The effect of vapor pressure on Cl isotope fractionation: Application to δ^{37}Cl value(s) of Mars. Z.D. Sharp[1], C.K. Shearer Jr.[2], F. M. McCubbin[2] and C. Agee[1,2], K. D. McKeegan[3] [1]Dept. Earth and Planetary Sci., Northrop Hall, University of New Mexico, Albuquerque, NM 87131, [2]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, [3]Dept. Earth and Space Sci., U.C.L.A., Los Angeles, CA 90095.

Introduction: The chlorine isotope composition of primitive terrestrial basalts shows a very limited range. Excluding samples that have interacted with a subducted component (*2*), the δ^{37}Cl value of basalts and cumulates cluster tightly around 0 per mil (Fig. 1). Chondrites have a similarly narrow range of δ^{37}Cl values indistinguishable from Earth (type 3 chondrites = -0.3±0.5, *n* = 6 (excepting Parnallee (*1*). The Moon has a wide range of δ^{37}Cl values, from -0.7 to +24‰ (*3*). Mars has a range of δ^{37}Cl values that is intermediate to the Earth and Moon, from -3.2 to +1.8‰ (Fig. 1 & 2). The large range for the Moon is interpreted as degassing of metal chlorides from an anhydrous silicate melt. The lowest value is equivalent to terrestrial and chondritic values – higher values are explained by vaporization and loss of light Cl. In contrast to the Moon, in which the δ^{37}Cl values range upward from a low value of near 0‰, the δ^{37}Cl values of martian meteorites have δ^{37}Cl values that are approximately equally distributed above and below 0‰. The spread of martian data may be related to a) different sources, b) interaction with crustal material or c) vaporization of light isotopes, as occurred on the Moon, but with a lower baseline value of -3‰.
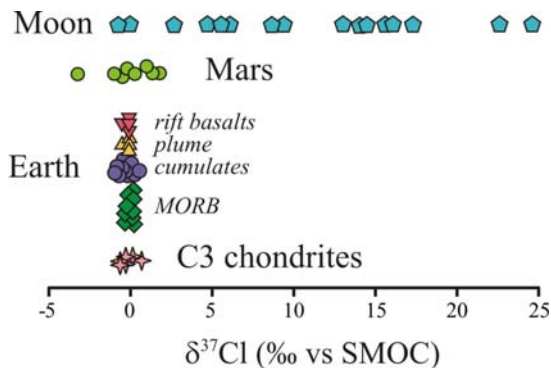

Fig. 1 Chlorine isotope composition of primitive materials from Earth, chondrites (1), lunar samples (3) and Mars (4).

One possibility for the lunar range that has not been considered is that isotope fractionation during vaporization occurs for all bodies, but the large fractionation of lunar materials is due to the fact that vaporization on the Moon occurred into a vacuum, in contrast to Earth and Mars, which both have atmospheres. Vaporization into a vacuum follows Graham's law, where the fractionation α is given by

$$\alpha = \sqrt{M1/M2} \quad (M1 = \text{Na}^{37}\text{C}, M2 = \text{Na}^{35}\text{Cl for NaCl}).$$

When an atmosphere is present, back diffusion occurs and α will be less than that expected by Graham's law. We determined how α is affected by a non-zero atmosphere by conducting evaporation experiments in vacuum and at 1 bar pressure (in air).
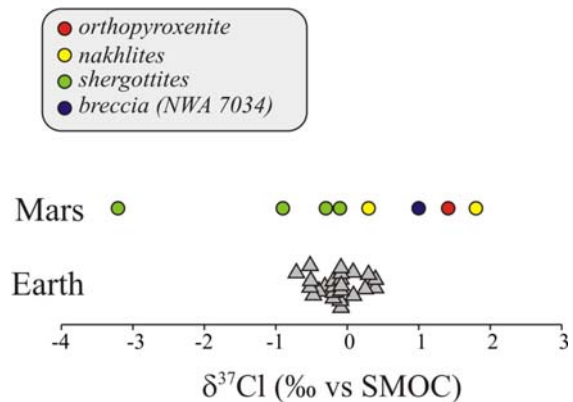

Fig. 2. Detail from Fig. 1 showing δ^{37}Cl values of martian meteorites by type (4).

