

Raman microscopy of selected chromate minerals

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Abstract:

A series of related chromate bearing minerals including crocoite, phoenicocroite, hemihedrite, iranite, macquartite, fornacite and vauquelinite have been analysed by Raman microscopy. These minerals are closely related and often have related paragenesis. Raman microscopy enables the selection of individual crystals of these minerals for Raman spectroscopic analysis. This is of importance as often the crystals are found adjacent to each other in the same matrix through paragenetic relationships. The Raman spectrum of crocoite shows three bands in the CrO_4 stretching region at 856, 841 and 825 cm^{-1} , phoenicocroite at 856, 848, 839 and 826 cm^{-1} , hemihedrite at 847, 837 and 824 cm^{-1} , iranite bands at 865, 846 and 818 cm^{-1} , macquartite at 857, 840 and 814 cm^{-1} . The Raman spectra of fornacite and vauquelinite are complicated by the presence of AsO_4 and PO_4 units in the structure and often the spectra are broad and vary with chemical composition. A comparison of the spectra of these minerals is made with that of the hexavalent chromate mineral edoylerite. Raman microscopy is a powerful and underutilized technique in terms of mineralogy for the study of closely related minerals such as these chromate minerals.

KEY WORDS: crocoite, phoenicocroite, fornacite, vauquelinite, iranite, macquartite, edoylerite, arsenate, phosphate, Raman spectroscopy

INTRODUCTION

A comparatively small number of minerals containing anions such as chromate, tungstate and molybdate are known. Many more minerals containing vanadates are known but many are rare. The discovery of chromates has a long and involved history.¹ Indeed S.A. Williams provides an excellent history of the chromate minerals together with their fundamental science.¹ Much interest in these minerals is shown by mineral collectors because of their inherent beauty. Included in these minerals are crocoite (PbCrO_4) and wulfenite (PbMoO_4). These types of minerals form through precipitation from solution in secondary mineral formation. The anion chromate may also be incorporated into other minerals such as phoenicocroite (Pb_2CrO_4)², embreyite ($\text{Pb}_5(\text{CrO}_4)_2(\text{PO}_4)\cdot\text{H}_2\text{O}$)³, vauquelinite

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($\text{Pb}_2\text{Cu}(\text{PO}_4)(\text{CrO}_4)(\text{OH})$)^{4,5}, fornacite ($\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{CrO}_4)(\text{OH})$)^{6,7}, hemihedrite ($\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2\text{F}_2$), iranite ($\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{F},\text{OH})_2$)⁸, and macquartite ($\text{Pb}_3\text{Cu}(\text{CrO}_4)(\text{SiO})_3(\text{OH})_4 \cdot 2\text{H}_2\text{O}$). Other minerals that could be included in this list of secondary minerals are molybdofofnacite ($\text{Pb}_2\text{Cu}[(\text{As},\text{P})\text{O}_4][\text{Mo},\text{Cr}\text{O}_4](\text{OH})$)⁹ and cassedannèite ($\text{Pb}_5(\text{VO}_4)_2(\text{CrO}_4)2 \cdot \text{H}_2\text{O}$).

It is probable that there is an intimate relationship between these chromate minerals. This mineral formation is a function of the anions present, the pH and the redox conditions. It is likely that the first mineral formed is phoenicocroite followed by crocoite as a result of the oxidation of galena. These minerals can be formed under a broad range of conditions. If copper or zinc is present crocoite may be eventually replaced by iranite, hemihedrite or vauquelinite. If phosphate anion is present the mineral formation after crocoite is embreyite followed by vauquelinite. Vauquelinite and fornacite are late-formed oxide-zone minerals and are often perched on or replace the re-formed crocoite. The paragenesis of iranite and hemihedrite is their formation in conditions at low Eh and pH above 7. It must also be recognised that these minerals are mobile and may be transported to locations other than where the minerals are formed. The minerals cocroite and phoenicocroite are monoclinic and have the scheelite structure. The Pb(II) cations in these structures are eight coordinate with the coordination sphere being trisdisphenoid of chromate oxygen atoms. Hemihedrite forms a series with iranite and has an acentric triclinic structure. Vauquelinite, fornacite and molybdofofnacite are isostructural members of the brackebuschite group.

