Sulphate efflorescent minerals from the El Jaroso ravine, Sierra Almagrera, Spain—a scanning electron microscopic and infrared spectroscopic study

Ray L. Frost,^a Daria L. Wain,^a B. Jagannadha Reddy,^a Wayne Martens,^a Jesus Martinez-Frias^{b,c} and Fernando Rull^{b,c}

^a*Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia. E-mail: r.frost@qut.edu.au*

^b*Centro de Astrobiología, INTA-CSIC, Associated to the NASA Astrobiology Institute, Ctra de Ajalvir km. 4, 28850 Torrejon de Ardoz, Madrid, Spain. E-mail: martinezfrias@mncn.csic.es*

^c*Cristalografía y Mineralogía, Unidad Asociada al Centro de Astrobiología INTA-CSIC, Universidad de Valladolid, 47006 Valladolid, Spain. E-mail: rull@fmac.uva.es*

Near infrared (NIR) spectroscopy is a technique that can be utilised to analyse minerals remotely through a fibre-optic cable. A suite of sulphate efflorescent minerals from the El Jaroso ravine, Sierra Almagrera, Spain have been analysed by ultraviolet, visible, NIR and mid infrared (IR) spectroscopy. Such a suite of minerals may be used to model the types of mineral deposits on Mars. The minerals were analysed by scanning electron microscopy and X-ray microanalysis (EDX) before spectroscopic analysis. Halotrichite was observed and the EDX analyses showed the mineral to be a mixture of heinrichite and pickeringite. The NIR spectrum of the efflorescent sample showed the sulphate deposit to be composed of a mixture of jarosite and halotrichites. The 7400 to 6400 cm⁻¹ (1351 to 1562 nm) NIR spectral region of the efflorescent sulphate minerals can be used to characterise the various sulphate deposits. The detection of a band at 8338 cm⁻¹ (1199 nm) reveals the presence of ferrous iron in jarosite which is unusual for the jarosite minerals. This can be caused by ferric iron reduction by thermophilic iron-oxidising bacteria. Mid IR spectra showed the characteristic OH stretching bands of the jarosites and the efflorescent mixtures. The position of water stretching vibrations at 2900 cm⁻¹ and lower shows strong hydrogen bonding as is also evidenced by water bending modes at around 1682 cm⁻¹.

Keywords: efflorescent minerals, evaporite, jarosite, halotrichite, sulphate, NIR spectroscopy

Introduction

Interest in the study of iron(II) sulphates arises from at least two perspectives. First, the observation of sulphates of iron on Mars by recent exploration (see for example: <http://www.news.cornell.edu/releases/rover/Mars.jarosite.html>) and second, by the formation of iron(II) and iron(III) sulphates in evaporate deposits.¹

Studies of these minerals have been undertaken for some considerable time.^{2–6} Interest in the chemistry of jarosites stems from a number of reasons. First, because of the discovery of jarosites on Mars.^{7,8} Such a discovery implies the presence of water on Mars either at present or at some time in the planetary past.^{9,10} Interest in such minerals and their thermal stability rests with the possible identification

of these minerals and dehydrated paragenetically-related minerals on planets such as Mars. There have been many studies on related minerals such as the Fe(II) and Fe(III) sulphate minerals.^{11–16} The formation of these minerals can occur through microbiological reduction of pyrite.^{17,18} Fe minerals such as Fe²⁺, Fe³⁺hydroxysulfate (copiapite), Fe³⁺ oxyhydroxide (goethite), KFe³⁺hydroxysulfate (jarosite) and Fe³⁺hydroxysulfate (schwertmannite) may form as weathering products in a pyrite oxidation process. Oxidation rates are dependent on temperature, pH, Eh, relative humidity, and the surface area of reactant pyrite.