Experimental procedure: NaCl was loaded onto a Pt loop in a glass vessel (Fig. 3). The loop was heated resistively until the NaCl melted and vaporized. The δ^{37}Cl values of the residual NaCl and the vaporized NaCl that had condensed on the glass walls were

Fig. 3 Pt loop in glass vessel used for vaporization experiments. Pt resistance heater holds molten NaCl while vapor condenses on the glass walls chilled to liquid nitrogen temperature.

measured using gas source mass spectrometry with CH_3Cl as an analyte (*5*).

Results: The measured $\Delta^{37}Cl_{melt\text{-}vapor}$ values were independent of vapor pressure over the range of 0 to 1 bar and were far less than those predicted by perfect Graham's law behavior ($\Delta^{37}Cl_{melt\text{-}vapor}$ = 1.003 to 1.0045 (measured) *vs.* 1.017 (expected)). A number of processes can reduce the fractionation from the ideal value predicted by Graham's law. These include stripping of the outer layer of the vaporizing species (onion-skin removal) due to slow diffusion of NaCl within the melt compared to the rate of NaCl (*g*) removal or vaporization of polymerized molecules instead of NaCl (*e.g.*, Na_2Cl_2 (*g*) gives an expected α of 1.008). Regardless of the reason for the low α values, we see no indication that vapor pressure has any effect on the fractionation during vaporization.

The results of our experiments support the initial conclusion of Sharp *et al.* (*3*) that the large range of isotope values for lunar samples is due to anhydrous degassing. The explanation for the moderate range of $\delta^{37}Cl$ values for the martian data is less clear. Three possibilities are considered. 1) The H/Cl ratio of martian magmas is less than for terrestrial materials (*6*), so that degassing of near-surface materials occurred essentially anhydrously, fractionating Cl isotopes in a manner similar to what is seen on the Moon. Because the diffusion rate of H is orders of magnitude faster than for Cl, a moderately hydrated sample could lose its H before losing all Cl, so that initial volatilization of Cl would occur as HCl (*g*), and subsequent volatilization would occur as NaCl (*g*) from an essentially anhydrous silicate. 2) Degassing occurred as HCl (g), as on Earth, and the range of $\delta^{37}Cl$ values is related to contamination of crustal material. In this case, the low values of the least contaminated basalts (LAR 06319) would most likely represent the mantle values for Mars, whereas the higher $\delta^{37}Cl$ values of the nakhlites, NWA 7034, and ALH 84001 would indicate crustal contamination. 3) The range of $\delta^{37}Cl$ values could be due to heterogeneous sources, suggesting that the martian mantle was never completely homogenized.

The shergottites all have $\delta^{37}Cl$ values less than 0‰ (Fig. 2) and generally have elevated water contents (*7*). The high water contents suggest that degassing occurred as HCl (*g*) without isotopic fractionation, consistent with their low $\delta^{37}Cl$ values. The lowest $\delta^{37}Cl$ value was measured in LAR 06319, an "enriched" olivine-phyric shergottites. It is also arguably the most primitive all the shergottites we have thus far analyzed.

However, the samples with high $\delta^{37}Cl$ values have equivalently high water contents. Chassigny also has elevated water contents (*8*) and evidence for interaction with aqueous salts (*9*) and NWA 7034 has the highest water content of any martian meteorite (*10*) and yet has one of the highest $\delta^{37}Cl$ values measured to date. There does not appear to be a strong correlation between the $\delta^{37}Cl$ value and water content.

Contamination from a crustal source may explain the range of $\delta^{37}Cl$ values for martian meteorites. If near-surface volatilization left the partially degassed samples with elevated $\delta^{37}Cl$ values, then incorporation of this material by subsequent intrusions, such as the nakhlites, NWA 7034, and ALH 84001, would result in high $\delta^{37}Cl$ values. The lowest value, found in the olivine-phyric shergotttite LAR 06319, would then represent the unmodified value of the martian mantle. If this is indeed the case, then why Earth and chondrites, which physically bracket Mars in the solar system, have $\delta^{37}Cl$ values of 0‰ is not clear. LAR is an enriched shergottites, and yet has the lowest $\delta^{37}Cl$ values. These results suggest that interaction with crustal material is not a necessary component of the enriched shergottites. Additional work on olivine-phyric shergottites as well as samples that have had interaction with near-surface material may help to better define the range and endmember values for martian materials.

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