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**This is the author-version of article published as:**

Frost, Ray and Wain, Daria and Martens, Wayde and Reddy, Jagannadha. (2007) The molecular structure of selected minerals of the rosasite group - An XRD, SEM and infrared spectroscopic study. *Polyhedron* 26(2):pp. 275-283.

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## The molecular structure of selected minerals of the rosasite group - an XRD, SEM and infrared spectroscopic study

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### Abstract

Minerals of the rosasite group namely, rosasite, glaucosphaerite, kolwezite, mcguinnessite have been studied by powder X-ray diffraction, scanning electron microscopy and infrared spectroscopy. X-ray diffraction shows the minerals to be complex mixtures with more than one rosasite mineral observed in each sample. SEM analysis shows the minerals to be fibrous in nature and the use of EDAX enabled the chemical composition of the minerals to be determined. The spectral patterns for the rosasite minerals are similar to that of malachite implying the molecular structure of is similar. The rosasite minerals are characterised by two OH stretching vibrations at  $\sim 3401$  and  $3311\text{ cm}^{-1}$ . Two intense bands observed at  $\sim 1096$  and  $1046\text{ cm}^{-1}$  are assigned to  $\nu_1(\text{CO}_3)^{2-}$  symmetric stretching vibration and the  $\delta$  OH deformation mode. Multiple bands are found in the  $800$  to  $900\text{ cm}^{-1}$  and  $650$  to  $750\text{ cm}^{-1}$  regions attributed to the  $\nu_2$  and  $\nu_4$  bending modes confirming the symmetry reduction of the carbonate anion in rosasites as  $C_{2v}$  or  $C_s$ . A band at  $\sim 560\text{ cm}^{-1}$  is assigned to a CuO stretching mode.

**Key words:** glaucosphaerite, kolwezite, mcguinnessite, nullaginite, rosasite, hydroxycarbonate, Infrared spectroscopy

### Introduction

The carbonates are a group of over 60 naturally occurring minerals containing the essential structural building block  $(\text{CO}_3)^{2-}$ . Most of these minerals are relatively rare and often in association with other building blocks such as hydroxyls, halogens, sulphate, silicate, phosphate, etc. The common simple rock-forming carbonates can be divided into three main groups: a) the calcite group, b) the dolomite group and c) the aragonite group. Peter Williams reports that whilst metal substitution in azurite is extremely uncommon, such is not the case for malachite [1]. Substitution of Cu(II) by other cations gives rise to the rosasite mineral group. In minerals related to malachite, ions identified together with Cu(II) are: Zn(II), Co(II), Ni(II) and Mg(II). The rosasite mineral group is monoclinic or triclinic hydroxy carbonates with the general formula  $A_2(\text{CO}_3)(\text{OH})_2$  or  $AB(\text{CO}_3)(\text{OH})_2$  where A and B is cobalt, copper, magnesium, nickel and zinc [2]. The most common congener of malachite is rosasite. Rosasite forms in the oxidation zones of zinc-copper deposits and the crystals are often fibrous and found in tufted aggregates. No single crystal study of rosasite has been forthcoming. Powder diffraction studies of rosasite suggest the mineral is triclinic [3]. The chemical composition of the rosasite minerals means that the minerals are highly

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colourful, often green to blue. Minerals in the rosasite group are related to the mineral malachite [4, 5]. Minerals in this group include rosasite  $[(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2]$  [6-8], glaucosphaerite  $[(\text{Cu,Ni})_2(\text{CO}_3)(\text{OH})_2]$  [9-11], kolwezite  $[(\text{Cu,Co})_2(\text{CO}_3)(\text{OH})_2]$  [12], mcguinnessite  $[(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2]$  [13-16], and nullaginite  $[(\text{Ni})_2(\text{CO}_3)(\text{OH})_2]$  [17-19]. Apart from rosasite the minerals are rare secondary minerals. Besides the chemical composition, the structural relationships between these minerals are demonstrated by the similarity of their powder diffraction patterns [20]. The space group symmetry and cell parameters are mainly derived from powder pattern indexing. Apart from that of malachite, no other structural determinations are available for the rosasite minerals. Rosasite as with the other minerals of this group form spheroidal aggregates in extremely thin fibrous crystals. Rosasite may be associated with aurichalcite, smithsonite and hemimorphite.

Infrared and Raman spectroscopy have been used to investigate carbonates including azurite and malachite [21, 22]. A detailed single crystal Raman study has been undertaken [5, 21]. However the vibrational spectroscopy of minerals of the rosasite group has not been undertaken. No infrared spectra of the minerals of the rosasite group have been forthcoming [22-25]. Also no NIR research on these minerals has been reported. An infrared stretching vibration of the hydroxyl unit of azurite was observed at  $3425\text{ cm}^{-1}$ , whereas two bands were reported for malachite at  $3400$  and  $3320\text{ cm}^{-1}$ . The observation of two bands for malachite suggests coupling of the hydroxyl stretching vibrations [5]. This coupling was not observed for azurite [5]. Azurite and malachite form the basis of pigments in samples of an archaeological or medieval nature [26-29]. Malachite has a characteristic intense band at  $\sim 430\text{ cm}^{-1}$  and for azurite an intense band at  $\sim 400\text{ cm}^{-1}$ . The deformation modes of azurite were reported at  $1035$  and  $952\text{ cm}^{-1}$  and at  $1045$  and  $875\text{ cm}^{-1}$  for malachite. [22, 30] Thus even though the two carbonate minerals have the same space group, the molecular structure of the minerals is sufficiently different to show infrared bands at slightly different wavenumbers. Differences between the spectra of malachite and azurite may be explained by the molecular structure of azurite being based upon a distorted square planar arrangement compared with a distorted octahedral arrangement about the copper in malachite.

The symmetric stretching bands of carbonate for azurite and malachite were observed at  $1090$  and  $1095\text{ cm}^{-1}$ . Goldsmith and Ross reported the infrared bending modes of carbonate at  $837$  and  $817\text{ cm}^{-1}$  for azurite and at  $820$  and  $803\text{ cm}^{-1}$  for malachite [21]. Two  $\nu_3$  modes were observed at  $1490$  and  $1415\text{ cm}^{-1}$  for azurite and at  $1500$  and  $1400\text{ cm}^{-1}$  for malachite [4, 5]. The observation of these two bands shows a loss of degeneracy. Such a conclusion is also supported by the observation of two  $\nu_4$  modes at  $769$  and  $747\text{ cm}^{-1}$  for azurite and  $710$  and  $748\text{ cm}^{-1}$  for malachite. The vibrational spectroscopy of these two minerals is complicated by this loss of degeneracy. Schmidt and Lutz report some vibrational spectroscopic data [31]. Two infrared bands at  $3415$  and  $3327\text{ cm}^{-1}$  were observed for malachite. Although the Raman spectra of the mineral brochantite  $[\text{Cu}_4(\text{OH})_6\text{SO}_4]$  have been reported, the Raman spectra of malachite and azurite were not [31].

In this work we report the X-ray diffraction, SEM analysis and infrared spectroscopy of minerals of the rosasite group and relate the spectroscopy to the mineral structure.

## **Experimental**

### **Minerals**

The minerals, their formula and origin used in this study are listed in Table 1. Selected minerals were obtained from the Mineral Research Company and other sources including Museum Victoria. The samples were phase analysed by X-ray diffraction for phase analysis and for chemical composition by EDX measurements.

### **X-Ray diffraction**

X-ray diffraction (XRD) patterns were recorded using CuK $\alpha$  radiation ( $n = 1.5418\text{\AA}$ ) on a Philips PANalytical X' Pert PRO diffractometer operating at 40 kV and 40 mA with 0.125° divergence slit, 0.25° anti-scatter slit, between 3 and 15° (2 $\theta$ ) at a step size of 0.0167°. For low angle XRD, patterns were recorded between 1 and 5° (2 $\theta$ ) at a step size of 0.0167° with variable divergence slit and 0.5° anti-scatter slit.

### **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), three 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 25kV 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.

### **Mid-IR spectroscopy**

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm<sup>-1</sup> range were obtained by the co-addition of 64 scans with a resolution of 4 cm<sup>-1</sup> and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc 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.

## Results and discussion

### X-ray diffraction

The XRD patterns of the rosasite mineral group are illustrated by those of rosasite and glaukosphaerite which are shown in Figures 1a and 1b. What is observed from the XRD patterns is that the mineral rosasite appears to be a mixture of rosasite, quartz and mcguinnessite. Glaukosphaerite appears to be a mixture of glaukosphaerite with some malachite and other impurities. In order to run an XRD pattern the mineral is scraped off a host rock and is ground before the XRD pattern is collected. This means that all minerals present are analysed. In terms of SEM and spectroscopy a more judicious selection can be made and only specific crystals analysed. In this instance the correct mineral is obtained. Roberts et al. showed that the mineral rosasite was monoclinic [32].