One of the difficulties associated with the analysis of jarosites and related minerals is that they often lack crystallinity, making detection using X-ray diffraction (XRD) techniques difficult. Vibrational spectroscopic techniques are

most useful in overcoming this difficulty. Near infrared (NIR) spectroscopy enables the spectra of such minerals to be readily obtained. Most efflorescent minerals are poorly crystalline as the loss of water from the structure causes the materials to become powdered. Another problem associated with the study of jarosites is their thermodynamic stability.¹⁹ Often, the minerals are formed from acid–sulphate rich environments such as acid mine drainage and acid–sulphate soils and, as such, their solubility is controlled by the climatic conditions in particular temperature. The minerals can precipitate in the day time as the solution evaporates and then redissolve at night when the temperature decreases. Such phenomena result in very complex mineral systems which involve jarosites and other sulphates, for example, iron(II)sulphates and potassium sulphate. The ability to be able to easily and readily detect minerals is of importance.^{20,21} NIR spectroscopy provides a suitable method for the analysis of these types of material and material mixtures.^{22–25} The other use of NIR spectroscopy is in the search for knowledge of minerals in the solar system.^{26–31} Hunt *et al.*^{20,21} first applied NIR spectroscopy to the study of minerals. It should be recognised that NIR spectroscopy is also known as proton spectroscopy, so this type of spectroscopy is most useful for measuring bonds involving hydrogen such as OH, NH, CH, etc. Thus, the technique appears most suitable for the measurement of hydrated, hydroxylated sulphates as might be found in soils and sediments that may exist on Mars.

Sulphate minerals are formed by the oxidation of sulphide minerals by a combination of oxidation, dehydration, and neutralisation reactions. In sulphate efflorescent deposits, gelatinous hydrated hydroxy sulphates such as the sulphate minerals including jarosites and halotrichites may be formed in solution and precipitate from this solution as a function of the pH and temperature.³² Such mixed sulphate species will depend upon the temperature and pH of the crystallisation.^{33,34} A typical deposit is found in the El Jaroso ravine. A recent study characterised jarosites in terms of their ultraviolet-visible (UV-vis) and NIR spectroscopy,³⁵ whereas other recent studies have characterised selected evaporate minerals by thermal analysis and Raman spectroscopic techniques.^{36–39} Thus it is important to understand the NIR spectroscopy of the efflorescent sulphate minerals: jarosites and halotrichites since these minerals are formed in mineral waste deposits, slag wastes and other environmental situations.^{40–42}

As part of a comprehensive study of the IR and Raman properties of minerals containing oxyanions, we report the NIR and mid infrared (IR) properties of the above named phases. A comparison is made with known jarosite and related sulphate minerals.

Experimental

Minerals

The minerals used in this study were obtained by two of the authors (Jesus Martinez-Frias and Fernando Rull). The minerals were collected from the El Jaroso ravine, Sierra

Almagrera, Spain. The jarosite minerals were obtained from Australian deposits.^{38,39,43,44} The minerals were analysed by X-ray diffraction for phase identification and by scanning electron microscopy (SEM) together with electron probe analysis for chemical composition.

SEM analysis

Mineral samples from The El Jaroso ravine were coated with a thin layer of evaporated carbon and secondary electron images were obtained using a scanning electron microscope (FEI Quanta 200 SEM, FEI Company, Hillsboro, Oregon, USA). For X-ray microanalysis (EDX), three samples were embedded in araldite resin and polished with diamond paste on a Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a Jeol 840A analytical SEM (Jeol Ltd, Tokyo, Japan) at 25 kV accelerating voltage. Preliminary analyses of the sulphate mineral samples were carried out on the FEI Quanta SEM using an EDAX X-ray microanalyser and microanalyses of the clusters of fine crystals were carried out using a full standards quantitative procedure on the Jeol 840 SEM using a Jeol-2300 energy-dispersive X-ray microanalysis system (Jeol Ltd, Tokyo, Japan). Oxygen was not measured directly but was calculated using assumed stoichiometry to the other elements analysed.

Infrared (IR) and NIR spectroscopy

NIR spectra were collected on a FT-IR spectrometer (Nicolet Nexus, Madison, Wisconsin, USA) with a Nicolet Near-IR Fibreport accessory. This is a fibre-optic probe and the probe is simply pointed at the mineral surface and the spectrum obtained. A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. The spot size was around 25 microns. Spectra were obtained from 11,000 to 4000 cm⁻¹ (909 to 2500 nm) by the co-addition of 64 scans at a resolution of 8 cm⁻¹. A mirror velocity of 1.2659 cm s⁻¹ was used. The spectra were transformed using the Kubelka–Munk algorithm to provide spectra for comparison with absorption spectra.

Infrared spectra were obtained using a Nicolet Nexus 870 FT-IR spectrometer (Nicolet Nexus, Madison, Wisconsin, USA) with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm⁻¹ range were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm s⁻¹. Spectra were co-added to improve the signal-to-noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the GRAMS software package (Galactic Industries Corporation, Salem, NH, USA). Band component analysis was undertaken using the Jandel “Peakfit” software package (Jandel Scientific, Postfach 4107, D-40688 Erkrath, Germany) which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function

with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of (r^2) greater than 0.995.

