

## Mid-infrared emission spectroscopy of sulfate and sulfate-bearing minerals

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### ABSTRACT

Mid-infrared thermal emission spectra were acquired and are presented for 37 different sulfate minerals representing Strunz classes 6/A–D as well as a few other miscellaneous sulfate-bearing minerals (Strunz class 3/C and 8/J). Sulfate vibrational modes are assigned to each spectrum; also assigned are the modes of component OH, H<sub>2</sub>O, and carbonate where applicable. A discussion also is presented regarding the effect of hydration state on the emissivity spectra; dehydration of the Ca-sulfate mineral series (e.g., gypsum-bassanite-anhydrite), as well as the Mg-sulfate series, causes the high-frequency edge of the sulfate  $\nu_3$  band to shift to a larger wavenumber.

**Keywords:** Mid-infrared, vibrational, spectroscopy, emissivity, emission, sulfate, spectra

### INTRODUCTION

Approximately 370 sulfate-mineral species are known to exist in nature (Hawthorne et al. 2000). Sulfate minerals are found in a variety of geologic settings, including volcanic, hydrothermal, evaporitic, and chemical-weathering environments. Some sulfate species are specific to single formational chemical environments, but others can form in several. Sulfates are formed in the presence of water of varying acidities and temperatures. In high-temperature volcanic and hydrothermal settings, metal-sulfate salts are common around active crater lakes, fumaroles, and hot springs, and may form volcanic aerosol particles. In low-temperature evaporite settings, preserved textural relationships (precipitation fabrics) between the sulfates and other salts can provide information regarding the precipitation sequence and mineral chemistry, thereby providing insight into the chemistry of the (sometimes ancient) surface waters. Chemical weathering can produce sulfate minerals that are entrained in soil or as crusts (or efflorescence) on host materials.

Sulfate minerals may be distinguished using thermal infrared (mid-infrared) spectroscopy. Early mid-infrared spectroscopic studies have shown that the aqueous sulfate anion (SO<sub>4</sub><sup>2-</sup>) produces four infrared absorption features at ~1105, ~983, ~611, and ~450 cm<sup>-1</sup> (corresponding to the asymmetric stretch,  $\nu_3$ ; symmetric stretch,  $\nu_1$ ; asymmetric bend,  $\nu_4$ ; symmetric bend,  $\nu_2$ , respectively) (Nakamoto 1986; also see Herzberg 1945; Hug 1997) of which only  $\nu_3$  and  $\nu_4$  are infrared active. These vibrations are modified when the sulfate anion is present within a solid-state medium, such as a mineral with a repeating molecular order, resulting in the potential appearance of all four sulfate vibrational modes in the spectrum.

The objective of this study is to present and discuss the mid-infrared emissivity spectra of a variety of sulfate-bearing minerals. A large suite of spectra are included to discuss the emissivity variations that arise over the mid-infrared wavelengths due to differences in chemistry, including hydration state of the samples. The results of this study will aid the interpretation of

thermal-infrared spectral data acquired in laboratories and those data acquired remotely of the Earth and other planetary bodies. The results of this study will be particularly relevant to the remote study of Mars, on which sulfate bedrock and sulfate-rich soils have been identified (e.g., Squyres et al. 2004; Squyres and Knoll 2005), and for which mid-infrared spectral data are plentiful (e.g., Christensen et al. 2001, 2003, 2004). Remote identification of specific sulfate minerals on Earth or elsewhere would enable the geologic setting in which the mineral formed to be determined. The spectra presented in this work are available through the Arizona State University Thermal Emission Spectral Library (<http://speclib.asu.edu>).

### SAMPLE DESCRIPTIONS

For this study, 62 sulfate-bearing mineral samples were studied, representing 37 different minerals (Table 1) that are reasonably common, available, and stable. These include the samples: afghanite, alunite, anglesite, anhydrite, antlerite, apthitalite (glaserite), apjohnite, barite, bassanite (hemihydrate), bloedite (blodite), brochantite, burkeite, celestine (celestite), coquimbite/paracoquimbite, creedite, ferricopiapite, glauberite, gypsum, hanksite, hexahydrate, jarosite, kainite, kieserite, linarite, minamiite, natrojarosite, pickeringite, plumbojarosite, polyhalite, potassium alum (potash alum; kalinite), rozenite, serpierite, sulfohalite, szomolnokite, thaumasite, thenardite, and zincobotryogen.

To confirm the mineralogic identification, all of the samples were analyzed by powder X-ray diffraction (XRD). The samples range in physical state from hand samples that are well-crystalline and dense, to less dense hand samples that are consolidated crystallites, to coatings, to loose particulate samples (powders) (Table 1).

### EXPERIMENTAL METHODS

The samples in this study were analyzed in thermal emission at ambient pressure using the Mars Space Flight Facility at Arizona State University. The spectrometer used is a modified Nicolet Nexus 670 E.S.P. FT-IR interferometer attached to an external glove box containing a temperature-stabilized sample chamber (maintained with circulating water behind the chamber wall). This spectrometer is equipped with a thermoelectrically stabilized DTGS detector and a CsI beam splitter

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**TABLE 1.** Listing of the sulfate-bearing minerals

Mineral*	Stoichiometric Composition	Sample and character***†	Locale
Afghanite‡	(Na, Ca, K) <sub>8</sub> (Si, Al) <sub>12</sub> O <sub>24</sub> (SO <sub>4</sub> , Cl, CO <sub>3</sub> )·12H <sub>2</sub> O	<b>S26, xl, cg</b>	Sar-e-Sang, Badakhshan, Afghanistan
Alunite	K <sub>2</sub> Al <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH) <sub>12</sub>	S14 S32 <b>S44, m, cg</b>	Sugar Loaf Butte, near Quartzite, AZ Marysvale, Piute Co., UT Marysvale, Piute Co., UT
Anglesite§	PbSO <sub>4</sub>	<b>S53, xl, cg</b>	Excepcion Mine, Villa Ahumada, Chihuahua, Mexico
Anhydrite	CaSO <sub>4</sub>	S9 <b>S16, m, cg</b>	Near Carson City, NV Near Carson City, NV
Antlerite	Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	<b>S10, m, cg</b>	Morenci, Greenlee Co., AZ
Aphthitalite (Glaserite)	(K,Na) <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>	S72 <b>S30, xl, cg</b>	Chucicamata, Chile Kuh-e-Namak, Region de Qom, Iran
Apjohnite	MnAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	<b>S38, cg, f</b>	Kern Co., CA
Barite	BaSO <sub>4</sub>	S1 <b>S2, m, cg</b>	Potosi, MO Northumberland Mine, Toquima Mtns, Nye Co., NV
Bassanite (Hemihydrate)	CaSO <sub>4</sub> ·1/2 H <sub>2</sub> O	S7 <b>S11, m, fg</b>	Near St. George, Wahsington Co., UT Locale unknown
Bloedite (Blodite)	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	<b>S33, xl, cg</b>	Soda Lake, San Luis Obispo Co., CA
Brochantite	Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub>	<b>S29, c, xl</b>	Ora Blanchard Claims, Blanchard Mine, Bingham, NM
Burkeite	Na <sub>2</sub> CO <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	S34 <b>S71, m, fg, pc</b>	Douglas Hill Copper Mine, Lyon Co., NV Searles Lake, San Bernardino Co., CA
Celestine (Celestite)	SrSO <sub>4</sub>	<b>S3, f, cg</b>	Near Calico, San Bernardino Co., CA
Coquimbite#	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9 H <sub>2</sub> O	S13 <b>S46, m, cg</b>	Maybee, MI Alcaparrosa, Chile
Creedite	Ca <sub>3</sub> Al <sub>2</sub> SO <sub>4</sub> (F,OH)·2H <sub>2</sub> O	S63 S28 <b>S36, xl, cg</b>	Atacama, Chile Navidad, Durango, Mexico Aguiles Serdan, Chihuahua, Mexico
Ferricopiapite	(Fe,Al,Mg)Fe <sub>3</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> ·20H <sub>2</sub> O	<b>S35, m, fg, pc</b>	Sierra Gorda, Chile
Glauberite	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	<b>S37, xl, cg</b>	Lake Bumbunga, near Lochiel, S.A., Australia
Gypsum**	CaSO <sub>4</sub> ·2 H <sub>2</sub> O	S52 S5 S6 <b>S8, xl, cg</b>	Bertram Siding, Salton Sea, Imperial Co., CA Near St. George, Washington Co., UT Mule Canyon, near Calico, San Bernardino Co., CA Near White City, Eddy Co., NM
Hanksite	KNa <sub>22</sub> (SO <sub>4</sub> ) <sub>9</sub> (CO <sub>3</sub> ) <sub>2</sub> Cl	S18 S24 <b>SL2, xl, cg</b>	Near White City, Eddy Co., NM Locale unknown Searles Lake, Trona, CA
“Hexahydrate” (likely kieserite)	MgSO <sub>4</sub> ·6 H <sub>2</sub> O	SL3 SL7 <b>152959, m, fg, pc</b>	Searles Lake, Trona, CA Searles Lake, Trona, CA Searles Lake, Trona, CA
Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	S39 <b>S51, m, fg, c</b>	Lehrite, Niedersachsen, Germany Barranco del Jarosa, Sierra Akmagrera, Spain
Kainite	KMgSO <sub>4</sub> Cl·3H <sub>2</sub> O	<b>S40, m, cg</b>	Copiapio Jarosite Mine, Dona Ana Co., NM
Kieserite	MgSO <sub>4</sub> ·H <sub>2</sub> O	<b>C5492-1, m, fg, pc</b>	Stassfurt, Harz, Germany Oficiana, Vegara, Chile
Linarite††	PbCu(SO <sub>4</sub> )(OH) <sub>2</sub>	<b>S27, xl, c</b>	Shine Mine, Bingham, NM
Minamiite‡‡	(Na,Ca,K) <sub>2</sub> Al <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH) <sub>12</sub>	<b>S76, m, fg</b>	Big Star Deposit, Maryvale, Piute Co., Utah
Natrojarosite	NaFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	<b>S48, m, fg, pc</b>	Sulfur Hole, Borate, San Bernardino Co., CA
Pickeringite§§	MgAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22 H <sub>2</sub> O	<b>S49, f, cg</b>	Corral Hollow, Alameda Co., CA
Plumbojarosite	PbFe <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH) <sub>12</sub>	<b>S15, fg, p</b>	Lomo de Toro Mine, Zimapan Hidalgo, Mexico
Polyhalite	K <sub>2</sub> Ca <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>4</sub> ·2H <sub>2</sub> O	<b>S50, m, fg</b>	NE of Carlsbad, Eddy Co., NM
Potassium Alum (Kalinite)	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	<b>S75, m, fg, pc</b>	Westeregeln, Niedersachsen, Germany
Rozenite	FeSO <sub>4</sub> ·4H <sub>2</sub> O	<b>JB626, m, cg, pc</b>	Iron Mountain, CA
Serpierite##	Ca(Cu,Zn) <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	<b>S61, xl, c</b>	Bayhorse Mine, Challis, Custer Co., ID
Sulfohalite	Na <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub> FCl	SL8 <b>S54, xl, cg</b>	Searles Lake, Trona, CA Searles Lake, near Trona, San Bernardino Co., CA
Szomolnokite	FeSO <sub>4</sub> ·H <sub>2</sub> O	S60 S78 <b>104276, xl, cg</b>	Markey Mine, Red Canyon, San Juan Co., UT Getchell Mine, near Golconda, Humboldt Co., NV Tintic Standard Mine, Dividend, UT
Thaumasite	Ca <sub>3</sub> Si(CO <sub>3</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub> ·12H <sub>2</sub> O	<b>S47, m, cg</b>	Fairfax Quarry, near Centerville, Fairfax Co., VA
Thenardite	Na <sub>2</sub> SO <sub>4</sub>	S74 <b>S22, m, cg</b>	Paterson, Passaic Co., NJ Salt Mine, Camp Verde, AZ
Zincobotryogen	ZnFe(SO <sub>4</sub> ) <sub>2</sub> (OH)·7H <sub>2</sub> O	S25 S66 SL16 <b>C5525-3, m, cg</b>	Soda Lake, San Benito Co., CA Camp Verde salt deposit, Yavapai Co., AZ Searles Lake, CA Mina Quetana, Calama, Chile

\* XRD data (to determine composition) were acquired mostly using a Rigaku Geigerflex powder diffractometer (at 40 kV and 35 mA) at a commercial lab (K/T GeoServices) using CuKα radiation and a 0.02° step size over the 2θ collection. Several samples were measured at Mount Holyoke College using a Rigaku Miniflex diffractometer and one (S46) was measured at Indiana University.

† Bold sample number denotes the sample whose spectrum is shown in the spectral-group figures.

‡ Composition assured by vendor (and a mineral example from the same vendor [Dan Weinrich Fine Minerals] and sample location is pictured on <http://www.webmineral.com/data/Afghanite.shtml>).

§ Sample S53 contains minor Celestine.

|| Sample S38 contains minor Kalinite/Halotrichite/Pickeringite.

# Sample S46 contains subequal amounts of coquimbite and paracoquimbite.

\*\* Sample S8 used to study particle-size effects; contains minor amount of bassanite.

†† Sample not pure: contains Pb-carbonate contaminant (cerussite).

‡‡ Sample not pure: approximately 90% minamiite, 8% alunite, 2% other.

§§ Sample S49 contains Kalinite/Apjohnite/Halotrichite.

||| Sample not pure: may contain goethite and other minerals.

## Composition confirmed by in-house analysis from sample provider [Excalibur Mineral Company].

\*\*\* Character of sample where m = massive, fg = fine-grained, cg = coarse-grained, xl = crystal form/faces visible (crystals at various orientations), pc = poorly consolidated; friable, c = coating, f = fibrous; p = particulate.

that allows the measurement of emitted radiation over the mid-infrared range of 2000 to 220  $\text{cm}^{-1}$  (5 to 45  $\mu\text{m}$ ). To reduce and maintain the amount of atmospheric water and  $\text{CO}_2$  vapor inside the spectrometer, external sample chamber, and glove box (and to reduce the degradation of the hydrophilic CsI beam splitter), the entire system is continuously purged with air scrubbed of water and  $\text{CO}_2$ .

