PATHWAYS OF SULFUR OXIDATION IN VOLCANIC SETTINGS – HOW UNANSWERED QUESTIONS ABOUT SULFATE ORIGIN ON MARS CAN BE ADDRESSED.

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Introduction: The excess of sulfur (S) relative to other elements expected from the weathering of Martian basalt in the rover landing sites has led to the conclusion that volcanic processes were the most important in S enrichment of the Martian regolith in equatorial regions [1-2]. In these models, S degassing and acid fog/rain weathering are believed to have been the key processes responsible for creating widespread acidic conditions on the surface. However, various Mg-, Na-, and Ca-sulfates detected on steep slopes and valley floors of Valles Marineris, on polar dunes of Olympia Undae, at the Phoenix landing site, and as sulfate-rich veins in Meridiani and Gale Crater [3] may represent more near-neutral pH conditions, thus, influenced less by volcanic activity and more by chemical weathering of bedrock.

Recent studies by our group have shown that stepwise oxidation of emitted H_2S by ferric iron (Fe^{3+}) and possibly other metals occurs in hydrothermal systems comprised of acidic hot springs and mud pots. This process leads to preferential formation of elemental S and sulfide minerals in the hot spring and mud pot sediments [4], which are later oxidized to sulfate (SO_4^{2-}) [5]. However, it is difficult to quantify the amount of SO_4^{2-} formed from Fe^{3+}-driven oxidation compared to O_2-driven oxidation, likely due to spatial variation caused by the heterogeneous and localized occurrences of H_2S emission, rapidly changing hydrological conditions, and ephemeral nature of the hot springs and mud pots in surface hydrothermal environments. Fe^{3+}-driven oxidation of hydrothermal sediments is proposed to be more dominant in closer proximity to acidic hot springs and mud pots because of higher Fe solubility in lower pH [5]. Conversely, the O_2-driven oxidation might be more important in cooler ephemeral drainages and stream networks further away from the main hydrothermal vents. Also, minor amounts of sulfate may be formed from direct H_2S oxidation by atmospheric O_2 at the water-air interface [4].

Goals & Significance for Mars: Further understanding and quantification of the oxidation pathways of hydrothermal S in modern volcanic systems on Earth is important because it can help better constraining hydrological and climatic conditions on early Mars (~3 billion years) when liquid water was still active on its surface. Sulfate minerals are abundant on the Martian surface and are believed to be associated with past volcanic emissions and oxidation of S-rich gases on the surface [1-3]. Because Mars has likely never had an O_2-rich atmosphere, understanding the role of metals such as Fe in the oxidation of volcanic/hydrothermal S is of great importance [4,5].

Field and experimental studies show that oxygen isotopes ($\delta^{18}O$) can be used to trace the mechanism of S oxidation to SO_4^{2-} because of large differences in $\delta^{18}O$ between atmospheric O_2 and water oxygen [6]. Further, distinctive O isotope fractionations occur between SO_4^{2-} and the oxygen source (O_2, water) during sulfur oxidation [7].

The main goal of this study was, therefore, to use the $\delta^{18}O$ of SO_4^{2-} forming in acidic hot springs and mud pots to estimate the quantities of SO_4^{2-} from oxidation of hydrothermal S via Fe^{3+} and O_2 pathways. Four different Mars analog environments were sampled: Iceland, Lassen, Valles Caldera, and Yellowstone in order to better quantify the amounts of hydrothermal SO_4^{2-} from these two oxidation pathways under different climatic conditions.

Results & Discussion: In the studied field sites, the oxidation process of hydrothermal S is accompanied by changes in the O isotopic composition of water (-15.5 to +6.3 ‰) related to evaporation and inflow of meteoric water, leading to a wide variation of $\delta^{18}O$ in the newly forming hydrothermal SO_4^{2-} (-8.8 to +5.5 ‰). Additionally, we recognize that the distinctive high $\delta^{18}O$ values (up to +13.7 ‰) likely accompany formation of SO_4^{2-} via direct oxidation of H_2S and/or hydrothermal S (e.g., elemental S, sulfide) by atmospheric O_2 in dry fumarolic environments.

The measured $\delta^{18}O$ of SO_4^{2-} for the acidic hot springs and mud pots from Iceland, Lassen, Valles Caldera and Yellowstone suggest that Fe^{3+}-driven oxidation of hydrothermal S appears to be important source of SO_4^{2-}. This process appears to contribute ~55 to 100 % of SO_4^{2-} when compared to contributions from O_2-driven oxidation and is more prevalent under wet conditions. Notably, the highest SO_4^{2-} contributions from Fe^{3+}-oxidation (~80-100%) were during wet conditions (e.g., snowmelt in Lassen; rain in Yellowstone and Iceland). These new estimates are in agreement with previous stoichiometric comparisons by [4] showing that under the measured elevated temperatures at the time of sampling there was significantly more Fe than O_2 available to form the measured SO_4^{2-} in the studied locations.

