

Halogen Content and Cl Isotope Systematics on Mars: From the Atmosphere to the Hydrosphere to the Lithosphere: J. J. Bellucci¹, M.J. Whitehouse¹, T. John², A.A. Nemchin¹, and J. F. Snape, ¹Department of Geosciences, Swedish Museum of Natural History, SE-104 05 Stockholm, Sweden. ²Institut für geologische Wissenschaften, Freie Universität, Berlin, Malteser Str. 74-100, 12249 Berlin, Germany *Corresponding Author's email: jeremy.bellucci@gmail.com

Introduction: The behavior of volatile species on a planetary body is key to understanding the late accretion history, the low temperature/atmospheric surface chemistry, and by inference, the potential for life. Therefore, the abundances of halogens (Cl, F, Br, and I), which are among the most atmo- and hydrophilic elements on a planetary body, in various geochemical reservoirs must be quantified. Halogens are hydrophilic and form ionic complexes in the presence of water, which inextricably links them to the hydrological cycle. Halogen complexes (e.g., salts (NaCl, KCl) or perchlorate (ClO₄-)) have significant effects, both positive and negative, on biological organisms. Specifically, ionic salts are requisite for life on Earth, while more complicated molecules are highly oxidizing and potentially harmful to humans (e.g., perchlorate (ClO₄-)). Therefore, understanding the halogen and any hydrological processes, the possibility of long-term habitability could be addressed.

Mars is enriched in volatiles compared to Earth (e.g., [1]). Additionally, Mars is highly stratified in terms of the concentration of halogens being significantly enriched in the crust when compared to the mantle (e.g., [2]). Recently observations from the surface of Mars have seen daily, transient hydrological activity, in the form of brines, which by definition have high concentrations of salts [3]. The Mars Odyssey Gamma Ray Spectrometer (GRS) has measured the concentration of Cl at the surface of Mars at 5000 µg/g [2]. The incompatibilities of F, Cl, Br, and I are all similar during melting (e.g., [4]). Therefore, the relative concentrations of each element should be similar between the crust and mantle.

An additional piece of geochemical information contained within the halogen group that can yield insights on the interaction of the atmosphere and lithosphere is Cl isotope systematics (measured in $\delta^{37}\text{Cl} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000$, and standard is SMOC (Standard Mean Ocean Chloride) with a defined value of 0.0‰). Cl isotopes do not fractionate significantly in planetary accretion, magmatic processes, or hydrothermal alteration, and are similar between the Earth's mantle, surface, the Moon, and primitive meteorites ($\pm 2\%$, [5-8]). However, during the atmospheric formation of perchlorate on Earth, which is likely the main Cl bearing phase on the Martian surface [9], Cl isotopes experience large fractionations, both positive and negative, in $\delta^{37}\text{Cl}$ and range from -14 to +5‰ [10]. The natural formation of perchlorate on Earth occurs in arid deserts (e.g., the Atacama), a similar environment to the surface of Mars. Since, the budget of the halo-

gens and the Cl isotopic composition of a rock is almost entirely controlled by phosphates, the halogen concentration(s) and Cl isotopic composition(s) in the phosphates of six Martian meteorites, spanning most of the available Martian lithologies have been investigated by Secondary Ion Mass Spectrometry (SIMS) using a Cameca 1280 ion microprobe at the Swedish Museum of Natural History (NORDSIM facility) and by electron microprobe x-ray mapping at the Freie Universität, Berlin following the analytical methods of [11]. The samples investigated here include four basalts, an ultra-mafic cumulate (Tissint, Zagami, LAR12011, RBT04262, and ALH84001), and the only explicitly crustal sample of Mars (NWA7533). Therefore, both the mantle and crustal systematics of the halogens and Cl isotopes on Mars have been investigated and are documented here.

Results and Discussion: The halogen concentrations in the sample set here range several orders of magnitude and range in $\delta^{37}\text{Cl}$ from -5.6 to +2.5‰, the latter being in agreement with Cl isotopic measurements by previous workers (Figure 1, e.g., [12]). It is evident that the most extreme $\delta^{37}\text{Cl}$ compositions, both positive and negative, correlate with increased concentrations in all other halogens. Sample LAR12011 has the largest range in both isotopic composition and halogen concentration. Additionally, electron probe x-ray maps of the phosphates in LAR12011 indicate strong late-stage igneous zoning with the crystal margins being enriched in halogens (Figure 2). The zone of halogen enrichment corresponds with a more extreme $\delta^{37}\text{Cl}$ value. Given the several orders of magnitude enrichment in the surface of Mars in halogens, any mixing between this and a depleted source (i.e., mantle) will result in isotopic overprinting. This late stage zoning is absent from the phosphates in the meteorite Tissint, which has the least extreme $\delta^{37}\text{Cl}$ value of all of the meteorites studied, indicating it has not undergone this process. Therefore, extreme $\delta^{37}\text{Cl}$ values reported here are likely the result of a three stage process whereby the Cl isotopic signature is created in the atmosphere/soil, that Cl is then incorporated into the surface brine(s) and then, along with the other halogens, infiltrated/mixed with primary magmas during crystallization through a process involving isotopic and halogen exchange between the reservoirs via hydrothermal activity and magma contamination. Sample NWA7533 is the only crustal sample available for study and is a regolith breccia with clasts that are at least 4.428 Ga [13]. Phosphates within these clasts display relatively constant halogen and Cl isotopic compositions ($\delta^{37}\text{Cl}$

