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# A Near Infrared spectroscopic study of the phosphate mineral pyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$

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## **Abstract**

Spectral properties as a function of composition are analysed for a series of selected pyromorphite minerals of Australian origin. The minerals are characterised by d-d transitions in NIR from 12000 to 8000  $\text{cm}^{-1}$  (0.83-1.25  $\mu\text{m}$ ). A broad signal observed at  $\sim 10000 \text{ cm}^{-1}$  (1.00  $\mu\text{m}$ ) is the result of ferrous ion impurity in pyromorphites and follows a relationship between band intensity in the near-infrared spectra and ferrous ion concentration. The iron impurity causes a change in colour from green-yellow to brown in the pyromorphite samples.

The observation of overtones of the OH-fundamentals, confirms the presence OH<sup>-</sup> in the mineral structure. The contribution of water-OH overtones in the NIR at 5100  $\text{cm}^{-1}$  (1.96  $\mu\text{m}$ ) is an indication of bonded water in the minerals of pyromorphite. Spectra in the mid-IR show that pyromorphite is a known mixed phosphate and arsenate complex,  $\text{Pb}_5(\text{PO}_4, \text{AsO}_4)_3\text{Cl}$ . A series of bands are resolved in the infrared spectrum of pyromorphite at 1017, 961 and 894  $\text{cm}^{-1}$ . The first two bands are assigned to  $\nu_3$ , the antisymmetric stretching mode and third band at 894  $\text{cm}^{-1}$  is symmetric mode of the phosphate ion. Similar patterns are shown by other pyromorphite samples with variation in intensity. The cause of multiple bands near 800  $\text{cm}^{-1}$  is the result of isomorphic substitution of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$  and the spectral pattern relates to the chemical variability in pyromorphite. The presence of  $(\text{AsO}_4)^{3-}$  is significant in certain pyromorphite samples.

*Key words:* Pyromorphite; Mimetite; Vanadinite; Phosphate; Arsenate; Near-IR and Mid-infrared spectroscopy; OH-overtones; Cation/anion substitution effects

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## 1. Introduction

The minerals of pyromorphite series vary in composition between the end members, pyromorphite  $Pb_5(PO_4)_3Cl$ , mimetite  $Pb_5(AsO_4)_3Cl$  and vanadinite  $Pb_5(VO_4)_3Cl$ . A general formula for the minerals can be represented as  $M[XO_4]Y$  where M-metals, for example, Ca, Pb;  $[XO_4]$  is  $[PO_4]$ ,  $[AsO_4]$  and  $[VO_4]$ ;  $Y = Cl, F, OH, H_2O$ . In this isomorphous series, the functional ions and cations are compositionally variant, with Ca frequently substituting for Pb and with P, As and V substituting mutually in the  $M[XO_4]$  position [1-3]. X-ray powder diffraction examination was used to record compositional differences and to examine the solid solution characteristics of the synthetic members of the pyromorphite series, pyromorphite, mimetite and vanadate [4]. Pyromorphite shares the same structure with apatite. Pyromorphite forms in the oxidized zone of lead deposits, where it forms very bright coloured, stacked with barrel-shaped crystals [5]. Green mimetite or yellow pyromorphite, identification between the two is difficult. Most crystals of mimetite-pyromorphite system are chemically zoned. Chemical variability in phosphohedyphane,  $Ca_2Pb_3(PO_4)_3Cl$  was observed by Kampf [6]. The crystal system of mimetite is known as a hexagonal (space group  $P6_3/m$ ). Mimetite has a dimorphic relationship with clinomimetite [7], which has a monoclinic system (space group  $P2_1/m$ ). The phase transition between the hexagonal system and monoclinic system occurs only through shifts of O(3) atom position in the crystal structure of mimetite [8,9].

Pyromorphite,  $Pb_5(PO_4)_3Cl$  (lead chlorophosphate), is analogous to mimetite with the phosphate  $(PO_4)^{3-}$  ion replacing the  $(AsO_4)^{3-}$  ion. Although the properties of the two minerals are almost the same, their colours are different. So, colour can usually be used to distinguish between the two, mimetite being yellow and Pyromorphite being yellow-green. Usually pyromorphite is green, mimetite yellow and vanadinite red [10]. Compositional variations in pyromorphite minerals cause change in colour, ranging from green, greenish-yellow, and yellow to brown. It is quite possible to distinguish the minerals of pyromorphite from their spectral properties. Practically all natural minerals of phosphorus are phosphates with anisodesmic structure made by tetrahedral radicals  $(PO_4)^{3-}$ . An over view on the diversity of phosphate minerals, distribution and genesis in Bulgaria presented by Kunov [11] provides sufficient proof for the cationic association in minerals.. Even though Kunov's review shows phosphates contain Fe and also other metals like Ca, Al, Mn, Cu, etc., their spectroscopic studies were not reported [11].

