Mid-infrared emission spectroscopy and visible/near-infrared reflectance spectroscopy of Fe-sulfate minerals†

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ABSTRACT

Sulfate minerals are important indicators for aqueous geochemical environments. The geology and mineralogy of Mars have been studied through the use of various remote-sensing techniques, including thermal (mid-infrared) emission and visible/near-infrared reflectance spectroscopies. Spectral analyses of spacecraft data (from orbital and landed missions) using these techniques have indicated the presence of sulfate minerals on Mars, including Fe-rich sulfates on the iron-rich planet. Each individual Fe-sulfate mineral can be used to constrain bulk chemistry and lends more information about the specific formation environment (e.g., Fe2+ sulfates are typically more water soluble than Fe3+ sulfates and their presence would imply a water-limited (and lower Eh) environment; Fe3+ sulfates form over a range of hydration levels and indicate further oxidation (biological or abiological) and increased acidification). To enable better interpretation of past and future terrestrial or planetary data sets, with respect to the Fe-sulfates, we present a comprehensive collection of mid-infrared thermal emission (2000 to 220 cm−1; 5–45 μm) and visible/near-infrared (0.35–5 μm) spectra of 21 different ferrous- and ferric-iron sulfate minerals. Mid-infrared vibrational modes (for SO42−, OH, H2O) are assigned to each thermal emissivity spectrum, and the electronic excitation and transfer bands and vibrational OH, H2O, and SO4 overtone and combination bands are assigned to the visible/near-infrared reflectance spectra. Presentation and characterization of these Fe-sulfate thermal emission and visible/near-infrared reflectance spectra will enable the specific chemical environments to be determined when individual Fe-sulfate minerals are identified.

Keywords: Mid-infrared, visible, near-infrared, spectroscopy, emissivity, reflectivity, sulfate, spectra, reflectance, vibrational, iron, emission, reflectance

INTRODUCTION

The 370–390 sulfate-mineral species (Hawthorne et al. 2000; Athenia Mineralogy at http://athena.unige.ch/athena/mineral/mnppc6.html, archived by WebCite at http://www.webcitation.org/6TTPwVErk) are indicators of aqueous environments, and can form over a broad range of geochemical conditions. Through evaluation of the chemical formulas of these numerous sulfate species, we determined that ~25% of known sulfate minerals are Fe-bearing (Fe2+, Fe3+). Fe2+ sulfate minerals tend to form in acidic environments at a range of temperatures, through precipitation due to evaporation of concentrated sulfuric acid solutions (e.g., H2SO4) such as may occur in volcanic hydrothermal/fumarolic/aerosol or acid mine drainage environments; conversely, many Fe3+ sulfates form at higher pH, in neutral to alkaline hydrothermal environments. Fe-bearing sulfates occur not only on Earth, but there is strong evidence for Fe-bearing sulfates occurring on Mars as well (e.g., Burns 1987). Fe3+ sulfates that form in a less oxidizing environment have been identified on Mars, and there is a great likelihood that szomolnokite (and/or other Fe3+ sulfates) (Bishop et al. 2009; Weitz et al. 2012) would be widespread because the martian environment is enriched in iron and sulfur (specifically dominated by Fe2+-bearing primary igneous minerals and sulfate). There is visible/near-infrared (VNIR) spectral evidence for a broad distribution of the similarly structured mono-hydrated sulfate species, kieserite, which is in solid solution with szomolnokite (e.g., Arvidson et al. 2005; Gendrin et al. 2005; Bishop et al. 2009; Murchie et al. 2009; Roach et al. 2009). Fe3+ sulfates also have been identified on Mars as jarosite in the Ca-,Mg-sulfate outcrops in Terra Meridiani using Mössbauer spectroscopy (Klingelhofer et

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