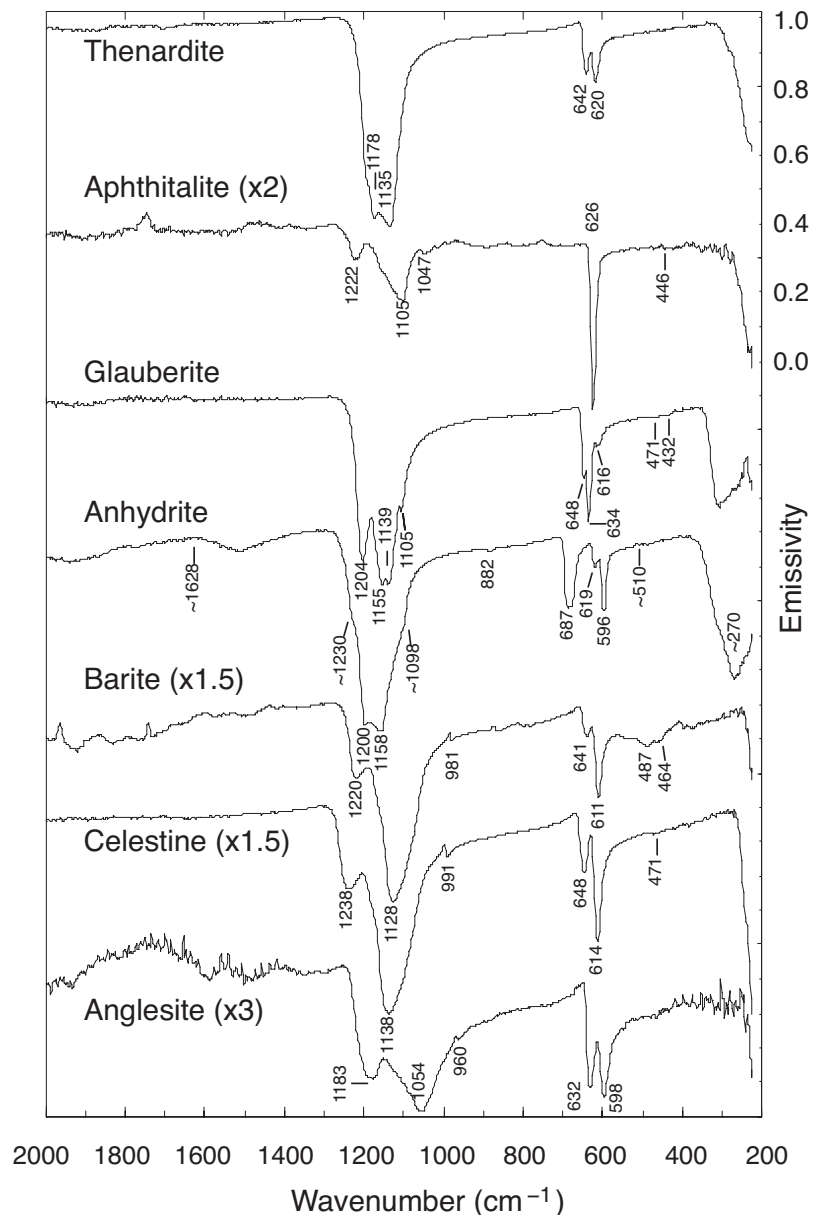
Each hand sample was heated to no more than 80  $^\circ\text{C}$  and routinely to lower temperatures (~35 to 50  $^\circ\text{C}$ ) for the samples that are easily dehydrated to deter the loss of structural water and maintain the sulfate coordination. Subsequent to an initial heating, each sample was placed into the sample chamber of the spectrometer and the passively emitted radiation was measured. The *particulate* samples were kept warm by actively heating the sample cups during the data acquisition period of 270 scans at 2  $\text{cm}^{-1}$  sampling. The *hand samples* could not be heated actively during the data acquisition, so each of the hand sample spectra was acquired over the shorter course of 160 scans at 2  $\text{cm}^{-1}$  sampling to mitigate the effects of sample cooling that produces an unwanted slope in the emissivity spectrum. Each sample was measured on at least three different occasions to co-add the spectra for better signal-to-noise and to produce a representative average spectrum. Additional details of the data calibration are presented in Christensen and Harrison (1993), Wenrich and Christensen (1996), and Ruff et al. (1997).

### SPECTRAL RESULTS AND ASSIGNMENT OF THE BANDS

The spectra of solid (nonparticulate), well-crystalline samples are preferred for clearer presentation of the fundamental, diagnostic absorption band positions and representative spectral shape of a mineral. This preference is based upon the relative simplicity of the solid sample spectrum that is free of multiple- and volume-scattering effects that occur in particulate spectra and are magnified with decreasing particle size (e.g., Lyon 1964; Aronson et al. 1966; Hunt and Vincent 1968; Vincent and Hunt 1968; Conel 1969; Hunt and Logan 1972; Aronson and Emslie 1973; Salisbury and Eastes 1985; Moersch 1992; Salisbury and Wald 1992; Wald 1994; Moersch and Christensen 1995; Wald and Salisbury 1995; Mustard and Hays 1997; Lane and Christensen 1998; Lane 1999; Cooper et al. 2002). However, some spectra presented here are of minerals in particulate form, or in poorly consolidated (yet solid) form, because well-crystalline, solid samples were not available. For these spectra, the fundamental absorption bands are shallower, and the bands that result from volume scattering are apparent and may dominate the spectra. Nonetheless, presentation of these spectra is useful, provided the effects of particle size, composition, and hydration state are understood as they correspond to distinct spectral behavior.

Throughout this paper, the sulfate spectra acquired in the laboratory will be presented

in groups according to their Strunz classifications (Strunz and Nickel 2001). In each spectral-group figure to be presented, only one spectrum of each mineral from Table 1 is shown (i.e., spectra of duplicate-mineralogy samples are not presented because they are similar to the presented spectra). Each phase produces a distinct spectrum as a result of the fundamental vibrational modes of the crystal structure (Table 2) and their associated overtones and combination bands. Mid-infrared sulfate spectra are dominated by the vibrational behavior of the S-O bonds in the sulfate anion, and in some cases, influenced by the presence of OH or  $\text{H}_2\text{O}$ , or even  $\text{CO}_3$ , in the structure. Cation complexation of  $\text{SO}_4^{2-}$  in a solid causes distortions of the sulfate polyhedra (e.g., Griffen and Ribbe 1979) away from simple  $T_d$  site symmetry and controls the resulting vibrational spectral features such as band splitting (removal of degeneracy) that results from the



**FIGURE 1.** Mid-infrared thermal emissivity spectra of anhydrous sulfates. The band depths of some spectra have been modified for easier comparison as noted by the parenthetical values. Spectra are offset for clarity.

lowered symmetry. Although S-O distances vary from mineral to mineral, the grand mean distance is 1.473 [Å (with minimum and maximum distances being 1.430 and 1.501 Å; Hawthorne et al. 2000)]. In a solid-state sulfate, internal vibrational features generally appear at  $\sim 1050$ – $1250$  ( $\nu_3$ ),  $\sim 1000$  ( $\nu_1$ ),  $\sim 500$ – $700$  ( $\nu_4$ ), and  $\sim 400$ – $500$  ( $\nu_2$ )  $\text{cm}^{-1}$  (e.g., Herzberg 1945; Nakamoto 1986; Vassallo and Finnie 1992; Bishop and Murad 2005), and at  $\leq 550$   $\text{cm}^{-1}$  due to lattice vibrations (e.g., Serna et al. 1986; Clark 1999) (including metal-oxygen, librational, and translational modes that occur at lower wavenumbers, respectively). The  $\nu_2$  band is known to be significantly weaker than the  $\nu_1$  mode and commonly is not observable in the infrared spectra of sulfates (Hezel and Ross 1966).

### Anhydrous sulfates

The samples of this classification (Strunz 6/A.) presented here include thenardite, apthitalite, glauberite, anhydrite, celestine, barite, and anglesite. The chemical structure of these sulfates is fairly simple and consists of tetrahedral sulfate groups whose O atoms are coordinated with interstitial cations. The larger the cation, the higher the coordination number (e.g.,  $\text{Ba}^{2+}$  in barite is coordinated with 12 O atoms, the smaller  $\text{Ca}^{2+}$  in anhydrite is coordinated with eight O atoms, and even smaller  $\text{Na}^+$  in thenardite is coordinated with only six O atoms).

Thenardite, apthitalite, and glauberite all contain  $\text{Na}^+$  and in the case of apthitalite and glauberite there is an additional cation of  $\text{K}^+$  and  $\text{Ca}^{2+}$ , respectively. Thenardite is a structurally simple sulfate whose sulfate polyhedra are closer to  $T_d$  symmetry than most other sulfates and whose spectrum is among the simplest (Fig. 1). For thenardite, there is not enough distortion of the sulfate polyhedra to exhibit a  $\nu_1$  mode, nor is a  $\nu_2$  band seen. The exhibited modes of the sulfate anion shown in emission are  $\nu_3$  and  $\nu_4$  doublets at 1178/1135 and 642/620  $\text{cm}^{-1}$ , respectively, representative of  $D_{2d}$  symmetry. However, there is a possible third  $\nu_3$  band appearing as a higher-frequency shoulder on the other  $\nu_3$  bands, suggestive of a more-distorted  $D_2$  symmetry (Steger and Schmidt 1964, using a transmission technique; Vassallo and Finnie 1992, using an emission technique). The  $D_2$  symmetry determined by Steger and Schmidt (1964) supports a third  $\nu_4$  (and  $\nu_3$ ) band that must be degenerate in the emission spectrum shown here because only a doublet is seen. This degeneracy is also the case for the transmission spectra of Moenke (1962) and in one of the two thenardite samples studied in Vassallo and Finnie (1992) (the second thenardite does show a weak third  $\nu_4$  band). The band that truncates at 220  $\text{cm}^{-1}$  represents a lattice mode vibration. Apthitalite, also known as glaserite, is unique to the anhydrous sulfate group in that its emission spectrum exhibits only a single, sharp, and very strong vibrational component of the  $\nu_4$  band (at 626  $\text{cm}^{-1}$ ), which also was noted by Moenke (1962) in transmission, whereas the other anhydrous sulfate spectra considered here have at least two and commonly three  $\nu_4$  components (Fig. 1). It is likely that in this case, the apthitalite  $\nu_4$  band is doubly degenerate because the sulfate anion in this mineral maintains  $C_{3v}$  symmetry (Adler and Kerr 1965), which predicts two  $\nu_4$  bands. Two  $\nu_3$  bands are present at 1222 and 1105  $\text{cm}^{-1}$  and the  $\nu_1$  sulfate fundamental vibration appears at 1047  $\text{cm}^{-1}$ . There are minor features in the spectrum around 450  $\text{cm}^{-1}$ , but it is unclear which minor deviation represents the  $\nu_2$  mode

[although it may be the small band at 446  $\text{cm}^{-1}$  as described in Ross (1974)]. A lattice mode is present but truncated at 220  $\text{cm}^{-1}$  (either a metal-O or an  $\text{SO}_4$  librational mode). Although a sample of arcanite ( $\text{K}_2\text{SO}_4$ ) was not obtained for this study, the spectrum would likely be similar to apthitalite due to its crystallographic similarities (Washington and Merwin 1921). This prediction appears to be borne out as shown by the transmission spectra of Moenke (1962); however, the apthitalite spectrum presented by Moenke's shows the  $\nu_3$  band to be more widely split than in the arcanite spectrum. The glauberite spectrum (Fig. 1) shows three components of the  $\nu_3$  band (at 1204, 1155, and 1139  $\text{cm}^{-1}$ ), one  $\nu_1$  band at 1105  $\text{cm}^{-1}$ , three components of the  $\nu_4$  band (at 648, 634, and 616  $\text{cm}^{-1}$ ), and two very weak  $\nu_2$  bands (471 and  $\sim 432$   $\text{cm}^{-1}$ ) that are difficult to discern in Figure 1. Ross (1974) and Adler and Kerr (1965) proposed either  $C_2$  or  $C_1$  symmetry. The bands presented here would satisfy either  $C_2$  or  $C_1$  symmetry, but cannot further identify which one is correct. The glauberite spectrum also shows the long-wave lattice mode that is present in all the anhydrous sulfates presented in this section.

The only cation in anhydrite is  $\text{Ca}^{2+}$ . The emissivity spectrum in Figure 1 clearly supports  $C_{2v}$  symmetry (e.g., Moenke 1959; Steger and Schmidt 1964; Hezel and Ross 1966, all using transmission data). Figure 1 shows at least two  $\nu_3$  bands at 1200 and 1158  $\text{cm}^{-1}$  with a possible third band appearing as a shoulder at  $\sim 1230$   $\text{cm}^{-1}$ , and three unequivocal components to the  $\nu_4$  band at 687, 619, and 596  $\text{cm}^{-1}$ . At  $\sim 1098$   $\text{cm}^{-1}$ , there is a shoulder in the spectrum, likely related to the  $\nu_1$  band (Fig. 1), but it is subtle. The  $\nu_1$  band of anhydrite is absent in the transmission spectrum presented by Adler and Kerr (1965), but is subtly present in the low-temperature anhydrite emission spectra of Vassallo and Finnie (1992) as a shoulder on a  $\nu_3$  band near 1000  $\text{cm}^{-1}$ . Ross (1974) and Steger and Schmidt (1964) assign the  $\nu_1$  band to 1013 and 1020  $\text{cm}^{-1}$ , respectively. More recently, Makreski et al. (2005) assigned a transmission band at 1013  $\text{cm}^{-1}$  to  $\nu_1$ . In the anhydrite spectrum presented here (Fig. 1), there is a distinct small band at 882  $\text{cm}^{-1}$  and an emissivity maximum at  $\sim 1628$   $\text{cm}^{-1}$ , both likely due to a minor amount of water being present in the "anhydrous" crystal, resulting from the Ca-OH and  $\text{H}_2\text{O}$  bending motions, respectively. A subtle  $\nu_2$  feature occurs at  $\sim 510$   $\text{cm}^{-1}$  (observed at 511  $\text{cm}^{-1}$  in Makreski et al. 2005) and a stronger lattice band appears at  $\sim 270$   $\text{cm}^{-1}$ . Comparison of the anhydrite spectrum to spectra of samples of similar composition with different hydration states (e.g., bassanite and gypsum) will be discussed in the "Hydrous sulfates" section.

