

# Identification of the rosasite group minerals—An application of near infrared spectroscopy

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## Abstract

The ability of near infrared reflectance spectroscopy to classify the rosasite group minerals from spectral characteristics is demonstrated. NIR spectroscopy can be regarded as an alternative tool for structure analysis. The spectra show that rosasite group minerals with different cations can be distinguished.  $\text{Ni}^{2+}$  in nullaginite  $[\text{Ni}_2(\text{CO}_3)(\text{OH})_2]$  is conspicuous through a single broad band absorption feature at  $8525\text{ cm}^{-1}$ , extended from  $11,000$  to  $7000\text{ cm}^{-1}$ . The effect of Ni on Cu is seen in the spectrum of glaukosphaerite  $[(\text{Cu}, \text{Ni})_2(\text{CO}_3)(\text{OH})_2]$  both by a red shift of the spectrum and reduction in intensity of bands with variable positions of band maxima for  $\text{Cu}^{2+}$  at  $6995\text{ cm}^{-1}$  and  $\text{Ni}^{2+}$  at  $7865\text{ cm}^{-1}$ . The spectrum of rosasite  $[(\text{Cu}, \text{Zn})_2(\text{CO}_3)(\text{OH})_2]$  is characterised by  $\text{Cu}^{2+}$  band at  $7535\text{ cm}^{-1}$ . Kolwezite  $[(\text{Cu}, \text{Co})_2(\text{CO}_3)(\text{OH})_2]$  is a spectral mixture of Cu and Co but optically separated by  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  peaks at  $8385$  and  $7520\text{ cm}^{-1}$ .

Vibrational spectra of carbonates show a number of bands in the  $7000\text{--}4000\text{ cm}^{-1}$  region attributable to overtones, combination of OH stretching and deformation modes. They appear to be uniform in nature since the structure of rosasite group minerals is identical. The complexity of these features varies between samples because of the variation in composition and hence is useful for discriminating different hydrous carbonates.

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## 1. Introduction

The diversity of carbonate minerals is remarkable. Many of these can be related to the coordination chemistry of cations in the solutions from which these minerals are formed. Carbonate minerals play an important role in determining the history of the Martian atmosphere, geology, and hydrology. These minerals are also a potential sink of atmospheric  $\text{CO}_2$  [1]. Thermal infrared spectra of the Martian surface indicate the presence of small amounts (2–5 wt.%) of carbonates. Carbonate minerals have unique absorptions throughout the near-infrared and thermal infrared spectral regions with electronic bands caused by d–d transitions from  $11,000\text{--}7000\text{ cm}^{-1}$  and overtone and combination bands in the range  $7000\text{--}4000\text{ cm}^{-1}$  whereas fundamental absorptions appear in the range  $4000\text{--}300\text{ cm}^{-1}$ . Such spectral features are aided in identifying the mineral species [2–7]. Minerals of rosasite group are OH-bearing simple carbonates of divalent cations. The knowledge of the spectral

reflectance properties of a range of these hydrous carbonate minerals certainly contribute to a definitive identification of carbonate minerals on Mars.

The minerals of rosasite group are monoclinic or perhaps triclinic hydroxy carbonates and are highly coloured often green to blue due to metal ions of most likely Cu, Ni, Co present as essential constituents of the atomic structure [8]. The minerals are fibrous in nature and the single crystal XRD studies have not been forthcoming. Minerals in rosasite group are related to the malachite mineral [9,10]. The malachite–rosasite group, with the general formula  $\text{A}_2^{2+}(\text{CO}_3)(\text{OH})_2$ , includes both common minerals, such as malachite ( $\text{A}^{2+} = \text{Cu}$ ) and rosasite ( $\text{A}^{2+} = \text{Cu}, \text{Zn}$ ), along with other minerals like mcguinnessite (Mg, Cu), glaukosphaerite (Cu, Ni), kolwezite (Cu, Co), nullaginite (Ni), pokrovskite (Mg), zincrosasite (Zn, Cu). Besides the chemical composition, the similarities of their powder patterns suggest close structural relationships between these minerals [11].

