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Halogen and Cl isotopic systematics in Martian phosphates: Implications for the Cl cycle and surface halogen reservoirs on Mars

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ABSTRACT

The Cl isotopic compositions and halogen (Cl, F, Br, and I) abundances in phosphates from eight Martian meteorites, spanning most rock types and ages currently available, have been measured *in situ* by Secondary Ion Mass Spectrometry (SIMS). Likewise, the distribution of halogens has been documented by x-ray mapping. Halogen concentrations range over several orders of magnitude up to some of the largest concentrations yet measured in Martian samples or on the Martian surface, and the inter-element ratios are highly variable. Similarly, Cl isotope compositions exhibit a larger range than all pristine terrestrial igneous rocks. Phosphates in ancient (>4 Ga) meteorites (orthopyroxenite ALH 84001 and breccia NWA 7533) have positive δ^{37}Cl anomalies (+1.1 to +2.5‰). These samples also exhibit explicit whole rock and grain scale evidence for hydrothermal or aqueous activity. In contrast, the phosphates in the younger basaltic Shergottite meteorites (<600 Ma) have negative δ^{37}Cl anomalies (−0.2 to −5.6‰). Phosphates with the largest negative δ^{37}Cl anomalies display zonation in which the rims of the grains are enriched in all halogens and have significantly more negative δ^{37}Cl anomalies suggestive of interaction with the surface of Mars during the latest stages of basalt crystallization. The phosphates with no textural, major element, or halogen enrichment evidence for mixing with this surface reservoir have an average δ^{37}Cl of −0.6‰, supporting a similar initial Cl isotope composition for Mars, the Earth, and the Moon. Oxidation and reduction of chlorine are the only processes known to strongly fractionate Cl isotopes, both positively and negatively, and perchlorate has been detected in weight percent concentrations on the Martian surface. The age range and obvious mixing history of the phosphates studied here suggest perchlorate formation and halogen cycling via brines, which have been documented on the Martian surface, has been active throughout Martian history.

1. Introduction

The behavior of volatile species on a planetary body is key to understanding its late accretionary history, low-temperature atmospheric/surface chemistry, and by inference, potential for life. The halogens (Cl, F, Br, and I) are amongst the most hydrophilic elements on a planetary body and, as such, quantification of their abundances in, and transfer between, various geochemical reservoirs has great potential as a tracer of surface processes. Specifically, halogens form ionic complexes in the presence of water, which inextricably links them to the hydrological cycle. Halogen complexes (e.g., halide salts (NaCl, KCl) or perchlorate (ClO_4^-) compounds) have significant effects, both positive and potentially negative, on biology (e.g., Srinivasan and Viraraghavan, 2009). Additionally, perchlorate can serve as an energy source for anaerobic reduction in microorganisms (Coates and Achenbach, 2004).

Halogens are in the same periodic group and are strongly incompatible during mantle melting but may show some overall dependence on pressure–temperature conditions (Joachim et al., 2015; Kendrick et al., 2012; Saal et al., 2002). Additionally, oxidized species of halogens (e.g., perchlorate and iodate) occur together on Earth in arid environments, providing further evidence for similar geochemical behavior in variable oxidation states (Lybrand et al., 2016). Together with abundances of the halogens, the Cl isotopic system yields important insights into the interactions between surficial, low-temperature reservoirs because Cl isotopes do not fractionate significantly in planetary accretion, magmatic processes, or hydrothermal alteration (Chiaradia et al., 2014;

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John et al., 2010; Kusebauch et al., 2015a; Selverstone and Sharp, 2011; Sharp et al., 2007, 2010, 2013). This has resulted in a similar Cl isotope composition between the Earth's mantle, its crust, the Moon, and primitive meteorites (Kusebauch et al., 2015a; John et al., 2010; Sharp et al., 2007, 2010, 2013). Phosphate minerals (e.g., apatite, merrillite) are ubiquitous in igneous rocks across a wide range of whole rock compositions and are extremely sensitive to post-crystallization fluid-driven alteration and/or metamorphic processes (Engvik et al., 2009; Kusebauch et al., 2015a). Since they control the majority of the halogen budget and the Cl isotopic composition of an igneous rock or meteorite (e.g., Roszjar et al., 2011), they provide an unparalleled tracer of processes affecting these elements, as well as being amenable to high spatial resolution *in situ* investigation on a sub-mineral grain scale.