Overall, because of the relatively large cations associated with the barite group of minerals (barite, celestine, and anglesite), their spectra appear different in shape than the smaller-cation sulfate spectra such as anhydrite that is structurally dissimilar (Fig. 1). The barite-group minerals themselves are isostructural, therefore their spectra are similar to each other, but the Christiansen feature and additional spectral features are offset by small amounts as a result of the different associated cations. The Christiansen feature and the more pronounced spectral features of  $\nu_3$  and  $\nu_4$ , and even the subtler  $\nu_1$ , are systematically offset to smaller wavenumber (lower energy) for the Sr- ( $\nu_3 = 1238, 1138$ ;  $\nu_4 = 648, 614$ ;  $\nu_1 = 991$   $\text{cm}^{-1}$ ), Ba- ( $\nu_3 = 1220, 1128$ ;  $\nu_4 = 641, 611$ ;  $\nu_1 = 981$   $\text{cm}^{-1}$ ), and Pb- ( $\nu_3 = 1183, 1054$ ;  $\nu_4 = 632, 598$ ;  $\nu_1 = 960$   $\text{cm}^{-1}$ ) sulfates, respectively, trending inversely with atomic

weight of the constituent cation. A single  $\nu_2$  band is visible for the celestine spectrum at  $471\text{ cm}^{-1}$  and  $\nu_2$  occurs as a doublet in the barite spectrum at  $487$  and  $464\text{ cm}^{-1}$ , but no  $\nu_2$  is obvious for the anglesite spectrum (albeit somewhat noisy). Similarly, the transmission studies of Hezel and Ross (1966) and Wylde et al. (2001) found anglesite (and celestine and barite) not to have a  $\nu_2$  band; nor is there an obvious  $\nu_2$  band in the anglesite spectrum of Moenke (1962). Here, the  $\nu_3$  and  $\nu_4$  fundamental sulfate-anion vibrations of the barite-group minerals are shown by two bands each, the  $\nu_1$  is non-degenerate (exhibiting only one band), and there is a single  $\nu_2$  feature (for celestine), all suggestive of  $C_{3v}$  symmetry; however, the transmission studies of Adler and Kerr (1965), Hezel and Ross (1966), and Wylde et al. (2001) showed three  $\nu_3$  bands (although the latter study shows only two strong  $\nu_3$  bands for celestine with a very weak third  $\nu_3$ ) that would be supportive of a  $C_s$  symmetry. Three  $\nu_3$  bands also were described for these isostructural minerals by Moenke (1962). The large splitting of the  $\nu_3$  bands is related to a large distortion of the sulfate tetrahedron. The band trends presented here for the barite-group minerals are consistent with those discussed in Adler and Kerr (1965) for infrared transmission spectra. However, the extra  $\nu_3$  band seen in the transmission data [and a theoretical third  $\nu_4$  band and second  $\nu_2$  required by  $C_s$  symmetry, as identified by Burgio and Clark (2001) for Raman data of barite and as seen here in the barite spectrum] suggest that there may be overlap in the position of the mid-infrared emissivity bands in this isostructural group that would prevent them from being resolved individually. Adler and Kerr (1965) did not discuss the  $\nu_4$  band due to their lack of data at the longer wavelengths, but Miller et al. (1960, using transmission data), Moenke (1962), and Wylde et al. (2001) did identify two  $\nu_4$  bands, equal to the number identified in this study.

#### Anhydrous sulfates with additional anions

The samples of this classification (Strunz 6/B.) presented here include antlerite, brochantite, linarite, alunite, minamiite, jarosite, natrojarosite, plumbojarosite, sulfosalite, burkeite, and hanksite. Some of these minerals produce more-complex sulfate spectra due to the presence of hydroxyl (OH) in their structures. Bands can be present in addition to those predicted by the crystal symmetry of the mineral due to hydroxyl groups bonded to one sulfate anion being hydrogen bonded to an adjacent sulfate anion (e.g., Araki 1961; Libowitzky 1999). These additional bands appear predominantly as OH in-plane ( $\delta$ ) and out-of-plane ( $\gamma$ ) bending modes. Antlerite and brochantite (both being Cu sulfates) have spectra that are roughly similar (Fig. 2); however, their sulfate anion site symmetries are different [ $C_s$  and  $C_1$ , respectively, according to Moenke (1962)].

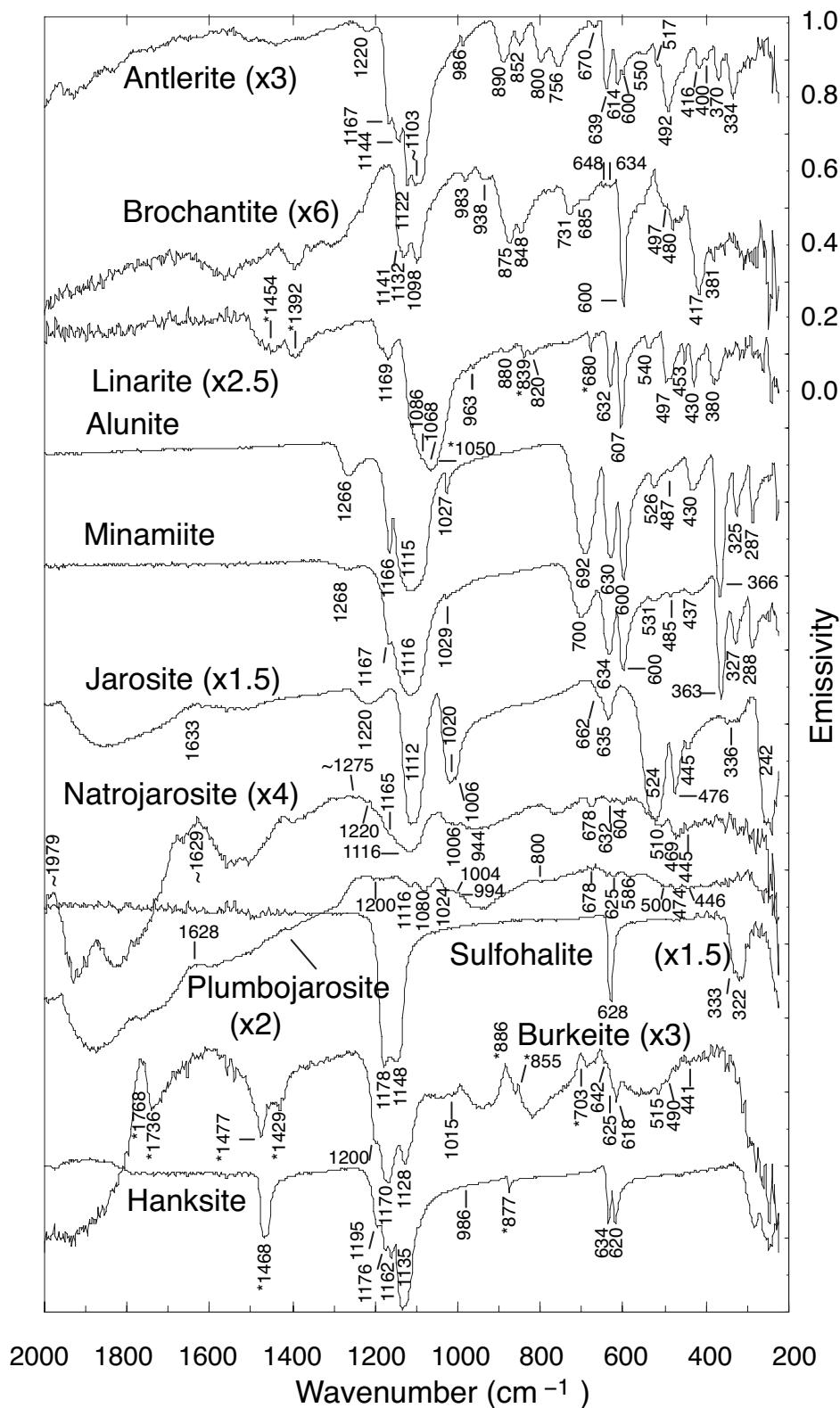
Antlerite, whose crystal structure was well-described by Hawthorne et al. (1989), displays three components of  $\nu_3$  (at  $1220$ ,  $1144$ , and  $\sim 1103\text{ cm}^{-1}$ ) and  $\nu_4$  (at  $670$ ,  $639$ , and  $614\text{ cm}^{-1}$ ) with an additional feature in the  $\nu_3$  range at  $1167\text{ cm}^{-1}$  due to OH in the crystal structure (Fig. 2). Antlerite contains four hydroxyls in the unit cell, hence four OH-bending vibrations clearly can be seen at  $890$ ,  $852$ ,  $800$ , and  $756\text{ cm}^{-1}$ . The  $\nu_1$  mode is displayed at  $\sim 986\text{ cm}^{-1}$ . The  $\nu_2$  vibrations occur at  $416$  and  $400\text{ cm}^{-1}$ , consistent with  $C_s$  symmetry of the sulfate that predicts two  $\nu_2$  bands. The weak  $600$  and  $550\text{ cm}^{-1}$  bands and the strong band at

$492\text{ cm}^{-1}$  are assigned to  $\gamma$ OH-bending modes. Additional bands at  $517$ ,  $370$ , and  $334\text{ cm}^{-1}$  can be attributed to Cu-O vibrations. Finally, a band seen as an emissivity maximum at  $\sim 1964\text{ cm}^{-1}$  is assigned as the first overtone of the  $\nu_1$  vibration (Martens et al. 2003), although that assignment is unproven.

Antlerite forms under pH conditions  $<4$  but if the pH is raised to  $\sim 4$ – $6$ , brochantite will form instead. Ross (1974) defined brochantite to have sulfate anions with  $C_1$  symmetry. This symmetry predicts three  $\nu_3$  bands; however, two are shown in Figure 2 at  $1132$  and  $1098\text{ cm}^{-1}$ , but the misshapen former band appears to be two unresolved bands, as is seen more clearly in the brochantite transmission spectrum of Moenke (1962); hence, the shoulder at  $\sim 1141\text{ cm}^{-1}$  is assigned to  $\nu_3$ , as also assigned in the brochantite transmission spectra of Schmidt and Lutz (1993) and Makreski et al. (2005). The  $\nu_1$  is displayed at  $983\text{ cm}^{-1}$  in agreement with Schmidt and Lutz (1993). Brochantite shows four bands at  $938$ ,  $875$ ,  $848$ , and  $731\text{ cm}^{-1}$  that are attributed to  $\delta$ OH-bending vibrations, and a deep band at  $600\text{ cm}^{-1}$  attributed to a  $\gamma$ OH-bending vibration. There are many OH lattice vibrational bands that overlie and even interact with the sulfate  $\nu_2$  and  $\nu_4$  vibrations, making the sulfate and OH band assignments difficult. However, I assign the  $\nu_4$  bands of brochantite to the features at  $\sim 685$ ,  $\sim 648$ , and  $\sim 634\text{ cm}^{-1}$ . Two  $\nu_2$  bands are predicted by  $C_1$  symmetry, but no  $\nu_2$  bands were assigned from the emissivity spectrum because it is not straightforward to differentiate these modes from Cu-O stretching modes in the same region (Schmidt and Lutz 1993). I have assigned some of the Cu-O stretching bands to the features at  $497$ ,  $480$ ,  $417$ , and  $381\text{ cm}^{-1}$ .

The spectral character of the linarite sample (Fig. 2) is somewhat similar in the  $\nu_3$  and  $\nu_4$  range to the anhydrous anglesite sample (Fig. 1) that also contains Pb. However, linarite exhibits more  $\nu_3$  bands that occur at  $1169$ ,  $1068$ , and either the small band at  $1050$  or  $1086\text{ cm}^{-1}$  [comparison to the linarite transmission spectrum of Omori and Kerr (1963) suggests the likelihood of the  $1086\text{ cm}^{-1}$  band; however, Moenke (1962) showed the  $1050\text{ cm}^{-1}$  band to be the strongest]. Comparison of the linarite spectrum to an emissivity spectrum of cerussite ( $\text{PbCO}_3$ , M.D. Lane, unpublished), a known contaminant in this linarite sample, suggests that the band at  $1050\text{ cm}^{-1}$  is due to carbonate contamination, and is not a  $\nu_3$  band. The sulfate  $\nu_4$  bands occur at  $632$  and  $607\text{ cm}^{-1}$ , but the sulfate symmetry of linarite, that of  $C_s$  (Ross 1974), predicts an unseen third  $\nu_4$  band. There is another band at  $680\text{ cm}^{-1}$ ; however, this band clearly is due to the  $\nu_4$  of the contaminant carbonate anion. Other bands due to the cerussite are also obvious at  $1454$  and  $1392\text{ cm}^{-1}$  (carbonate  $\nu_3$  bands) and at  $839\text{ cm}^{-1}$  (carbonate  $\nu_2$ ) (Huang and Kerr 1960). Linarite also shows a sulfate  $\nu_1$  at  $963\text{ cm}^{-1}$ . Although not apparent in the anhydrous anglesite sample, linarite exhibits two  $\nu_2$  bands assigned at  $453$  and  $430\text{ cm}^{-1}$ . There is also a deep band at  $\sim 500\text{ cm}^{-1}$  that Ross (1974) attributed to  $\gamma$ OH using the transmission data of Moenke (1962). The OH groups in the structure add other spectral bands to linarite that are not seen in the anglesite spectrum. For example, a doublet at  $880$  and  $820\text{ cm}^{-1}$  is due to OH deformation ( $\delta$  bending) as is the band at  $540\text{ cm}^{-1}$  ( $\gamma$  bending). The mode observed at  $380\text{ cm}^{-1}$  may be a metal-O vibration.

The mid-infrared features of alunite and/or jarosite and/or varieties thereof are discussed in other works: Shokarev et al. [1972; using transmission ( $4000$ – $240\text{ cm}^{-1}$ )], Powers et al. [1975; using



**FIGURE 2.** Mid-infrared thermal emissivity spectra of anhydrous sulfates with additional anions, where the asterisks denote bands from carbonate contamination (in linarite) or carbonate in the mineral structure. The band depths of some spectra have been modified for easier comparison as noted by the parenthetical values. Spectra are offset for clarity.

transmission ( $4000\text{--}200\text{ cm}^{-1}$ ), Serna et al. [1986; using Raman ( $3700\text{--}50\text{ cm}^{-1}$ ) and transmission ( $4000\text{--}100\text{ cm}^{-1}$ )], Breitinger et al. [1997; using Raman ( $<1500\text{ cm}^{-1}$ ) and transmission ( $3600\text{--}400\text{ cm}^{-1}$ )], Sasaki et al. [1998; using Raman ( $1300\text{--}200\text{ cm}^{-1}$ ) and diffuse reflectance ( $4000\text{--}400\text{ cm}^{-1}$ )], Sejkora and Ďuda [1998; using transmission ( $4000\text{--}400\text{ cm}^{-1}$ )], and Bishop and Murad [2005; using reflectance ( $\sim 33000\text{--}200\text{ cm}^{-1}$ ) and transmission ( $4000\text{--}400\text{ cm}^{-1}$ )]. The emissivity spectra presented here of alunite and jarosite (Fig. 2) are different in shape from their transmittance and reflectance counterparts, but exhibit many of the same spectral features.