### SEM images

SEM images of rosasite, glaucosphaerite, kolwezite and pokrovskite are shown in Figures 2a, 2b, 2c and 2d. The crystals of the three minerals are acicular and may be up to 0.5 mm in length. The minerals appear to be fibrous in nature. The images show the hydroxycarbonates to be botryoidal and forming crusts. This is best illustrated by the SEM image of pokrovskite (Figure 2d). Figures 3 show the typical EDAX analyses of rosasite, glaukosphaerite, kolwezite and mcguinnessite. The results of the analyses are reported in 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  $(\text{Cu}_{1.5}\text{Zn}_{0.5})_2(\text{CO})_3(\text{OH})_2$ . 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  $(\text{Cu}_{1.1}\text{Ni}_{0.7}\text{Mg}_{0.06})_2(\text{CO})_3(\text{OH})_2$ . A similar formula exists for the mineral kolwezite from Zaire namely  $(\text{Cu}_{1.33}\text{Co}_{0.67})_2(\text{CO})_3(\text{OH})_2$ . 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 mcguinnessite from California gives a cation ratio of Cu/Mg as 1:1. Other measurements record a ratio of Mg/Cu as 1.5/0.5.

### Infrared spectroscopy

The minerals of the rosasite group have not been studied by single crystal X-ray diffraction. Invariably because most of the crystals are composed of thin fibres.

Extensive powder X-ray diffraction suggests the minerals are triclinic, although Anthony et al. states the minerals are monoclinic [33]. This statement is apparently based upon the assumption the structures are similar to that of malachite. The structure shows that two of the three oxygens bond to separate copper atoms but one carbonate oxygen bonds to two copper atoms. The OH unit serves to bridge two copper atoms. The model of the structure of malachite shows that the carbonate anion is of  $C_{2v}$  symmetry if the two cations bonding to the carbonate anion are identical [4, 5]. If however the two cations are different (e.g. Cu and Ni or Cu and Zn) then the symmetry of the carbonate anion would be  $C_s$ . The mineral glaucosphaerite is equally enigmatic and may be monoclinic. Williams reported the structure of the rosasite group of minerals to be triclinic [1]. It is not necessarily true that rosasite has the same structure as malachite [1]. In the structure of rosasite some of the copper atoms in the model of malachite are replaced by zinc atoms.

The infrared spectra of selected minerals of the rosasite group in the OH stretching region are shown in Figure 4. Rosasite is characterised by two intense bands at 3401 and 3311  $\text{cm}^{-1}$  with two additional bands at 3139 and 3486  $\text{cm}^{-1}$ . The bands at 3486, 3401 and 3311  $\text{cm}^{-1}$  are attributed to OH stretching vibrations whereas the bands at 3228 and 3139  $\text{cm}^{-1}$  are ascribed to adsorbed water. If we use a Libowitzky type empirical formula [34] calculation of the hydrogen bond distances in the structure can be estimated. The bands at 3486, 3401, 3311 and 3139  $\text{cm}^{-1}$  lead to hydrogen bond distances of 2.877, 2.80, 2.75 and 2.68 Å. The conclusion may be made that there are three different hydrogen bond distances of the OH units which are a weaker hydrogen bond strength than the hydrogen bond formed from adsorbed water. The mineral glaucosphaerite has infrared bands at 3529, 3402, 3309, 3191 and 3022  $\text{cm}^{-1}$ . The bands at 3402 and 3309  $\text{cm}^{-1}$  are in almost identical positions to those of rosasite. Because of the broad spectral profile in the OH stretching region variation in the bands at 3191 and 3022  $\text{cm}^{-1}$  may occur. This makes the fitting of bands difficult. Similarly for the mineral kolwezite the two OH stretching vibrations are observed at 3401 and 3307  $\text{cm}^{-1}$ . The infrared spectrum of mcguinnessite appears different. The two bands at 3407 and 3316  $\text{cm}^{-1}$  are in common with the spectra of the other minerals. The other intense band at 3545  $\text{cm}^{-1}$  may be due to an impurity. Powder X-ray diffraction shows that these minerals are not 100 % pure and are often mixed with other minerals of the rosasite group or related minerals.

The infrared spectra of selected rosasite minerals in the 900 to 1200  $\text{cm}^{-1}$  region are shown in Figure 5. For rosasite two intense bands are observed at 1096 and 1046  $\text{cm}^{-1}$ . The first band is assigned to the  $\nu_1$  symmetric stretching mode of the carbonate unit. Bands have been observed in the infrared spectra of malachite at 1095  $\text{cm}^{-1}$  and 1090  $\text{cm}^{-1}$  for azurite [4, 5]. The infrared spectrum of hydrocerrusite showed an intense band at 1090  $\text{cm}^{-1}$  [35]. Interestingly the  $(\text{CO}_3)^{2-}$   $\nu_1$  band of the rosasite minerals should not be infrared active [5, 36-38]. However because of symmetry reduction of the carbonate anion the band is activated. An intense Raman band is observed at 1096  $\text{cm}^{-1}$  for rosasite and is assigned to the  $\nu_1$   $(\text{CO}_3)^{2-}$  symmetric stretching vibration [5, 36-38]. The intense band at 1046  $\text{cm}^{-1}$  is assigned to the  $\delta$  OH deformation mode. For malachite two bands attributed to OH deformation modes are found at 1045 and 875  $\text{cm}^{-1}$  [5]. For hydrocerrusite the OH deformation modes were observed at 1047 and 1040  $\text{cm}^{-1}$ . It is noted that in the infrared spectrum of rosasite an intense shoulder occurs at 1023  $\text{cm}^{-1}$ . This band is also assigned to an OH

deformation mode [39, 40]. In the Raman spectrum of rosasite a low intensity band is observed at  $1056\text{ cm}^{-1}$  and is ascribed to this vibrational mode [5, 36, 38, 41].

For the mineral kolwezite two intense infrared bands are observed at  $1096$  and  $1047\text{ cm}^{-1}$ . The first band is assigned to the  $\nu_1(\text{CO}_3)^{2-}$  vibrational mode and the second band to a  $\delta$  OH deformation mode. As for rosasite in the infrared spectrum a long tail on the low wavenumber side is observed and a component band may be resolved at  $1012\text{ cm}^{-1}$ . This band is a second  $\delta$  OH deformation mode. The position of this second band appears to vary between the rosasite minerals. In the IR spectrum of mcguinnessite, two bands are observed at  $1046$  and  $1004\text{ cm}^{-1}$ . Both bands are ascribed to  $\delta$  OH deformation modes. The  $\nu_1(\text{CO}_3)^{2-}$  symmetric stretching mode is observed at  $1099\text{ cm}^{-1}$ . A second band is observed at  $1084\text{ cm}^{-1}$ . The observation of a second band supports the concept of two different carbonate units in the mcguinnessite structure. In the Raman spectrum the intensity of bands assigned to  $\delta$  OH deformation modes is low and for mcguinnessite a band is observed at  $1060\text{ cm}^{-1}$ . In the infrared spectrum of glaukosphaerite the  $\delta$  OH deformation mode is observed at  $1047\text{ cm}^{-1}$ . However the spectral profile on the lower wavenumber side of this band is complex and may be resolved into a series of overlapping bands. Two bands are observed at  $1099$  and  $1078\text{ cm}^{-1}$  and are assigned to the  $\nu_1$  symmetric stretching modes; again supporting the concept of two different carbonate units in the glaukosphaerite structure. Only a single  $\nu_1$  symmetric stretching mode band for rosasite was observed.

The infrared spectra of selected rosasite minerals in the  $1225$  to  $1625\text{ cm}^{-1}$  region are shown in Figure 6. The infrared spectrum of rosasite in this spectral region are characterised by strong bands centred upon  $1488$  and  $1388\text{ cm}^{-1}$  which may be resolved into four bands at  $1522$ ,  $1488$ ,  $1425$  and  $1388\text{ cm}^{-1}$ . These bands are attributed to the  $\nu_3$  antisymmetric  $(\text{CO}_3)^{2-}$  stretching modes. In the IR spectrum of malachite two bands are observed at around  $1500$  and  $1400\text{ cm}^{-1}$  [5]. For hydrozincite two bands are observed at  $1515$  and  $1400\text{ cm}^{-1}$ . It would appear that there are two pairs of bands for rosasite namely ( $1522$  and  $1425\text{ cm}^{-1}$ ) and ( $1488$  and  $1388\text{ cm}^{-1}$ ). The observation of two sets of bands for rosasite suggests that there are two independent carbonate units in the crystal structure. Such sets of bands are also observed for each of the other rosasite minerals. For kolwezite two sets of bands are found at ( $1522$  and  $1426\text{ cm}^{-1}$ ) and ( $1486$  and  $1390\text{ cm}^{-1}$ ) and for glaukosphaerite ( $1531$  and  $1425\text{ cm}^{-1}$ ) and ( $1493$  and  $1401\text{ cm}^{-1}$ ). The intensities for mcguinnessite are opposite to that of rosasite in this spectral region; bands are observed for this mineral at ( $1542$  and  $1432\text{ cm}^{-1}$ ) and ( $1497$  and  $1391\text{ cm}^{-1}$ ).

