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Metavivianite an intermediate mineral phase between vivianite, and ferro/ferristrunzite – a Raman spectroscopic study

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Abstract

A comparison between the minerals vivianite, metavivianite, and ferro/ferristrunzite is made using Raman spectroscopy. The Raman spectrum of metavivianite is broad and more closely resembles the spectrum of ferro/ferristrunzite than vivianite. This is not unexpected since both minerals are triclinic. Metavivianite is characterised by a broad profile in the hydroxyl stretching region with bands observed at 3368 and 3133 cm^{-1} . The width of the bands indicates the structure of metavivianite is disordered. In the PO stretching region bands are observed at 1123, 1060, 1005 and 958 cm^{-1} and are assigned to the symmetric stretching modes. Vivianites with partial oxidation are characterised by a sharp OH stretching band observed around 3480 cm^{-1} in the Raman spectrum. It is proposed that metavivianite is a transitional oxidation phase between the vivianite and the ferro/ferristrunzite end members.

Key Words- ferric, ferristrunzite, phosphate, vivianite, metavivianite, Raman spectroscopy

1. Introduction

The vivianite group of minerals are of wide interest because of their widespread occurrence in nature. The minerals are of the general formula $A^{3+}(XO_4)_2 \cdot 8H_2O$ where A^{2+} may be Co, Fe, Mg, Ni, Zn and X is As or P. Vivianite and baricite are, respectively, the Fe- and Mg-dominant phosphates in the group. Extensive solid solution formation occurs between baricite and vivianite. Isomorphous substitution in this group occurs readily, and intermediate compositions are often observed. Further, the minerals are susceptible to auto-oxidation and air oxidation. The minerals are also light sensitive. This light sensitivity may assist in the self-catalytic oxidation. The minerals occur in the corrosion coatings of water pipes, in soils from peat bogs, morasses, and in sediments (HENDERSON et al. 1984). These minerals have been found in sediments in New Zealand (ANTHONY et al. 2000). The vivianite minerals are all monoclinic with point group 2/m (ANTHONY et al. 2000). Vivianite can oxidise either through self-catalytic oxidation or through air oxidation. Such oxidation is apparently photo-catalytically induced. Hence

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$(\text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (vivianite) oxidises to $(\text{Fe}^{2+})_{3-x}(\text{Fe}^{3+})_x(\text{PO}_4)_2(\text{OH})_x \cdot (8-x)\text{H}_2\text{O}$ (metavivianite). It should be noted that the two minerals vivianite and metavivianite are not phase related nor is there a compositional relationship. Metavivianite is triclinic iron(II,III) phosphate hydroxide hydrate and was first described by Ritz et al. (RITZ et al. 1974). Apparently the monoclinic symmetry is preserved up to $x=1.2$. If the value of x exceeds 1.4 then metavivianite is formed. Kerchenite is also an oxidised vivianite mineral (CHUKHROV & ERMILOVA 1956; CHUKHROV & RUDNITSKAYA 1966; EFREMOV 1953). It is probable that kerchenite and metavivianite are one and the same mineral (RODGERS 1986); however, the original description of kerchenite is not sufficiently detailed to be certain.

There are two minerals based on strunzite, namely ferrostrunzite and ferristrunzite that are isostructural with strunzite. The formulae of these minerals are $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (strunzite), $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot (5\text{H}_2\text{O} \cdot \text{OH})$ (ferrostrunzite), and $\text{Fe}^{3+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot (5\text{H}_2\text{O} \cdot \text{OH})$ (ferristrunzite) (VOCHTEN & DE GRAVE 1990; VOCHTEN et al. 1995). Strunzite, $\text{MnFe}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, is triclinic, space group $P1$. The strunzite mineral exhibits a well-marked monoclinic pseudocell with the pseudosymmetry of $C2/c$ space group. The atomic arrangement consists of chains built up by Fe coordination octahedra sharing vertices; PO_4 tetrahedra link together adjacent octahedra. Parallel chains are connected by PO_4 groups to form thick slabs. Parallel slabs are connected by Mn coordination octahedra, to form the three-dimensional framework (FANFANI et al. 1978). Likewise ferrostrunzite is triclinic with prismatic flattened crystals. Ferristrunzite is also triclinic but the crystals are acicular, rounded and elongated.