### Emissivity

Alunite displays two  $\nu_3$  features at  $1266$  and  $1115\text{ cm}^{-1}$ . The  $\nu_1$  feature occurs at  $1027\text{ cm}^{-1}$  as supported by the study of Serna et al. (1986) and Breitinger et al. (1997), the two  $\nu_4$  bands occur at  $692$  and  $630\text{ cm}^{-1}$ , and a single  $\nu_2$  band occurs at  $430\text{ cm}^{-1}$ . The observation of these bands supports  $C_{3v}$  symmetry of the sulfate tetrahedron. A sharp band at  $1166\text{ cm}^{-1}$  is due to  $\delta\text{OH}$ , so identified because deuteration greatly shifts this band to lower frequency (Breitinger et al. 1997). Breitinger et al. also demonstrated that this  $\delta\text{OH}$  band undergoes a Fermi resonance with the  $1115\text{-cm}^{-1}$   $\nu_3$  band. Additional bands are exhibited at:  $600\text{ cm}^{-1}$  (due to  $\gamma\text{OH}$ ), and  $526$  and  $487\text{ cm}^{-1}$  (both due to Al-O). Bands at  $366$ ,  $325$ , and  $287\text{ cm}^{-1}$  have been attributed to Al-O bonds for the octahedral structural components (Serna et al. 1986).

The minamiite spectrum (Fig. 2) is virtually identical to that of alunite. Because they are from the same crystal system (i.e., trigonal-rhombohedral), their spectra should be quite similar; however, the cations  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in the minamiite

**TABLE 2.** Band assignments of the fundamental vibrational modes in sulfate-bearing minerals (in  $\text{cm}^{-1}$ )

Mineral	$\delta\text{H}_2\text{O}$	$\nu_3$	$\delta\text{OH}$	$\nu_1$	$\text{H}_2\text{O}$ libration	$\delta\text{OH}$	$\nu_4$	$\gamma\text{OH}$	$\nu_2$	$\text{H}_2\text{O}$ libration	M-O or lattice
Afghanite†		1171 1128 1022					609 590 540?				434
Alunite		1266 1115	1166	1027			692 630	600	430		526 487 366 325 287
Anglesite		1183 1054		960			632 598				trunc.
Anhydrite	~1628	1200 1158 ~1230?		~1098? (sh)		882	687 619 596		510		270
Antlerite		1220 1144 ~1103	1167	~986		890 852 800 756	670 639 614	600 550 492	416 400		517 370 334
Aphthitalite		1222 1105		1047			626		446?		trunc.
Apjohnite	~1690	1115 1080 1054		992		944	705 640 580				trunc.
Barite		1220 1128		981			641 611		487 464		trunc.
Bassanite	1630	1171 1158 1093		1000			664 630 600				~240
Bloedite		~1190 (sh) 1158 1121		992		820 719	~653 (sh) 634 (sh) 614		469 428		310 trunc.
Brochantite		~1141 (sh) 1132 1098		983		938 875 848 731	~685 ~648 ~634	600			497 (sh) 480 417 381 ~297
Burkeite‡		1200 (sh) 1170 1128		1015		~625 (sh) ~642 (sh) 618			441?		515? 490? (sh) trunc.
Celestine		1238 1138		991			648 614		471		trunc.
Coquimbite		1180 1100		1013		890 816	685 650 597		480 443		278
Creedite		1180 1154 1098 1043		983		806 772	676 640 570		497 478		386 trunc.
Ferricopiapite	1649 1444	1220 ~1116 ~1050		997			600 552		~467		trunc.
Glauberite		1204 1155 1139		1105			648 634 616		471 ~432		308
Gypsum	1621	1155		1010*		877*	676 604 595? (sh)			475	trunc.
Hanksite§		1195 1176 1162 1135		986			634 620				285 249
"Hexahydrate" (likely kieserite)		1254 1222 (sh) 1180		1045	917		676 643 614		462?		409 375 358 322 trunc.

Notes: (sh) = Band occurs as a shoulder on a larger band; trunc. = Band is truncated, so band minimum is not known.

\* Band location is identifiable only because of Type III band behavior (Hunt and Vincent, 1968) in a fine-grained (<10  $\mu\text{m}$ ) sample.

† Afghanite exhibits additional vibrational modes due to carbonate anions in the mineral structure (~1560–1387  $\text{cm}^{-1}$ ,  $\nu_3$ ; 887  $\text{cm}^{-1}$ ,  $\nu_2$ ; 735  $\text{cm}^{-1}$ ,  $\nu_4$ ; ~400–250  $\text{cm}^{-1}$ , lattice mode) and Si-Al-O bending modes at 682 and 662  $\text{cm}^{-1}$ .

‡ Burkeite exhibits additional vibrational modes due to carbonate anions in the mineral structure (1477 and 1429  $\text{cm}^{-1}$ ,  $\nu_3$ ; 886  $\text{cm}^{-1}$ ,  $\nu_2$ ; 703  $\text{cm}^{-1}$ ,  $\nu_4$ ).

§ Hanksite exhibits additional vibrational modes due to carbonate anions in the mineral structure (1468  $\text{cm}^{-1}$ ,  $\nu_3$ ; 877  $\text{cm}^{-1}$ ).

|| Thaumassite exhibits additional vibrational modes due to carbonate anions in the mineral structure (1392  $\text{cm}^{-1}$ ,  $\nu_3$ ; 880  $\text{cm}^{-1}$ ,  $\nu_2$ ; 329  $\text{cm}^{-1}$ , lattice mode) and Si-O (765 and 680  $\text{cm}^{-1}$ ,  $\nu\text{Si-O}$ ; 494 and ~460  $\text{cm}^{-1}$ ,  $\delta\text{Si-O}$ ).

# Linarite contains contaminant cerussite and hence has observable carbonate bands at 1454, 1392, 1050, 839, and 680  $\text{cm}^{-1}$ .

TABLE 2.—Continued

Mineral	$\delta\text{H}_2\text{O}$	$\nu_3$	$\delta\text{OH}$	$\nu_1$	$\text{H}_2\text{O}$ libration	$\delta\text{OH}$	$\nu_4$	$\gamma\text{OH}$	$\nu_2$	$\text{H}_2\text{O}$ libration	M-O or lattice
Jarosite	1633	1220 1112	1020	1006			~662 (sh) 635		445		524 476 ~336 ~242 285
Kainite	1654	1181 1135 1128			1020	809 744	660 643 602		468 441?		
Kieserite		1256 ~1213 (sh) 1183		1045	919		669 641 ~610		458?		~352
Linarite#		1169 1086 (sh) 1068		963		880 820	632 607	540 497	453 430		380
Minamiite		1268 1116	1167	1029			700 634	600	437		531 485 363 327 288
Natrojarosite	1629	1220 ~1165 (sh) 1116	~1010 (sh)~1006				678 ~632	604	445		510 469 trunc. trunc.
Pickeringite	~1680	1115 1080 1047		985		~945	~705 ~646 (sh) ~588		480		
Plumbojarosite	~1628	1200 1116 1080	1024	1004?			~678 ~6250	586	446		50 474 trunc.
Polyhalite	1651	~1231 (sh) 1192 1172 1102		~1010 988	744 687		657 623 602		471?		244
Potassium Alum	~1690	1226 (sh) 1128 1055		993			~653 (sh) 593		~443?		trunc.
Rozenite	~1680	~1220 (sh) 1100 ~1013		992		818 ~760 735 ~692	~660 (sh) ~645 (sh) 602 641 600		468? ~467		384
Serpierite	~1665	1144 1123 1098		983		825 ~687					
Sulfohalite		1178 1148 322					628				333 (sh)
Szomolnokite		1226 (sh) 1195 1149		1018	846		626 606 554		361?		trunc.
Thaumasite	1712	~1135 (sh) 1095 1066 (sh)		999			636 588 642 620				trunc. trunc.
Thenardite§		1178 1135									
Zincobotryogen	1660	1220 1164 (sh) 1132 1068 1031	1010?	999		806?	602 545 485		393?		280

Notes: (sh) = Band occurs as a shoulder on a larger band; trunc. = Band is truncated, so band minimum is not known.

\* Band location is identifiable only because of Type III band behavior (Hunt and Vincent, 1968) in a fine-grained (<10  $\mu\text{m}$ ) sample.

† Afghanite exhibits additional vibrational modes due to carbonate anions in the mineral structure (~1560–1387  $\text{cm}^{-1}$ ,  $\nu_3$ ; 887  $\text{cm}^{-1}$ ,  $\nu_2$ ; 735  $\text{cm}^{-1}$ ,  $\nu_4$ ; ~400–250  $\text{cm}^{-1}$ , lattice mode) and Si-Al-O bending modes at 682 and 662  $\text{cm}^{-1}$ .

‡ Burkeite exhibits additional vibrational modes due to carbonate anions in the mineral structure (1477 and 1429  $\text{cm}^{-1}$ ,  $\nu_3$ ; 886  $\text{cm}^{-1}$ ,  $\nu_2$ ; 703  $\text{cm}^{-1}$ ,  $\nu_4$ ).

§ Hanksite exhibits additional vibrational modes due to carbonate anions in the mineral structure (1468  $\text{cm}^{-1}$ ,  $\nu_3$ ; 877  $\text{cm}^{-1}$ ).

|| Thaumasite exhibits additional vibrational modes due to carbonate anions in the mineral structure (1392  $\text{cm}^{-1}$ ,  $\nu_3$ ; 880  $\text{cm}^{-1}$ ,  $\nu_2$ ; 329  $\text{cm}^{-1}$ , lattice mode) and Si-O (765 and 680  $\text{cm}^{-1}$ ,  $\nu\text{Si-O}$ ; 494 and ~460  $\text{cm}^{-1}$ ,  $\delta\text{Si-O}$ ).

# Linarite contains contaminant cerussite and hence has observable carbonate bands at 1454, 1392, 1050, 839, and 680  $\text{cm}^{-1}$ .

have a smaller radius than  $\text{K}^+$ , hence the minamiite spectral features likely should be offset to higher wavenumbers (higher frequency) due to the stronger bonds. The bands are shifted minimally and may be due partially to the impurity of the minamiite, which is contaminated by ~8% alunite. The largest shifts, albeit small, are seen in the position of the  $\nu_4$  bands. For minamiite, they are located at 700 and 634  $\text{cm}^{-1}$ . The depths of some of

the minamiite features are shallower relative to the same bands in alunite (i.e., the bands at 1268, 1167, 1029, 700, 531, and 437  $\text{cm}^{-1}$ ). These band-depth differences likely are crystal-axis orientation effects.

Jarosite, natrojarosite, and plumbojarosite are all also isostructural to alunite. Jarosite exhibits two  $\nu_3$  bands at 1220 and 1112  $\text{cm}^{-1}$ , a  $\nu_1$  band at 1006  $\text{cm}^{-1}$ , and a single  $\nu_2$  at 445  $\text{cm}^{-1}$ . The

jarosite spectrum shows a subtle shoulder at  $\sim 662$  on a stronger feature at  $635\text{ cm}^{-1}$  suggesting two  $\nu_4$  bands [as also was seen in the transmission spectra of Powers et al. (1975), Serna et al. (1986), and Bishop and Murad (2005)]. These bands suggest  $C_{3v}$  sulfate symmetry as supported by other studies (e.g., Adler and Kerr 1965; Ross 1974; Lazaroff et al. 1982). Additional modes of jarosite are shown to occur at  $\sim 1020$  (due to  $\delta\text{OH}$ ) and 524, 476,  $\sim 336$ , and  $\sim 242\text{ cm}^{-1}$  due to Fe-O lattice modes. Shokarev et al. (1972) and Lazaroff et al. (1982) assigned the former two bands to  $\tau\text{OH}$ -translational modes and the band at  $\sim 336\text{ cm}^{-1}$  to a  $\tau\text{SO}_4$ -translational mode using their transmission spectra. The broader lattice-mode band at  $524\text{ cm}^{-1}$  suggests a possible superposed  $\gamma\text{OH}$  mode on the higher frequency side of the feature as observed by both Serna et al. (1986) and Sasaki et al. (1998). An emissivity maximum at  $1633\text{ cm}^{-1}$  results from  $\delta\text{H}_2\text{O}$ . Jarosites and alunites are isostructural, but the sulfate tetrahedra are more distorted in alunite, hence the split between the  $\nu_3$  modes is  $\sim 151\text{ cm}^{-1}$  in alunite and  $108\text{ cm}^{-1}$  in jarosite. This relationship of the  $\nu_3$  bands is similar to that noted by Serna et al. (1986).

Natrojarosite differs from jarosite through the replacement of  $\text{K}^+$  by  $\text{Na}^+$  in the structure. Theoretically, natrojarosite should exhibit the same features as jarosite but with bands shifted to higher frequencies as a result of the smaller cation ( $\text{Na}^+$ ) in the structure. Inspection of Figure 2 shows otherwise, primarily because the natrojarosite spectrum exhibits features that result from scattering in a particulate sample. For example, the decreased emissivity at  $\sim 1275\text{ cm}^{-1}$  and the broad, bowl-shaped feature with an emissivity minimum at  $\sim 944\text{ cm}^{-1}$  result from the finer effective particle size of the natrojarosite. The natrojarosite spectrum does, however, display a  $\nu_3$  feature at  $\sim 1116\text{ cm}^{-1}$  that occurs at a slightly higher wavenumber than the jarosite counterpart. This relationship also was seen by Sasaki et al. (1998) and Bishop and Murad (2005). A second  $\nu_3$  feature is not distinct, but may be a small feature at ( $\sim 1220\text{ cm}^{-1}$ ). The former  $\nu_3$  feature is broadened on the higher-frequency side likely due to another  $\nu_3$  band that is apparent at  $\sim 1165\text{ cm}^{-1}$ . Three  $\nu_3$  features were identified in Sasaki et al. (1998) likely due to the presence of both Na and Fe cations, even though the  $C_{3v}$  sulfate symmetry predicts only two  $\nu_3$  features. The feature at  $\sim 1006\text{ cm}^{-1}$  is the  $\nu_1$  band, but its higher-frequency breadth is due to a superposed  $\delta\text{OH}$  band. The  $\nu_4$  feature of natrojarosite occurs at  $678\text{ cm}^{-1}$ . Although not as clear as the previous band, another  $\nu_4$  feature occurs at  $\sim 632\text{ cm}^{-1}$ . These  $\nu_4$  bands of natrojarosite show broader splitting than in jarosite. The  $\nu_2$  band is assigned at  $445\text{ cm}^{-1}$  (just as in jarosite), and other bands occur at  $604\text{ cm}^{-1}$  (due to  $\gamma\text{OH}$ ), and at  $510$  and  $469\text{ cm}^{-1}$  [due to Fe-O vibrations; Shokarev et al. (1972) and Lazaroff et al. (1982) assign these two bands to  $\tau\text{OH}$ -translational modes]. An emissivity maximum at  $1629\text{ cm}^{-1}$  is due to the bending vibration of water ( $\delta\text{H}_2\text{O}$ ) (e.g., Sejkora and Āuda 1998, using transmission data). The emissivity maximum at  $\sim 1979\text{ cm}^{-1}$  is thought to be the overtone of the  $\delta\text{OH}$  feature (Bishop and Murad 2005) that occurs at  $\sim 1010\text{ cm}^{-1}$ ; however, Bishop and Murad (2005) also suggest that this band could be the overtone of a  $\nu_3$  band, but that assignment does not seem to fit the emissivity data as well as the  $\delta\text{OH}$  overtone assignment. Future deuteration studies could verify the proper assignment. Other features that arise from combinations and overtones occur, but have not been assigned.