Apart from crocoite, no vibrational spectroscopic information is available on these chromate minerals. The Raman spectra of chromate anion in solution gives the ν_1 symmetric stretching mode at 847 cm^{-1} ; the ν_3 mode at 884 cm^{-1} ; the ν_2 mode at 348 cm^{-1} and the ν_4 mode at 368 cm^{-1} . Farmer reports the infrared spectrum of barium chromate with ν_1 at 860 cm^{-1} , ν_3 at $949, 894, 873\text{ cm}^{-1}$ and ν_4 at $419, 389$ and 375 cm^{-1} .¹⁰ The ν_2 band was not given. The Raman spectrum of crocoite has been reported by Wilkins.¹¹ For crocoite all the allowed vibrations ($1\text{A}_1 + 1\text{E} + 2\text{T}_2$) are Raman active, but only the T_2 symmetry species are ir active. All degeneracies are removed in crocoite and the resulting 9A vibrational modes are all Raman and ir active. Cr-O distances in crocoite are unusually small (av. 1.65 \AA .) indicating a substantial amount of multiple-bonding character in the chromate ion. This leads to strong Raman interactions. The Raman frequencies observed are $838, 853, 825, 400, 377, 359, 336, 326\text{ cm}^{-1}$; lattice modes are $184, 135, \text{ and } 36\text{ cm}^{-1}$.¹¹ To the best of the knowledge of the authors, no vibrational spectroscopy of the minerals other than crocoite have been reported. In this paper we report the Raman spectra of a series of paragenetically related chromate minerals and relate the spectra to the structure of the minerals.

EXPERIMENTAL

Minerals:

The following minerals were obtained from the South Australian Museum and Museum Victoria and have been characterized. The minerals were checked for phase composition using X-ray diffraction and for chemical composition using the electron probe.

Crocoite originated from Dundas, Tasmania, Australia.
Phoenicocroite – sample G21953 originated from the Rat Tail Claim, Potters Cramer, Arizona, USA
Phoenicocroite – sample M4703 originated from Beresovsk, Siberia, Russia.
Hemihedrite –sample G13893 originated from the Rat Tail Claim, Potters Cramer, Arizona, USA
Hemihedrite –sample M37144 and sample 33405 originated from Wickenburg, Maricopa Co., Arizona, USA
Fornacite –sample G10953 originated from Renevilkle, Zaire.
Fornacite –sample M37124 originated from Whim Creek Copper Mine, Pilbara, Western Australia.
Vauquelinite –sample G15573 and sample M48032 originated from Kintore Open Cut, Broken Hill, NSW.
Iranite was supplied by the Mineral Research Co.
Macquartite was supplied by the Mineral Research Co.

The selection of minerals from these related phases for Raman spectroscopic analysis must be undertaken with care. Often the crystals are found together through paragenetic relationships. This means different crystals are found adjacent to or mixed with related minerals.

Raman microscopy

The crystals of the chromate minerals were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a thermo-electrically cooled Charge Coupled Device (CCD) detector. Raman spectra were excited by a Spectra-Physics model 127 Nd-Yag laser (785 nm) and acquired at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . The crystals were oriented to provide maximum intensity. All crystal orientations were used to obtain the spectra. Power at the sample was measured as 1 mW. The incident radiation was scrambled to avoid polarisation effects. Further details have been published.¹²⁻¹⁶

Spectralcalc software package GRAMS. 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 Gauss-Lorentz 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 regression coefficient of R^2 greater than 0.995.