Some infrared data exist for the vivianite-group phosphate minerals (FARMER 1974); however, most infrared data predates the advent of Fourier transform infrared spectroscopy (GEVORK'YAN & POVARENENYKH 1973; GEVORK'YAN & POVARENENYKH 1980; HUNT 1977; HUNT et al. 1972; OMORI & SEKI 1960; SITZIA 1966). Some Raman studies of the vivianite phosphate minerals have been undertaken (MELENDRES et al. 1989; PIRIOU & POULLEN 1984), and recently Frost et al. reported a Raman spectroscopic comparison of the minerals vivianite, bobierite and baricite (FROST et al. 2002; JOHNSON et al. 2002). However, no Raman spectroscopic investigation of the vivianite-metavivianite related phosphate minerals has been forthcoming, and certainly no detailed comparison of vivianite and metavivianite has been undertaken using vibrational spectroscopy. Possible autoxidation of the minerals is a major difficulty in studying these minerals, and this process is probably photocatalytically enhanced. The use of X-ray diffraction may cause changes in the structure during measurement, and indeed, even the use of the longer excitation wavelengths in Raman spectroscopy may also change the oxidation state of the iron(II) in the vivianite. Simple grinding of the mineral in air will change the chemical composition of the mineral. Since there is currently a lack of comprehensive spectral knowledge of the vivianite phosphate minerals, particularly of the difficult-to-study vivianite-metavivianite-kerchenite-ferro/ferristrunzite series, the determination of molecular structure of vivianite-metavivianite minerals using Raman spectroscopy has been undertaken as part of a wider comprehensive study of the vibrational spectroscopy of secondary minerals.

2. EXPERIMENTAL

2.1 Analysis of samples

Vivianite and metavivianite were obtained from the Mineralogical Research Company (San Jose, California, USA). The vivianite originated from Monserrat Mine, Poopo, Bolivia. This particular specimen was selected because almost no oxidation was observed based on its colour. The colour was a light blue. The metavivianite (labelled oxykerchenite) originated near the City of Kerch, Crimean Peninsula, Ukraine. Specimens of strunzite (M36370; Hagendorf, Bavaria, Germany) and ferristrunzite (M42815; Blaton, Hainaut Province, Belgium) were obtained from the collections of Museum Victoria, Australia and were confirmed using powder X-ray diffraction methods. Both were from their respective mineral type localities. The sample of ferrostrunzite from Arnberg, Sauerland, Germany was obtained from Professor R. Vochten. SEM-EDS analyses indicated no As or transition metals, other than Mn and Fe, to be present. The minerals were checked by X-ray diffraction and Mössbauer spectroscopy.

2.2 Raman microprobe spectroscopy

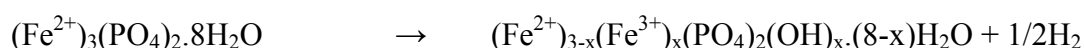
Crystals of the minerals were orientated on a polished metal surface on the stage of an Olympus BHSM microscope equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm⁻¹ between 100 and 4000 cm⁻¹. Repeated acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio in the spectra, which were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

Infrared spectra were collected using a Nicolet infrared microscope using an ATR technique with silica plates. 64 scans were collected with a resolution of 4 cm⁻¹. Spectroscopic manipulations such as baseline adjustment, smoothing and normalization were performed using the 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 specific parameters to be fixed or varied accordingly. Band fitting was carried out 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 correlations of r² greater than 0.995.