The plumbojarosite sample is a particulate sample, hence its spectrum shows evidence of volume scattering. Volume scattering is manifested as broad emissivity minima at  $>1240\text{ cm}^{-1}$  and  $\sim 1050$  to  $820\text{ cm}^{-1}$ . Sasaki et al. (1998) noted that the  $\text{Pb}^{2+}$  cations occupy only half of the sites of  $\text{K}^+$  in jarosite and  $\text{Na}^+$  in natrojarosite (i.e., in a unit structure there is an  $\text{SO}_4^{2-}$  adjacent to  $\text{Pb}^{2+}$  ions and an  $\text{SO}_4^{2-}$  adjacent to vacant sites); a related difference is that the crystallographic unit-cell  $c$  parameter ( $33.85\text{ \AA}$ ) is about twice that of jarosite and natrojarosite ( $17.22$  and  $16.72\text{ \AA}$ , respectively). Sasaki et al. (1998) found that the  $c$  parameter affects the stretching modes ( $\nu_1$  and  $\nu_3$ ) but not the bending modes ( $\nu_2$  and  $\nu_4$ ). This causality allows plumbojarosite to exhibit three  $\nu_3$  bands—at  $1200$ ,  $1116$ , and  $1080\text{ cm}^{-1}$ —when only two  $\nu_3$  bands are predicted for the sulfate symmetry. Three  $\nu_3$  bands are consistent with the number observed by Sasaki et al. (1998). It is unclear where the  $\nu_1$  mode appears; it could be either [or both due to the peculiar unit structure of plumbojarosite mentioned above and seen in Sasaki et al. (1998)] of the two shoulders at  $1004$  and  $994\text{ cm}^{-1}$  on the deeper volume-scattering feature. Between the possible  $\nu_1$  and the  $\nu_3$  bands lies a feature at  $1024\text{ cm}^{-1}$  due to  $\delta\text{OH}$ . The  $\nu_4$  bands appear at  $\sim 678$  and  $\sim 625\text{ cm}^{-1}$  (the inflection within this second band is thought to be noise in the spectrum) and the  $\nu_2$  band occurs at  $446\text{ cm}^{-1}$ . Other bands include an emissivity maximum at  $\sim 1628\text{ cm}^{-1}$  due to the bending vibration of water ( $\delta\text{H}_2\text{O}$ ) (e.g., Omori and Kerr 1963), an unidentified band at  $800\text{ cm}^{-1}$  [similar in position to an unassigned band in natrojarosite in the transmission spectrum of Bishop and Murad (2005)], a  $\gamma\text{OH}$  band at  $586\text{ cm}^{-1}$ , and bands at  $500$  and  $474\text{ cm}^{-1}$  due to Fe-O vibrations.

The other sulfates in this class exhibit simpler spectra regardless the presence of being another anion in the structure such as F and Cl in sulfohalite,  $\text{CO}_3$  in burkeite, and  $\text{CO}_3$  and Cl in hanksite (Fig. 2). The spectrum of isometric sulfohalite, whose structure is composed of sulfate anions surrounded by 12 Na cations as well as NaF and NaCl octahedra, exhibits traditional features related to the internal vibrations of the sulfate anion. The  $\nu_3$  doublet features occur at  $1178$  and  $1148\text{ cm}^{-1}$  and a  $\nu_4$  singlet occurs at  $628\text{ cm}^{-1}$ . This isometric crystal exhibits no apparent  $\nu_1$  or  $\nu_2$  bands, suggestive of a fairly undeformed sulfate tetrahedron; the lack of  $\nu_1$  and  $\nu_2$  plus the two  $\nu_3$  bands suggest  $D_{2d}$  symmetry. This symmetry permits two  $\nu_4$  bands but only one is visible, hence the  $\nu_4$  band must be doubly degenerate. However, Omori (1970) suggested  $T_d$  symmetry for the sulfate anions in sulfohalite. By using factor group analysis (on the space group  $O_h^2$  and site group  $T_d$  of the  $\text{SO}_4$  ion) and the calculated force constants of the Urey-Bradley force field (Urey and Bradley 1931), Omori calculated the normal modes of vibration of sulfohalite that he attributes to combination bands of the lattice modes in the far infrared. His mathematical determinations match well the bands in his transmission spectrum which is similar to the measured emissivity spectrum of sulfohalite (Fig. 2) and predict the splitting seen in the  $\nu_3$  bands, due to combinations of the  $\text{SO}_4$  molecular vibrations and long-wavelength lattice modes [i.e., internal-external combination bands (Mitra 1963)]. The deep bands that occur superposed at  $\sim 333$  and  $322\text{ cm}^{-1}$  were attributed by Omori (1970) to lattice vibrations that arise from the  $\text{Na}_6\text{Cl}$  and  $\text{Na}_6\text{F}$  octahedra. Another lattice-mode band is present, but truncated at  $220\text{ cm}^{-1}$ .

Although White (1974) stated that "...detailed interpretation is impossible" (p. 273) of spectra of minerals with complex structures, including burkeite, I disagree with that view and my interpretation follows. The burkeite spectrum (Fig. 2) clearly shows spectral evidence of both the  $\text{SO}_4$  and  $\text{CO}_3$  anions. The spectral character at  $>1250\text{ cm}^{-1}$  is dominated by the behavior of the carbonate anion (e.g., the emissivity maximum at  $1768\text{ cm}^{-1}$  and the neighboring band at  $1736\text{ cm}^{-1}$ ; the emissivity minimum at  $1477$  and  $1429\text{ cm}^{-1}$  due to  $\text{CO}_3\text{ v}_3$ ). Carbonate also causes the emissivity maxima at  $886\text{ cm}^{-1}$  ( $\text{CO}_3\text{ v}_2$ ),  $855$ , and  $703\text{ cm}^{-1}$  ( $\text{CO}_3\text{ v}_4$ ) (Lane and Christensen 1997). These are maxima because they are transparency features [Type II and Type III behaviors, as classified by Hunt and Vincent (1968)] related to the friable nature of the sample that has a fine powder on the surface. A fine-grained spectrum of carbonate can be seen in Lane (1999) for comparison and for detailed discussion of the similar spectral features. The sulfate anion in burkeite causes features at  $1200$ ,  $1170$ , and  $1128\text{ cm}^{-1}$  all related to the sulfate  $\text{v}_3$  asymmetric-stretching vibration. The weak emissivity minimum at  $1015\text{ cm}^{-1}$  is due to the sulfate  $\text{v}_1$  and the band at  $618\text{ cm}^{-1}$  is due to  $\text{v}_4$ , and it is likely that the shoulders at  $642$  and  $625\text{ cm}^{-1}$  are also likely  $\text{v}_4$  features. These bands suggest the possibility of  $\text{C}_{2v}$ ,  $\text{C}_2$ ,  $\text{C}_s$ , or  $\text{C}_1$  symmetry of the sulfate, but it is not clear which one is correct. All of these possibilities predict one to two  $\text{v}_2$  bands; however, it is not clear which of the spectral feature(s) represent this mode; perhaps it is the band at  $441\text{ cm}^{-1}$ . The bands at  $515$  and  $490\text{ cm}^{-1}$  possibly are due to metal-O bonds. Finally, burkeite exhibits a very strong feature truncated at  $220\text{ cm}^{-1}$ , representing a lattice mode.

Hanksite also contains features related to constituent carbonate. These carbonate bands occur at  $1468$  and  $877$  ( $\text{v}_3$  and  $\text{v}_2$ , respectively). Omori and Kerr (1963) also noted these carbonate bands in their hanksite transmission spectrum. There are four sulfate  $\text{v}_3$  bands at  $1195$ ,  $1176$ ,  $1162$ , and  $1135\text{ cm}^{-1}$  due to both K and Na being bound to the sulfate anions. The sulfate  $\text{v}_1$  band appears as a subtle feature at  $986\text{ cm}^{-1}$ . Two strong bands at  $634$  and  $620\text{ cm}^{-1}$  represent the sulfate  $\text{v}_4$  mode. The lower-wavenumber bands at  $285$  and  $249\text{ cm}^{-1}$  are lattice modes.

### Hydrous sulfates

The samples of this classification (Strunz 6/C.) presented here include kieserite, szomolnokite, rozenite, hexahydrate, coquimbite/paracoquimbite, pickeringite, apjohnite, potassium alum, bloedite, polyhalite, bassanite, and gypsum. For this subclass, each mineral contains bound  $\text{H}_2\text{O}$ , in various abundances. It should be noted that this study did not extend to the higher frequencies at which bound water is best studied due to the presence of the strong OH-stretching modes ( $\sim 4000\text{--}3000\text{ cm}^{-1}$ ) and at even higher frequencies due to water overtones ( $\sim 6500\text{--}7000\text{ cm}^{-1}$ ). However, continued research with the samples studied in this work is being conducted with other spectroscopic techniques (e.g., Lane et al. 2004), including the higher frequency region.

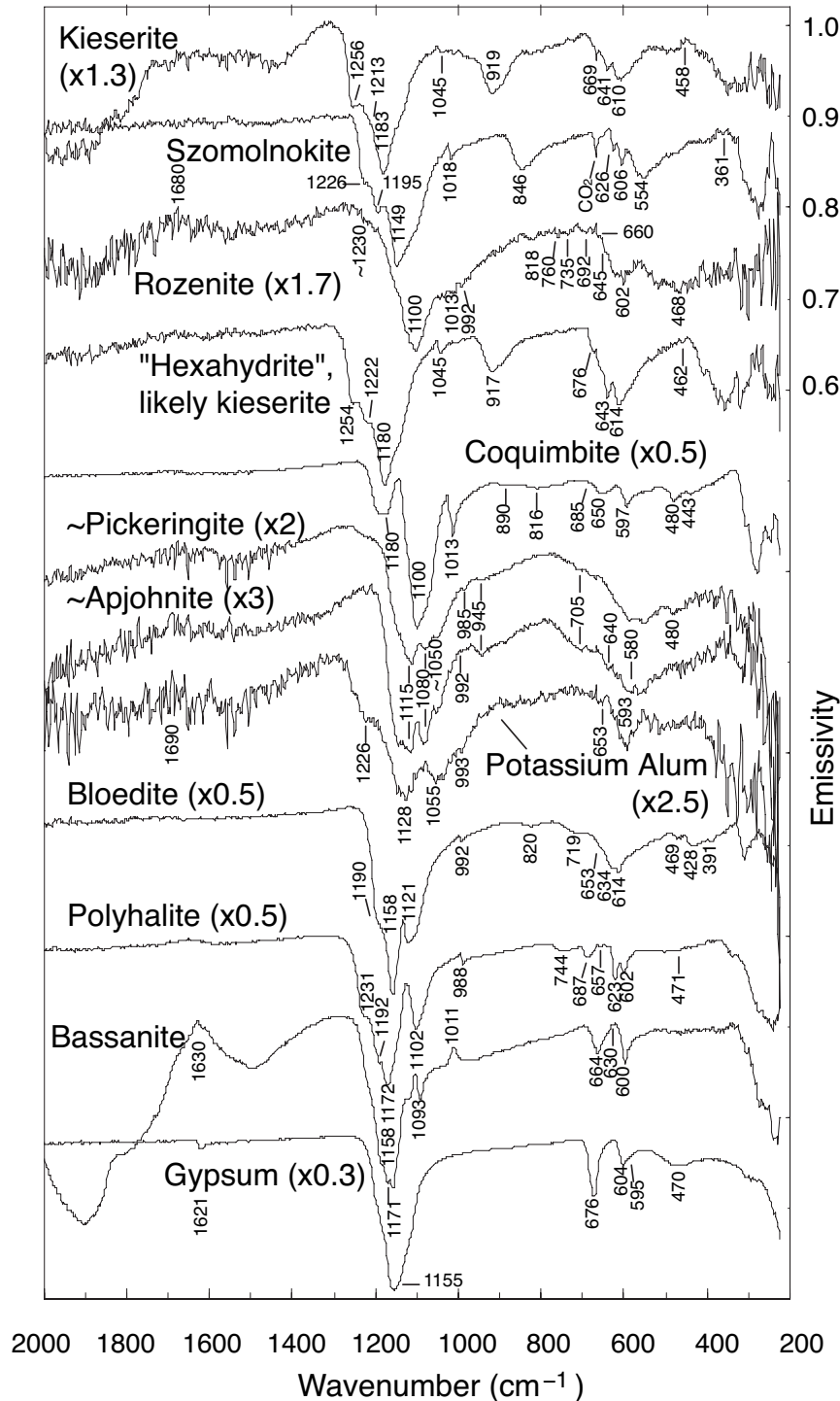
A kieserite spectrum is shown in Figure 3. The sulfate  $\text{v}_3$  bands in this monohydrate are present at  $1256$  and  $1183\text{ cm}^{-1}$  with a subtle third band at  $\sim 1213\text{ cm}^{-1}$ . The  $\text{v}_1$  band is seen at  $1045\text{ cm}^{-1}$  and three  $\text{v}_4$  bands occur at  $669$ ,  $641$ , and  $\sim 610\text{ cm}^{-1}$ . The feature at  $458\text{ cm}^{-1}$  is assigned to the  $\text{v}_2$  band. The sulfate tetrahedra in kieserite are known to be in  $\text{C}_2$  site symmetry (e.g., Hezel and Ross 1966; Stoilova and Lutz 2002). This symmetry

predicts the three  $\text{v}_3$  and  $\text{v}_4$  bands and a single  $\text{v}_1$  band, but also an additional  $\text{v}_2$  band that is unassigned here. There is a pronounced feature at  $919\text{ cm}^{-1}$  that is uncommon but otherwise is seen only in szomolnokite (also a monohydrated Fe-sulfate) of the other sulfates in this paper. This uncommon band likely is due to the unusual librational modes of the water molecule seen in kieserite-group minerals but not in other hydrates in which water molecules form a similar coordination (Grodzicki and Piszczek 1998). The presence of this band is a reliable indicator of monohydrated kieserite-group sulfates. This water libration band also appears very distinctly in the kieserite transmission spectrum of Moenke (1962). The long-wave, broad band at  $\sim 350\text{ cm}^{-1}$  is due likely to the M-O vibration in the coordinated sulfate anion (Ferraro and Walker 1965).

