (EM) under a mass resolving power (MRP) of ~ 2000 . δD (for 76535 and 79215) was measured on the same apatite grains at an MRP of ~ 500 , after concentration measurements.

Concentration measurements. After Cl isotope analysis, C, H, F, S, and Cl were obtained with a 10x10 μm rastering Cs⁺ beam of ~ 3 nA. To avoid cracks and contamination, ion images of $^{12}\text{C}^-$, $^{16}\text{O}^1\text{H}^-$, $^{31}\text{P}^-$, and $^{35}\text{Cl}^-$ were examined for each grain; the smallest field aperture and electronic gating were used. $^{12}\text{C}^-$, $^{16}\text{O}^1\text{H}^-$, $^{18}\text{O}^-$, $^{19}\text{F}^-$, $^{31}\text{P}^-$, $^{32}\text{S}^-$, and $^{35}\text{Cl}^-$ were collected with an EM or a Faraday cup at an MRP of ~ 5000 . Measured ion ratios were calibrated against in-house apatite

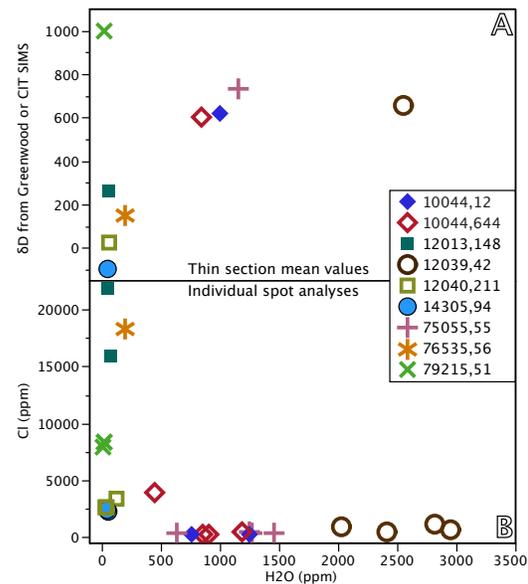


Figure 1. Measurements of δD and [Cl] in lunar apatite plotted against [H] as ppm H_2O . A: New δD data combined with data from [3,6], presented as thin section averages to facilitate comparison between analyses of different apatite crystals in the same thin sections. B: [Cl] vs [H], showing an inverse relationship between them.

standards; the largest component of uncertainty arises from blank corrections. H_2O values < 100 ppm are within uncertainty of zero.

Results: Hydrogen concentrations [H] range from within uncertainty of zero to ~ 3000 ppm H_2O , while [Cl] ranges from 200-22000 ppm (Fig. 1). High [Cl] values (> 2000 ppm) are observed only in apatites with < 500 ppm H_2O ; conversely, apatites with > 500 ppm H_2O have < 1200 ppm Cl (Fig. 1b).

$\delta^{37}\text{Cl}$ values range from $+1.6$ to $+32.8\%$ (Fig. 2), consistent with previous observations of very high $^{37}\text{Cl}/^{35}\text{Cl}$ ratios in lunar samples [4]. The highest $\delta^{37}\text{Cl}$ values are exclusively in apatite with low [H] (< 200 ppm H_2O), but apatite grains with $\delta^{37}\text{Cl} < +18\%$ show a wide range of [H], including the apatites from 12039,42 with 2000-3000 ppm H_2O and $\delta^{37}\text{Cl}$ of $+15$ to $+17\%$. The relationship between $\delta^{37}\text{Cl}$ and [Cl] is somewhat the opposite, with greater dispersion in [Cl] for those apatites with high $\delta^{37}\text{Cl}$, including those from 12013,148 and 76535,56 with [Cl] >1.5 wt.% and $\delta^{37}\text{Cl} \geq +25\%$.

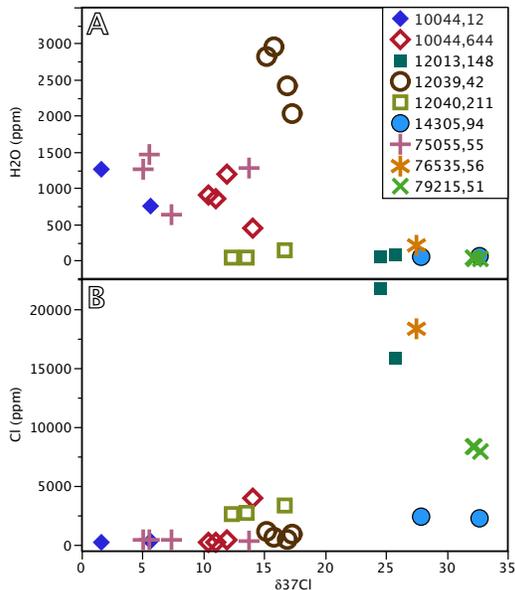


Figure 2. Concentrations of H₂O (A) and Cl (B) in apatite versus $\delta^{37}\text{Cl}$. Although the highest $\delta^{37}\text{Cl}$ values are only found in apatite with low-H₂O, samples like 12039 show a large, positive Cl-isotope fractionation ($> +15\%$) at high H₂O content (2000-3000 ppm H₂O). This is not consistent with the idea [4] that anhydrous conditions are required for extreme Cl fractionation. The highest $\delta^{37}\text{Cl}$ values ($> +25\%$) represent a wide range of [Cl], which is not consistent with a simple fractionation story.