RESULTS AND DISCUSSION

The Raman spectra of the chromate bearing minerals in the CrO stretching region are shown in Figure 1. The results of the band component analyses are reported in Table 1. The Raman spectrum of crocoite shows three bands in the CrO

stretching region at 856, 841 and 825 cm^{-1} . The band at 841 cm^{-1} is the most intense and is assigned to the ν_1 symmetric stretching vibration. These values are in agreement with those enunciated by Wilkins where bands at 853, 838 and 825 cm^{-1} were reported.¹¹ The bandwidth of the 841 cm^{-1} band is 5.0 cm^{-1} ; whereas the bandwidth of the 856 cm^{-1} band is 10.4 cm^{-1} . The band at 825 cm^{-1} is a very low intensity band. Phoenicochroite is monoclinic: space group C2/m with $Z=4$.² Thus the factor group analysis of phoenicochroite is identical to that of crocoite.¹ The Raman spectrum of phoenicochroite from Beresovsk, Russia shows four bands in the CrO stretching region with bands observed at 856, 848, 839 and 826 cm^{-1} . Only three bands were observed in the Raman spectrum of phoenicochroite from Rat Tail Claim, Potter Cramer, Arizona at 847, 836 and 824 cm^{-1} . The widths of these bands are 11.6, 5.6 and 8.7 cm^{-1} .

It is probable that hemihedrite is isomorphous with iranite and displays triclinic hemihedral symmetry.¹⁷ The Raman spectrum of the two minerals is however sufficiently different to suggest that the minerals are not phase related. The minerals have the related formula hemihedrite $(\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2\text{F}_2)$ and iranite $(\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{F},\text{OH})_2)$.⁸ The only difference appears that hydroxyl units may isomorphically substitute for F in the structure of iranite. The minerals have been synthesised.⁴ The Raman spectrum of hemihedrite shows three bands in the CrO stretching region at 847, 837 and 824 cm^{-1} . The bands of hemihedrite are very sharp with bandwidths of 6.5, 5.5, and 5.8 cm^{-1} . In contrast iranite shows a complex set of overlapping bands. For iranite bands are observed at 865, 846 and 818 cm^{-1} . Additional bands are observed at 916, 891 and 790 cm^{-1} . Further the band widths are considerable broader than for hemihedrite. The bandwidths of the 865, 846 and 818 cm^{-1} bands are 18.0, 12.0 and 23.2 cm^{-1} .

The Raman spectrum of macquartite shows two low intensity bands at 968 and 936 cm^{-1} . It is not known how these bands may be assigned. One possibility is that they are the ν_1 symmetric stretching vibrations of SO_4 and PO_4 ions. The authors are not aware of isomorphous substitution in chromate minerals; however such a phenomenon is highly likely. The other possibility is that these bands are due to SiO stretching vibrations as the mineral macquartite $(\text{Pb}_3\text{Cu}(\text{CrO}_4)(\text{SiO})_3(\text{OH})_4.2\text{H}_2\text{O})$ contains SiO units. The mineral is also monoclinic with space group C2/m. The Raman spectrum of macquartite shows three bands at 857, 840 and 814 cm^{-1} . The most intense band is the band at 814 cm^{-1} ; however the band at 840 cm^{-1} is assigned to the ν_1 symmetric stretching mode.

The two minerals fornacite and vauquelinite appear to form from solid solutions. The minerals have the formula fornacite $(\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{CrO}_4)(\text{OH}))^{6,7}$ and vauquelinite $(\text{Pb}_2\text{Cu}(\text{PO}_4)(\text{CrO}_4)(\text{OH}))^{4,5}$. However subtle differences exist in the crystal structure.^{5,7} Some differences occur in coordination around the Pb ions and in the arrangement of symmetry elements in the two minerals.⁷ Considerable variation is observed in the spectra of both fornacite and vauquelinite. This no doubt results from the formation of a continuous series of solid solutions, the composition of which may vary in the one mineral deposit and even in the one mineral example. Further the spectrum of fornacite appears to be superimposed on the spectra of cerussite and other oxidation products of galena. The Raman spectrum of fornacite from the Whim Creek Copper mine, Pilbara, Western Australia, shows a complex set of overlapping bands in the Raman spectrum (Figure 1). Low intensity bands are