Single crystal studies are available for malachite and rosasite [12]. The other minerals are characterized by microcrystalline fibrous habit. For these phases, space group symmetry and cell parameters are derived from powder pattern indexing.

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Table 1  
Table of the rosasite group minerals, the EDAX analyses, their chemical formulae and their origin

Mineral	Origin	Formula	Analysis
Nullaginite	Otway Prospect, Western Australia	$\text{Ni}_2(\text{CO}_3)(\text{OH})_2$	NiO: 68.67
Glaukosphaerite	Carr Boyd Nickel Mine, Carr Boyd Rocks, Western Australia	$(\text{Cu, Ni})_2(\text{CO}_3)(\text{OH})_2$	CuO: 41.6%; NiO: 25.2%
Mcguinnessite	Red Mountain, Mendocino County, California	$(\text{Mg, Cu})_2(\text{CO}_3)(\text{OH})_2$	CuO: 39.6% MgO: 23.27%
Rosasite	Mapimi, Durango, Mexico	$(\text{Cu, Zn})_2(\text{CO}_3)(\text{OH})_2$	CuO: 35.7%; ZnO: 36.5%
Kolwezite	Mupine, Shaba Province, Zaire	$(\text{Cu, Co})_2(\text{CO}_3)(\text{OH})_2$	CuO: 48.4%; CoO: 23.0%
Pokrovskite	Sonoma County, California	$\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot (1/2) \text{H}_2\text{O}$	MgO: 50.80

An accurate structural model of malachite is available for a long time [13], whereas the crystal structure of rosasite and of the isostructural mineral mcguinnessite were only recently solved from powder data [14]. Malachite is monoclinic,  $P2_1/a$ , with  $a = 9.502$ ,  $b = 11.974$ ,  $c = 3.24 \text{ \AA}$  and  $\beta = 98.75^\circ$ , whereas rosasite,  $P2_1/a$ , displays cell constants  $a = 12.897$ ,  $b = 9.370$ ,  $c = 3.162 \text{ \AA}$  and  $\beta = 110.26^\circ$ . Both the structures are built up by the same “modules”, namely “octahedral” walls of edge-sharing  $\text{A}^{2+}$  polyhedra, linked together through corner sharing to form infinite layers, and “triangular”  $\text{CO}_3$  groups, which assure the interlayer connection.

Infrared and Raman spectroscopy have been used to investigate carbonates including azurite and malachite [15,16]. NIR spectroscopy of the minerals of rosasite group has not been undertaken. However IR studies have been made very recently on these minerals (see first paper by Frost et al.). An infrared stretching vibration of the hydroxyl units of azurite was observed at  $3425 \text{ cm}^{-1}$ , whereas two bands were reported for malachite at  $3400$  and  $3320 \text{ cm}^{-1}$ . The rosasite mineral group is characterised by two OH stretching vibrations in the range  $3545\text{--}3310 \text{ cm}^{-1}$  and a broad band from  $3190\text{--}3120 \text{ cm}^{-1}$  due to adsorbed water [17]. The deformation modes of azurite were reported at  $1035$  and  $952 \text{ cm}^{-1}$  and at  $1045$  and  $875 \text{ cm}^{-1}$  for malachite. [16,18]. For rosasite group minerals, these modes have been recognised by three intense bands at  $1046$ ,  $870$  and  $818 \text{ cm}^{-1}$  [17]. Thus even though these carbonate minerals have the same space group, the molecular structure of the minerals is sufficiently different to show near-IR and IR bands at slightly different wavenumbers. Differences between the spectra of malachite, azurite and rosasite group minerals may be explained by the molecular structure of azurite being based upon a distorted square planar arrangement compared with a distorted octahedral arrangement of copper in malachite and rosasite. A variety of hydrous carbonate minerals are expected to show different spectral properties.