Addressing unanswered questions for Mars:

Recognizing complex S oxidation pathways during volcanic activity in the presence of water - Our new quantitative measures of oxidation pathways signify the importance of Fe^{3+}-driven oxidation of hydrothermal S to SO_4^{2-} in the surface volcanic settings under rapid changes of shallow hydrological conditions and seasonal climate fluctuations. This is significant given that Mars never had O_2-rich atmosphere and abundant hydrosphere but is enriched in sulfate minerals, often accompanied by elevated Fe in the sediments [1]. In volcanic rocks, iron is mainly present as Fe^{2+} in the mafic minerals such as pyroxene, olivine and magnetite. Therefore, there has to be exposure to atmospheric O_2 over some period of time in order to oxidize Fe^{2+} to Fe^{3+} on Earth. Conversely, the photochemical processes might have dominated oxidation of Fe^{2+} to Fe^{3+} on the martian surface and enhanced oxidation of hydrothermal S to SO_4^{2-} [4,5]. This is supported by experimental studies showing that UV photo-oxidation of Fe^{2+} to Fe^{3+} is efficient and could have occurred on short-time scales on Mars, particularly in dry or shallow aqueous systems [8].

Revising concept of mineralogical eras - The Fe^{3+}-driven oxidation model for acidic hydrothermal settings offers invaluable insight into the formation of sulfate-rich deposits under low water-to-rock ratios controlled by intermittent hydrological and climate conditions in volcanic settings on Earth. It is expected that similar processes were also common on early Mars when liquid water and volcanism were still active on its surface. Current geochemical models use the concept of mineralogical eras [9] to explain aqueous alterations of the martian surface. For instance, clay minerals are believed to be mainly formed as a result of moderately wet conditions during the Noachian period (~4.1 to 3.8 Ga). In contrast, sulfate formation primarily occurred during the drier Hesperian period (~3.8 to 3.0 Ga) with increased volcanic activity accompanied by S degassing that led to atmospheric (acid rain) deposition of sulfate in the form of sulfuric acid [1,2]. The latter would have involved chemical weathering and later deposition of sulfate-rich sediments during the transition to a drier climate in the end of Hesperian. However, if the model of step-wise oxidation of $H_2S \rightarrow$ elemental S/sulfide $\rightarrow SO_4^{2-}$ by Fe^{3+} is considered [4,5], the previous suggestions for the role of S degassing and atmospheric deposition of SO_4^{2-} on Mars might be greatly overestimated. This is because significant portions of the emitted S would have been initially trapped in surface hydrothermal deposits as elemental S and sulfide and then subsequently oxidized to SO_4^{2-}. Therefore, there is a need to revise previous geochemical models for Mars. For example, it would be crucial to address whether the formation of Noachian clays and Hesperian sulfates could be viewed as a result of secondary aqueous alteration products occurring on terrains with bedrock depleted and enriched, respectively, in hydrothermal S minerals. When addressed, this would allow for better characterization of hydrological and climatic conditions on early Mars.

New approach to address S excess in sediments - In-situ measurements carried out by rovers often point to the "excess" of S in martian sediments [1-3]. Some of this uncertainty might stem from our inability to directly measure mineralogical composition, the presence of amorphous materials, and/or inaccuracy of geochemical models used in interpretation of bulk elemental analysis on Mars [5]. However, the presence of hydrothermal elemental S and/or S intermediates from its subsequent oxidation could be an alternative explanation for S excess in surface deposits, given the history of widespread volcanism on Mars. Our previous experimental study suggests that oxidation of elemental S by Fe^{3+} is less efficient than by O_2, particularly at low temperatures [5]. Therefore, more elemental S of hydrothermal origin (e.g., S excess) could be expected in the surface sediments under cold and O_2-depleted martian conditions. Accordingly, it was suggested that elemental S might be still present and account for the S excess measured in some of the Gusev sediments [10]. Additionally, the S excess could be related to the presence of amorphous S intermediates (e.g., sulfites, thiosulfates) formed through slow and incomplete oxidation of hydrothermal elemental S to more oxidized S phases under relatively dry conditions on the martian surface. The latter is consistent with in situ detections of amorphous sulfites by the SAM instrument on the Curiosity rover in Gale crater [11].

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