

DIAGNOSTIC ABSORPTION FEATURES IN SULFATE REFLECTANCE SPECTRA ACROSS OMEGA WAVELENGTH RANGE. E. A. Cloutis, Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9, e.cloutis@uwinnipeg.ca.

Introduction: The Mars Express Omega instrument has detected sulfate minerals across large parts of the Martian surface [1]. In order to enhance the interpretation of the observational spectra for Omega and CRISM, we have undertaken a systematic spectral-compositional-structural study of a wide range of sulfate minerals. Discrimination of specific sulfates is important for constraining the geological and climatic evolution of Mars because many sulfates form, or are stable, only under restricted conditions [e.g., 2].

Experimental Procedure: A total of 31 sulfates were included in this study: alunite, amarantite, angle-site, anhydrite, apjohnite, barite, botryogen, butlerite, copiapite, coquimbite, ferricopiapite, fibroferrite, gypsum, halotrichite, hexahydrite, hydronium jarosite, jarosite, kieserite, kornelite, magnesiocopiapite, melanterite, metavoltine, natrojarosite, pickeringite, rhomboclase, romerite, rozenite, sideronatrite, szomolnokite, and voltaite. Samples were hand-crushed and dry sieved to <45 μm and characterized by XRD, XRF, and reflectance spectroscopy (0.3-25 μm) [3].

Results: Across the wavelength range covered by the Omega instrument (0.35-5.2 μm), sulfates can exhibit a large number of absorption bands, many of which are unique to sulfates.

0.43-1.0 μm region: Fe^{3+} . All Fe^{3+} -bearing sulfates whose iron atoms are joined through shared oxide or hydroxide ions exhibit a spin-forbidden narrow absorption band, or closely overlapped bands, near 0.43 μm . This feature differs in appearance from that of other non-sulfate, Fe^{3+} -bearing minerals. Additional Fe^{3+} absorption bands are normally present in the 0.5-0.63 and 0.78-0.95 μm regions, with the latter being generally more intense than the former (Fig. 1).

0.9-1.2 μm region: Fe^{2+} . Fe^{2+} -bearing sulfates exhibit a single absorption band near 0.9 μm , or two bands near 0.9-0.95 and 1.17 μm , depending on how the Fe^{2+} is coordinated (by H_2O and/or SO_4) (Fig. 1).

1.4, 1.9, 3 μm regions: $\text{OH}/\text{H}_2\text{O}$. The wavelength position and number of absorption bands in the 1.4, 1.9 and 3 μm regions can be related to the number of distinct sites occupied by $\text{OH}/\text{H}_2\text{O}$, as well as the degree of hydrogen bonding. However, other $\text{OH}/\text{H}_2\text{O}$ -bearing minerals also exhibit bands in these regions.

1.8 μm region. Absorption bands in this region are present for nearly all OH and/or H_2O -bearing species, with up to 3 narrow bands being present between 1.6 and 1.87 μm (Table 1, Fig. 2). Features in this region are attributable to hydrogen bonding, and are combina-

tions of 3- μm region O-H stretching fundamentals plus 8- to 10- μm region S-O bending fundamentals.

2.1-2.7 μm region. Up to 11 absorption bands may be present in this region (e.g., alunite); anhydrous species have no absorptions in this region (Table 2; Fig. 2). Band assignments can be grouped as follows: OH stretches plus SO bends, OH stretches plus OH rotations, SO bending or stretching overtones. The number of bands and differences in wavelength positions makes them very useful for sulfate discrimination.

4-5 μm region: S-O . The region from ~3.9 to ~5.2 μm is characterized by overtones and combinations of strong ν_3 S-O bending fundamentals in the 8-10 μm region. Their number and intensity follows that of the 8-10 μm region fundamentals. The wavelength positions and relative band depths in this region are very useful for sulfate species discrimination (Fig. 3).

Discussion: The large number of samples available for this study also allowed a number of other issues to be addressed, including cation substitution, hydration-dehydration, and accessory phases.

Cation substitutions. The spectrum-altering effects of cation substitutions are a function of how strongly the sulfate structure is affected by the substitution. For jarosite-natrojarosite, K-Na substitution results in small (generally <30 nm) but measurable changes in almost all absorption band positions, including OH and SO bands. In other cases (copiapite-ferricopiapite: Fe^{2+} - Fe^{3+} substitution) there are no reliable systematic spectral differences. Other cation substitution pairs range between these extremes.