UV-vis spectroscopy

A UV-vis spectrophotometer (Varian Cary 3, Melbourne, Australia), equipped with a diffuse reflectance accessory (DRA) was employed to record the electronic spectrum of the sample in the region between 200 and 900 nm (50,000 to 11,110 cm^{-1}). The diffuse reflectance measurements were converted into absorption (arbitrary units) using the Kubelka–Munk function [$f(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$]. Data manipulation was performed using Microsoft Excel.

Results and discussion

SEM and EDX analysis

The SEM image of a halotrichite from Jaroso, Spain is shown in Figure 1. The image shows elongated crystals of a halotrichite type mineral together with jarosite crystals. The chemical analysis of the halotrichite is given in the SEM image in Figure 2. From this analysis, the halotrichite formula is given by $(\text{Zn}, \text{Mg}, \text{Mn}^{2+}, \text{Fe}^{2+})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$. The formula of the mineral is closest to that of dietrichite or is a solid solution of dietrichite and pickingerite. Other mineral samples of a fibrous nature were analysed as pickingerite.

UV-vis, IR and NIR spectroscopy

The NIR and the UV-vis spectra overlap, and often the NIR information, can be more readily obtained from the red end of the UV-vis spectrum, as is shown in Figure 3. The NIR spectral regions may be conveniently divided into four regions: (a) the high wavenumber region $> 7500 \text{ cm}^{-1}$ ($> 1333 \text{ nm}$). This region

Figure 1. SEM image of sulphate efflorescent minerals showing jarosite and the halotrichite dietrichite (100 microns across).

Figure 2. EDAX analysis of the halotrichite dietrichite.

is where some electronic bands characteristic of Fe^{2+} and Fe^{3+} ions are observed. The spectra are shown in Figure 4; (b) the high wavenumber region between 7500 and 6000 cm^{-1} (1333 to 1667 nm) attributed to the first overtone of the fundamental hydroxyl stretching mode (Figure 5); (c) the 6200 – 5400 cm^{-1} (1612 to 1852 nm) region attributed to water combination modes of the hydroxyl fundamentals of water. The spectra are shown in Figure 6; (d) the 5500 – 4000 cm^{-1} (1852 to 2500 nm) region attributed to the combination of the stretching and deformation modes of the jarosites, halotrichite and related iron(II), iron(III) sulphates. The spectra are shown in Figure 7. The mid IR region may also be divided by spectral regions: (a) the 3800 to 1800 cm^{-1} region where OH fundamental vibrations are observed (Figure 8), (b) 1750 to 1250 cm^{-1} region where the water bending modes are observed (Figure 9) and (c) the low wavenumber region from 1200 to 500 cm^{-1} where the oxyanion fundamentals are observed (Figure 10). The results of the NIR spectral data are reported in Table 1 and the results of the mid-IR spectral data in Table 2.

The 50,000 to $10,000 \text{ cm}^{-1}$ (200 to 1000 nm) spectral region

Fe^{2+} and $\text{Fe}^{3+}/\text{Mn}^{2+}$ are the main candidates in sulphate minerals that dominate in the electronic spectra as can be seen in their spectra shown in Figures 3 and 4. Ferric/ferrous ions show characteristic bands in their electronic spectra in this spectral region. The d^5 ion in a complex has five valence electrons occupying three in t_{2g} and two in e_g orbitals and is considered as a high-spin configuration. Ions with d^5 configuration such as Fe(III) and Mn(II) have a sextet ground state, $^6A_{1g}$ and a series of quartet excited states ($^4T_{1g}$, $^4T_{2g}$, 4E_g , $^4A_{1g}$ and $^4A_{2g}$). The transitions are actually spin-forbidden based on crystal-field theory. However, extended visible region spectra of jarosites include a sharp band around 435 nm ($23,000 \text{ cm}^{-1}$) and a shoulder at 650 nm and a broad band

Table 1. The NIR spectral data of efflorescencia, oxida-efflorescencia, natrojarosita, jarosite, and halotrichite..