Discussion: The fact that apatites from 12039,42 have H₂O > 2000 ppm and $\delta^{37}\text{Cl} > +15\%$ suggests ^{37}Cl enrichments can be generated in magmas with significant dissolved water (i.e., assuming apatite water contents are proportional to water contents of parent melts). Although it is not possible to determine the precise H₂O content of a magma from measurements of [H] in apatite, all experimental data available regarding the partitioning of H between apatite and melt indicates that H is incompatible in apatite at low OH/F ratios, i.e. that these apatites contain less H₂O than their parent magmas. Our data precludes the hypothesis of [4] (that high $\delta^{37}\text{Cl}$ can arise only in anhydrous processes), as well as any simple relationship between $\delta^{37}\text{Cl}$ and H₂O. Nevertheless, it is noteworthy that the highest $\delta^{37}\text{Cl}$ values are clearly associated with relatively low H₂O, and thus these data, taken by themselves, might permit some variation on the hypothesis of [4].

A related inference from [4] is that Cl loss to an anhydrous vapor should enrich the residual Cl in ^{37}Cl . From this we would predict that the most fractionated samples (highest $\delta^{37}\text{Cl}$) would have the lowest Cl contents. This relationship between [Cl] and $\delta^{37}\text{Cl}$ is not observed, see Figure 2b – the most Cl-rich samples also have the highest $\delta^{37}\text{Cl}$. Similarly, Cl distribution in some individual apatite grains is not homogeneous

(based on Cl- ion image), showing Cl-rich rims or sectors. However, there is no difference in Cl isotopic composition between Cl-poor or Cl-rich portions of the same grain.

Whatever mechanisms are causing the extreme fractionation of chlorine isotopes, they are capable of producing a reservoir that is unusually rich in Cl and high in $\delta^{37}\text{Cl}$. This seems to preclude ^{37}Cl enrichment by preferential outgassing of ^{35}Cl from magmas (at least, as the sole mechanism). We also note that this extreme composition is consistently associated with low δD (Fig. 1a). This component is most abundant in apatites from highlands sample 12013 and 76535 (and possibly 14305), and thus may represent a highlands component. The δD value of this latter end member ($\leq -100\%$) is consistent with a contribution from solar wind hydrogen ($< -995\%$), suggesting that it could represent a crust/regolith component.

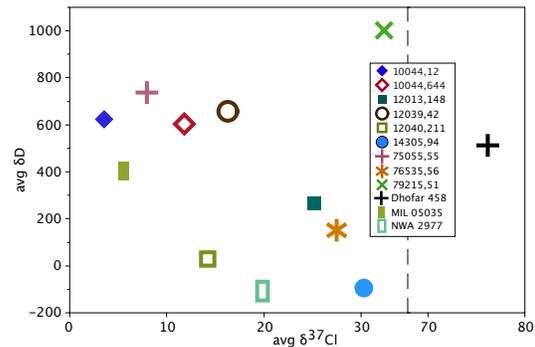


Figure 3. Measurements of δD vs. $\delta^{37}\text{Cl}$, thin section averages. Data for the last three samples from [8].

Most of the samples analyzed here appear consistent with mixing between this highland component and a second characterized by low Cl/H, low $\delta^{37}\text{Cl}$, high H and high δD (Figs. 1,3); however, several do not. Apatites from 79215,51 and Dho458 [8] fall off the trend to high δD and/or high $\delta^{37}\text{Cl}$. 79215 might be distinct because of its unusual history of metasomatism [7].

The distinctive $\delta^{37}\text{Cl}$ values of lunar materials provide clues to the origins of their volatiles but do not appear to provide a simple signature for low-H magmas on the Moon. The diversity of volatile compositions in lunar apatite suggests additional unrecognized volatile components or fractionation processes.

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References: [1] Boyce J.W. et al. 2010 *Nature* 466, 466-469. [2] McCubbin F.M. et al. 2010, *PNAS* 107, 11223-11228. [3] Greenwood J.P. 2011, *Nature Geosci.* 4, 79-82. [4] Sharp Z.D. et al., 2010 *Science* 329, 1050-1053. [5] Sharp Z.D. et al., 2010 *GCA* 74, 264-263. [6] Greenwood J.P. et al. 2012 *Lunar Planet. Sci.* 43rd, Abstr. 2089. [7] Treiman A. et al. 2013, *Lunar Planet. Sci.* 44th. [8] Wang Y. et al. 2012 *MaPS*, Abstr. #5170.