Mars is enriched in halogens compared to Earth (Sharp and Draper, 2013) and highly stratified, with orders of magnitude higher abundances of halogens in the crust relative to the mantle (Filiberto et al., 2016; Hecht et al., 2009; Keller et al., 2006; McCubbin et al., 2016). Significant progress has been made in understanding the surface halogen and chloride chemistry of the surface of Mars via orbiters and landers (e.g., Farley et al., 2016; Hecht et al., 2009; Keller et al., 2006; Martin-Torres et al., 2015), but how the hydrosphere and atmosphere of Mars interact with the lithosphere remains ambiguous. The only samples currently available to directly study these interactions on Mars are Martian meteorites. Martian meteorites are currently categorized into six groups: Shergottites, an augite-basalt (NWA 8159), Chassignites, Nakhlites, an orthopyroxenite ALH 84001, and NWA 7533 and its pairs (e.g., Agee et al., 2013, 2014; Humayun et al., 2013; Mittlefehldt, 1994; Nyquist et al., 2001 and references therein). Shergottites are the most widely available, classified into basaltic and lherzolitic types (e.g., Nyquist et al., 2001) and further subdivided, on the basis of light rare earth element concentrations and radiogenic isotope compositions, into a spectrum from depleted, through intermediate, to enriched varieties (e.g., Borg et al., 2005; Brennecka et al., 2014). The enriched Shergottites generally have a younger age (∼170 Ma) than the depleted Shergottites (∼300–580 Ma) (e.g., Borg et al., 2005; Brennecka et al., 2014).

Phosphates in some Martian meteorites are explicitly not in igneous equilibrium with their host rocks, having widely varying compositions on a sub-grain scale, complex inner structures, and a chemistry that strongly indicates interaction with the Martian crust or a Cl-rich crustal fluid (Howarth et al., 2016; McCubbin et al., 2016; Shearer et al., 2015). In order to investigate and try to constrain the halogen and chlorine cycle on Mars, the halogen concentrations and Cl isotopic composition of the phosphates of eight Martian meteorites, spanning most of the available Martian lithologies, have been investigated here by Secondary Ion Mass Spectrometry (SIMS) and by electron microprobe x-ray mapping. The samples investigated in this study include six Shergottites (4 enriched, 2 depleted), the ultramafic cumulate (ALH 84001), and the only explicitly crustal sample from Mars (NWA 7533). Two additional Shergottites, Nakhla, and two sections of Chassigny were also surveyed but yielded no suitable targets. This sample set, containing two ancient samples (>4 Ga) that are most likely derived from the Southern Hemisphere and six young (<600 Ma) samples that are suggested to originate from the Northern Hemisphere, based on crystallization ages and impact crater densities (e.g., Nyquist et al., 2001), therefore allows the investigation of the halogen and Cl isotopic cycle on Mars from different reservoirs, surface locations, and times.

1.1. *Martian phosphates*

Northwest Africa (NWA) 7533 is identified as a regolith breccia (Agee et al., 2013; Humayun et al., 2013). NWA 7533 has evolved clasts that contain zircon and phosphates with U–Pb ages of 4.42 Ga and 1.35 Ga, respectively (Bellucci et al., 2015a; Humayun et al., 2013). As a regolith breccia, there is likely to be a difference between clast- and matrix-hosted apatites, the former linked to formation at 4.42 Ga while the latter can, in principle, have crystallized originally or could have been modified at any time between 4.42 Ga and 1.35 Ga (Bellucci et al., 2015a). The presence of sulfides in cracks is a critical observation (Lorrand et al., 2015) that points to likely hydrothermal activity during amalgamation of the breccia at 1.35 Ga. Additionally, a single merrillite grain in a pair of NWA 7533 shows replacement by Cl-rich apatite indicating interactions with Cl-rich fluids (Shearer et al., 2015).