The infrared spectrum of the low wavenumber region are shown in Figure 7. The infrared spectrum is limited to the cut-off point at  $550\text{ cm}^{-1}$  at which point the diamond ATR cell absorbs the infrared radiation. However such a cut off point does not effect the infrared spectroscopy of minerals containing carbonate as all of the bands are above  $550\text{ cm}^{-1}$ . The mineral rosasite shows two intense infrared bands at  $870$  and  $818\text{ cm}^{-1}$ . These bands are assigned to the  $\nu_2$  bending modes of the  $(\text{CO}_3)^{2-}$  units. The observation of two  $\nu_2$  bands is in harmony with the observation of two sets of bands in the  $\nu_3$  antisymmetric stretching region. The infrared spectrum of malachite shows two bands at  $820$  and  $803\text{ cm}^{-1}$  ascribed to  $\nu_2$  bending modes as does azurite at  $837$  and  $817\text{ cm}^{-1}$  [5]. Hydrocerrusite infrared spectrum shows two bands at  $850$  and  $834\text{ cm}^{-1}$ . The  $\sim 880\text{ cm}^{-1}$  band for rosasite is not symmetrical and may be

resolved into two component bands at 889 and 870  $\text{cm}^{-1}$ . The infrared spectrum of the mineral glaucosphaerite is very similar to that of rosasite with two bands observed at 886 and 819  $\text{cm}^{-1}$ . The infrared spectrum of the mineral kolwezite is also similar in this spectral region, even though the profile is more complex. The spectrum of mcguinnessite is more complex with a number of bands observed at 870, 847, 833, 819 and 803  $\text{cm}^{-1}$ . The bands at 870 and 819  $\text{cm}^{-1}$  are related to the  $\nu_2$  bending modes. The other bands may be due to impurities.

For rosasite a number of bands are observed at 781, 748 and 710  $\text{cm}^{-1}$ . These bands are assigned to the  $\nu_4 (\text{CO}_3)^{2-}$  bending modes. For malachite two infrared bands are observed at 748 and 710  $\text{cm}^{-1}$  which are assigned to this vibration [4, 5]. Another mineral with similar formulation to rosasite, hydrozicite has bands in this region at 738 and 710  $\text{cm}^{-1}$ . The infrared spectrum of hydrocerrusite has  $\nu_4 (\text{CO}_3)^{2-}$  bending modes at 700, 687 and 676  $\text{cm}^{-1}$ . Two bands are observed around 570  $\text{cm}^{-1}$  for rosasite; it is not known if these bands are due to  $\nu_4 (\text{CO}_3)^{2-}$  bending modes. However this assignment seems unlikely. These bands are due to CuO stretching vibrations [41-45]. The infrared spectrum of kolwezite displays bands at 747, 728 and 710  $\text{cm}^{-1}$ . The results for glaucosphaerite include bands at 749, 737 and 668  $\text{cm}^{-1}$ . A low intensity band is observed at 570  $\text{cm}^{-1}$  and is ascribed to the CuO stretching vibration. The IR spectrum of mcguinnessite also shows an intense band at 559  $\text{cm}^{-1}$  which is assigned to CuO stretching vibration [42, 45-47].

## CONCLUSIONS

XRD studies of the rosasite mineral group showed the minerals are mixtures of members of the rosasite minerals. Normally one of the rosasite minerals is predominant. EDAX has been used to determine the chemical composition of the mineral. The rosasite from Rosas mine, Narcao, Cagliari, Sardegna (Sardinia), Italy analysed as CuO 53.7 and ZnO 18.3 % giving rise to the formula  $(\text{Cu}_{1.5}\text{Zn}_{0.5})_2(\text{CO})_3(\text{OH})_2$ . Glaucosphaerite from the Carr Boyd Nickel mine analysed as CuO 41.6 % and NiO 25.2 % giving rise to the formula  $(\text{Cu}_{1.1}\text{Ni}_{0.7}\text{Mg}_{0.06})_2(\text{CO})_3(\text{OH})_2$ . Similarly the mineral kolwezite from Zaire has a formula  $(\text{Cu}_{1.33}\text{Co}_{0.67})_2(\text{CO})_3(\text{OH})_2$ .

The infrared spectral patterns for the minerals rosasite, glaucosphaerite, kolwezite and mcguinnessite are similar and may be compared with that of malachite. This implies the molecular structure is similar to malachite. The single crystal structure of the members of the rosasite mineral group remains undetermined. The question arises as to why there are similar infrared spectral patterns for the rosasite minerals. It means the minerals must have the same structure or at least related structures. Malachite is monoclinic with point group  $2/m$ . Therefore it can be inferred that the structure of the rosasite group of minerals is monoclinic. This conclusion is in agreement with the assumptions of Anthony et al. who state that rosasite and related minerals have monoclinic structure by analogy with malachite [33].

## **Acknowledgments**

The financial and infra-structure support of the Queensland University of Technology, Inorganic Materials Research Program is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

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<b>Mineral</b>	<b>Locality of origin</b>	<b>Formulae</b>	<b>Analysis (% by mass)</b>
Rosasite	Mapimi, Durango, Mexico	$(\text{Cu,Zn})_2(\text{CO})_3(\text{OH})_2$	CuO 35.7 % ZnO 36.5 %
Glaukosphaerite	Carr Boyd Nickel Mine, Carr Boyd Rocks, W.A. [17, 19]	$(\text{Cu,Ni})_2(\text{CO}_3)(\text{OH})_2$	CuO 41.6 % NiO 25.2 %
Kolwezite	Mupine, Shaba Province, Zaire [33]	$(\text{Cu,Co})_2(\text{CO})_3(\text{OH})_2$	CuO 48.4 % CoO 23.0 %
McGuinnessite	Red Mountain, Mendocino County, California [16]	$(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2$	CuO 39.6 % MgO 23.7%

**Table 1 Table of the hydroxycarbonate minerals, their chemical formulae and origin**

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Table 1 Table of the rosasite minerals, the EDAX analysis, their chemical formulae and their origin.

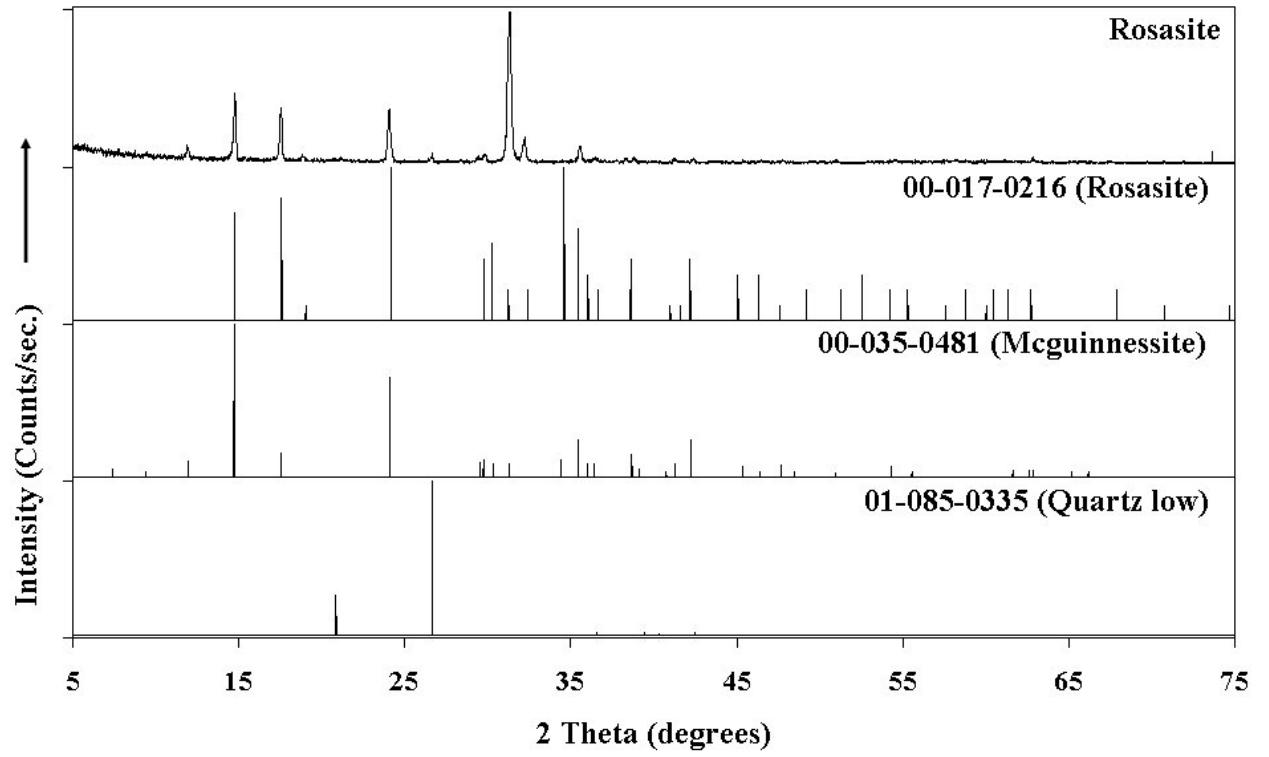
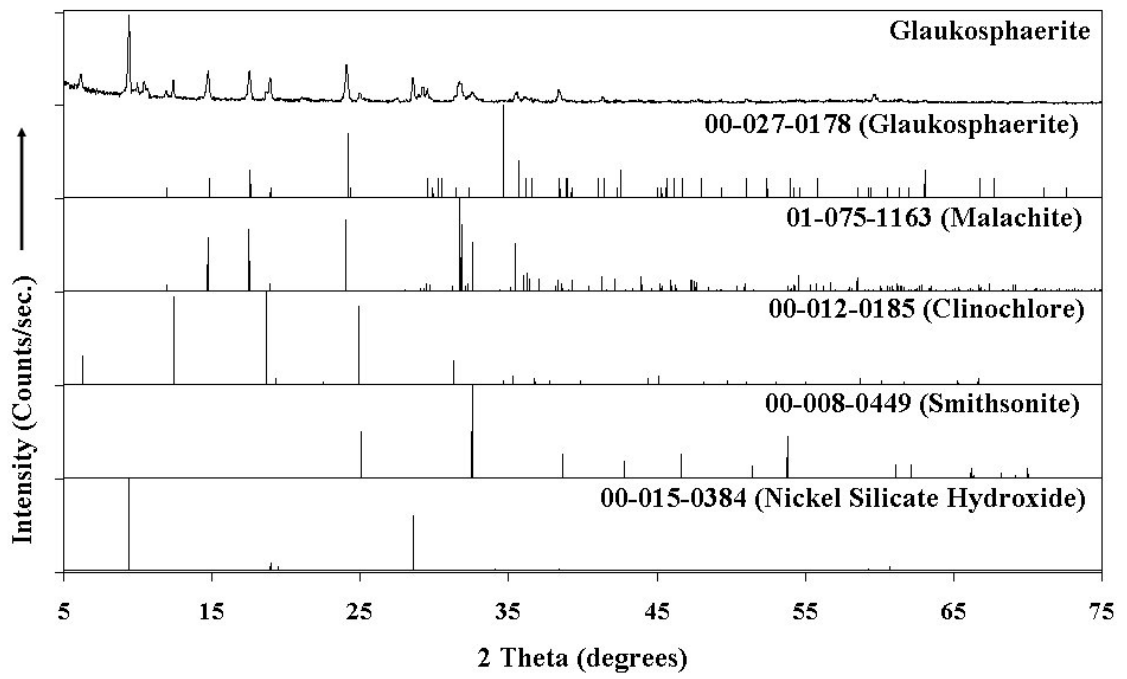