The purpose of this study is to apply the technique of NIR reflectance spectroscopy and to determine the range of spectral variability which this class of rosasite group minerals exhibits and whether they are plausible candidates for identification in Martian spectra.

## 2. Experimental

### 2.1. Minerals

The minerals, their formula and origin used in this study are listed in Table 1. Selected minerals were obtained from the Min-

eral Research Company and other sources including Museum Victoria. The samples were phase analysed by X-ray diffraction and for chemical composition by EDX measurements.

### 2.2. SEM analysis

Mineral samples of the rosasite were coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), samples were embedded in Araldite resin and polished with diamond paste on 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 at  $25 \text{ kV}$  accelerating voltage. Preliminary analyses of the rosasite mineral samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system. Oxygen was not measured directly but was calculated using assumed stoichiometries to the other elements analysed.

### 2.3. Near-infrared spectroscopy

Near IR spectra were collected on a Nicolet Nexus FT-IR spectrometer with a Nicolet Near-IR Fibreport accessory. A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from  $11,000$  to  $4000 \text{ cm}^{-1}$  by the co-addition of 64 scans at a resolution of  $8 \text{ cm}^{-1}$ . A mirror velocity of  $1.266 \text{ m/s}$  was used. The spectra were transformed using the Kubelka–Munk algorithm to provide spectra for comparison with absorption spectra.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package 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  $0.995$ .

### 3. Results and discussion

#### 3.1. SEM analysis

The EDX quantitative analyses were made on different areas of the samples. One set of EDX spectra of rosasite minerals selected and deconvoluted to determine the composition. The results are reported in the Table 1.

The rosasite sample used in this work analysed to a Cu/Zn ratio of close to 1:1. As such if the atom ratio of Cu/Zn is 1:1 then every second position in the model will be taken up by a Zn atom. Rosasite does not necessarily maintain a ratio of 1:1. For example the rosasite from Rosas mine, Narcao, Cagliari, Sardegna (Sardinia), Italy analyses as CuO 53.7 and ZnO 18.3%. This gives a formula of the Narcao rosasite as  $(\text{Cu}_{1.5}\text{Zn}_{0.5})_2(\text{CO})_3(\text{OH})_2$ . SEM analysis enables the chemical composition of the mineral to be estimated. Such analysis is important because the chemical composition will have an influence on the NIR spectra. The presence of for example Cu or Mn will effect the NIR spectra greatly.

According to Anthony et al. a glaucosphaerite sample from Kasompi, Congo gave a formula of  $(\text{Cu}_{1.23}\text{Zn}_{0.71})_2(\text{CO})_3(\text{OH})_2$  [33]. It is noted that the Cu/Zn ratio is not 1:1 and the total cations is not 2.0, but 1.94. The mineral glaucosphaerite from the Carr Boyd Nickel mine analyses as CuO 41.6% and NiO 25.2%. This gives the formula of glaucosphaerite as  $(\text{Cu}_{1.1}\text{Ni}_{0.7}\text{Mg}_{0.06})_2(\text{CO})_3(\text{OH})_2$ . Again the presence of Ni will change the spectra in the NIR region. A similar description exists for the mineral kolwezite from Mupine, Shaba Province, Zaire where the EDAX measurement gives an analysis of CuO 48.4%:CoO 23.0%. This then leads to the formula  $(\text{Cu}_{1.33}\text{Co}_{0.67})_2(\text{CO})_3(\text{OH})_2$ . The fact that the two cation ratio is not 1:1 may have implications for the structure of the mineral and therefore for the vibrational spectroscopy of the mineral. The mineral mcguinnessite gave an analysis of CuO 39.6%:MgO 23.7%. This leads to a formula of the mcguinnessite from Red Mountain, Mendocino County, California as  $(\text{Mg}, \text{Cu})_2(\text{CO}_3)(\text{OH})_2$ .