Hydration-dehydration. The spectrum-altering effects of water are best demonstrated by gypsum and anhydrite. Both are sheet sulfates with gypsum containing interlayer water. Spectrally, this results in the appearance of H_2O -associated absorption bands (as expected), but also changes in positions of all the major SO fundamentals and their overtones (Fig. 3).

Accessory phases. A number of sulfate samples contained fine-grained goethite \pm hematite (up to ~10 %). By comparing pure and "contaminated" samples, we found that the spectrum-altering effects of these iron oxides/hydroxides are generally limited to the region below ~1 μm (Fig. 1). Longer wavelength sulfate absorption band positions were not affected.

Summary. Sulfate minerals are a spectrally diverse group, exhibiting numerous diagnostic absorption features in the 0.3-5.2 μm region. Of particular utility for sulfate detection and species discrimination, are the 1.8,

2.1-2.7, and 4.5.2 μm regions. Other potentially useful regions are overlapped by other minerals (e.g., 1.4, 1.9, 3 μm regions) or can be strongly affected by accessory phases (0.4-1 μm region).

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References: [1] Mustard J.F. et al. (2004) AGU, Fall 2004, abstr. #P24A-07. [2] Buckby T. et al. (2003) *Min. Mag.*, 67, 263. [3] <http://www.planetary.brown.edu/relab/>.

Table 1. 1.8 μm region absorption bands.

Mineral	Position (μm)	Position (μm)	Position (μm)
<i>OH-bearing</i>			
Jarosite	1.84-1.85		
Natrojarosite	1.85-1.86		
Alunite	1.777		
<i>H₂O-bearing</i>			
Kieserite	1.75		
Voltaite	1.8		
Rhomboclase	1.8		
Gypsum	1.751	1.78	
Amarantite	1.78		
Coquimbite	1.75		
Romerite	1.75		
Rozenite+melanterite	1.62	1.75	
Hexahydrite	1.75		
Pickeringite	1.75		
<i>OH- and H₂O-bearing</i>			
Sideronatrite	1.748	1.803	1.867
Ferricopiapite	1.78		
Copiapite	1.78		
Botryogen	1.622	1.751	1.811
Fibroferrite	1.78		

Table 2. Absorption bands in the 2.1-2.7 μm region.

Mineral	Band Positions (μm)
Jarosite	2.08, 2.21, 2.27, 2.30, 2.41, 2.46, 2.51, 2.59, 2.61
Natrojarosite	2.07, 2.23, 2.27, 2.30, 2.42, 2.46, 2.52, 2.61
Alunite	2.07, 2.16, 2.18, 2.21, 2.32, 2.40, 2.42, 2.48, 2.51, 2.56, 2.68
Kieserite	2.13, 2.42, 2.55
Szomolnokite	2.10, 2.41, 2.55
Voltaite	2.55
Rhomboclase	2.45, 2.58
Gypsum	2.17, 2.22, 2.28, 2.43, 2.48, 2.55
Amarantite	2.55

Coquimbite	2.1, 2.55
Romerite	2.10, 2.40, 2.60
Rozenite+	
melanterite	2.44, 2.53
Hexahydrite	2.45, 2.54
Pickeringite	2.1, 2.55
Hydronium	
jarosite	2.28, 2.45, 2.6
Sideronatrite	2.09, 2.15, 2.18, 2.24, 2.28, 2.36, 2.43, 2.46, 2.50, 2.58, 2.68
Ferricopiapite	2.04, 2.41, 2.46, 2.55
Copiapite	2.10, 2.42, 2.47, 2.53
Botryogen	2.05, 2.28, 2.43, 2.54
Fibroferrite	2.05, 2.40, 2.47, 2.55

Fig. 1. Reflectance spectra (0.3-2.7 μm) of rozenite+melanterite (black), voltaite (red), natrojarosite (blue), and natrojarosite containing ~10% goethite (green). **Fig. 2.** Reflectance spectra (1.6-2.7 μm) of alunite (black), sideronatrite (red), and botryogen (blue). **Fig. 3.** Reflectance spectra (3-11 μm) of jarosite (black), sideronatrite (red), anhydrite (blue), and gypsum (green).