Szomolnokite also is a monohydrated sulfate and it is considered to be an end-member in a solid-solution series with kieserite (Jambor et al. 2000). The szomolnokite hand sample is well-crystalline and provided strong spectral features (Fig. 3). This szomolnokite spectrum closely resembles that of kieserite; however, the szomolnokite spectral features are shifted to longer wavelengths by roughly  $20\text{--}100$  wavenumbers. The internal vibrational bands due to the sulfate anion are distinct in the spectrum shown in Figure 3 and consist of three  $\text{v}_3$  bands at  $1226$ ,  $1195$ , and  $1149\text{ cm}^{-1}$ . The  $\text{v}_1$  band appears as a small feature at  $1018\text{ cm}^{-1}$ . Features at  $626$ ,  $606$ , and  $554\text{ cm}^{-1}$  result from the  $\text{v}_4$  vibrations. The unusual emission feature at  $846\text{ cm}^{-1}$  is due to water libration (Grodzicki and Piszczek 1998), as was seen in the kieserite spectrum at  $919\text{ cm}^{-1}$ . The sharp feature at  $\sim 669\text{ cm}^{-1}$  is due to the improper removal of atmospheric  $\text{CO}_2$  in the sample chamber and is not related to the mineral sample itself. The many sulfate-related absorption features result from the distortions of the  $\text{SO}_4$  tetrahedron, and the number of bands supports the  $\text{C}_2$  site symmetry for sulfate anion in szomolnokite, a kieserite-group mineral (Hezel and Ross 1966). This symmetry additionally predicts two  $\text{v}_2$  bands, one of which could be represented by the feature at  $361\text{ cm}^{-1}$  but the assignment is uncertain. The truncated band at  $\sim 275$  likely is due to a Fe-O vibration.

The mineral rozenite is closely related to szomolnokite because the former is known to dehydrate readily to the latter. The water in rozenite causes an emissivity maximum at  $\sim 1680\text{ cm}^{-1}$  (due to the  $\delta\text{H}_2\text{O}$  mode), a band at  $818\text{ cm}^{-1}$ , and weaker bands at  $\sim 760$ ,  $735$ , and  $692\text{ cm}^{-1}$  that likely result from  $\delta\text{OH}$  (Fig. 3). Rozenite exhibits a deep  $\text{v}_3$  feature at  $1100\text{ cm}^{-1}$  and two small shoulder features at  $\sim 1013$  and  $1195\text{--}1260\text{ cm}^{-1}$  that also are representative of the  $\text{v}_3$  bands. The  $\text{v}_1$  band appears at  $992\text{ cm}^{-1}$ . The rozenite spectrum shows a fairly broad  $\text{v}_4$  band centered at  $\sim 602\text{ cm}^{-1}$  with two other  $\text{v}_4$  bands that appear as subtle shoulders on the higher frequency side at  $\sim 660$  and  $645\text{ cm}^{-1}$ , and a possible  $\text{v}_2$  band at  $468\text{ cm}^{-1}$ . The emissivity bands present in the monoclinic rozenite spectrum cannot identify further the sulfate site symmetry beyond either  $\text{C}_1$  or  $\text{C}_2$ .

The hexahydrate spectrum shown in Figure 3 appears almost identical to the kieserite spectrum also shown in that figure and discussed above. Both spectra exhibit the uncommon feature at  $\sim 920\text{ cm}^{-1}$  thought to be unique to and diagnostic of the monohydrated, kieserite-group sulfates (Grodzicki and Piszczek 1998), as is seen also in the spectrum of monohydrated szomolnokite discussed above. Kieserite readily hydrates to hexahydrate



**FIGURE 3.** Mid-infrared thermal emissivity spectra of hydrous sulfates. The band depths of some spectra have been modified for easier comparison as noted by the parenthetical values. Spectra are offset for clarity.

dration/dehydration trends of the Mg sulfates, and better assessment/control of their hydration must be done to understand fully the spectral differences between the mineral species. On the basis of the "hexahydrate" spectrum shown, the bands occur as follows: three  $\nu_3$  at 1254, 1222, and 1180  $\text{cm}^{-1}$ ;  $\nu_1$  at 1045  $\text{cm}^{-1}$ ; water libration at 917  $\text{cm}^{-1}$ ;  $\nu_4$  at 676, 643, and 614  $\text{cm}^{-1}$  and  $\nu_2$  possibly at 462  $\text{cm}^{-1}$ ; however, these likely are the appropriate band assignments for kieserite, not actual hexahydrate. The long-wave, broad band at  $\sim 358 \text{ cm}^{-1}$  and its neighboring inflections are due likely to M-O vibrations in the coordinated sulfate anion (Ferraro and Walker 1965).

The coquimbite/paracoquimbite sample is well-crystalline and contains approximately subequal amounts of the two minerals, which are polytypic. The coquimbite/paracoquimbite spectrum (Fig. 3) shows two clear  $\nu_3$  features at 1180 and 1100  $\text{cm}^{-1}$ ; the shape of the 1100  $\text{cm}^{-1}$  band suggests that there may be another weaker  $\nu_3$  band at slightly lower frequency [three bands were seen in transmission data of Moenke, (1962) as reported by Ross (1974)]. A strong  $\nu_1$  feature is present at 1013  $\text{cm}^{-1}$ . Three  $\nu_4$  bands occur at 685, 650, and 597  $\text{cm}^{-1}$ ; however, the 685  $\text{cm}^{-1}$  band is very small, but distinct in this very clean spectrum. The  $\nu_2$  features occur at 480 and 443  $\text{cm}^{-1}$  with strong lattice modes occurring at  $< 350 \text{ cm}^{-1}$ . The bands that result from the water in the coquimbite structure can be seen at  $\sim 890$  and  $816 \text{ cm}^{-1}$  (bending modes).

Neither the pickeringite nor apjohnite samples are pure, as determined by XRD analyses; each sample con-

tains both of the above plus subordinate amounts of kalinite and halotrichite  $[\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}]$ . These mineral assemblages are quite common due to the extensive solid solution between them and that they are all halotrichite-group minerals (Jambor et al. 2000), except for kalinite. For this reason these two spectra are very similar and discussed together. These spectra each show three  $\nu_3$  bands at  $\sim 1115$ ,  $\sim 1080$ , and  $1047\text{--}1054 \text{ cm}^{-1}$ . Two  $\nu_3$

contains both of the above plus subordinate amounts of kalinite and halotrichite  $[\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}]$ . These mineral assemblages are quite common due to the extensive solid solution between them and that they are all halotrichite-group minerals (Jambor et al. 2000), except for kalinite. For this reason these two spectra are very similar and discussed together. These spectra each show three  $\nu_3$  bands at  $\sim 1115$ ,  $\sim 1080$ , and  $1047\text{--}1054 \text{ cm}^{-1}$ . Two  $\nu_3$

bands for pickeringite in Ross (1974) are listed as occurring at 1085 and 1025  $\text{cm}^{-1}$ ; however, the latter is a carryover typo from Moenke (1962), which still is being propagated incorrectly in the literature (e.g., see Frost et al. 2000, 2005) and actually is seen clearly in the Moenke spectrum at 1125  $\text{cm}^{-1}$ . Although only two  $\nu_3$  bands were identified from Moenke (1962), the Moenke pickeringite spectrum very closely resembles the Moenke halotrichite spectrum in which a subtle band at  $\sim 1068 \text{ cm}^{-1}$  also was identified as a  $\nu_3$  band (Ross 1974). Considering the similarity between the Moenke pickeringite and halotrichite spectra and of the “pickeringite” and “apjohnite” spectra of this study, and the fact that they are all halotrichite-group minerals, the band assignments I give to the  $\nu_3$  bands are supported. A  $\nu_1$  band is seen at 985  $\text{cm}^{-1}$  (this band is subtle in the “apjohnite” spectrum and occurs at 992  $\text{cm}^{-1}$ ). A clearer band occurs at  $\sim 945 \text{ cm}^{-1}$  in both spectra that likely is due to the bending mode of the OH in the structures. The bending mode of  $\text{H}_2\text{O}$  appears as an emissivity maximum at  $\sim 1680 \text{ cm}^{-1}$  (Ross 1974). The  $\nu_4$  bands can be seen at  $\sim 705, 640,$  and  $580 \text{ cm}^{-1}$ , but these bands are fairly ill-defined, likely as a result of extensive solid solution and the impurities of the minerals. A band in “pickeringite” occurs at  $\sim 480 \text{ cm}^{-1}$  that likely is due to a  $\nu_2$  mode [a band at 480  $\text{cm}^{-1}$  in the halotrichite spectrum of Moenke (1962) also was identified as  $\nu_2$ ]; however, no additional  $\nu_2$  band is obvious [but is predicted by either  $C_1$  or  $C_2$  site symmetry (Ross 1974)]; nor are any clear  $\nu_2$  bands seen in the “apjohnite” spectrum. These spectra are fairly noisy though, due to keeping the sample temperatures low during measurement to prevent water from being driven out of the samples.

Due to low temperatures during data acquisition, the potassium alum (that is, potash alum or kalinite) spectrum (Fig. 3) is also a bit noisy. However, three  $\nu_3$  bands are seen at 1226, 1128, and 1055  $\text{cm}^{-1}$ , whereas the  $\nu_1$  band is seen at 993  $\text{cm}^{-1}$ . A pronounced  $\nu_4$  feature occurs at  $\sim 593 \text{ cm}^{-1}$  and a second likely  $\nu_4$  band occurs at  $\sim 653 \text{ cm}^{-1}$ , but a third  $\nu_4$  band was not assigned, even though it is predicted by what appears to be  $C_{2v}$  sulfate symmetry on the basis of the other bands presented here. This symmetry determination is consistent with the results of Frost and Klopogge (2001) but is inconsistent with the  $C_{3v}$  symmetry of Campbell et al. (1970) and Ross (1974) that would only allow two  $\nu_3$  bands. However, the Moenke (1962) transmission data that Ross interpreted as having only two  $\nu_3$  bands does indeed show a band at 1075  $\text{cm}^{-1}$  that I interpret as a third  $\nu_3$  band (disallowed by  $C_{3v}$  symmetry), reinforcing my interpretation of  $C_{2v}$  sulfate symmetry in potassium alum. A vibrational band related to the water bending mode is seen as a subtle emissivity maximum at  $\sim 1690 \text{ cm}^{-1}$  (Frost et al. 2000), and the general absorption at  $\sim 500 \text{ cm}^{-1}$  may be due to a water libration mode and a superposed  $\nu_2$ , although these individual bands are not distinct in this spectrum.

The bloedite spectrum (Fig. 3) exhibits three  $\nu_3$  bands at 1190 (shoulder), 1158, and 1121  $\text{cm}^{-1}$ , and a  $\nu_1$  band at 992  $\text{cm}^{-1}$ . The  $\nu_4$  bands were assigned at 653 (shoulder), 634, and 614  $\text{cm}^{-1}$  and two  $\nu_2$  bands are seen at 469 and 428  $\text{cm}^{-1}$ . These band assignments are consistent with  $C_1$  sulfate symmetry (Ross 1974). The bands seen at 820 and 719  $\text{cm}^{-1}$  are due to the water-bending modes present in the mineral. The features at 391  $\text{cm}^{-1}$  and lower frequency likely are lattice modes.

Polyhalite (Fig. 3) exhibits  $\nu_3$  features at 1231 (shoulder),

1172, and 1102  $\text{cm}^{-1}$ ; an additional small band at 1192  $\text{cm}^{-1}$  is also likely a  $\nu_3$  mode associated with another of the three cations in the mineral (K, Mg, Ca) that also are coordinated to the sulfate anion and offer various sulfate polyhedral distortions. A sharp  $\nu_1$  feature occurs at 988  $\text{cm}^{-1}$  with an additional small  $\nu_1$  band at 1010  $\text{cm}^{-1}$  due to the many sulfate distortions. The  $\nu_4$  bands occur at 623 and 602 with a small third band at 657  $\text{cm}^{-1}$ . The 744 and 687  $\text{cm}^{-1}$  bands are water librational modes (Ross 1974; Gadsden 1975). The emissivity maximum at 1651  $\text{cm}^{-1}$  is the manifestation of the  $\text{H}_2\text{O}$ -bending mode (e.g., Omori and Kerr 1963; Ross 1974). The  $\nu_2$  bands are small enough not to be able to assign properly; however, the symmetry of the sulfate anion ( $C_1$ , Ross 1974) predicts two bands, one of which may be the band at  $\sim 471 \text{ cm}^{-1}$ . The band at  $\sim 244 \text{ cm}^{-1}$  that is truncated at longer wavelengths is interpreted as a lattice mode. The emissivity spectrum presented here appears with fewer bands than the “very complex” transmission spectrum of Moenke (1962) described by Ross (1974) that suggests five  $\nu_3$  bands, two  $\nu_1$  bands, three  $\nu_4$  bands, three  $\nu_2$  bands, and several water-bending and librational bands, likely because of the different sulfate-coordinated cations in the structure (K, Mg, Ca). Nonetheless, the correlation between the two spectra is simple to make because the overall shape of the spectra are very similar and the assignments of the bands given here for the emissivity spectrum agree with those presented by Ross.

