Halogen and Cl isotope compositions of Martian phosphates: Implications for surface chemistry and bulk Mars

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The Cl isotopic compositions and halogen (Cl, F, Br, and I) abundances in phosphates from eight and ten Martian meteorites, respectively, have been measured *in situ* by Secondary Ion Mass Spectrometry (SIMS). The sample set here spans most rock types and ages currently available for Mars. Additionally, the distribution of halogens has been documented by x-ray mapping. X-ray maps illustrate intercrystalline zoning that cannot have been magmatically produced and agrees with previous studies suggesting that Martian phosphates record interactions with surface brines. Halogen concentrations range over several orders of magnitude, including some of the highest 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 pronounced negative δ^{37}Cl anomalies suggestive of interaction with fluids from 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 Cl isotope composition for Mars, the Earth, and the Moon. Oxidation and reduction of chlorine to and from perchlorate is the only process known to strongly fractionate Cl isotopes, both positively and negatively. The age range and obvious mixing history of the phosphates studied here suggest perchlorate formation, via oxidation reactions, and halogen cycling in brines have been active throughout Martian history and are confirmed by current surface observations.