Figure 1a



**Figure 1b**

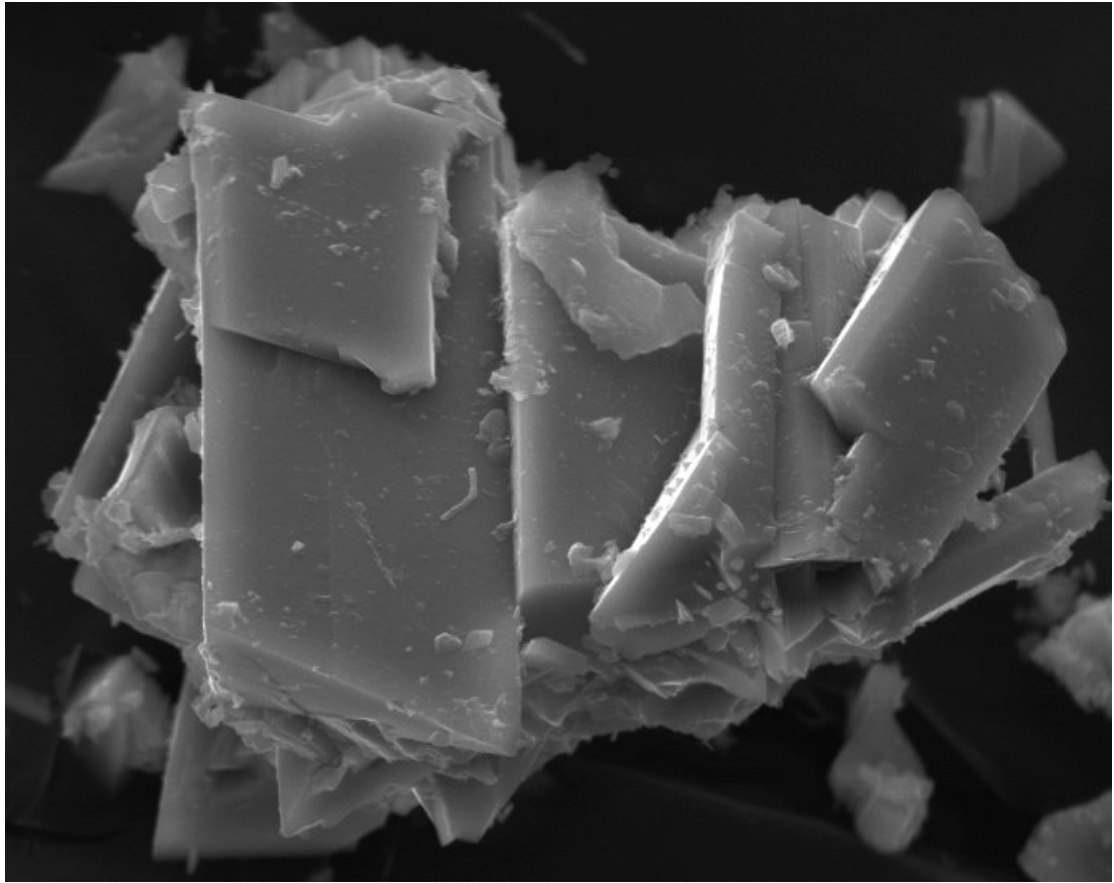
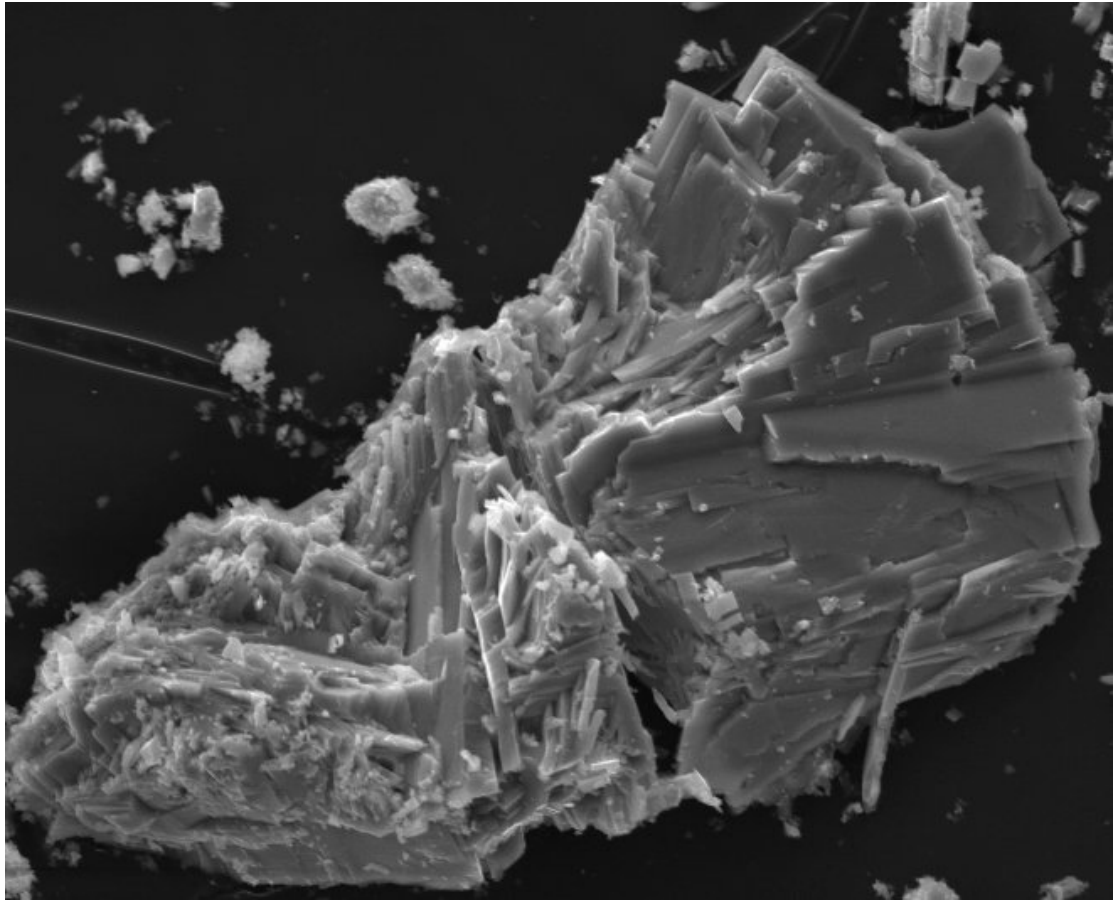
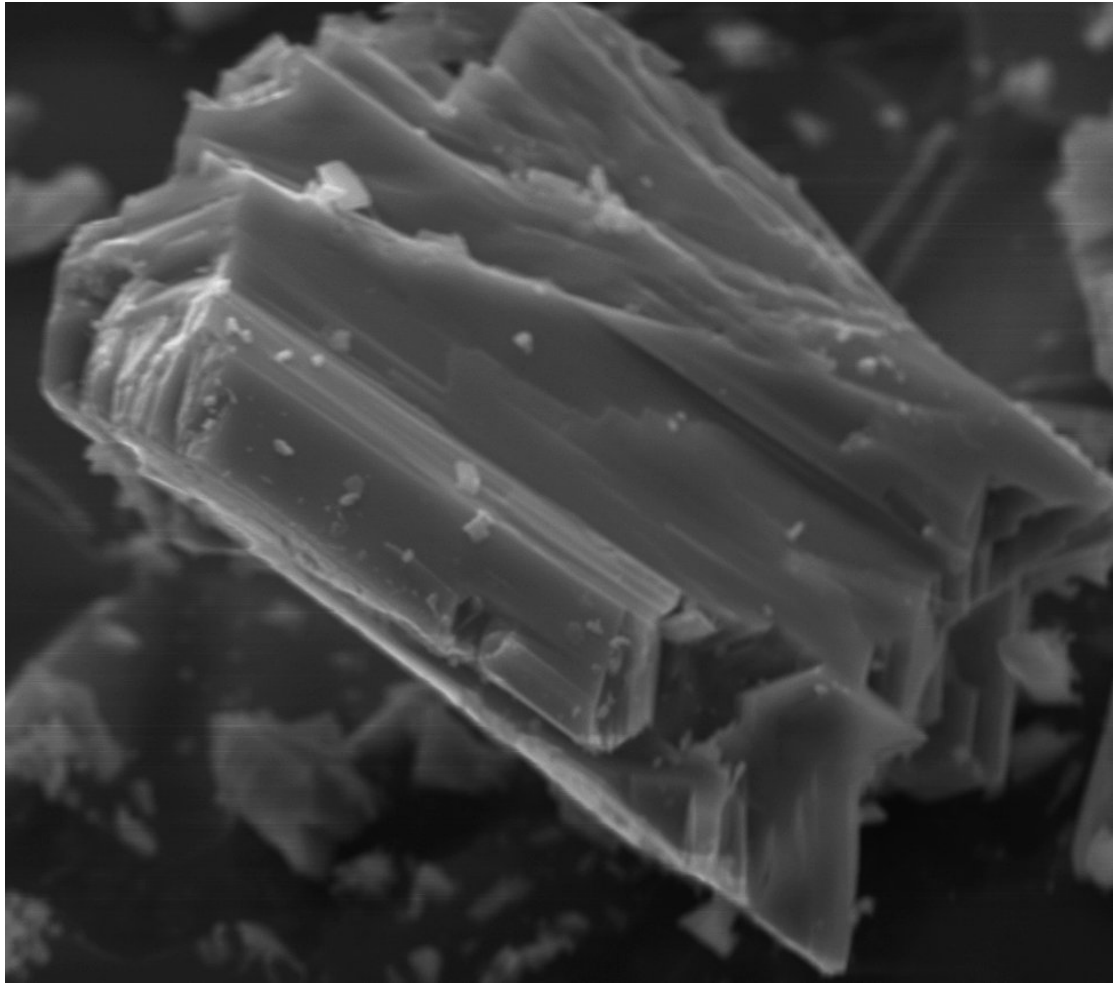