observed at 916, 890 and 872 cm^{-1} . The first band may be assigned to the ν_1 symmetric stretching mode of PO_4 anions and the last two bands to the ν_3 antisymmetric stretching modes of AsO_4 units. The most intense band is observed at 847 cm^{-1} and this band is assigned to the ν_1 CrO_4 symmetric stretching mode. A second intense band is observed at 830 cm^{-1} and is ascribed to the ν_1 symmetric stretching mode of AsO_4 units. This spectrum, although complex, clearly shows the substitution of chromate by arsenate and phosphate. What the spectrum also shows is that the substitution is minor. Figure 2 shows a second set of spectra of fornacite and vauquelinite. This set of spectra shows more clarity. The CrO_4 symmetric stretching vibration is clearly exemplified by the intense band observed at around 830 cm^{-1} . The PO_4 stretching vibration by a band at around 930 cm^{-1} . In the spectrum of fornacite a distinct band can be observed at 880 cm^{-1} which corresponds to the ν_3 antisymmetric stretching mode. The question arises as to where is the ν_1 symmetric stretching mode of AsO_4 . This band must be combined with the profile of the ν_1 of CrO_4 . Figure 1 shows the Raman spectrum of edoylerite ($(\text{Hg}^{2+})_3\text{Cr}^{6+}\text{O}_4\text{S}_2$). This mineral shows a single intense band at 840 cm^{-1} which is assigned to the ν_1 symmetric stretching mode of the Cr^{6+}O_4 units. It is apparent that the presence of AsO_4 units shifts the profile from around 840 to 830 cm^{-1} .

The Raman spectra of the low wavenumber region of the selected chromium minerals are shown in Figure 3. The Raman spectrum of crocoite shows a series of bands at 402, 379, 360, 339 and 327 cm^{-1} . The position of these bands is in excellent agreement with that reported by Wilkins.¹¹ Farmer reported the infrared spectrum of chromates with ν_4 modes observed for barium chromate at 419, 389 and 375 cm^{-1} . One probable assignment is that the first three bands at 402, 379 and 360 cm^{-1} are attributable to the ν_4 modes and that the two bands at 339 and 327 cm^{-1} to the ν_2 modes. It is interesting to compare the spectrum of crocoite with that of phoenicochroite in this region, since the two minerals have the same symmetry. The Raman spectrum of phoenicochroite shows five bands at 398, 377, 356, 339 and 322 cm^{-1} . The bands are well separated and show greater intensity than for crocoite. The first three bands are assigned to the ν_4 bending modes and the last two bands to the ν_2 symmetric bending modes. The Raman spectrum of hemihedrite shows four bands at 376, 351, 337 and 319 cm^{-1} . The assignment of the bands is as for phoenicochroite.

The Raman spectrum of iranite shows a complex set of overlapping bands. Bands are observed at 404, 380, 369, 333 cm^{-1} . These bands correspond to the bending modes of the CrO_4 units. The first three bands correspond to the ν_4 bending modes of the CrO_4 units and the band at 333 cm^{-1} to ν_2 bending modes of the CrO_4 units. Additional bands are observed at 389, 354 and 333 cm^{-1} . These bands may correspond to SiO bending modes. The Raman spectrum of macquartite displays two low intensity bands at 463 and 439 cm^{-1} . These bands are attributed to the bending modes of the (SiO_3) units in macquartite. A broad band is centred upon 374 cm^{-1} and is assigned to the ν_4 bending modes of the CrO_4 units. Two bands are observed at 349 and 340 cm^{-1} and are attributed to the ν_2 bending modes of the CrO_4 units. The Raman spectrum of fornacite displays a strong resemblance to that of iranite, even though the spectrum in the CrO_4 stretching region was different. The Raman spectrum shows complexity in this region. Bands are observed at 400, 388, 381, 369, 354, 343, 332 and 305 cm^{-1} . The mineral fornacite does contain AsO_4 units and it is likely some of these bands may be assigned to the bending modes of AsO_4 units.