Allan Hills (ALH) 84001 is a coarse-grained orthopyroxenite. ALH 84001 has a crystallization age of 4091 ± 30 Ma determined by ^{176}Lu–^{176}Hf (2σ, Lapen et al., 2010). ALH 84001 has experienced post-crystallization aqueous alteration that precipitated carbonates at 3900 ± 40 to 4040 ± 100 Ma based on Rb–Sr and Pb–Pb isochrons, respectively (Borg et al., 1999). The analyzed phosphate in ALH84001 was apatite.

The Shergottites studied here encompass both the enriched and depleted varieties. The enriched Shergottites analyzed in this study are Roberts Massif (RBT) 04262, Larkman Nunatuk (LAR) 12011, NWA 4864, and Zagami, with the depleted Shergottites represented by Tissint and Sayh al Uhamymir (SaU) 005. The crystallization ages of these samples are all <600 Ma (e.g., Bellucci et al., 2015b; Brennecka et al., 2014; Borg et al., 2005; Lapen et al., 2010; Shafer et al., 2010, Table 1). Based on previous literature, the apatites and merrillites in RBT 04262 and LAR 12011 are explicitly not in equilibrium with the host rock, are zoned in F, Cl, and OH$^-$ and likely have interacted with Cl-rich fluids on the Martian surface, while Zagami has apatite in equilibrium with the whole rock and has been used to calculate a magmatic water content (Howarth et al., 2016; McCubbin et al., 2016). Published information is unavailable for the rest of the analyzed Shergottites.

2. Analytical methods

Halogen concentrations (Cl, F, Br, and I) and stable Cl isotopic compositions (reported as δ^{37}Cl, where $\delta^{37}\text{Cl} = [(^{37}\text{Cl}/^{35}\text{Cl})_{sample}/(^{37}\text{Cl}/^{35}\text{Cl})_{standard} - 1]*1000$, expressed relative to Standard Mean Ocean Chloride with a defined value of 0.0‰; Kaufmann et al., 1984) were measured using a CAMECA IMS1280 large-geometry secondary ion mass spectrometer at the NordSIMS facility, Swedish Museum of Natural History. The procedures used here closely follow those of Kusebauch et al., 2015b, 2015c and Marks et al., 2012. Samples (polished thin sections or epoxy-mounted, polished rock chips) were first cleaned using ethanol and distilled water and then coated with 30 nm of Au. Prior to spot analyses, the analytical positions were sputtered for 120 s over a 25 × 25 μm raster area to remove the Au coating and any remaining surface contamination. For both concentration and isotope analysis, secondary ions of halogens species were sputtered from the surface using a ∼15 μm, ∼2 nA Cs$^+$ Gaussian focused, raster- (10 μm) homogenized primary beam with an impact energy of 20 kV. An low-energy, normal-incidence electron beam was used in conjunction with the primary Cs$^+$ beam to counteract any charging effects on the surface of the sample. Secondary ions were centered in a 2500 μm field aperture, which provides a ca. 30 μm field of view on the sample that is smaller than the combined spot and pre-sputter area, thus precluding admission of surface contaminant halogens to the mass spectrometer. For halogen concentration measurements, secondary ions were filtered at high mass resolution ($M/\Delta M = 5000$) and species of ^{19}F$^-$, ^{37}Cl$^-$, ^{127}I$^-$, and a matrix peak of ^{40}Ca^{31}P$^-$ were then measured in either an electron multiplier (<10^6 cps) or Faraday cup (>10^6 cps) in mono-collection mode using a peak hopping routine. Measurement of

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