#### 3.2. NIR spectroscopy

The reflectance spectra ( $11,000\text{--}4000\text{ cm}^{-1}$ ) of rosasite group minerals covering a wide range in composition show diagnostic absorption bands related to electronic process involving electronic transitions due to transition metal ions (as listed in Table 1), and vibrational process involving hydroxyl units. Many of these absorption bands are relatively broad and overlapping. However, by the application of spectral analysis methods like continuum removal and derivative analysis permit minerals to be distinguished. The spectral differences between the minerals are illustrated in plots showing major absorption band centres and their spectral feature positions. NIR spectral features are subdivided into three regions (Figs. 1–3): the first region is the high wavenumber region  $11,000\text{--}5400\text{ cm}^{-1}$ ; spectra of the samples are shown in the Fig. 1. This is the window where characteristic electronic bands are caused by d–d transitions of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions in the higher

energy range,  $11,000\text{--}7000\text{ cm}^{-1}$  whereas in the lower region,  $7000\text{--}5400\text{ cm}^{-1}$  bands are attributed to the first overtones of the fundamental hydroxyl stretching modes, and combinational modes of OH stretching and bending modes. The second region,  $5400\text{--}4700\text{ cm}^{-1}$  where bands appear due to the first overtones of the water–OH stretching fundamentals and lastly the  $4600\text{--}4000\text{ cm}^{-1}$  region attributed to the combination of the stretching and deformation modes of rosasite minerals and are related to divalent ions of Mg, Zn, Cu, Ni, and Co hydroxides. The spectra are shown in Fig. 3. The results of the NIR spectra are reported in Table 2.

##### 3.2.1. The $11,000\text{--}7000\text{ cm}^{-1}$ spectral region

The six minerals studied here contain iron group ions in variable composition. NIR spectroscopy shows distinct spectral features. Crystal field effects due to valence states of Cu, Ni and Co are clearly reflected in their spectra as depicted in Fig. 1, from  $11,000$  to  $7000\text{ cm}^{-1}$ . A brief theory is offered here to explain the spectral features in each case followed by the assignment of the bands.

Rosasite  $[(\text{Cu}, \text{Zn})_2(\text{CO})_3(\text{OH})_2]$  displays a very broad feature chiefly, cupric ion character. Cu(II) has one unpaired electron corresponding to  $d^9$  configuration. So, there is only one free ion term,  ${}^2D$  and is split into ground  ${}^2E$  and excited  ${}^2T_2$  states in octahedral crystal field. But  ${}^2E$  splits under Jahn–Teller