A similar situation exists for the Raman spectrum of vauquelinite in this region. The Raman spectrum of vauquelinite is similar to that of macquartite. In some ways this is not unexpected as both minerals contain CrO_4 units. Bands are observed at 375, 348 and 332 cm^{-1} . The first band is broad and is attributed to the ν_4 bending modes whilst the two bands at 348 and 332 cm^{-1} are assigned to the ν_2 bending modes. The Raman spectrum of vauquelinite does show a broad profile over the 430 to 570 cm^{-1} region with two peaks at 538 and 520 cm^{-1} . These bands are assigned to the ν_4 modes of PO_4 units. The Raman spectrum of edoylerite shows three bands at 382, 368 and 363 cm^{-1} . These bands are assigned to the ν_4 modes of CrO_6 units. Two additional bands are observed at 340 and 325 cm^{-1} and are attributed to the ν_2 bending modes of CrO_6 units. A very intense band is observed in the Raman spectrum of edoylerite at 269 cm^{-1} .

CONCLUSIONS

The study of the chromate minerals is of importance in mineralogy. A close paragenetic relationship exists between the minerals. The minerals result from secondary mineral formation following the oxidation of galena and the formation of cerussite. In the presence of chromate ions phoenicochroite forms and the formation of crocoite follows in the paragenetic relationship. In all probability cerussite also forms in the oxidation process. The implication in terms of Raman spectroscopy is that is highly likely that the same mineral matrix will contain cerussite, possibly anglesite, phoenicochroite and crocoite. If copper and zinc are present then the crocoite may be further replaced by iranite, hemihedrite and vauquelinite. The formation of these latter three minerals will depend on the conditions of the secondary mineral formation such as pH, anion speciation, anion and cation concentration, and temperature.

Chromate minerals lend themselves to Raman microscopic analysis and often the paragenetically related minerals are found in the same matrix. This means that analysis by other methods such as X-ray diffraction would produce an analysis of a mixture of the minerals. Scanning electron microscopy allows for the identification of individual minerals and the use of an electron probe enables the chemical composition of the mineral to be obtained. Such latter techniques are time consuming. Raman microscopy has the advantage of rapid identification of the chromate minerals in the same mineral matrix.

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Table 1 Results of the Raman spectroscopic analysis of selected chromate minerals (band positions in wavenumbers/cm⁻¹).

crocoite	phoenocochroite	hemihedrite	iranite	macquartite	fornacite	vauquelinite	molybdoformacite	Suggested assignments
		1055	916 891	968 936	916 890 872		1089 1048 1014	v ₁ symmetric stretching of SO ₄ and PO ₄ And v ₃ symmetric stretching of CrO ₄
856 841 825	856 848 839 826	847 837 824	865 846 818	857 840 814	867 847 830	843 827	855	v ₁ symmetric stretching of CrO ₄
		693 680 672 667	790 535	463 439	790 778		713 666 558	
402 379 360 339 327	398 377 356 339 322	376 351 337 319	404 389 380 369 354 343 333	374 349 340	400 388 381 369 354 343 332 305	375 348 332	387 355 320	v ₄ and v ₂ bending modes
	215 176	212	307 240 222	194			278 226 196	Lattice modes

			196 163 139					
184 135	143	171 142		152	159 139 122		159 152	

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Figure 1 Raman spectra of the CrO stretching region of cocroite, phoenicochroite, hemihedrite, iranite, fornacite, vauquelinite and edoylerite

Figure 2 Raman spectra of fornacite and vauquelinite

Figure 3 Raman spectra of the CrO low wavenumber region of cocroite, phoenicochroite, hemihedrite, iranite, fornacite, vauquelinite and edoylerite

LIST OF TABLES

Table 1 Results of the Raman spectroscopic analysis of selected chromate minerals (band positions in wavenumbers/cm⁻¹).