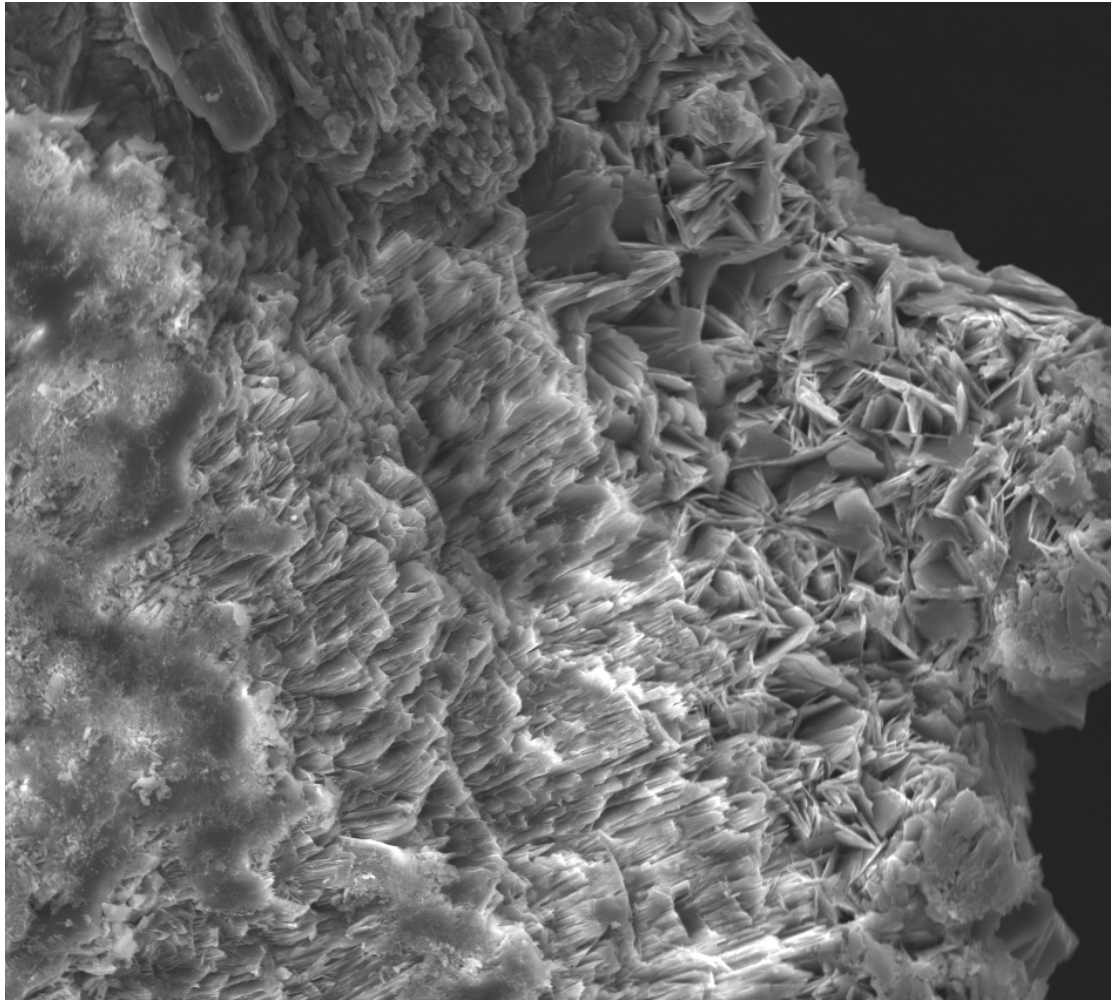
Figure 2a SEM image of rosasite



**Figure 2b SEM image of glaukosphaerite**



**Figure 2c SEM image of kolwezite**