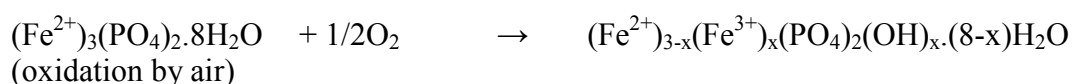
3. Results and Discussion

3.1 Chemical oxidation

The following chemical reactions are envisaged as the oxidation of vivianite as iron(II) phosphate.



(self oxidation)



Further oxidation may result in the formation of the ferro or ferristrunzite minerals.



The oxidation of the primary iron(II) phosphate, vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ yields a cascade of products spanning the redox conditions applying to vivianite and the redox conditions applying to the fully oxidized state. Initially, the oxidation of vivianite leads to $(\text{Fe}^{2+})_{3-x}(\text{Fe}^{3+})_x(\text{PO}_4)_2(\text{OH})_x \cdot (8-x)\text{H}_2\text{O}$, in which the monoclinic crystal structure is preserved up to $x = 1.2$, and overall charge balance is conserved by converting some of the water of crystallization to hydroxyl anions. Oxidation past $x = 1.4$ apparently can lead first to a triclinic structure with the same charge-compensated formula, $(\text{Fe}^{2+})_{3-x}(\text{Fe}^{3+})_x(\text{PO}_4)_2(\text{OH})_x \cdot (8-x)\text{H}_2\text{O}$ as vivianite. At present, only this triclinic phase, according to Rodgers 1986, is correctly denoted as metavivianite (RODGERS 1986), which is now known to be a misnomer since vivianite and metavivianite are not dimorphous, but differ compositionally (i.e., there is no phase transition connecting these forms).

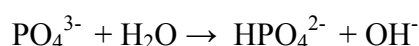
3.2 Hydroxyl stretching and deformation vibrations.

The vibrational spectra of the strunzite-related minerals based upon the formulae: $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}^{3+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot [5\text{H}_2\text{O} \cdot \text{OH}]$, may be conveniently broken up into spectroscopic regions: (a) the hydroxyl stretching region of the hydroxyl units and of the coordinated water (b) the phosphate PO stretching region (c) the phosphate OPO bending region (d) the low wavenumber region including the metal oxygen stretching vibrations. Factor group analysis predicts four bands in the hydroxyl-stretching region of the ferri-strunzite minerals of which two are infrared active and two are Raman active.

The Raman spectrum of the hydroxyl-stretching region of vivianite, metavivianite, ferristrunzite and ferrostrunzite are shown in Figure 1. The Raman spectrum of the metavivianite suffers from a lack of signal to noise; nevertheless bands can be identified at 3368 and 3133 cm^{-1} . Even though the spectrum is noisy, the observation of the spectrum has implications for the structure of the metavivianite. Such Raman spectra are indicative of disordered structures where little to no long range order is observed. Such observations have been made with other minerals including kaolinites and hydrotalcites. The Raman spectrum of vivianite shows two intense bands at 3279 and 3130 cm^{-1} with a low intensity band at 3012 cm^{-1} . A low intensity band is also observed at 3509 cm^{-1} . For ferristrunzite these two bands are observed at 3465 and 3367 cm^{-1} . A Ferrostrunzite Raman spectrum shows two bands at 3492 and 3405 cm^{-1} . It is suggested that the hydroxyl unit is hydrogen bonded to the adjacent phosphate unit and by cooling to liquid nitrogen temperature, this bond is strengthened. The Raman band at 3483 cm^{-1} is apparently Raman active/infrared inactive. This suggests that this vibration results from a centre of symmetry. Such a result exists if the hydroxyl unit points towards a second oxygen in an O-H—O

arrangement. In agreement with the factor group analysis two Raman and two infrared modes for ferri and ferrostrunzite are observed.