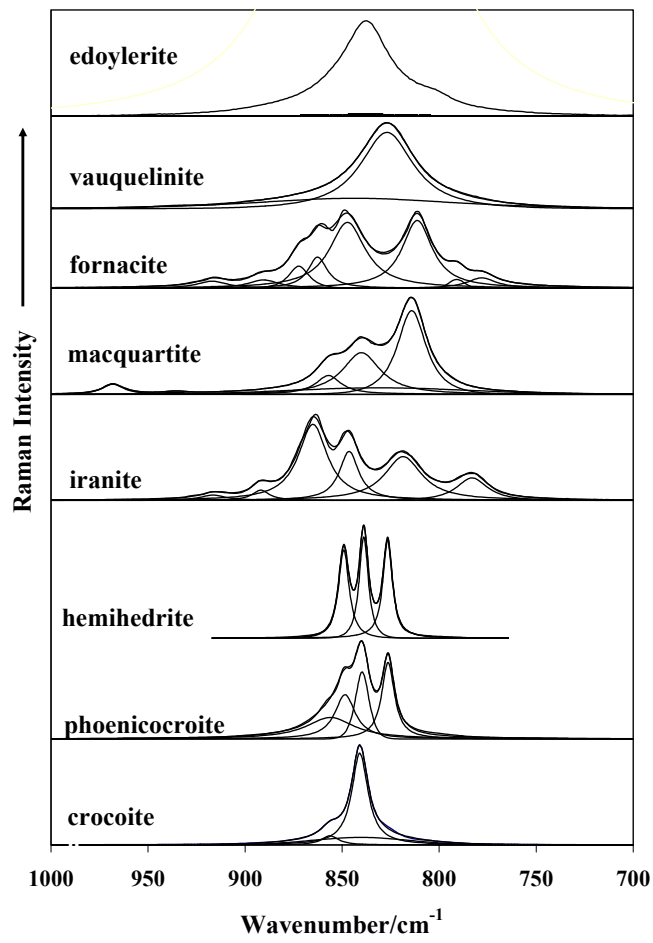


Figure 1

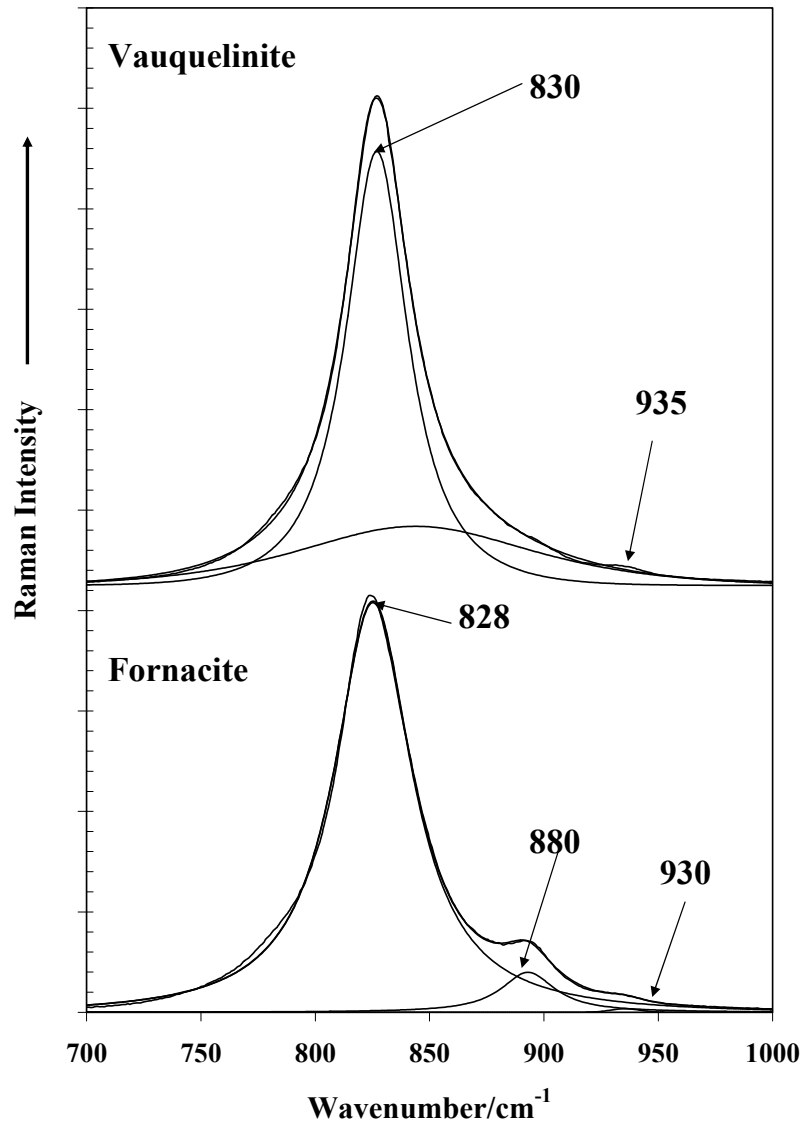