Eflorescencia			Eflorescencia oxidada			Natrojarosita			Jarosite			Halotrichite (Spain)			Halotrichite (California)		
Centre	FWHM*	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area
			8851	241.2	0.83				8607	70.9	0.04	8835	191.4	0.14			
			8557	252.9	0.96				8506	119.4	0.15	8503	240.1	0.71	8493	189.3	0.36
			8374	422.9	2.49				8338	365.7	0.78	8304	236.9	0.39			
									8280	32.5	0.02						
									8090	108.6	0.21	8081	256.6	0.39			
			7976	420.9	1.53				7969	103.1	0.16	7891	123.5	0.12			
			7717	146.8	0.31												
			7405	106.0	0.16	7408	158.5	1.80				7563	61.8	0.09	7507	182.1	1.17
7038	144.8	4.28							7296	156.7	0.48	7290	45.8	0.08	7403	126.0	0.72
6906	165.8	12.31	7016	165.0	5.08				7023	208.1	5.51						
			6891	156.4	11.96	7095	81.2	1.87	6913	88.7	6.04	6974	193.8	7.15	6960	197.2	9.69
									6826	140.2	4.09	6865	181.3	3.39	6781	262.0	7.90
6751	91.5	1.66										6738	259.9	9.24			
6729	290.7	9.94	6750	137.5	2.62	6788	123.5	7.05									
									6701	161.1	6.63						
						6594	294.8	2.69	6509	169.8	3.68	6527	204.8	0.98			
									6342	277.3	2.50	6156	85.5	0.09			
5809	340.8	7.36	5924	298.2	3.53							5800	193.2	0.94			
			5734	249.4	4.29				5725	130.7	3.13	5723	78.2	0.33	5706	269.5	3.94
5613	180.4	1.49							5616	91.1	0.68	5626	150.4	1.02			
									5612	135.1	0.50						
			5577	151.9	1.31												
						5413	59.6	2.12									
			5239	91.5	4.34	5366	36.8	0.68	5217	139.5	15.05						
5158	148.8	31.81	5160	111.4	14.77	5174	144.3	17.92	5149	80.1	15.41	5167	154.2	28.44	5167	122.5	20.89
									5120	42.9	3.23						
5051	77.2	2.72	5062	102.6	6.06	5031	240.1	35.36	5074	62.3	6.00	5040	162.4	19.46	5058	255.3	41.18
									5027	78.5	9.85						

Table 1. The NIR spectral data of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite (continued).

Efflorescencia			Efflorescencia oxidada			Natrojarosite			Jarosite			Halotrichite (Spain)			Halotrichite (California)		
Centre	FWHM*	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area
4989	188.4	9.24	4999	274.0	29.93	4815	138.8	5.27	4946	51.6	0.47	4942	129.3	5.22			
4814	320.6	12.42										4869	227.2	17.27	4826	303.0	11.69
			4766	221.8	5.08	4740	66.3	1.63									
									4692	99.0	1.17	4650	268.9	3.58			
4549	136.7	2.10	4572	207.0	2.21	4542	94.0	10.71	4589	104.8	3.78				4548	170.2	2.46
									4505	79.5	4.96	4517	100.0	0.96			
						4416	60.0	8.55	4416	90.3	4.20						
						4391	42.7	2.21									
						4352	33.2	1.13	4321	92.2	1.26						

FWHM is the full width of the band at half maximum peak height

Table 2. Results of the Mid-IR spectral data of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite.

Efflorescencia			Efflorescencia Oxidada			Natrojarosite			Jarosite			Spain			California			Suggested assignment
Centre	FWHM*	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	
3530	57.9	1.47	3527	21.1	0.19	3627	43.4	0.39	3592	72.5	2.11				3694	16.5	0.04	ν (H ₂ O)
3488	72.1	1.55	3512	136.4	4.31	3515	155.2	1.57	3545	47.1	2.84	3538	137.7	1.49	3573	34.6	0.17	“
3381	269.5	13.44	3364	228.7	12.28	3365	77.1	7.68	3401	60.7	10.87	3397	214.9	10.12	3493	189.0	4.36	“
						3342	188.5	15.72	3337	122.1	5.13							ν (OH)
									3247	302.4	11.13							“
									3239	30.1	0.39	3228	267.2	22.30	3263	321.3	24.19	“
																		“
3087	396.0	50.15	3083	364.3	46.25										3031	307.9	13.73	2 δ (H ₂ O)
2814	256.7	5.25	2813	290.6											2873	341.3	25.89	
2512	431.8	9.65	2489	392.1	9.82							2484	352.6	9.98	2501	361.4	13.82	

Table 2. Results of the Mid-IR spectral data of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite (continued).