In the hydroxyl-stretching region in both the infrared and Raman spectrum of vivianite and the ferri/ferro strunzites, a sharp band is observed at around 3490 cm^{-1} . The intensity of the band is higher in the infrared spectrum. One possible explanation of this band is that it is due to hydroxyl groups associated with the presence of Fe^{3+} . If some oxidation of the ferrous ion to ferric occurs then this charge would need to be counterbalanced by the negative of the hydroxyl unit as no other negative charges could originate from the phosphate anion. (WILDNER et al. 1996) This then could mean that a free proton is available to form HPO_4 units. The following reaction is envisaged.



Any phenomena such as the migration of a proton to a phosphate anion can be measured using vibrational spectroscopy. Likewise the bonding of a hydroxyl unit to the metal could be observed. The band observed at 3504 , 3468 and 3487 cm^{-1} for vivianite, ferristrunzite and ferro strunzite may be attributed to the OH stretching unit coordinated to the iron(III) cation. Some early publications based upon infrared data suggested that infrared bands at around 3450 cm^{-1} were attributable to definite OH stretching bands in natural vivianite lending partial support to the charge-compensated formula, $(\text{Fe}^{2+})_{3-x}(\text{Fe}^{3+})_x(\text{PO}_4)_2(\text{OH})_x \cdot (8-x)\text{H}_2\text{O}$, for partially oxidized vivianite (TIEN & WAUGH 1969). The more recent work on lipscombite by Vochten and De Grave 1981 seems consistent with a significantly lower value (-3350 cm^{-1}) for OH stretching for this anhydrous mineral (VOCHTEN & DE GRAVE 1981).

3.3 Phosphate vibrations

Raman spectra of aqueous phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} . Such bands will become more complex in a crystal structure involving more than one cation and degeneracy will be lost. Farmer reports the infrared spectrum of triploidite with formula $(\text{Mn,Fe})_2\text{PO}_4\text{OH}$ with the (ν_1) at 957 cm^{-1} , (ν_3) at 1090 , 1058 , 1030 and 1010 cm^{-1} , (ν_2) at 420 cm^{-1} and the ν_4 mode at 595 , 570 , 486 cm^{-1} . An hydroxyl stretching frequency of 3509 cm^{-1} was given. The chemical formula of this mineral is close to that of strunzite and so similar spectra could be expected.

The Raman spectra of the PO_4 stretching region of vivianite, ferristrunzite, ferrostrunzite and metavivianite are shown in Figure 2. The Raman spectrum of the hydroxyl stretching region of metavivianite resembles that of vivianite whereas the Raman spectrum of the PO_4 stretching region of metavivianite more closely resembles that of the ferri/ferro strunzites. The bands are broad, indicating disorder in the structure. Bands are observed at 1123 , 1060 , 1005 and 958 cm^{-1} with bandwidths of 109.9 , 64.7 , 46.9 and 50.9 cm^{-1} . In the Raman spectrum of vivianite a single intense band is observed at 949 cm^{-1} with low intensity bands observed at 1081 , 1050 and 1015 cm^{-1} . The 949 cm^{-1} band is assigned to the Raman active PO stretching vibration. The position of this band is in excellent agreement with the previously

published result. (PIRIOU & POULLEN 1987) The bands at 1081, 1050 and 1015 cm^{-1} are assigned to the phosphate PO antisymmetric stretching vibrations. The 1081 cm^{-1} band is very low in intensity.

For ferristrunzite three Raman bands are observed at 1022, 1008 and 985 cm^{-1} . and for ferrostrunzite three bands are observed at 1010, 987 and 974 cm^{-1} . The observation of more than one symmetric stretching vibration means that the PO stretching vibrations are non-equivalent. Upon obtaining the spectra at 77K, better band separation is found and three bands are observed for strunzite at 1009, 992 and 973 cm^{-1} . For ferristrunzite, three Raman bands are observed at 1026, 1004 and 980 cm^{-1} . Four Raman bands are observed for ferrostrunzite at 1011, 993, 989 and 973 cm^{-1} at 77K. The observation of three Raman bands suggests that the degeneracy of the phosphate symmetric stretching mode is lost. The symmetric stretching modes of phosphate are observed at higher wavenumbers for the ferristrunzite compared with that of strunzite. The position of these infrared bands fits well with the Raman result. Vochten reported a single band at 975 cm^{-1} (VOCHTEN & DE GRAVE 1990). For ferristrunzite an intense infrared band at 983 cm^{-1} with a second band at 963 cm^{-1} was observed. The Raman spectra of the PO stretching region clearly show a difference between the spectra of the ferri and ferro-strunzites.