Figure 2

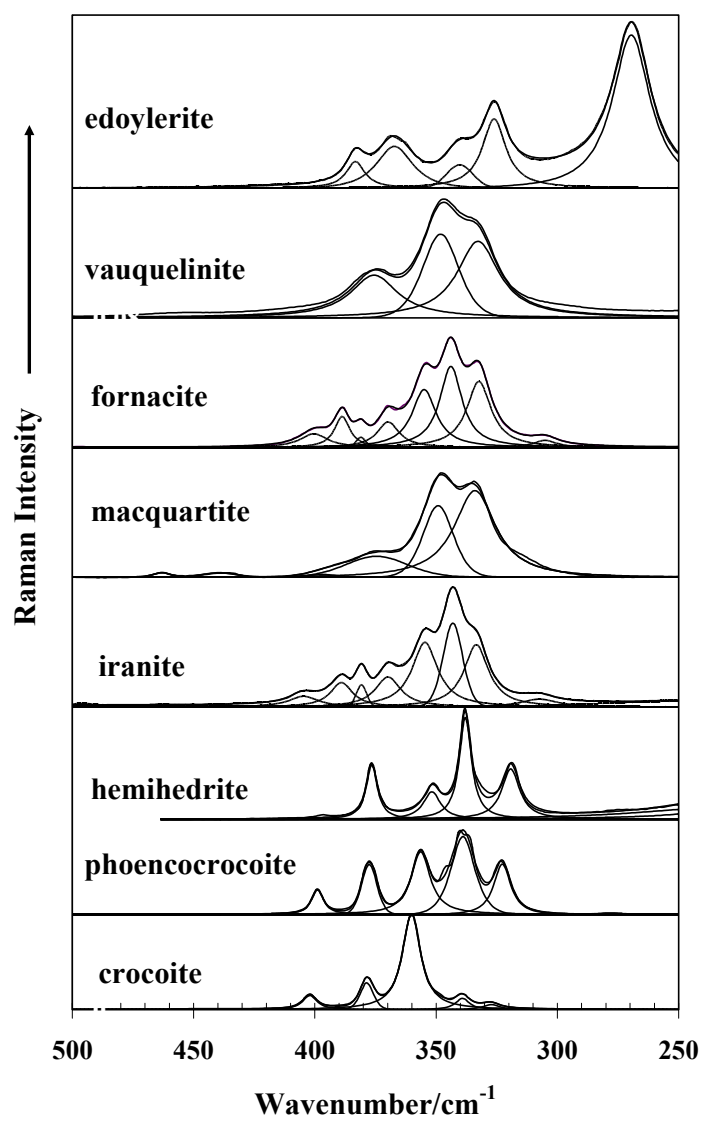


Figure 3