Efflorescencia			Efflorescencia Oxidada			Natrojarosite			Jarosite			Spain			California			Suggested Assignment
Centre	FWHM*	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	
						2042	68.8	0.29	2220	186.2	0.77							
						1980	36.3	0.10										
1695	22.1	0.19	1692	41.0	0.23				1682	17.1	0.59							δ (H ₂ O)
1662	22.7	0.14										1650	73.8	1.65	1654	89.3	1.89	"
1638	54.9	2.08	1639	52.6	1.18	1644	91.8	1.05				1602	159.4	1.82	1604	121.3	1.36	"
			1611	159.0	1.83				1619	17.0	2.14							"
1553	220.6	1.32																
			1443	96.6	0.43	1425	36.5	0.17				1453	167.6	0.68	1492	197.9	1.18	
1220	22.4	0.39																ν_3 (SO ₄) ²⁻
1186	32.4	0.54	1182	92.3	1.54	1179	65.7	3.66										"
1146	47.3	1.06							1151	45.1	5.13	1134	51.0	1.19	1145	42.5	0.81	"
1098	52.7	4.80	1093	13.1	0.05	1089	43.7	9.34	1110	76.9	23.62	1105	28.4	0.97	1107	40.4	3.26	"
1065	55.7	3.24	1085	76.2	7.41							1076	40.2	2.62	1075	26.7	1.05	"
									1053	40.7	-1.50	1047	55.2	5.84	1048	43.3	3.62	"
			1020	18.1	0.19	1025	26.6	1.73	1017	116.8	23.28				1017	139.8	2.46	"
						1003	27.6	3.72										ν_1 (SO ₄) ²⁻
993	42.4	2.47	989	37.3	2.78	985	75.3	11.93				988	18.3	0.12	992	9.4	0.06	ν_1 (SO ₄) ²⁻
945	59.1	1.37	954	91.8	1.63							949	77.3	1.36	949	29.5	0.54	ν_1 (SO ₄) ²⁻
						897	74.2	3.45	901	48.9	1.32				918	71.6	0.72	δ (OH)
						795	52.5	0.76	798	16.0	0.33							"
									779	33.8	0.68							"
709	70.7	0.28	712	79.1	0.29							717	61.7	0.14	709	66.0	0.24	"
						680	19.6	0.04	669	14.4	1.50							ν_4 (SO ₄) ²⁻
						668	13.4	0.06										"
634	11.1	0.09				626	15.2	0.53							626	17.6	0.09	"
									600	16.3	1.48							"
591	39.2	0.35	590	25.1	0.19				582	31.1	0.66	587	61.6	0.38	580	66.1	0.51	"
552	27.2	0.21	552	22.7	0.12	534	12.6	0.12										ν FeO
						524	9.2	0.06										"

FWHM is the full width of the band at half maximum peak height

Figure 3. UV-vis reflectance spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 50,000 to 16,667 cm^{-1} (200 to 600 nm) region.

near 900 nm (15,385 and 11,110 cm^{-1}).^{20,45–48} Ferric iron-bearing sulphates besides jarosite exhibit variable spectral behaviour (Figure 3). In the present study, for jarosite from the El Jaroso ravine, Sierra Almagrera, Spain, the shoulder band located at 481 nm and sharp band at 414 nm (20,790 and 24,150 cm^{-1}) are attributed to ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{E}_g(\text{G})$, ${}^4\text{A}_{1g}(\text{G})$, transitions.^{20,35,45,46,49} These two transitions are shifted to the red side of the spectrum and the UV band near 400 nm (25,000 cm^{-1}) is split into two components at 431 nm and 389 nm (23,150 and 25,705 cm^{-1}) for natrojarosite. A strong and broad band that appears near 320 nm (31,250 cm^{-1}) in all the five minerals is attributed to ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition and an additional sharp band arises due to the presence of Mn^{2+} at 284 nm (35,200 cm^{-1}) in halotrichite is assigned to ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ transition.^{50,51} The rise in absorption in the range 250–200 nm (40,000–50,000 cm^{-1}) is due to metal–ligand charge transfer.⁵² The halotrichite spectrum characterised by two sharp bands around 300 nm is a common feature in Mn-bearing minerals.⁵³ This feature is distinctly different from that of jarosites. The Fe(III) bands in the electronic spectra of jarosites are broad and distinctly different from that of Mn(II) bands in halotrichite (Figure

3). The cause of shifts for the two strong bands at 357 and 310 nm (28,000 and 32,260 cm^{-1}) to higher energy side in efflorescencia can be ascribed to the spectral mixture of jarosites and halotrichite.