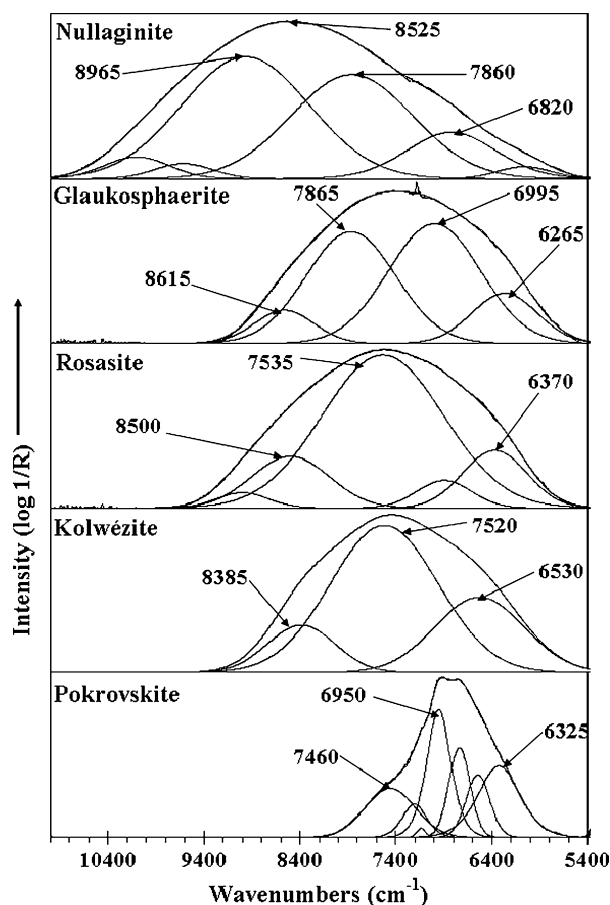
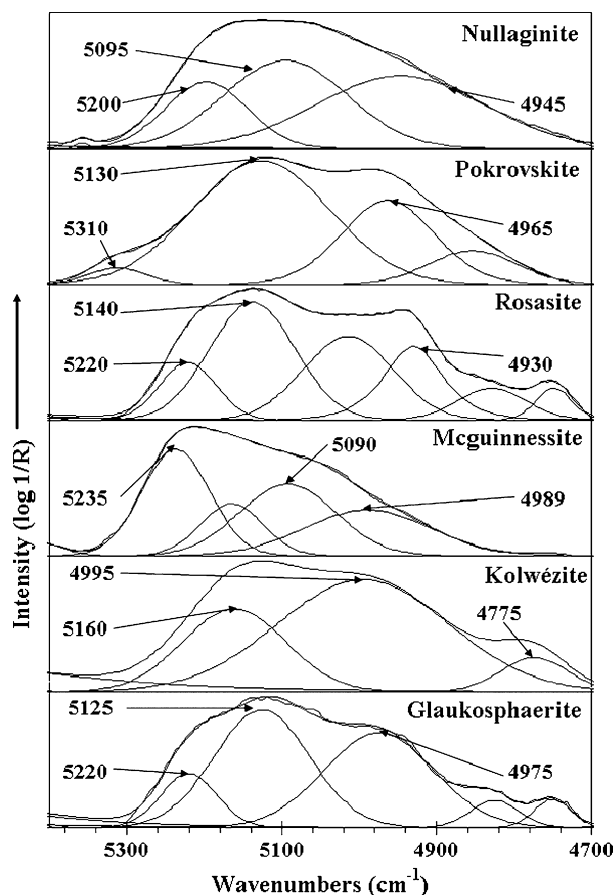


Fig. 1. NIR spectra of rosasite, glaucosphaerite, kolwezite, pokrovskite and nullaginite in the  $11,000\text{--}5400\text{ cm}^{-1}$  region.



Table 2 (Continued)

Glaukosphaerite	Kolwézite			Mcguinnessite			Rosasite			Pokrovskite			Nullaginite			Suggested Assignment			
	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area				
4507	90.7	2.08	2.08	4503	81.1	1.67	4506	72.1	1.83	4511	54.0	1.42	4536	57.9	1.73	4526	32.0	0.11	
																4500	34.4	0.08	
4396	126.6	4.11	0.74	4446	57.5	0.74	4465	43.5	2.17	4476	40.8	0.57							
																4413	2.43	0.23	
4317	72.2	0.95	17.46	4409	47.2	0.98	4404	98.1	17.46	4368	53.0	1.15	4367	31.4	0.21	4405	48.8	0.38	
																4305	19.6	0.02	
4247	73.1	0.91	0.60	4243	31.1	0.13	4240	34.9	2.06	4262	22.2	0.09	4262	62.0	1.21	4269	43.2	0.16	
																4244	31.0	0.49	
4164	155.0	4.26	3.00	4201	58.9	3.00	4201	58.9	3.00	4158	7.9	0.03	4157	7.9	0.03	4151	27.8	0.05	
																4129	31.9	0.07	
4057	78.4	0.61														4129	27.9	0.05	

Fig. 2. NIR spectra of glaukosphaerite, kolwézite, mcguinnessite, rosasite, pokrovskite and nullaginite in the 5400–4700  $\text{cm}^{-1}$  region.