3.4 Low wavenumber vibrations

The low wavenumber region of the four minerals is shown in Figure 3. The difficulty in the study of this spectral region is a combination of the complexity of the overlap and the number of bands. The difficulty rests with the attribution of the multiple bands found in this region. In aqueous solutions of the phosphate ion, the band observed at 420 cm^{-1} is assigned to the ν_2 bending mode. For metavivianite, the spectral features in the Raman spectrum are not resolved. Broad bands are observed centred upon 443 and 580 cm^{-1} . The lack of resolution and the width of the bands again suggest that the mineral is highly disordered. For vivianite two bands are observed at 423 and 456 cm^{-1} , with the latter being the most intense. The observation of two bands for the OPO bending region suggests the loss of degeneracy of the bending mode. For aqueous systems the ν_4 mode of phosphate is observed at 567 cm^{-1} . For vivianite four bands are observed at 584, 569, 545 and 530 cm^{-1} . The 569 cm^{-1} band is intense and sharp. These bands are assigned to the ν_4 modes of vivianite. The spectral data reported by Griffith is at variance with these results (GRIFFITH 1970). Farmer reported infrared bands at 590, 560 and 475 cm^{-1} (FARMER 1974). In the Raman spectrum, for vivianite two intense bands are observed at 236 and 186 cm^{-1} .

The region between 370 and 570 cm^{-1} is complex for both vivianite and the ferri-ferrostrunzites with a considerable number of overlapping bands. For ferristrunzite bands are observed at 454 and 399 cm^{-1} and are attributed to the OPO symmetric bending modes. The bands are observed at 474, 434 and 408 cm^{-1} for ferristrunzite. In the Raman spectrum of ferristrunzite three bands are observed at 576, 533 and 503 cm^{-1} at 298K and 575, 528 and 505 cm^{-1} at 77K. These results are in good agreement with the infrared bands reported by Vochten at 580 and 511 cm^{-1} . For ferrostrunzite three bands are observed at 568, 531 and 509 cm^{-1} , which shift to 573, 550 and 512 cm^{-1} at 77K. The observation of the multiplicity of bands in the ν_2

and ν_4 regions is significant because it means that the symmetry of the phosphate ion is lost and has been reduced from T_d to probably C_s .

Model for the oxidation of vivianite

A model is proposed in which metavivianite is a transitory oxidation state mineral between vivianite and ferro/ferristrunzite. Raman spectroscopy shows that the spectral features of metavivianite resemble that of both vivianite and ferri/ferrostrunzite. Vivianite is monoclinic and point group $2/m$. Metavivianite is triclinic iron(II) phosphate hydrate and was first described by Ritz et al. (RITZ et al. 1974). It is apparent that the crystal structure of the iron(II) phosphate is dependent upon the degree of oxidation. Apparently the monoclinic symmetry is preserved up to $x = 1.2$. If the value of x exceeds 1.4 then metavivianite is formed. Both ferristrunzite and ferrostrunzite are triclinic just as metavivianite. It is suggested that metavivianite (syn. kerchenite) is intermediate in the oxidation process between vivianite and ferro/ferristrunzite. Even very pure vivianite shows a Raman band near 3480 cm^{-1} , which gives an indication that the mineral has undergone some partial oxidation.