The 10,000 to 7500 cm^{-1} (1000 to 1333 nm) spectral region

A few resolvable bands in the range 1000 to 1324 nm or 10,000–7550 cm^{-1} (Figure 4) from the complex band profiles are obtained for halotrichite, jarosite and efflorescencia. Halotrichite ($\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$) displays a maximum absorption at 8502 cm^{-1} with a component at 8304 cm^{-1} , another intense band at 8081 cm^{-1} and two shoulders on either side of the central band. The two main bands at 8502 and 8081 cm^{-1} (marked with *) with a separation of 421 cm^{-1} are due to ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition of Fe(II) in an octahedral site. A single broad band at 8338 cm^{-1} (marked with *) in the jarosite spectrum implies an undistorted octahedral site for Fe^{2+} . Efflorescencia oxidada shows a broad band profile in which two strong bands are identified at 8374 and 7976 cm^{-1} (marked with *). It is apparent that the NIR spectrum of efflorescencia oxidada

Figure 4. NIR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 9050 to 7550 cm^{-1} (1105 to 1324 nm) region.

is a spectral mixture of jarosite and halotrichite. The two main bands of halotrichite at 8502 and 8081 cm^{-1} appear in efflorescencia oxidada as strong broad bands at 8374 and 7976 cm^{-1} (marked with *) having separation at 398 cm^{-1} and the undistorted band of jarosite appears more strongly at 8374 cm^{-1} (see Figure 4 marked with *). Similar intense crystal field bands of Fe(II) have been observed in several silicate minerals containing both ferrous and ferric ions^{54,55} and in some selected iron (II) and iron(III) sulphates.⁵⁶ The detection of Fe(II) band (8338 cm^{-1}) in the NIR region is an evidence for partial reduction of some ferric iron into ferrous iron through reduction by thermophilic iron-oxidizing bacteria.

The 7400 to 6400 cm^{-1} (1351 to 1562 nm) spectral region

The spectral region in the 7500 to 6000 cm^{-1} region shows the first overtone of the OH stretching vibration (Figure 5). A number of conclusions can be readily made: (a) the sulphate precipitates labelled efflorescencia and efflorescencia-oxida have nearly identical spectra in this spectral region, (b) the spectra of the natrojarosite and jarosite are very different

which is unexpected and (c) the efflorescencia spectrum appears as the summation of the spectra of the halotrichite and the jarosite. The NIR spectra of the two halotrichites (heinrichite and pickeringite) are identical. The efflorescencia sample is characterised by broad bands at 7038 , 6906 and 6729 cm^{-1} . The bands are shifted for the efflorescencia oxidada sample. The NIR spectrum of jarosite in this spectral region is characterised by bands at 7026 , 6914 , 6701 and 6509 cm^{-1} . The natrojarosite spectrum shows bands at 7095 , 6788 and 6594 cm^{-1} . The difference in the spectra shows that jarosites with different cations can be distinguished. Bishop and Murad³⁵ reported the NIR and mid-IR spectra of synthetic jarosites and alunites and assigned the bands. They reported NIR bands of natural jarosite at 6808 , 6560 , 5406 and 5165 cm^{-1} . The NIR results for a synthetic jarosite showed bands at 7015 , 6817 and 5400 cm^{-1} . These results show that the NIR spectra of a synthetic jarosite cannot be compared with those of the natural sample. Considerable variation in the spectra occurs for jarosites from different origins.

The NIR spectra of halotrichite in this spectral region give bands at 6974 and 6738 cm^{-1} .

Figure 5. NIR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 7000 to 6000 cm^{-1} (1429 to 1667 nm) region.

Figure 6. NIR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 6000 to 5500 cm^{-1} (1667 to 1818 nm) region.