effect and the excited state,  ${}^2T_2$  also splits indicating distortion of octahedral symmetry. Three spin-allowed transitions are generally observed for Cu(II) [19,20]. Three bands, one in NIR and two in the visible region have been reported for several Cu(II) complexes in tetragonally distorted octahedral coordination [21,22]. One intense band reported for Cu(II) in conicalcrite [ $\text{CaCuAsO}_4\text{OH}$ ] at  $8585\text{ cm}^{-1}$  was assigned to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transition [23]. The NIR band for rosasite,  $\text{CaCuAsO}_4\text{OH}$  centered at  $7535\text{ cm}^{-1}$  with a shoulder  $8500\text{ cm}^{-1}$  (Fig. 1) is due to Cu(II) and is assigned to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transition. The band shift to lower energy when compared to conicalcrite shows the effect of Zn on copper ion.

The divalent nickel ion in octahedral coordination is responsible for the green colour of the mineral [24]. Crystal field splittings of Ni(II) and site distortion have been explained in Ni-bearing mineral. Three spin-allowed bands are mainly observed [25–27]. In Ni–Mg carbonate minerals, gaspeite, three broad bands at  $8130$ ,  $13,160$  and  $22,730\text{ cm}^{-1}$  were assigned to  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ ,  ${}^3A_{2g}(\text{F}) \rightarrow T_{1g}(\text{F})$  and  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$  spin-allowed transitions and observed a splitting for the first band [28]. The spectrum of nullaginite [ $\text{Ni}_2(\text{CO}_3)(\text{OH})_2$ ] is an unique character of Ni(II) with a strong broad feature from  $11,000$  to  $7000\text{ cm}^{-1}$ . A band is centred at  $8525\text{ cm}^{-1}$  is a direct measure of crystal field splitting energy ( $\Delta_0$ ). This band is split into two bands with maxima at  $8965$  and  $7860\text{ cm}^{-1}$  is



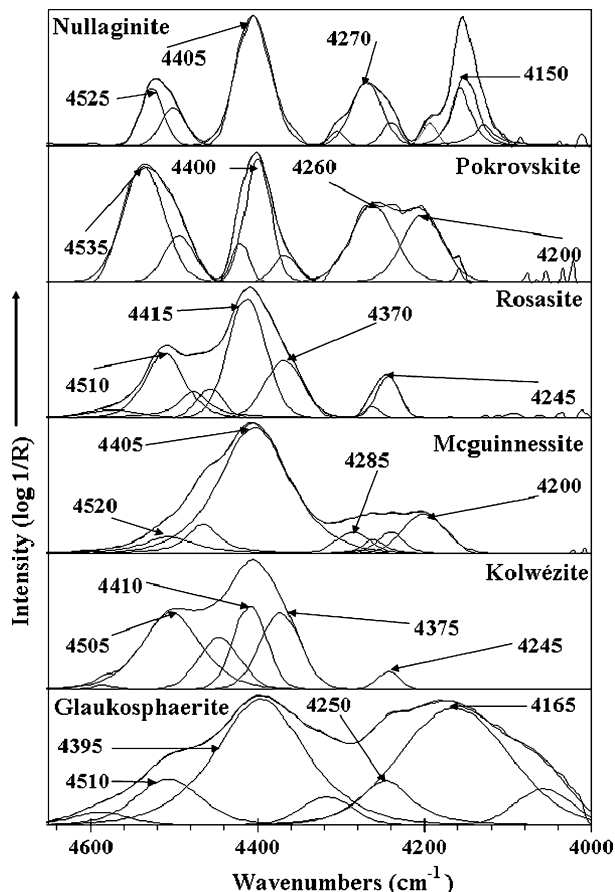


Fig. 3. NIR spectra of glaukosphaerite, kolwezite, mcguinnessite, rosasite, pokrovskite and nullaginite in the 4600–4000  $\text{cm}^{-1}$  region.

attributed to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  transition. Copper and nickel are the two major constituents of the glaukosphaerite mineral,  $(\text{Cu}, \text{Ni})_2(\text{CO}_3)(\text{OH})_2$ . Both the Cu and Ni contribute to its optical spectrum which gives rise to a broad band profile from 9400 to 7000  $\text{cm}^{-1}$ . It is resolved into four bands. The band at 7865  $\text{cm}^{-1}$  with a split component on the red side at 8615  $\text{cm}^{-1}$  identified as 10Dq band of Ni(II) and is assigned to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  transition whereas the second intense band at 6995  $\text{cm}^{-1}$  attributed to Cu(II) by comparing this with 7535  $\text{cm}^{-1}$  band in the spectrum of rosasite. In this case, the band causes a shift due to the presence of Ni as major constituent of the mineral.