Conclusions

A number of important conclusions may be made. (1) the Raman spectra of metavivianite can be obtained with difficulty; (2) the spectra of vivianite and ferri/ferrostrunzite are different from metavivianite; (3) the spectral features of metavivianite are broad compared with either vivianite and ferri/ferrostrunzite (4) Raman spectroscopy has the advantage that low wavenumber region for these phosphate minerals can be determined. One way of studying the oxidation of vivianite is to consider that vivianite and ferro/ferristrunzite as simply end-members and that metavivianite is an intermediate oxidation phase between these two end members.

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List of Figures

Figure 1 Raman spectra of the OH stretching region of metavivianite, vivianite, ferristrunzite and ferrostrunzite.

Figure 2 Raman spectra of the PO stretching region of metavivianite, vivianite, ferristrunzite and ferrostrunzite.

Figure 3 Raman spectra of the OPO bending region of metavivianite, vivianite, ferristrunzite and ferrostrunzite.

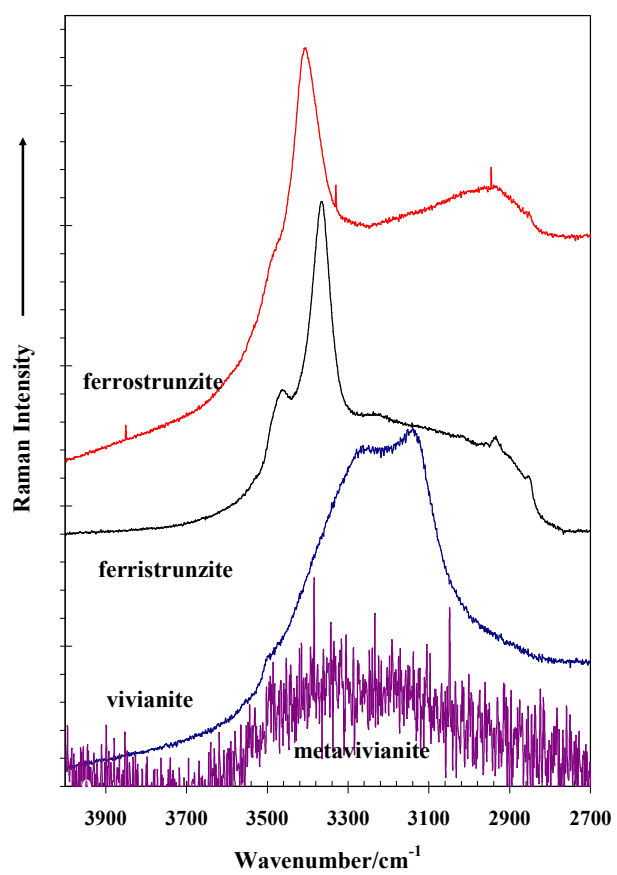


Figure 1

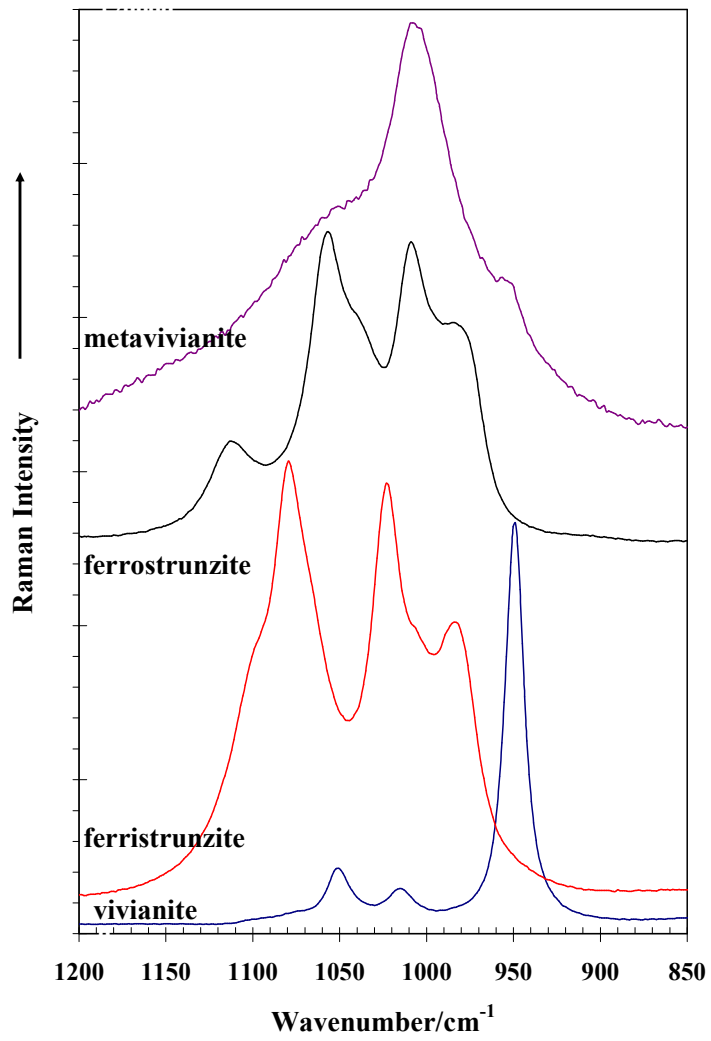


Figure 2

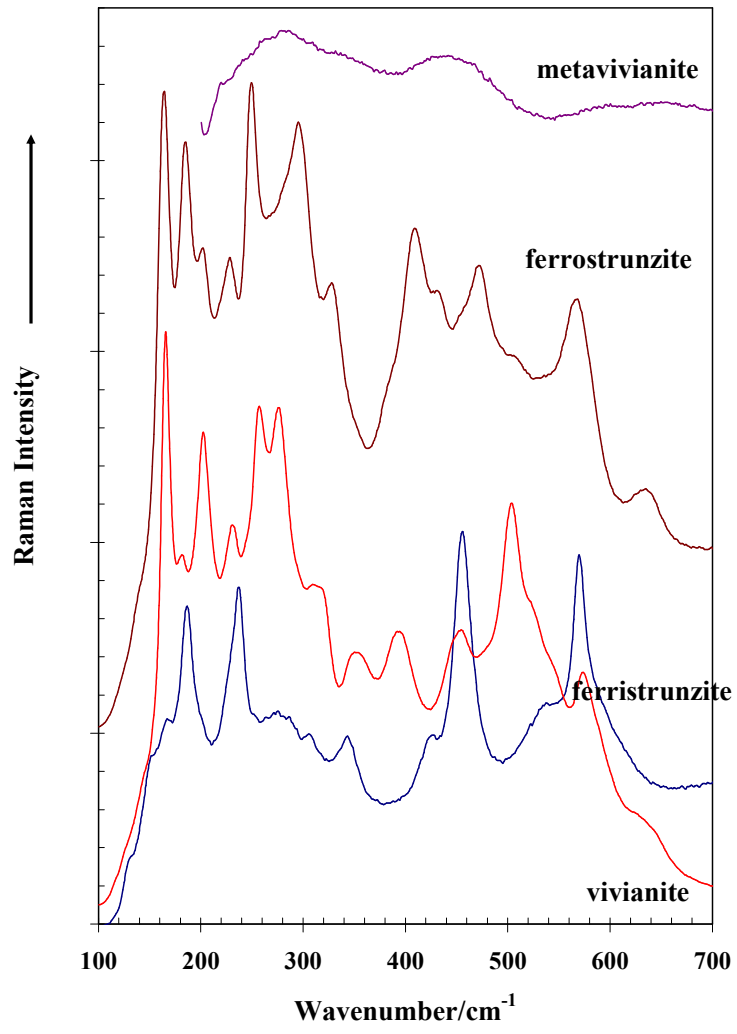


Figure 3