**Figure 2d SEM image of pokrovskite**

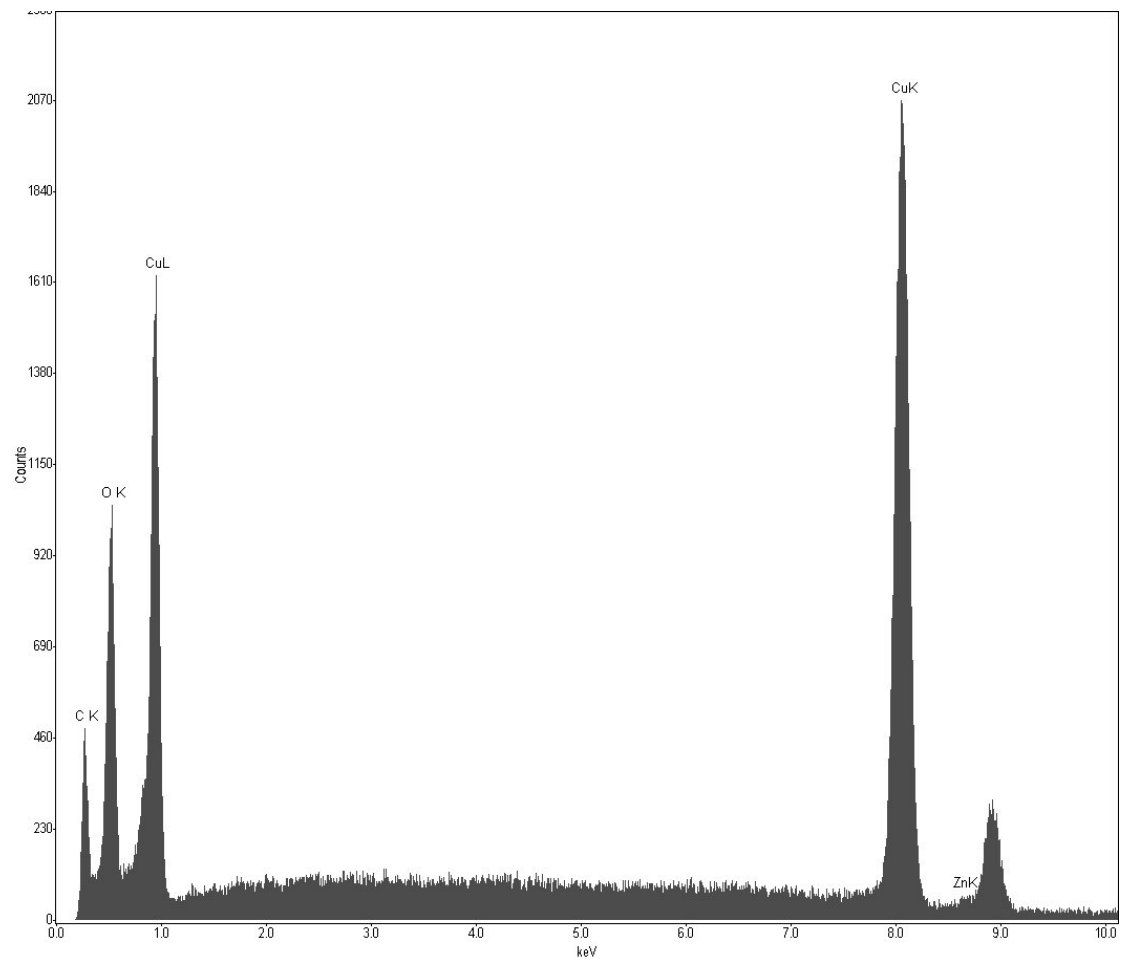
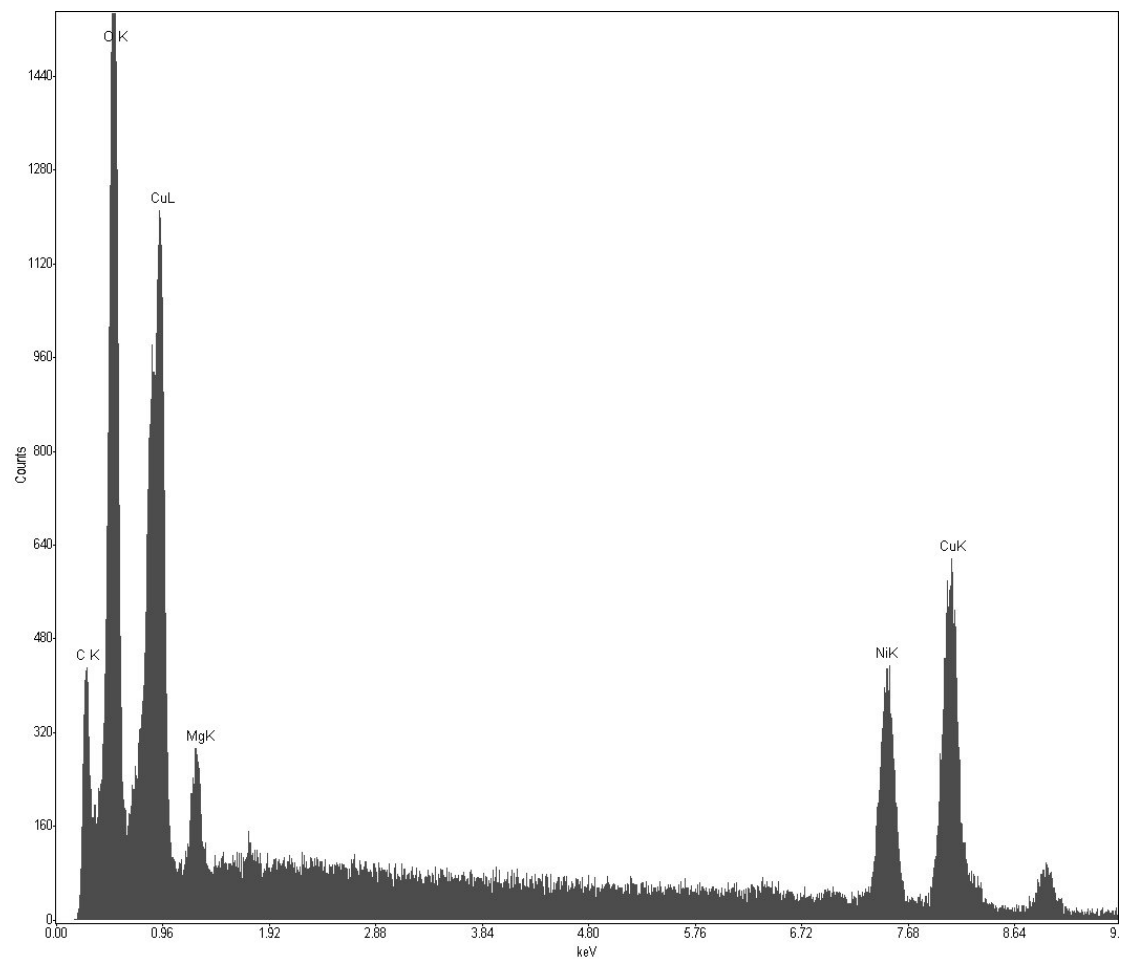
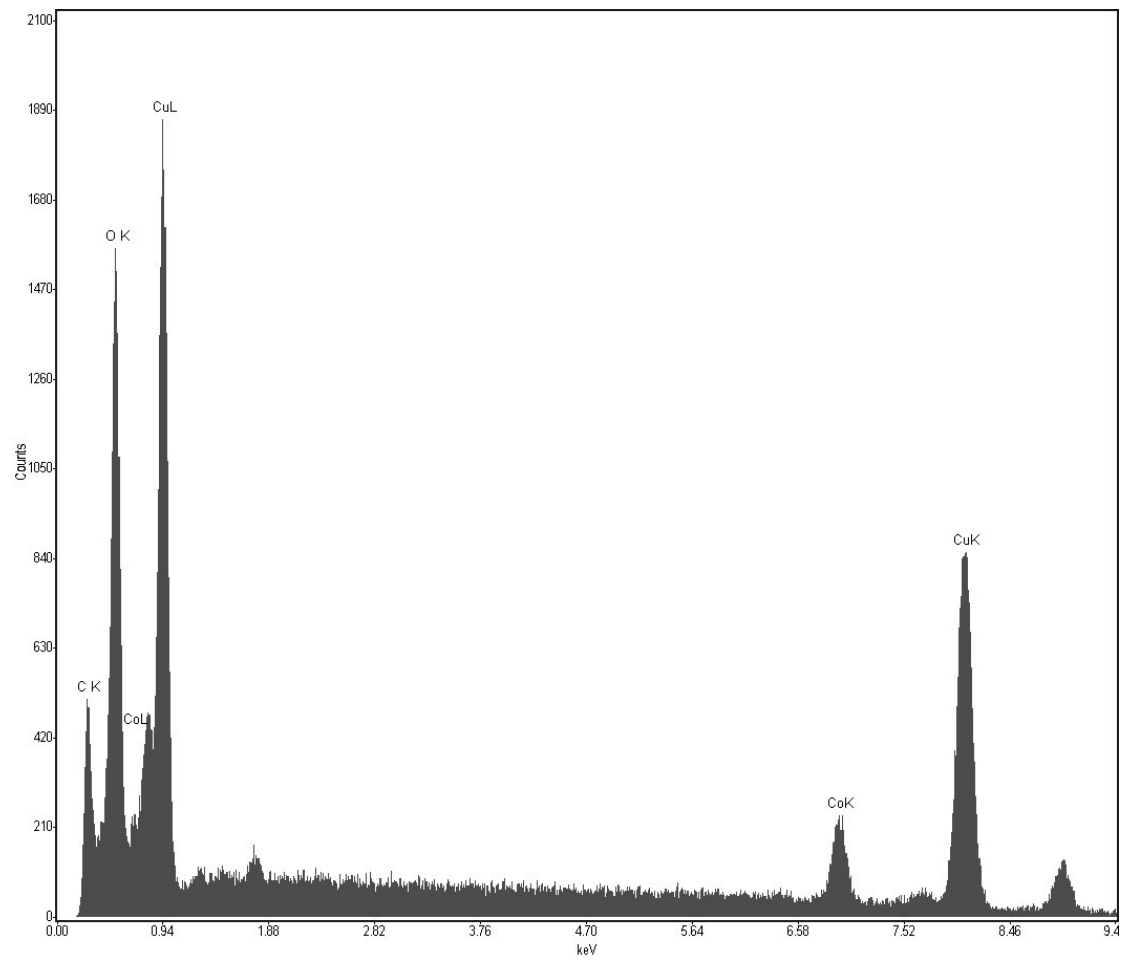


