

**DETECTION OF JAROSITE AND ALUNITE WITH HYPERSPECTRAL IMAGING: PROSPECTS FOR DETERMINING THEIR ORIGIN ON MARS USING ORBITAL SENSORS.** G. A. Swayze<sup>1</sup>, G. A. Desborough<sup>1</sup>, R. N. Clark<sup>1</sup>, R. O. Rye<sup>2</sup>, R. E. Stoffregen<sup>3</sup>, K. S. Smith<sup>1</sup>, and H. A. Lowers<sup>1</sup>, <sup>1</sup> U.S. Geological Survey, MS964, Box 25046 DFC, Denver, CO 80225, [gswayze@usgs.gov](mailto:gswayze@usgs.gov), <sup>2</sup> U.S. Geological Survey, MS963, Box 25046 DFC, Denver, CO 80225, <sup>3</sup> AWK Consulting Engineers, Inc., 10 Duff Rd., Suite 304, Pittsburgh, PA, 15218.

Recent identification of jarosite at Meridiani Planum [1] has generated intense interest because its mode of formation may constrain past conditions on the planet. The small footprint (18 m) of the Mars Reconnaissance Orbiter CRISM spectrometer may allow recognition and mapping of jarosite and other sulfate minerals from orbit in the coming months on a planetary scale. Alunite is commonly associated with jarosite in terrestrial deposits [2, 3] and has been recognized in Hawaiian basalts [4] used as analogs for Martian volcanic rocks. Given this, it is likely that CRISM scientists will eventually find alunite on the Martian surface. Alunite, like jarosite, may potentially form on Mars in a number of modes ranging from high-temperature environments associated with magmatic fluids, to lacustrine or supergene environments (formed possibly from CO<sub>2</sub>-facilitated oxidation [5] of Fe<sup>2+</sup> in sulfides and H<sub>2</sub>S in aqueous fluids).

Determining the origin of alunite and jarosite in terrestrial environments can be accomplished using stable isotopes; however, this method requires laboratory analyses [2, 3]. A spectroscopic tool that could be used from orbit to distinguish between such environments may prove valuable in selecting future landing sites with the highest potential for preserving evidence of past life.

Jarosite and alunite have detectable spectral features in the 1.3 to 2.5 micron region that can be used to determine their Na and K composition in the laboratory [6]. Reflectance spectra of jarosites and alunites synthesized at different temperatures (95 to 200C and 150 to 450C respectively) show OH-related vibrational absorptions that become narrow and more intense in the higher-temperature samples. A possible explanation for this behavior is the protonation of hydroxyls that charge balance Fe and Al deficiencies in low-temperature synthetic jarosite and alunite. Replacement by H<sub>2</sub>O of one or more of the three hydroxyls, which are each hydrogen bonded to an apical sulfate oxygen, disrupts strong vibrational coupling, thereby weakening the spectral absorptions. When these samples are heated, the protonated hydroxyls are liberated as "excess water," and recrystallization produces fully hydroxylated crystals with intense spectral features that resemble those of natural high-temperature jarosite and alunite. Synthetic hydronium jarosite and alunite spectrally resemble low-temperature synthetic Fe-deficient jarosite and Al-deficient alunite, respectively. Proton transfer from the H<sub>3</sub>O<sup>+</sup> ion to the OH site in synthetic hydronium jarosite increases chemical disorder on its OH sites [7], also resulting in muted spectral features. This also applies to hydronium alunite.

Temperature-dependent spectral variations have been observed for 70 natural alunite samples formed at temperatures ranging from 20 to 400C. Spectral observations of 19 natural jarosite samples showed only a temperature dependency for a recently formed stalactitic hydronium-bearing jarosite from Iron Mountain, California. This jarosite had broad, weak absorptions characteristic of the low-temperature synthetic jarosites. All the other jarosite samples, including those formed in supergene environments (<80C), have narrow, intense absorptions similar to high-temperature synthetic jarosites. A likely explanation for the spectral similarity of all aged jarosites is the tendency for them to recrystallize into alkali endmembers over time. XRD analysis of 32 natural hydrothermal and supergene K- and Na-jarosites determined that intermediate compositions are absent, and instead, mixtures of discrete K and Na endmembers typify most samples [8]. The recrystallization likely results in loss of protonated hydroxyls in the lattice that are diagnostic of formation temperatures. This is not the case for natural alunite, which apparently does not undergo extensive recrystallization over time.

If alunite is exposed on the surface of Mars over a sufficiently large area, then the CRISM spectrometer should detect it and determine its K and Na composition as has been shown using AVIRIS spectra collected over Cuprite, Nevada [9]. This spectrophotometer also could be used to differentiate between alunite in high-temperature, relict, acid-sulfate hydrothermal systems and low-temperature, acid-saline lacustrine sediments. Selection of Martian landing sites to seek evidence of past life could be guided by sulfate alteration minerals. Which has the greatest probability of preserving evidence of life, alunite-bearing, low-temperature supergene and lacustrine rocks or alunite-bearing, hydrothermally-altered rocks? This spectrophotometer and others like it may be useful tools for selecting interesting landing sites from Mars orbit.

**References:** [1] Klingelhoffer et al. (2004) *Science*, 306, 1740. [2] Rye et al. (1992) *EcoGeol*, 87, 225. [3] Rye and Alpers (1997) USGS OFR97-88. [4] Wolfe et al. (1997) USGS Prof Paper 1557. [5] Papike et al. (2006) *GCA*, 70, 1309. [6] Bishop and Murad (2005) *AmMin*, 90, 1100. [7] Grohol et al. (2003) *PhysRevB*, 67, 064401. [8] Desborough et al. (2006) *ICARD*, 458. [9] Swayze et al. (2003), *JGR*, 108(9), 5105.