The 6200 to 5400 cm^{-1} (1613 to 1852 nm) spectral region

The NIR spectra in the 6200 and 5400 cm^{-1} region show broad bands exist in this spectral region (Figure 6). The NIR spectrum of jarosite shows two bands at 5724 and 5614 cm^{-1} . The bands for the efflorescencia are at 5809 and 5613 cm^{-1} . The bands shift to lower wavenumbers for the efflorescencia oxidada sample. The band positions reported here differ from those reported by Bishop and Murad.³⁵ These authors attributed bands in these positions to the combination of the νOH and δOH fundamentals. Bands in this region are normally attributed to the combination of water bands, i.e. $\nu\text{H}_2\text{O}$ and $\delta\text{H}_2\text{O}$. It is probable that the differences between the results reported in this work and published results can be attributed to the variation in chemical composition of the natural mineral samples.

The 5500 to 4000 cm^{-1} (1818 to 2500 nm) spectral region

The spectrum of efflorescencia in the 5500–4000 cm^{-1} region (Figure 7) shows bands at 5158, 4989 and 4814 cm^{-1} .

Figure 7. NIR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 5500 to 4000 cm^{-1} (18,918 to 2500 nm) region.

The spectra of efflorescencia-oxidada show bands at 5160, 4999 and 4766 cm^{-1} . The NIR spectrum in this spectral region of jarosite show bands at 5232, 5141, 5035 and 4504 cm^{-1} . Bishop and Murad reported bands for a natural jarosite at 5165, 4514 and 4417 cm^{-1} . They reported bands for a synthetic jarosite at 5145, 4410, 4065 and 4000 cm^{-1} . The spectrum of the Spanish natrojarosite displayed bands at 5174, 5031, 4815, 4542 and 4416 cm^{-1} . Chemical analysis of this jarosite shows the mineral is a cationic mixture with sodium being the predominant cation. Bands in this region are attributed to overtone and combination bands. Bishop and Murad assigned bands to the third overtone of the sulphate antisymmetric stretching vibration. The probability of the third overtone of the fundamental having significant intensity is negligible.

The 3800 to 1800 cm^{-1} spectral region

The OH stretching region of the natural minerals is shown in Figure 8. The IR spectrum of jarosite shows bands at 3504, 3401 and 3247 cm^{-1} . The bands at 3504 and 3401 cm^{-1} may be assigned to the jarosite OH stretching vibrations. The band at 3247 cm^{-1} is ascribed to the first overtone of the

Figure 8. Mid-IR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 3800 to 2900 cm^{-1} region.

water bending mode. Bishop and Murad reported IR bands for a natural jarosite at 3550, 3410 and 3384.³⁵ Some variation of band positions between sample spectra was observed. For a synthetic jarosite, they observed bands at 3550, 3410 and 3385 cm^{-1} . The IR spectrum of halotrichite shows bands at 3228, 2943 and 2484 cm^{-1} . The spectrum of efflorescencia shows bands at 3381, 3087 and 2512 cm^{-1} , whilst the spectrum of the efflorescencia-oxidada sample gave bands at 3364, 3083 and 2489 cm^{-1} .

The 1750 to 1250 cm^{-1} spectral region

This IR spectral region is significant for information on water bending modes (Figure 9). The IR spectrum of jarosite shows two strong bands at 1682 and 1619 cm^{-1} . The high wavenumber band is indicative of strong hydrogen bonding of water and the 1619 cm^{-1} band to weakly hydrogen bonded water. The spectrum of the natrojarosite mineral shows a broad band at 1643 cm^{-1} . The spectrum of halotrichite shows a broad band around 1650 cm^{-1} . The spectrum of the efflorescencia sample gave two bands at 1695 and 1638 cm^{-1} . The spectrum of the efflorescencia-oxidada sample shows bands in similar positions. The first overtone of this band

can show as an additional band in the OH stretching region around 3100 cm^{-1} .

The 1250 to 525 cm^{-1} spectral region

The IR spectra of the sulphate fundamental vibrations are shown in Figure 10. Sulphates, as with other oxyanions, lend themselves to Raman spectroscopy.⁵⁷ In aqueous systems, the sulphate anion is of T_d symmetry and is characterised by Raman bands at 981 cm^{-1} (ν_1), 451 cm^{-1} (ν_2), 1104 cm^{-1} (ν_3) and 613 cm^{-1} (ν_4). Reduction in symmetry in the crystal structure of sulphates such as jarosites will cause the splitting of these vibrational modes. For jarosites the space group is $R3m = C_3^2$ and six sulphate fundamentals should be observed. The factor group analysis of jarosites and alunites has been published by Serna *et al.*⁵⁸ Ross reports the interpretation of the infrared spectra for the sulphate anion in alums as ν_1 , 981 cm^{-1} ; ν_2 , 465 cm^{-1} ; ν_3 , 1200, 1105 cm^{-1} ; ν_4 , 618 and 600 cm^{-1} .⁵⁹ Water stretching modes were reported at 3400 and 3000 cm^{-1} , bending modes at 1645 cm^{-1} and librational modes at 930 and 700 cm^{-1} .⁶⁰ In the structure of alums, six water molecules surround each of the two cations. This means the sulphate ions are distant from

Figure 9. Mid-IR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 1750 to 1250 cm^{-1} region.