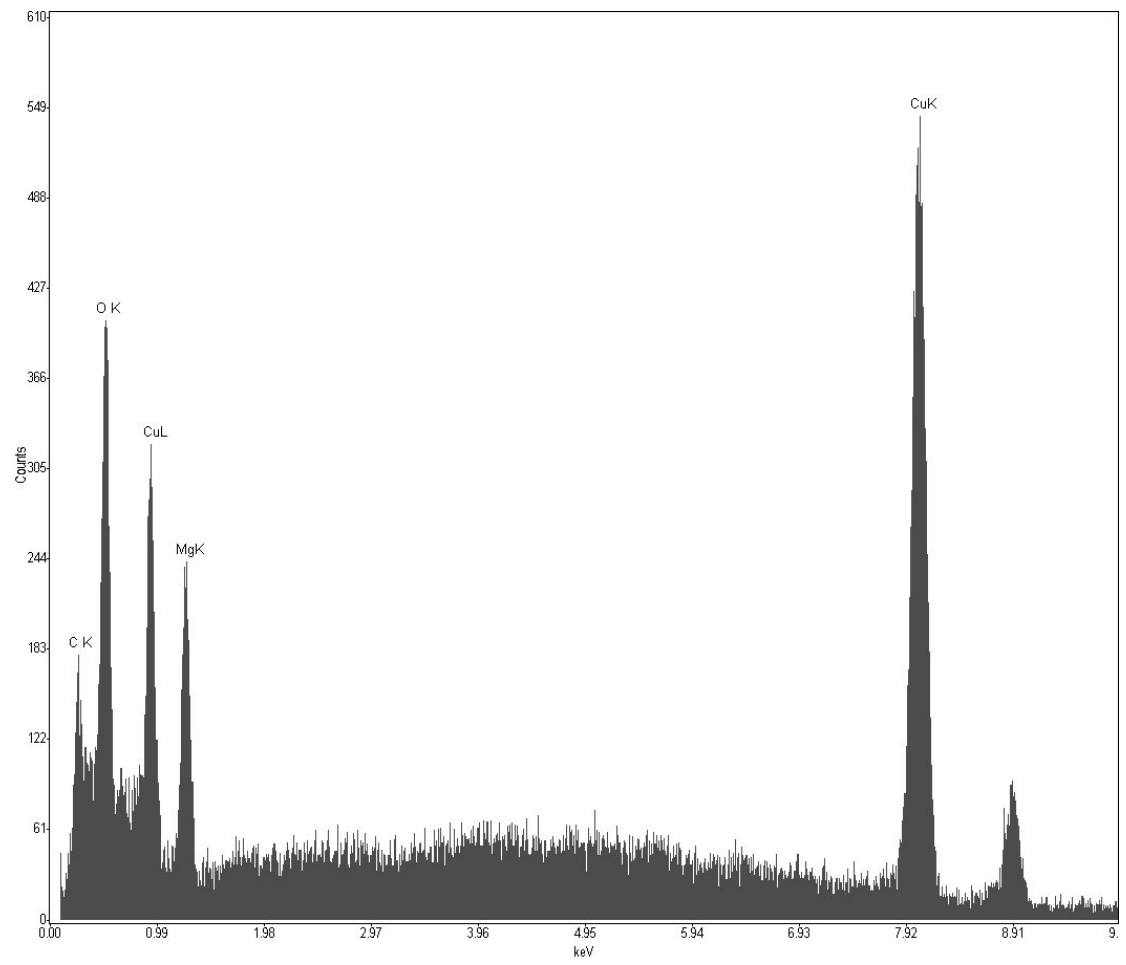
Figure 3a EDX of roasite



**Figure 3b Glaucosphaerite**



**Figure 3c EDAX of kolwezite**



**Figure 3d Mcguinnessite**

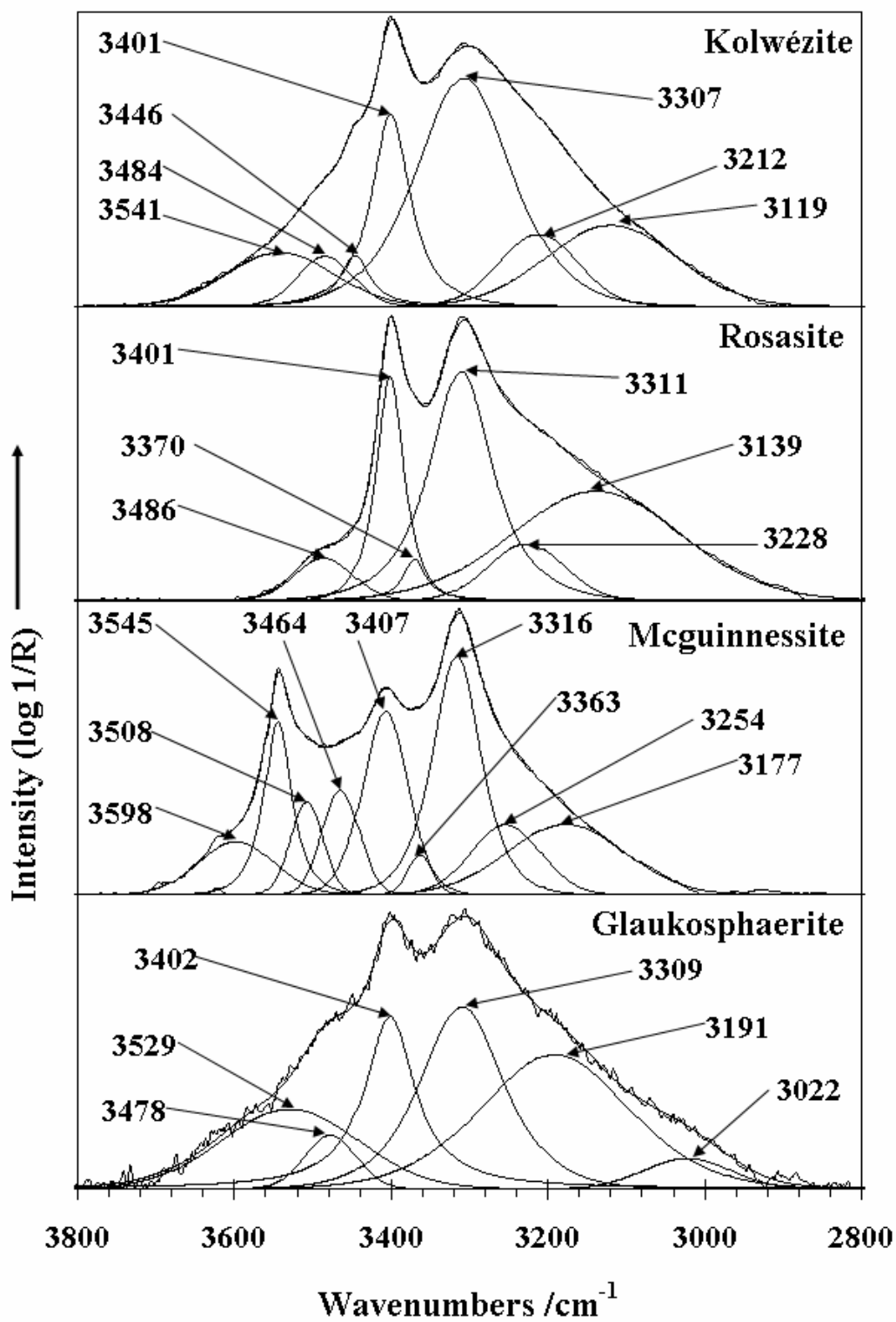