For  $\text{Co}^{2+}$ , ( $3d^7$ ) the free ion terms are same as that for  $d^3$ -ions ( $\text{Cr}^{3+}$ );  ${}^4\text{F}$ , the ground term and  ${}^4\text{P}$ ,  ${}^2\text{G}$ ,  ${}^2\text{H}$ ,  ${}^2\text{D}$ ,  ${}^2\text{F}$ , excited terms. In the crystal field, the  $\text{Co}^{2+}$  has three spin-allowed transitions from the ground state,  ${}^4\text{T}_{1g}(\text{F})$  to  ${}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{A}_{2g}(\text{F})$  excited states. Two main absorption regions are observed in  $\text{Co}^{2+}$  spectra in octahedral coordination that correspond to quartet–quartet transitions: (a) 10,000–7000  $\text{cm}^{-1}$  (in the near-IR) relates to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  transition; (b) 20,000–17,000  $\text{cm}^{-1}$  the most intense  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition [29]. Kolwezite,  $(\text{Cu}, \text{Co})_2(\text{CO}_3)(\text{OH})_2$  shows a spectral mixture of copper and cobalt. Optically they are separated from one another. The  $\text{Cu}^{2+}$  band at 7520  $\text{cm}^{-1}$  is similar to that of rosasite spectrum with slightly variable intensity. The second

band that appeared at 8385  $\text{cm}^{-1}$  is in the cobalt spectrum range 10,000–7000  $\text{cm}^{-1}$ . Hence it is termed as  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  spin-allowed transition of  $\text{Co}^{2+}$  ion [29] and this transition is expected to show a broad-intense band. But in this case it is different with the intensity of  $\text{Co}^{2+}$  band (8385  $\text{cm}^{-1}$ ) diminished most obviously at the expense of copper as its concentration is very high in the mineral. Mcguinnessite  $[(\text{Mg}, \text{Cu})_2(\text{CO}_3)(\text{OH})_2]$  did not reveal the presence of copper since the mineral matrix suppressed electronic bands.

The spectrum of pokrovskite,  $[\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot (1/2)\text{H}_2\text{O}]$  is entirely different when compared with the spectra of other the minerals of the rosasite group (Fig. 1). The position of the bands for pokrovskite is different compared with the position of the bands for the other rosasite group minerals (Table 2). In the case of all the other minerals, possible substitutions of cations of Cu, Ni and Co for Mg are responsible for the result of broad band with splittings. Pokrovskite is a magnesium carbonate that shows a narrow band with structure at 6950  $\text{cm}^{-1}$  which implies non-involvement of transition metal ions as Mg is only major constituent of atomic structure of the mineral. SEM analysis of pokrovskite also shows Fe and Mn as minor impurities. The sharp band located at 6950  $\text{cm}^{-1}$  with a split band of 6370  $\text{cm}^{-1}$  are the first overtones of the OH fundamentals. This is in conformity with the IR bands as has been demonstrated the rosasite mineral group is characterised by two strong OH stretching vibrations in the range 3545–3310  $\text{cm}^{-1}$  [17]. The 7460  $\text{cm}^{-1}$  band appears as a shoulder to the main band seems to be the combination modes of OH stretching and Mg–OH or Fe–OH modes. The observation of weak bands in other minerals between 6265 and 6820  $\text{cm}^{-1}$  indicates strong OH bonding in pokrovskite.