~+2‰). Matrix phosphates have a significantly larger range in both halogen concentration and Cl isotopic compositions ($\delta^{37}\text{Cl}$ from +1.4 to +2.5‰). X-ray maps of clast phosphates indicate some zoning in F and Cl. NWA7533 has a history of hydrothermal alteration, as seen in hydrothermal sulfides [14]. The range observed in $\delta^{37}\text{Cl}$ is therefore, likely associated with hydrothermal overprinting. Lastly, this isotopic and concentration data would have been lost during traditional analyses and this study highlights the need for more *in situ* investigations of stable isotopes in Martian meteorites.

Conclusions: The extreme heterogeneity and Cl isotopic compositions measured in igneous rocks here are most likely caused by late stage mixing with a surface reservoir(s), likely brines/surficial water, with an extreme Cl composition(s). Similarly, the heterogeneity observed in the only crustal sample examined here (NWA7533) likely reflects heterogeneous mixing during hydrothermal processes that have been previously documented for this meteorite. These extreme $\delta^{37}\text{Cl}$ compositions are a likely a result of perchlorate formation in the Martian atmosphere, which, on Earth, creates a similar spread in Cl isotopic compositions both in positive and negative $\delta^{37}\text{Cl}$. Therefore, any Martian samples that have interacted with the surface of Mars (i.e., Martian meteorites) cannot be used to confidently determine the bulk or initial Cl isotopic composition of Mars directly. However, the least extreme Cl isotopic composition ($\delta^{37}\text{Cl} \sim 0\text{‰}$) is observed in Tissint, which is not enriched in other halogens and does not display Cl or F zoning in x-ray maps. This least extreme mixing end member (in $\delta^{37}\text{Cl}$) is assumed to represent the Martian mantle and is therefore very likely chondritic, which is similar to the Earth and Moon. The Cl isotopic compositions are distinct among petrological types, which is more likely a reflection of their eruption in different surface localities on Mars and interaction with local brines. Since the Cl-isotopic compositions are likely a reflection of local halogen and Cl-isotopic reservoirs, a stable isotopic reservoir inventory can be constructed of different surface localities and mixing end-members (brines/surface water). These data should be used in conjunction with other stable isotopic systematics (e.g., O, S, and Fe) to access the full breadth of atmospheric, hydrologic/hydrothermal, and potentially biotic processes taking place on Mars and recorded in Martian meteorites.

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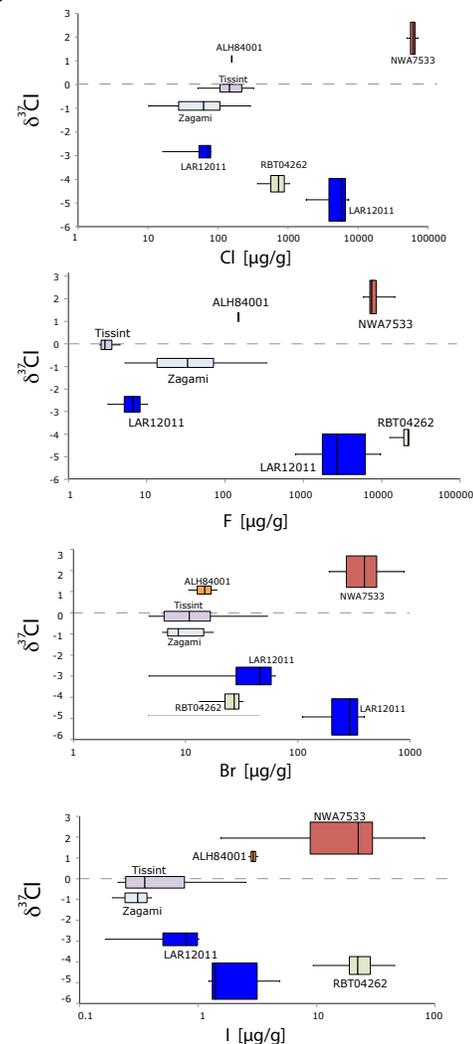


Figure 1. $\delta^{37}\text{Cl}$ vs. halogen concentrations in $\mu\text{g/g}$ in phosphates from the Martian samples studied here.

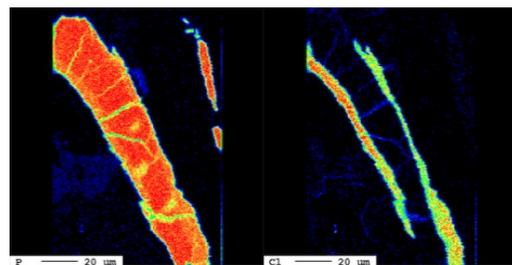


Figure 2. P and Cl x-ray maps of a phosphate in LAR12011 indicating strong zoning of Cl concentrations. The enriched zone has the most extreme $- \delta^{37}\text{Cl}$ measured in any Martian meteorite to date.