Figure 10. Mid-IR spectra of efflorescencia, oxida-efflorescencia, natrojarosite, jarosite, and halotrichite in the 1200 to 500 cm^{-1} region.

the cations and co-ordinate to the water molecules. Ross also lists the infrared spectra of the pseudo-alums formed from one divalent and one trivalent cation. Halotrichite has infrared bands at ν_1 , 1000 cm^{-1} , ν_2 , 480 cm^{-1} , ν_3 , 1121, 1085, 1068 cm^{-1} and ν_4 , 645, 600 cm^{-1} . Pickeringite, the Mg end member of the halotrichite–pickeringite series, has infrared bands at ν_1 , 1000 cm^{-1} , ν_2 , 435 cm^{-1} , ν_3 , 1085, 1025 cm^{-1} and ν_4 , 638, 600 cm^{-1} .⁵⁹ Ross also reports a weak band at $\sim 960 \text{ cm}^{-1}$ which is assigned to a second OH librational vibration.⁵⁹

This spectral region shows the fundamental vibrations of the $(\text{SO}_4)^{2-}$ units (Figure 10) with the bands at around 1100 and 1000 cm^{-1} assigned to the ν_3 $(\text{SO}_4)^{2-}$ antisymmetric stretching vibrations. The shoulder at 897 cm^{-1} for natrojarosite is ascribed to the ν_1 $(\text{SO}_4)^{2-}$ symmetric stretching vibrations. Sasaki *et al.*⁶¹ showed that these bands were cation sensitive. The bands observed at 669, 600 and 582 cm^{-1} for jarosite are assigned to the ν_4 $(\text{SO}_4)^{2-}$ bending modes. The ν_2 $(\text{SO}_4)^{2-}$ bending modes are not observed as they occur below the cut-off point for the diamond ATR cell. Bishop and Murad reported bands for both the synthetic and natural minerals at 663 and 630 cm^{-1} .³⁵

Conclusions

Compositional variability in jarosite [$\text{KFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$] and natrojarosite [$\text{NaFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$] has minimal effect on band positions (in the UV-vis spectrum). Eflorescencia and eflorescencia oxidada show almost identical spectral features but these spectral features are distinctly different from jarosites and halotrichite. NIR spectroscopy has the distinct advantage that the technique can be used remotely. This means that no handling of the minerals is needed. Further although it is not specifically known whether planets, for example Mars, have deposits of jarosites and related sulphate minerals, NIR spectroscopy can be used at remote distances and may be employed to identify the presence of these minerals.

The detection of the Fe(II) band at 8338 cm^{-1} in NIR shows the presence of ferrous iron which is unusual for the jarosite minerals. The detection of this Fe(II) band (8338 cm^{-1}) in NIR is evidence for the process of some ferric iron reduction into ferrous iron by thermophilic iron-oxidising bacteria.^{18,62,63} The appearance of sharp bands in the UV region and absence of Fe^{3+} band near 500 nm in the visible region of the spectrum provide proof of the presence of Mn(II) in halotrichite and its spectral features are distinctly different from those of jarosites due to ferric iron. All sulphate minerals release metals and acids when they dissolve and, therefore, represent a potentially significant environmental risk. Our study using NIR spectroscopy enables us to identify minerals that occur in mine wastes and slags of significant environmental risk, as occurs in the El Jaroso ravine.

There is probably no place on earth which could match the environment found on Mars (see <http://tierra.rediris.es/jarosite/>). The amazing recent discovery in Mars'

Meridiani Planum region of an iron-bearing sulphate called jarosite (<http://www.news.cornell.edu/releases/rover/Mars.jarosite.html>), which contains hydroxyl as a part of its structure, is strong mineralogical evidence that liquid water once flowed through these rocks. The minerals found in the El Jaroso ravine hydrothermal system provide a potential model for the exploration of minerals on Mars.

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