The visible and infrared spectral properties of jarosite and alunite

JANICE L. BISHOP1,2,* AND ENVER MURAD3

1SETI Institute, 515 North Whisman Road, Mountain View, California 94043, U.S.A.
2NASA-Ames Research Center, Mail Stop 239-4, Moffett Field, California 94035, U.S.A.
3Bayerisches Geologisches Landesamt, D-95603 Marktredwitz, Germany

ABSTRACT

The visible and infrared spectral properties of two natural jarosite minerals and a suite of synthetic jarosites and alunite samples are described here. The fundamental stretching and bending vibrations observed in the infrared region for SO4^2– and OH– are compared with the near-infrared overtones and combinations of these vibrations. Shifts were observed in the SO4^2– and OH– bands for Al^3+ vs. Fe^3+ at the octahedral sites and K+ vs. Na+ at the “A” (frequently monovalent) sites. Crystal-field theory bands were observed for jarosite near 435, 650, and 900–925 nm and were compared to those of iron oxides. Spectral bands near 1.76, 2.17, 2.53, 4.5, 8–10, and 15–24 μm (corresponding to ~5670, 4600, 3970–4150, 2100–2300, 1000–1225, and 420–675 cm^-1, respectively) for alunite and near 0.43, 0.91, 1.85, 2.27, 2.63, 4.9, 8–10, and 15–24 μm (corresponding to ~23000, 10990, 5400, 4350–4520, 3800–4150, 1950–2200, 1000–1190, and 440–675 cm^-1, respectively) for jarosite would be most useful for detecting these minerals using remote sensing on Earth or Mars. These minerals are important indicators of alteration processes, and this study contributes toward combined visible/near-infrared and mid-infrared spectral detection of these two alunite-group minerals.

INTRODUCTION

Jarosite and alunite are frequently observed on Earth and may also occur on Mars (Klingelhöfer et al. 2004). Fine-grained alunite forms via sedimentary or low-temperature processes, whereas alunite veins are formed by hydrothermal activity. Alunite has also been found in metamorphic rocks. Aqueous alteration of alunite in the presence of silica leads to the formation of kaolinite, muscovite or K-feldspar. Alunite dissolution in low-silica environments forms böhmite, γ-AlOOH. Jarosite is a common weathering product of oxidized iron sulfides under acidic conditions and frequently forms in concert with ferric oxyhydroxides. Laboratory experiments and field observations have shown that jarosite typically forms at pH values below 3, whereas schwertmannite precipitates preferentially in concert with ferric oxyhydroxides. Laboratory experiments and field observations have shown that jarosite typically forms at pH values below 3, whereas schwertmannite precipitates preferentially at pH values between 3 and 4, and ferricydrite is observed at pH 5 and above; goethite has been observed to form throughout the pH range (2.5 to 8) of sulfide oxidation (Bigham and Murad 1997; Bigham et al. 1996). Detailed and up-to-date descriptions of the structures and occurrences of the minerals of the alunite-jarosite group have been given in the recent MSA Reviews in Mineralogy and Geochemistry volume on sulfates, in particular in the chapters by Stoffregen et al. (2000), Bigham and Nordstrom (2000), and Dutrizac and Jambor (2000).

As described by Burns (1987, 1988), jarosites could form on Mars through chemical alteration of sulfide minerals, whose presence on Mars is indicated from analysis of Martian meteorites (e.g., McSween 1985). Remote sensing of these minerals could therefore provide information about surface processes such as alteration of sulfides, acid aqueous conditions, or volcanic processes. Jarosite formation could occur at low temperatures and the nature and type of ferric sulfate-bearing rocks, or gossans, produced on Mars are expected to be similar to those formed on Earth. Thermodynamic calculations of mineral stabilities and chemical weathering on Mars indicate that iron sulfides would oxidize to Fe(II) sulfate without water and to Fe(III) sulfate plus ferric oxides/oxyhydroxides with water (Gooding 1978). Oxidation rates of sulfides on Mars in equatorial melt-waters would be about 10^3 times slower than on Earth, but would still occur over geologic time (Burns and Fisher 1993). Moses et al. (1987) noted that FeS2 is oxidized to Fe(II) sulfate faster at lower pH, but that abiotic oxidation of Fe(II) to Fe(III) is slower at lower pH. Oxidation of Fe(II) to Fe(III) could be biomediated or photo-induced in order to facilitate jarosite formation from FeS2 at low pH. Temple and Delchamps (1953) noted early on that aqueous Fe(III) at low pH is a more aggressive oxidant for pyrite than dissolved oxygen. This could be important for Mars where there is likely to be more ferric iron than oxygen. Burns and Fisher (1990) performed acid leaching experiments on pyrrhotite (Fe1-xS) and proposed an acid groundwater weathering scenario for Mars where pyrrhotite would be transformed to pyrite, then to goethite plus jarosite. Jarosite is highly insoluble and would resist further reaction, but goethite could convert to hematite over time.

The alunite group has the formula AMn(SO4)2(OH)6, where A is usually a monovalent cation (K+, Na+, or Li+) and M is typically Al3+ (alunite), Fe3+ (jarosite), or another trivalent cation (Dutrizac and Jambor 2000). The structure is composed of SO4^2– tetrahedra and MO3(OH)4 octahedra, both somewhat distorted and each forming a layer in the a direction (Stoffregen et al. 2000). Each SO4^2– tetrahedron has one O atom bound to Al or Fe, producing a symmetry of C3v instead of Td (Adler and Kerr 1965). The ionic radii for octahedrally coordinated Al^3+ and high spin Fe^3+ are 0.535 Å and 0.645 Å, respectively (Shannon 1976), and the valence electrons for Al^3+ are in p orbitals while those for Fe^3+...