Tracing martian surface interactions with the triple O isotopic composition of meteoritic phosphates

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Introduction: There is ample evidence that Mars once had an ocean and thus, the possibility to sustain life. As such, it is critical to quantify the interactions between the lithosphere and hydrosphere on Mars. Martian meteorites are the only direct samples of Mars available for isotope analyses on Earth. While most of these rocks are igneous in origin and, thus, are expected to have stable isotope systematics in equilibrium with the martian mantle, some of these samples have minerals which have interacted with the surface and have recorded evidence of these interactions (e.g., [1]). Oxygen, in particular, is a useful isotopic tracer of interactions between some minerals, the atmosphere and the hydrosphere. Specifically, photochemical reactions in the atmosphere result in large, measurable mass independent oxygen isotope fractionations that are recorded in alteration products, reset minerals, or minerals that formed while interacting with surface water [2-3].

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 zoning that strongly indicates interaction with the martian crust or a Cl-rich crustal fluid [4,5]. Some of these phosphates have halogen elemental ratios nearly identical to those in the alteration products measured in the nakhlites and those measured at Meridiani rocks by the Opportunity lander [4]. Samples that do not have zoned phosphate crystals or halogen enrichments, have a $\delta^{37}\text{Cl}$ within uncertainty of the Earth, the Moon, and chondritic materials [4]. Thus, the origin of the variable halogen ratios and $\delta^{37}\text{Cl}$ have been attributed to oxidized, halogen-rich species, specifically perchlorate, on the martian surface [4].

Perchlorate formation on Earth fractionates Cl isotopes both positively and negatively in $\delta^{37}\text{Cl}$ (resulting in values ranging from -14 to +5%), and generates positive $\Delta^{17}\text{O}$ values of between +4 to +10% [6]. Natural perchlorate occurs on the Earth in arid deserts (e.g., the Atacama), similar to the martian surface, and forms through photochemical reactions in the upper atmosphere [6]. The formation processes of perchlorate are not well understood on Earth or on Mars. However, perchlorate has been measured at several landing sites on Mars. The ratio of ClO$_4^-$/Cl was measured as 4.4 in at least one surface location suggesting the oxidized Cl species is the most prevalent [7]. Further, the Cl isotope composition of the martian surface has been measured in situ in four locations and has a $\delta^{37}\text{Cl}$ value ranging from -51 to -1% [8]. On Earth, there are covariations in $\delta^{37}\text{Cl}$ and $\Delta^{17}\text{O}$ in perchlorate [6]. As some martian phosphates show textural and chemical evidence (including halogen ratios, and Cl isotope compositions) for exchange reactions with the martian hydrosphere while others are in equilibrium with the bulk sample, the goal for this study is to further investigate these phosphates via their triple O isotope compositions using Secondary Ion Mass Spectrometry (SIMS). Here we will present the triple isotope composition of phosphates from three enriched shergottites (Zagami, RBT 04262 and LAR 12011), one depleted shergottite (Tissint), an orthopyroxenite (ALH 84001), and a regolith breccia (NWA 7533). These compositions will be used to provide further constraints on the interactions with the martian surface recorded by these minerals and define the O-isotope composition of the oxidized surface of Mars (Figure 1).

Figure 1. $\Delta^{17}\text{O}$ vs. $\delta^{37}\text{Cl}$ weighted averages for phosphates measured by SIMS in individual martian meteorites and individual phosphates from NWA 7533. $\delta^{37}\text{Cl}$ values for all meteorites presented here and the assumed martian mantle value for $\delta^{37}\text{Cl}$ are from [4].

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