### 3.2.2. The 5400–4700 $\text{cm}^{-1}$ spectral region

Fig. 2 shows the spectra of carbonates in the 5400–4700  $\text{cm}^{-1}$  region. A broad absorption feature near 5100  $\text{cm}^{-1}$  is invariably accompanied by a feature in the 5000–4800  $\text{cm}^{-1}$  and these are contributed by water–OH overtones of the two IR bands observed in the range 3250–3100  $\text{cm}^{-1}$  due to adsorbed water in the minerals. They appear to be uniform in nature because the structure of the rosasite group minerals are identical. The complexity of these features varies between samples because of the variation in composition and hence is useful for discriminating different hydrous carbonates. As Ni is the major cation in nullaginite, its spectrum is characterized by a broad feature at 5095  $\text{cm}^{-1}$  with two shoulders on either side at 5200 and 4945  $\text{cm}^{-1}$ . Glaukosphaerite shows almost similar spectrum with additional bands of variable intensities. An intense band at 5130  $\text{cm}^{-1}$  with a component, 4965  $\text{cm}^{-1}$  is seen in the spectrum of pokrovskite, Mg-carbonate whereas the bands in mcguinnessite are less intense. There is an increase in complexity in the spectra of rosasite and kolwezite due to the presence of cations of Zn, Co and Cu.

### 3.2.3. The 4600–4000 $\text{cm}^{-1}$ spectral region

Rosasite minerals exhibit absorption bands in the 4600–4000  $\text{cm}^{-1}$  region and show slight differences in terms of band

positions and intensities. The band positions of the samples that are well-defined minima in this region are shown in the Fig. 3. Although there are small shifts in band positions, the minerals of the group exhibits at least two absorption features whose peaks are observed at around 4535–4505 and 4415–4400  $\text{cm}^{-1}$ . Most probably, they emerge with two or more partially overlapping bands. The spectral character of the two main peaks around 4500 and 4400  $\text{cm}^{-1}$  is probably second order overtones of the most intense C–O stretching bands centred upon 1488 and 1388  $\text{cm}^{-1}$  in infrared spectra of carbonates [17,30]. Cloutis et al. showed that the second order overtone resulting from C–O stretching bands at 7  $\mu\text{m}$  (1420  $\text{cm}^{-1}$ ) [30]. Frost et al. reported intense Raman bands at around 1500  $\text{cm}^{-1}$  [17]. The complexity of bands with variable intensities from 4285–4165  $\text{cm}^{-1}$  are attributable to the combination of the OH-stretching and deformation modes of M–OH where M may be Mg, Cu, Ni, Co or Zn in wide range of composition in rosasite mineral group.

#### 4. Conclusions

Near infrared reflectance spectral analyses of hydroxy carbonates of the rosasite group minerals may be used as an indicator of specific mineralogy for the study of carbonates in Martian spectra, based upon the complexity of bands due to electronic and vibrational processes. The electronic spectra of transition series elements-bearing hydrous carbonates in a wide range of composition show broad bands in 11,000–7000  $\text{cm}^{-1}$  region due to ions of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in glaukosphaerite, kolwezite, mcguinnessite, rosasite, pokrovskite and nullagine.

These carbonates exhibit unique absorptions throughout near-infrared region of 7000–4000  $\text{cm}^{-1}$ : (a) the first overtone of the OH stretching vibration bands in the range 7000–4800  $\text{cm}^{-1}$ ; (b) the spectral character of the two main peaks around 4500 and 4400  $\text{cm}^{-1}$  probably second order overtones of the most intense C–O stretching bands centred upon 1488 and 1388  $\text{cm}^{-1}$  in the infrared spectra of carbonates and (c) the complexity of bands with variable intensities are disposed from 4285–4165  $\text{cm}^{-1}$  are attributable to the combination of OH-stretching and deformation modes of M–OH where M may be Mg, Cu, Ni Co or Zn in wide range of composition of the rosasite mineral group.

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