Figure 4

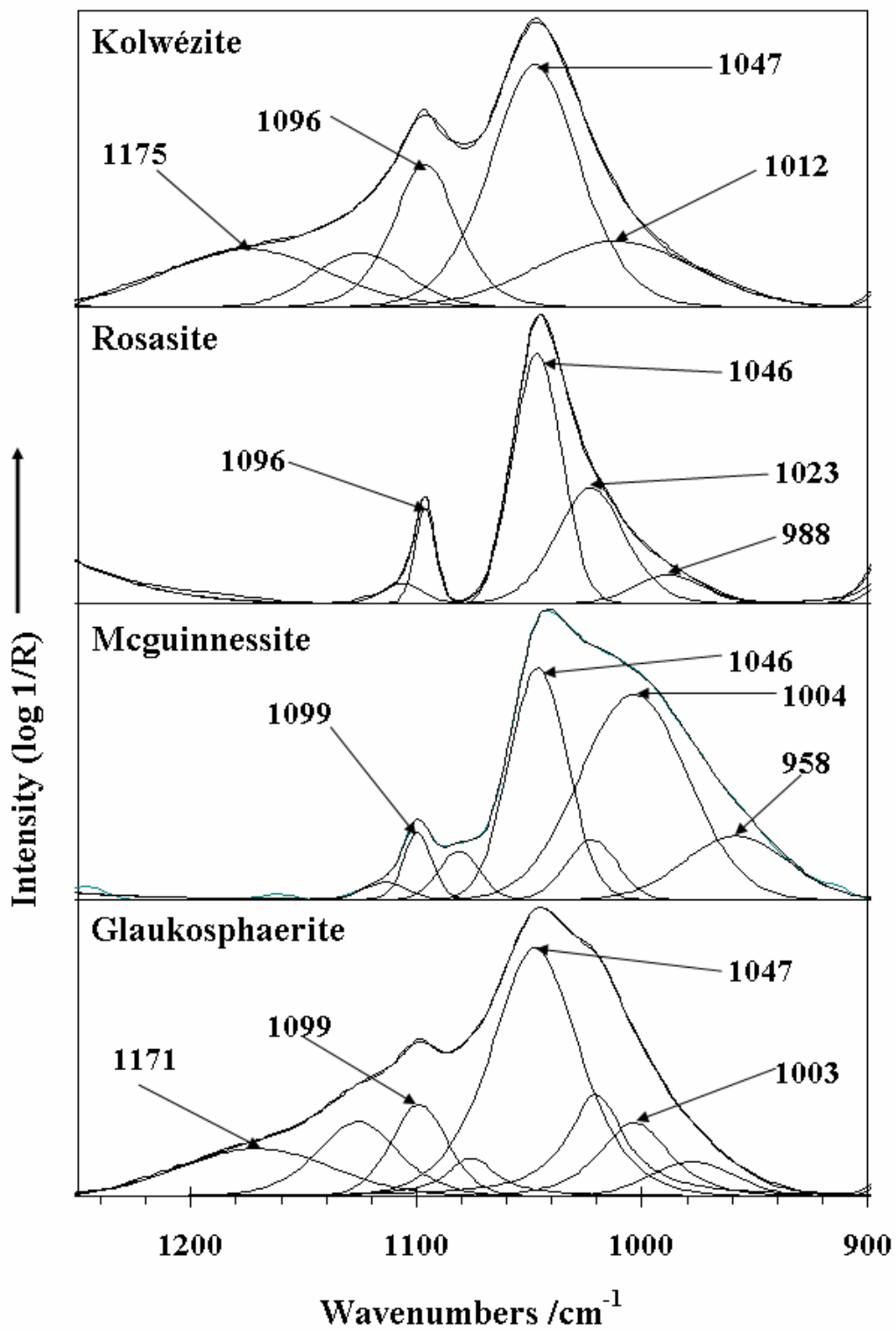


Figure 5

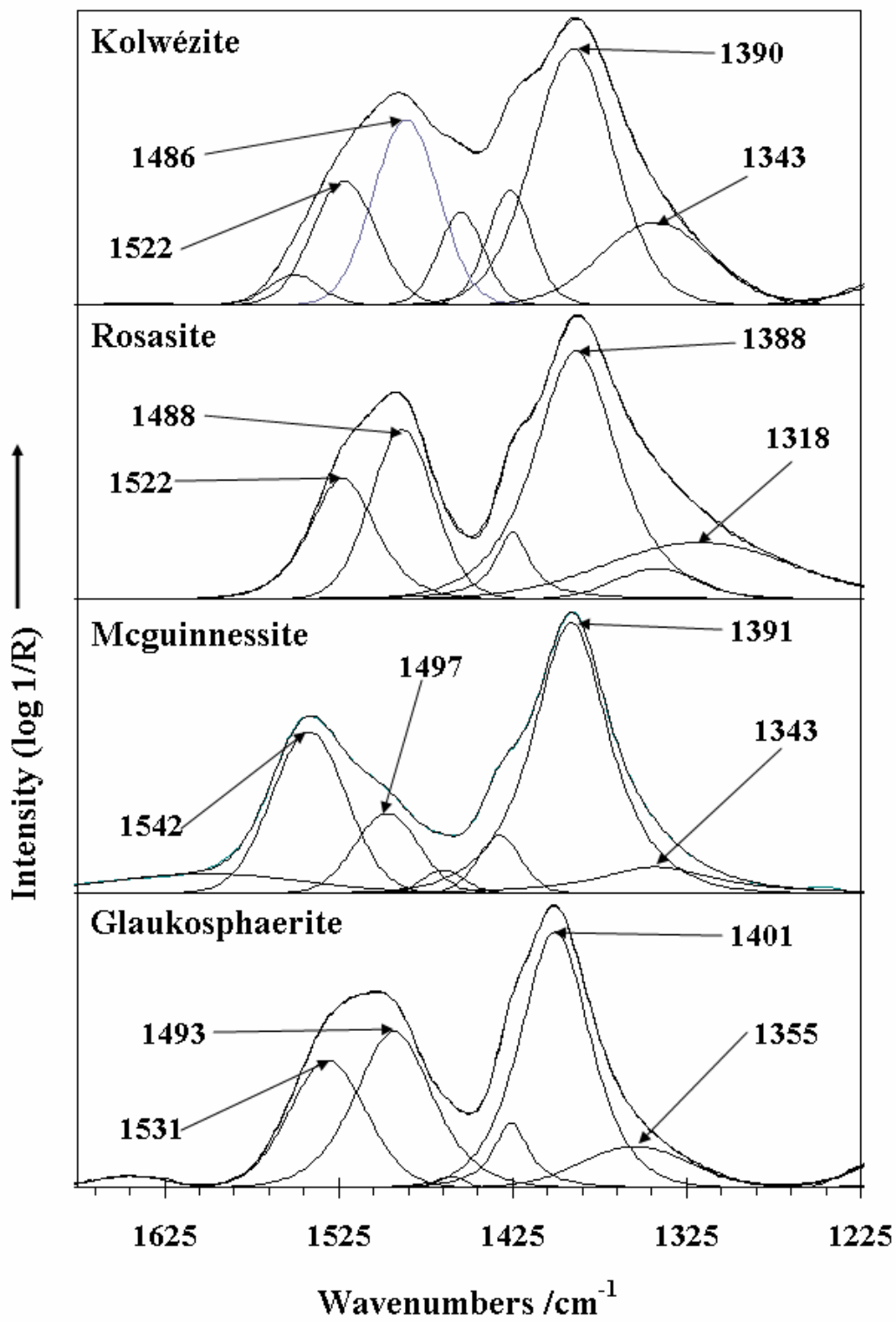


Figure 6

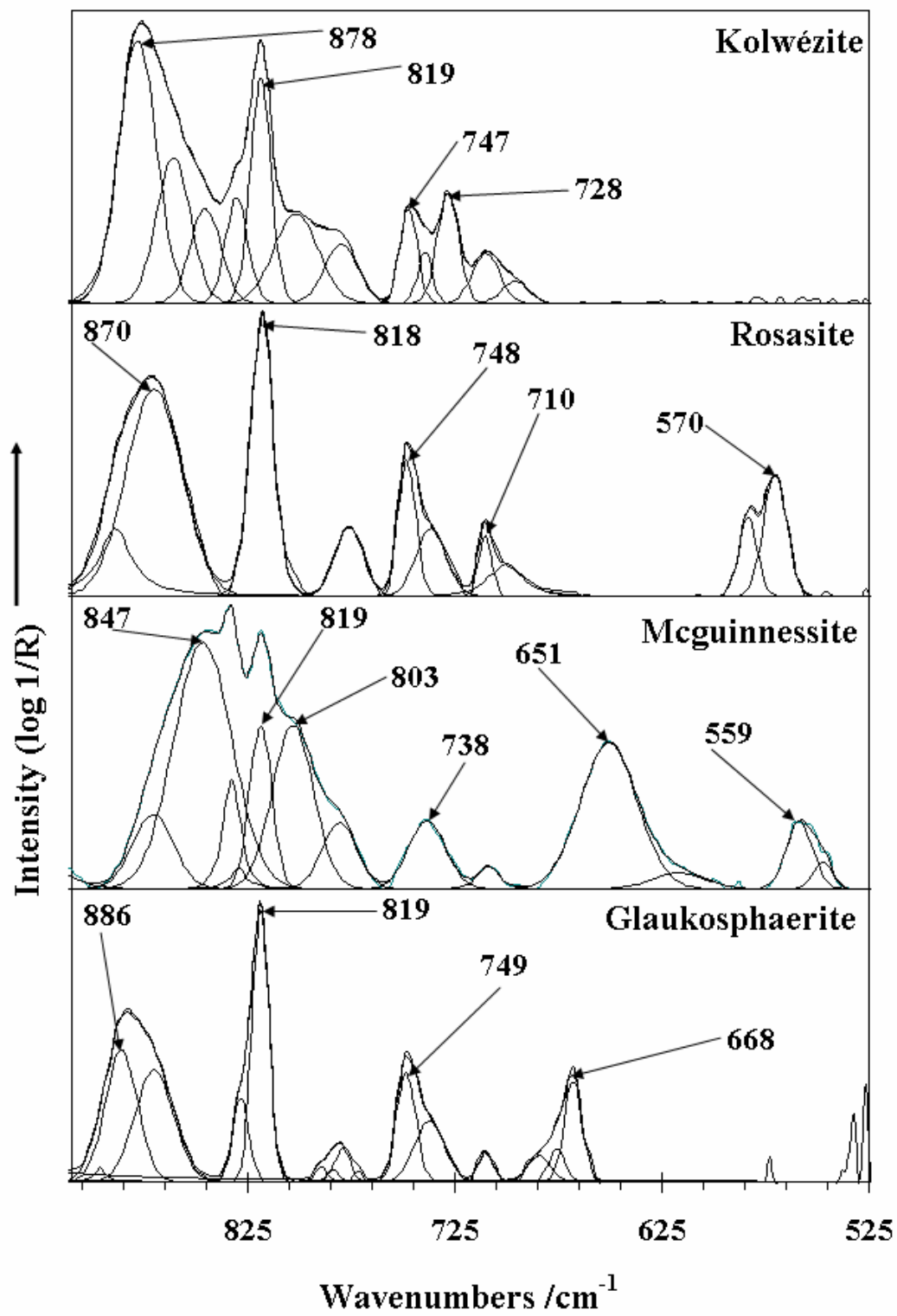


Figure 7