Bassanite (hemihydrate) is a Ca-sulfate whose hydration state ( $0.5 \text{ H}_2\text{O}$ ) falls between that of anhydrite ( $\text{CaSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The bassanite  $\nu_3$  features (Fig. 3) occur at 1171, 1158, and 1093  $\text{cm}^{-1}$ . The  $\nu_1$  feature is not a sharp peak, but rather is observed as the downward trend of the spectrum (at 1000  $\text{cm}^{-1}$ ) on the low-frequency side of a sharp emissivity maximum at 1011  $\text{cm}^{-1}$ . Two distinct  $\nu_4$  bands are seen as sharp features at 664 and 600  $\text{cm}^{-1}$  and a small additional  $\nu_4$  band occurs between them at 630  $\text{cm}^{-1}$ . A truncated band occurs at  $\sim 240 \text{ cm}^{-1}$  that is thought to result from a Ca-O mode (Ferraro and Walker 1965). The  $\nu_2$  bands, if present, are unclear among the spectral noise, but were identified at  $\sim 465$  and  $\sim 420 \text{ cm}^{-1}$  in the transmission spectrum of Moenke (1962) as reported by Ross (1974). All of these bands considered together do not distinguish uniquely the sulfate site symmetry between  $C_2$  and  $C_1$  (Ross 1974). It is unlikely, however, that the symmetry is  $D_2$ , also listed by Ross as a possibility, because an otherwise unpredicted  $\nu_1$  band is seen here that also has been identified in other works (e.g., Sarma et al. 1998, using Raman data; Prasad et al. 2005, using transmission and Raman data). An emissivity maximum at 1630  $\text{cm}^{-1}$  represents the  $\delta\text{H}_2\text{O}$  mode.

The gypsum spectrum (Fig. 3) shows one obvious  $\nu_3$  mode at 1155  $\text{cm}^{-1}$ ; however, the slightly bowed non-Lorentzian shape suggests the possibility of other bands that also are predicted by the  $C_2$  site symmetry of the sulfate tetrahedron (Hass and Sutherland 1956; Hezel and Ross 1966; Berenblut et al. 1971). In fact, several distinct  $\nu_3$  bands were seen using polarized reflectance, as demonstrated by three unique extinction coefficient maxima (Hass and Sutherland 1956).  $C_2$  symmetry suggests there should be one  $\nu_1$  band; however, this  $\nu_1$  band is not perceptible in the emissivity spectrum, likely because the  $\nu_1$  band is very weak, as is also the case for the transmission spectrum of Moenke (1962). The simplicity of the  $\nu_3$  band(s) (i.e., the lack of splitting) sug-

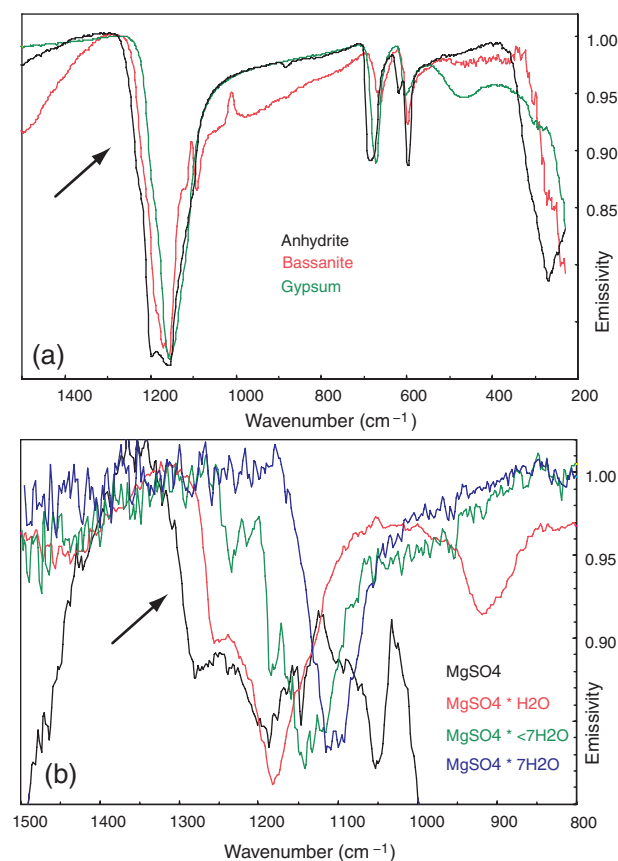
gests minimal distortion. Crowley and Hook (1996) presented a gypsum spectrum acquired using directional-hemispherical reflectance that also does not show a  $\nu_1$  band, and Vassallo and Finnie (1992) showed a  $\nu_1$  band in gypsum that disappears with increasing experimental temperatures. Two  $\nu_4$  bands are seen at 676 and 604  $\text{cm}^{-1}$  with a possible shoulder on the lower-frequency band at  $\sim 595 \text{ cm}^{-1}$  (a third  $\nu_4$  band?), consistent with the two  $\nu_4$  bands observed in transmission by both Putnis et al. (1990) and Prasad et al. (2005), regardless of the  $C_2$  symmetry predicting three bands. Three  $\nu_4$  bands were observed by Hass and Sutherland (1956) using a reflection technique, but two were extremely close together (at 602 and 604  $\text{cm}^{-1}$ ). A broad band is seen at  $\sim 470 \text{ cm}^{-1}$  that was assigned by Hass and Sutherland (1956) to a water libration and their rationale is reasonable and probable; however, in Raman spectra there are two  $\nu_2$  bands that occur in much the same position (e.g., Berenblut et al. 1971; Sarma et al. 1998; Prasad et al. 2001; Knittle et al. 2001), so the sulfate  $\nu_2$  vibration may contribute to some, albeit minor, degree (Vassallo and Finnie 1992). A lattice mode occurs at longer wavelengths and is truncated at 220  $\text{cm}^{-1}$ . In gypsum, the water molecules are quite interactive with the CaO and  $\text{SO}_4$  groups (Sarma et al. 1998) and cause a distinct, sharp band ( $\delta\text{H}_2\text{O}$ ) in the emissivity spectrum at 1621  $\text{cm}^{-1}$  (e.g., Hass and Sutherland 1956).

With the addition of water in the gypsum structure, it exhibits a sheet structure, unlike bassanite and anhydrite whose chains of  $\text{SO}_4$  tetrahedra and  $\text{CaO}_8$  dodecahedra are in three-dimensional frameworks. Interestingly, there exists a step-wise trend in both the lattice mode and in the  $\nu_3$  band from anhydrite to bassanite to gypsum. These bands for the anhydrous Ca-sulfate occur at higher frequency than for the bassanite, and the same trend is also true between bassanite and the more-hydrated Ca-sulfate (gypsum) (Fig. 4a). In this sequence the phase transitions are associated with a structural change related to the dehydration and rehydration process (Sarma et al. 1998); however, the structural modification due to water between anhydrite and bassanite is small, so the dehydration-rehydration process is reversible. This is not true for gypsum to bassanite/anhydrite in which the dehydration-rehydration process is irreversible (Hummel et al. 2001). It is interesting to note that the same trend of the  $\nu_3$  band shifting to higher frequency (higher wavenumber) with decreasing water content also was observed in: (1) a separate emission study (M.D. Lane, unpublished) of Mg-sulfates (Fig. 4b), which included  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , oven-dried  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (resulting in water loss),  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  (kieserite), and anhydrous  $\text{MgSO}_4$  reagent; (2) in Fe-sulfates ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , rozenite), under unpurged and purged conditions (Bishop et al. 2005, using emission and reflectance data); and (3) in polyhydrated, monohydrated, and anhydrous Cu-sulfates (Ferraro and Walker 1965, Table VI). Chio et al. (2004) also show this trend in Raman data for the  $\nu_1$  band, shifting to higher frequency from gypsum to bassanite to anhydrite. They suggest that, because anhydrite does not have any molecular water, the S-O bond is stronger than in gypsum. Also, the hydrogen bonding in bassanite is considerably weaker than that in gypsum due to a longer  $\text{OH} \cdots \text{O}$  bonding distance, and the weakened hydrogen bonding in bassanite leads to a stronger S-O bond (thus the higher-frequency of the  $\nu_1$  band).

Decreasing the particle size of a mineral sample causes the fundamental vibrational band depths to shallow and in some cases

to invert, and also causes volume scattering features to appear and deepen. The latter often enhances the spectral contrast associated with very weak bands, thereby allowing their position to be identified.

To study particle size effects for a sulfate mineral, a fine-grained,  $<10 \mu\text{m}$  powder was made of the gypsum sample and the emissivity spectrum was obtained (not shown). Differences between emissivity spectra of particulate and consolidated hand samples are due primarily to the increasing number of grain/air interfaces per unit volume with decreasing particle size and the associated increase in scattering due to reflections and refractions from both external (multiple scattering) and internal (volume scattering) sides of the grain. The fine-grained gypsum sample showed typical Type I, II, and III behaviors as defined by Hunt and Vincent (1968). Type I behavior occurred in the  $\nu_3$  region of gypsum (at  $\sim 1155 \text{ cm}^{-1}$ ). Type II behavior was seen at  $\sim 1621$ ,  $\sim 676$ , and  $\sim 604 \text{ cm}^{-1}$ . Additionally, in the transparency/volume scattering region located between the  $\nu_3$  and  $\nu_4$  bands, some sharp, Type III emissivity maxima were observed (i.e., very small, weak bands became more prominent and appeared as sharp emissivity maxima within broad emissivity troughs as particle size decreased and spectral contrast was enhanced). These sharp maxima in the fine-grained sample spectrum enabled



**FIGURE 4.** Emissivity spectra of (a) Ca-sulfates and (b) Mg-sulfates showing the shift to higher frequency (larger wavenumber) of the  $\nu_3$  (see arrow) and lattice modes (in Ca sulfates) associated with the dehydration of the mineral.

the otherwise very weak and previously unseen  $\nu_1$  feature and equally weak  $\delta\text{OH}$  feature to be identified in gypsum (at  $\sim 1010$  and  $\sim 877$   $\text{cm}^{-1}$ , respectively).

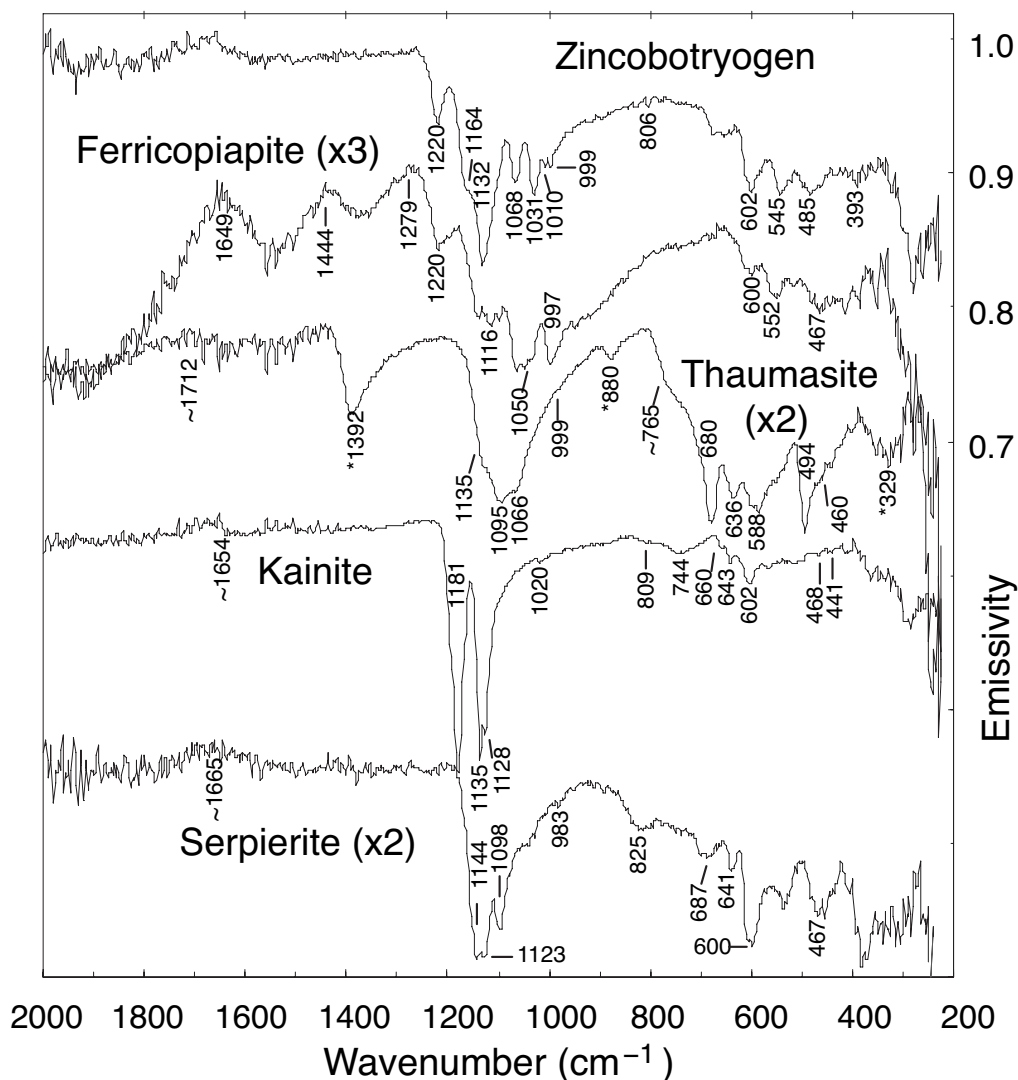
### Hydrous sulfates with additional anions

The samples of this classification (Strunz 6/D.) presented here include zincobotryogen, ferricopiapite, thaumasite, kainite, and serpierite. Both zincobotryogen and ferricopiapite are members of the copiapite group minerals. The spectra for each of these samples are shown in Figure 5.

