CHEMICAL AND SPECTRAL PROPERTIES OF SULFATES PRODUCED BY MAGMATIC GAS/MINERAL SURFACE REACTION ON MARS

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Introduction: Much of our understanding of the composition and properties of the Martian surface has been gained through orbital and in situ observations in the IR-range of the electromagnetic spectrum. These remote observations have determined that the crust of Mars is composed primarily of basalt [1]; it has been shaped largely by volcanic processes throughout much of its recent history [2]; and the planet’s surface is enriched in S and Cl [3]. On Mars, it is likely that recent (Amazonian) volcanism would have been relatively dry compared to more water-rich terrestrial magmas, with elevated (S+Cl)/OH ratios [4], possibly reflecting the dehydration of the Martian mantle over time. Since magmatic gas from water-poor magma can transport a significant amount of iron and alkalis [5], martian gas may have had a significantly different degree of reactivity with surface materials and produced a different suite of alteration minerals than seen in terrestrial fumerolic environments. Understanding the products of these reactions and how these products modify the observed spectral signature of common surface constituents are the focus of this study.

Methods: We conducted experiments to simulate interaction between magmatic gas and minerals on the martian surface by placing a gas source (glass of Irvine composition supersaturated with volatiles) at the bottom of a long silica glass tube, drawing a capillary in the tube, and placing a mineral chunk (target) separated from the tube by Pt wire above the capillary before evacuating and sealing the tube (Fig 1). The tube was suspended in a vertical furnace in a strong calibrated thermal gradient such that the source was at a temperature of ~1200 °C, and the target mineral was at a known temperature between 300° and 800° C. The experiment was kept at elevated temperature for 12-24 hours, allowing the source to melt and degas, and the vapor to interact with the target mineral. The source magma was produced using several powdered oxides, silicates and iron metal to match the composition of the Martian Rock Irvine, as analyzed by MER Spirit [6]. Chunks of Mars analog minerals (olivine, plagioclase and pyroxene), approximately 0.5cm in diameter were used to simulate the Martian crust. A detailed description of the experimental methods is described in [7].

IR spectroscopy. Each of the target minerals was analyzed by TIR and VNIR prior to and following exposure to magmatic vapor. TIR spectra were acquired in the range of 100-2000 cm⁻¹ using a Thermo Fisher Nicolet 6700 FTIR spectrometer. VNIR spectra were acquired in the range of 350 to 2500 nm with bidirectional reflectance spectra collected using an ASD FieldSpec3 Max spectrometer. To mitigate any hydration or alteration of phases deposited on target minerals following degassing experiments, the VNIR measurements were taken from inside an atmosphere-purged bag filled with N₂ gas. After the second set of spectra were acquired, samples were analyzed using SEM/EDS to determine the mineralogy of phases forming on the target mineral surfaces. This allowed for the comparison of the actual mineralogy of these coatings to the mineralogy determined by a least squares regression of the IR spectra dataset.

Results: Following the experiments, all target minerals appeared to have been discontinuously encrusted with vapor deposits and the products of gas/mineral surface interactions. SEM/EDS analysis of the targets found them to be coated with an abundance of sulfates, chlorides, and silica. Thin coatings of elemental S were also noted in several experiments. As sulfates were not found in the vapor deposits of our previous experiments [8], these were likely formed by the interaction of SO₂ in the gas with the mineral surfaces through migration of cations to the surface from the mineral interior. This is also in keeping with the native S and silica seen on the surface [9].
As anticipated, sulfate chemistry was largely dependent on the mineralogy and temperature of the target. For example, Ca-sulfate formed on augite and plagioclase targets and magnesium sulfate on olivine. Notably, these sulfates were absent on targets that were held at 700°C. In addition, examples of Fe-K sulfates, with morphology similar to jarosite as reported by other workers [10] was identified (Fig. 2).

Substantial changes to the spectra of the target minerals were observed, with development of features consistent with the mineralogy of the vapor-deposited and alteration phases determined by SEM/EDS, despite very small abundances. Oriented olivine (peridot) and plagioclase grains also showed noticeable differences in their spectra, demonstrating that these changes are caused by deposition of vapor deposits and surface interaction and not simply because of changes in grain orientation.

Changes were noted in both the VNIR and TIR spectra of target minerals. All VNIR spectra collected showed at least some darkening, with many examples showing a blue slope, characteristic of small particle coatings. Spectra of several target minerals show increased depth of the 1.9 μm band consistent with the presence of a sulfate phase (Fig. 3). The olivine shows a slightly weakened 1 μm, ferrous iron band, consistent with masking of the underlying olivine by some spectrally neutral material in that region.

TIR spectra of all grains showed changes following interaction with the gas, while most preserved the overall shape of the spectra. Oriented grains (Fig 4.) showed the most substantive changes in the 800-1200 cm\(^{-1}\) range; the plagioclase grain shows shallowed spectral contrast, and the olivine shows spectral shape changes consistent with transmission through a thin coating. Linear least-square deconvolutions of the spectral data show that sulfate signatures can be resolved for some experiments, although it appears that their detection is inconsistent.

**Summary:** Our experiments show that sulfates can be produced on silicate grains by interaction of low-OH S- and Cl-bearing magmatic gas with mineral surfaces. Our previous results on degassing experiments [8] indicated that the fO\(_2\) decreases with dropping temperature along the tube although it is not buffered; therefore, sulfate formation on the mineral surfaces likely involves SO\(_2\) reaction and formation of the reduced S seen on the surfaces. IR data from this study show that it is a useful tool for detecting mineralogy of minor coatings. Even small quantities of sulfates can make appreciable changes to VNIR and TIR spectra.


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