The zincobotryogen spectrum has many bands for this complex, monoclinic salt, due to the additional presence of OH and  $\text{H}_2\text{O}$  in the structure and its low symmetry. The  $\nu_3$  bands occur at 1220, 1132, and 1031, with additional  $\nu_3$  bands at 1164 (shoulder) and 1068  $\text{cm}^{-1}$ . These five  $\nu_3$  bands exhibited in zincobotryogen are similar to the five  $\nu_3$  bands shown for botryogen in the transmission data of Moenke (1962) as assigned by Ross (1974). The  $\nu_1$  band is small but clear at 999  $\text{cm}^{-1}$ . It is possible that the small band at 1010  $\text{cm}^{-1}$  is due to water in the mineral ( $\delta\text{OH}$ ), as it occurs just to the high-frequency side of the  $\nu_1$  band, similar to that band relationship in jarosite. And a small feature at 806  $\text{cm}^{-1}$

also could result from an OH-bending vibration. Constituent water additionally causes a bending mode ( $\delta\text{H}_2\text{O}$ ) to be seen at 1660  $\text{cm}^{-1}$  (e.g., Ross 1974). Three strong  $\nu_4$  bands are present at 602, 545, and 485  $\text{cm}^{-1}$ . The  $\nu_2$  band may occur at  $\sim 393$   $\text{cm}^{-1}$  and there is a strong lattice band at  $\sim 280$   $\text{cm}^{-1}$ . Ferricopiapite, a triclinic mineral, exhibits  $\nu_3$  bands at 1220,  $\sim 1116$ , and 1050  $\text{cm}^{-1}$ . The  $\nu_1$  clearly occurs at 997  $\text{cm}^{-1}$ . The  $\nu_4$  bands occur at 600 and 552  $\text{cm}^{-1}$ , although this latter band is assigned by Ross (1974), in the similar copiapite spectrum of Moenke (1962), to be an OH-bending mode. The  $\nu_2$  band is exhibited at  $\sim 467$   $\text{cm}^{-1}$  and a strong lattice mode is truncated at 220  $\text{cm}^{-1}$ . The sulfate symmetry of ferricopiapite is  $C_1$  (as it is for copiapite), which allows for one more  $\nu_4$  and one more  $\nu_2$  band than is seen in the emissivity spectrum (Fig. 5). Scattering features related to the small effective particle size of the sample also are seen as the general decrease in emissivity at  $>1649$   $\text{cm}^{-1}$ . One notable doublet occurs between 1649 and 1279  $\text{cm}^{-1}$ . This doublet is due to the water present in the structure of the mineral and is pronounced due to the scattering of the emitted energy from this friable sample. The water in the structure causes the emissivity maxima at  $\sim 1649$  and  $\sim 1444$   $\text{cm}^{-1}$  that result from splitting of the

**FIGURE 5.** Mid-infrared thermal emissivity spectra of hydrous sulfates with additional anions, where the asterisks denote bands from carbonate in the mineral structure. The band depths of some spectra have been modified for easier comparison as noted by the parenthetical values. Spectra are offset for clarity.



H<sub>2</sub>O deformation mode. The emissivity spectra of fine-grained szomolnokite, kieserite, coquimbite, kornelite, and a few other hydrous sulfate samples that display scattering features (none of which are shown here) also exhibit this doublet at variable wavenumber positions; however, this doublet is not seen in their coarse-particle (crystalline) counterparts [e.g., the doublet is not seen in the spectra of (para)coquimbite, kieserite, or szomolnokite samples shown in Fig. 3] nor in any fine-grained non-hydrous sulfate samples. The scattering in the emissivity spectra allows this doublet to be identified, but this doublet also is seen clearly in the transmission data for goslarite and illesite of Moenke (1962), which also are hydrated sulfate minerals.

Thaumasite is a complex hydrated Ca-sulfate mineral (of the ettringite group) that bears anionic compounds of CO<sub>3</sub>, SO<sub>4</sub>, and OH in addition to the bound H<sub>2</sub>O molecules. It is an unusual mineral in that it is the only mineral known to contain Si that coordinates with six hydroxyl groups and is stable at ambient pressures and temperatures (e.g., Edge and Taylor 1971; Lewandowska and Rospondek 2002; Jacobsen et al. 2003). The CO<sub>3</sub>-related features occur at 1392 (CO<sub>3</sub> v<sub>3</sub>), 880 (CO<sub>3</sub> v<sub>2</sub>), and 329 (CO<sub>3</sub> lattice mode) cm<sup>-1</sup>. The sulfate v<sub>3</sub> features occur at ~1135 (shoulder), 1095, and 1066 cm<sup>-1</sup>. The sulfate v<sub>1</sub> appears at 999 cm<sup>-1</sup>, albeit weak. And two strong sulfate v<sub>4</sub> bands occur at 636, and 588 cm<sup>-1</sup>. A strong sulfate lattice mode band is truncated at the long-wavelength end of the spectrum. The spectral features that result from the Si-O vibrations in the unusual Si(OH)<sub>6</sub><sup>2-</sup> groups occur at: ~765 cm<sup>-1</sup> (very broad shoulder) due to Si-O stretching, 680 cm<sup>-1</sup> (also due to νSi-O), and two δSi-O bending modes at 494 and ~460 cm<sup>-1</sup> (shoulder) (Lewandowska and Rospondek 2002, using transmission data). The δH<sub>2</sub>O mode occurs at ~1712 cm<sup>-1</sup> as an emissivity maximum (e.g., Lewandowska and Rospondek 2002).

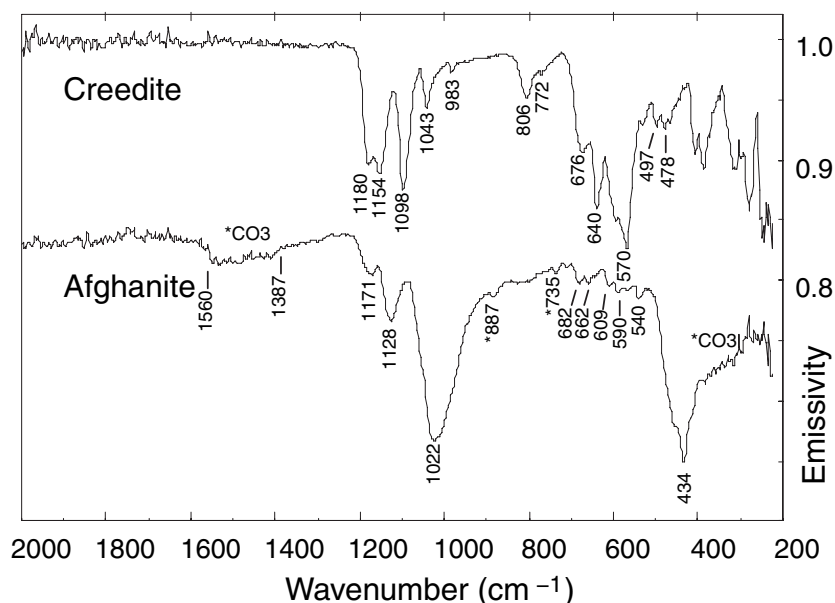
The chemical formula of kainite may be written as MgSO<sub>4</sub>·KCl·3H<sub>2</sub>O, which identifies the constituent chloride and sulfate components. Kainite is one of the few sulfates that contains chloride. Chlorides typically do not exhibit spectral features in the infrared and, accordingly, the spectral features of kainite are all associated with the sulfate and water vibrations. Three strong and sharp v<sub>3</sub> features are exhibited at 1181, 1135, and 1128 cm<sup>-1</sup>. The v<sub>1</sub> feature occurs at 1020 cm<sup>-1</sup>. Three discrete v<sub>4</sub> features occur at 660, 643, and 602 cm<sup>-1</sup>. A v<sub>2</sub> mode is exhibited at 468 cm<sup>-1</sup> and a second v<sub>2</sub> may occur at ~441 cm<sup>-1</sup>. A sulfate lattice mode is truncated at the long-wavelength edge of the spectrum. Water vibrations are seen at ~1654 cm<sup>-1</sup> (δH<sub>2</sub>O) (e.g., Omori and Kerr 1963) and at 809 and 744 cm<sup>-1</sup> (both δOH modes). The amount of sulfate anion bands seen, and the low number of degeneracies, suggests

a fairly low site symmetry perhaps as high as C<sub>2v</sub> (if only one v<sub>2</sub> band) and as low as C<sub>1</sub>.

The sample of serpierite used for this study was a small (~5 × 5 mm) bluish crystal growth on a larger substrate that was masked during data acquisition. Overall there is a slope in this spectrum that is due to sample cooling during the scanning (Fig. 5). Despite the slope in the spectrum, the spectral features of the monoclinic serpierite sample are clear. There are numerous spectral features in this complex Cu sulfate due to the presence of both OH and H<sub>2</sub>O in the structure and the mineral's lack of symmetry. The emissivity features in Figure 5 occur as follows: three v<sub>3</sub> features at 1144, 1123, and 1098 cm<sup>-1</sup>; a clear v<sub>1</sub> mode at 983 cm<sup>-1</sup>; two clear v<sub>4</sub> features at 641 and 600 cm<sup>-1</sup>; and a broad band at ~467 cm<sup>-1</sup> with superposed structure that represents the region of v<sub>2</sub> with an unclear number of bands. The Moenke (1966) transmission data discussed in Ross (1974) show a similar number of bands: three v<sub>3</sub> bands at 1125, 1108, and 1065 cm<sup>-1</sup>; a v<sub>1</sub> at 990 cm<sup>-1</sup>; two v<sub>4</sub> at 648 and 610 cm<sup>-1</sup>; however, unlike the emissivity spectrum, the Moenke (1966) data show two discrete v<sub>2</sub> bands at 475 and 445 cm<sup>-1</sup>. The Raman spectrum from Frost et al. (2004) also is similar in the number of bands: three v<sub>3</sub> bands at 1131, 1122, and 1077 cm<sup>-1</sup>; a v<sub>1</sub> at 988 cm<sup>-1</sup>; two v<sub>4</sub> at 645 and 605 cm<sup>-1</sup>; however, unlike the emissivity spectrum, the Frost et al. (2004) data show three discrete v<sub>2</sub> bands at 475, 445, and 421 cm<sup>-1</sup>. A lattice mode in the emissivity spectrum (Fig. 5) occurs at ~400 cm<sup>-1</sup>. As a result of the water in the serpierite, a water-bending mode occurs as an emissivity maximum at ~1665 cm<sup>-1</sup> and two δOH modes are seen at 825 and 687 cm<sup>-1</sup>. These three water modes were also shown in Moenke (1966) as assigned by Ross (1974).

#### Sulfate-bearing minerals (not officially sulfates)

Although not officially "sulfates," some minerals contain a sulfate anion group in their structure and display sulfate anion vibrational modes in their mid-infrared spectra (Fig. 6). The samples of this classification presented here include creedite (a fluoride group halide; Strunz 3/C.) and afghanite (a cancrinite



**FIGURE 6.** Mid-infrared thermal emissivity spectra of sulfate-bearing minerals that are not officially sulfates, where the asterisks denote bands from carbonate in the mineral structure. Spectra are offset for clarity.

group silicate; Strunz 8/J.).

The creedite spectrum (Fig. 6) exhibits and is dominated by a large number of absorption features related to the vibrations of the sulfate anion. Features at 1180, 1154, 1098, and 1043  $\text{cm}^{-1}$  result from sulfate  $\nu_3$  vibrations. A distinct  $\nu_1$  feature occurs at 983  $\text{cm}^{-1}$ , three  $\nu_4$  features are seen at 676, 640, and 570  $\text{cm}^{-1}$ , and two  $\nu_2$  features are seen at 497 and 478  $\text{cm}^{-1}$ . The water in the structure causes bands to arise at 806 and 772  $\text{cm}^{-1}$  due to  $\delta\text{OH}$ .

The mineral structure of afghanite is described in detail in Ballirano et al. (1996). The afghanite emissivity spectrum (Fig. 6) contains features related to the carbonate and sulfate anionic groups in the structure. The carbonate features include the broad  $\text{CO}_3 \nu_3$  absorption from  $\sim 1560$  to 1387  $\text{cm}^{-1}$ , the  $\text{CO}_3 \nu_2$  at 887  $\text{cm}^{-1}$ , and the  $\text{CO}_3 \nu_4$  at 735  $\text{cm}^{-1}$ . The breadth of the long-wavelength lattice band at  $\sim 400$  to 250  $\text{cm}^{-1}$  likely is due to the superposed carbonate lattice mode on a sharper metal-O mode at 434  $\text{cm}^{-1}$ . The sulfate anion features include three  $\nu_3$  modes at 1171, 1128, and 1022  $\text{cm}^{-1}$ . The  $\nu_1$  mode is not distinct. The sulfate  $\nu_4$  bands occur at 609 and 590  $\text{cm}^{-1}$ . It is also possible that the band at 540  $\text{cm}^{-1}$  represents a  $\nu_4$  vibration. The features at 682 and 662  $\text{cm}^{-1}$  may represent Si-Al-O bending modes (Ballirano et al. 1996). As discussed for the kainite spectrum above, the Cl in the mineral does not exhibit specific features in the spectrum.

### FINAL REMARKS

Sulfate anions in minerals may exhibit bands in the IR at  $\sim 1050$ – $1250$  ( $\nu_3$ ),  $\sim 1000$  ( $\nu_1$ ),  $\sim 500$ – $700$  ( $\nu_4$ ), and  $\sim 400$ – $500$  ( $\nu_2$ )  $\text{cm}^{-1}$  due to asymmetric and symmetric stretching and bending of the  $\text{SO}_4$  anion. The number and position of the fundamental bands are dependent upon the sulfate symmetry and the degree of deformation of the anion. Additional spectral emissivity features may arise due to OH and  $\text{H}_2\text{O}$  in the molecular structure of some sulfates. Several sulfates also contain anionic carbonate in the structure that causes additional spectral emissivity features; however, constituent Cl does not cause spectral bands to arise.

The amount of hydration in minerals with similar chemistry will affect the high-frequency position of the  $\nu_3$  fundamental bands. This position change is seen in the Ca-, Mg-, Fe-, and Cu-sulfate series in which the  $\nu_3$  band occurs at a lower-frequency (lower wavenumber) position with higher states of hydration.

A water librational band that occurs at 846  $\text{cm}^{-1}$  in szomolnokite and 919  $\text{cm}^{-1}$  in kieserite is unique in appearance and restricted to these two monohydrated sulfates studied here. It is predicted that this band will be present in the emissivity spectra of other monoclinic kieserite-group sulfates (e.g., szmikite, gunningite) and may be used as an indicator for monohydrated sulfates.

Finally, particle size also affects the sulfate spectra, as discussed for gypsum, and fine-grained sulfates can exhibit Type I, II, and III band behaviors. Coarse, crystalline samples exhibit spectra dominated by the absorption bands associated with the fundamental vibrational modes of the constituent anion(s), whereas fine-grained samples have spectra that can be dominated by multiple- and volume-scattering features and show diminished or inverted fundamental modes. As a result of the inversion of fundamental bands and neighboring increased spectral contrast, the position of previously indistinct vibrational modes may be discerned in fine-grained samples.

The unique spectral character of sulfates (and sulfate-bearing minerals) allows their emissivity spectra to be used for identification of these minerals, spectral determination of unknown composition, and in some cases, identification of the physical state of the mineral (coarse vs. particulate). Knowing these characteristics can provide insight into the geologic setting in which they are found, whether by fieldwork or through airborne or orbital remote sensing techniques.

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