Pyromorphite,  $Pb_5(PO_4)_3Cl$  belongs to the chloroapatite group,  $M_5(PO_4)_3Cl$  where M may Ca, Pb, Cd or Ba. The M atom has two crystallographically different M(1) and M(2) sites. The chloroapatite group crystallizes in hexagonal or monoclinic structures. For example, cadmium chloroapatite,  $M = Cd$ , [12], strontium chloroapatite,  $M = Sr$  [13] and barium chloroapatite,  $M = Ba$  [14] crystallize in hexagonal,  $P6_3/m$ , and stoichiometric chloroapatite,  $M = Ca$ , crystallizes in a monoclinic,  $P2_1 / b$  [15]. X-ray single-crystal analyses of green and brown pyromorphites,  $Pb_5(PO_4)_3Cl$  from two mines in Japan were performed and classified into hexagonal crystal system with space group  $P6_3/m$  for pyromorphites [16]. The cell parameters are  $a = 1.0022$  and  $0.9993$  nm and  $c = 0.7348$  and  $0.7334$  nm for green and brown samples respectively.

Thus no significant difference was observed in their structures. Structural features of some calcium phosphates of biological interest were described by Mathew and Takagi [17]. The importance of hydroxyapatite (OHAp) considered being a prototype for the inorganic component of bones and teeth as a biological mineral in dental research. Infrared spectroscopic study of the three stoichiometrically related minerals; cornetite, libethenite and pseudomalachite have been made by Martin and Frost [18]. The vibrational modes in the phosphate stretching and bending regions appear in the range, 996-917  $\text{cm}^{-1}$  for  $\nu_1$ , 452-420  $\text{cm}^{-1}$  for  $\nu_2$ , 1095-1031  $\text{cm}^{-1}$  for  $\nu_3$  and 648-525  $\text{cm}^{-1}$  for  $\nu_4$ . Farmer report shows infrared bands for pyromorphite at 1030 and 970  $\text{cm}^{-1}$  assigned to phosphate mode,  $\nu_3$ , anti-symmetric stretching vibrations and at 572 and 542  $\text{cm}^{-1}$  for  $\nu_4$ , bending modes [19]. The infrared spectrum of mimetite is different from pyromorphite, displacing bands at 815, 803 and 783  $\text{cm}^{-1}$  attributed to arsenate  $\nu_3$ , antisymmetric stretching vibrations and at 415 and 383  $\text{cm}^{-1}$  assigned to arsenate  $\nu_4$  bending modes [19]. IR spectra of lead apatites were investigated by Levitt et al., [20] and Levitt and Condrate [21]. Raman studies have been reported for several minerals [22-29].

A recent study of Raman spectroscopy on pyromorphite minerals shows the reduction of symmetry for  $(\text{PO}_4)^{3-}$  units from the observation of multiple bands for  $\nu_4$  and  $\nu_2$  bending vibrations and the presence of isomorphic substitution for  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$  units through the  $\nu_1$  symmetric stretching bands at 824 and 851  $\text{cm}^{-1}$  [30]. The information on the application of NIR spectroscopy of minerals is very limited and in particular, the near-infrared spectroscopic studies have not been made on pyromorphites series. The present work is undertaken to study the spectral properties as a function of composition and isomorphic substitution of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$  in the series of selected pyromorphite minerals from different geographical locations of Australia.

## 2. Experimental

### 2.1. Minerals

A selection of pyromorphite minerals were provided by The South Australian Museum (Adelaide, Australia). Table 1 reports the pyromorphite minerals together with their origin and chemical analysis. All the minerals selected for the present investigation are from Australian mineral deposits. The minerals were analysed by XRD for phase identification [30] and scanning electron microscopy (SEM) was employed for composition analysis. The EDX measurements were made for chemical composition of the samples and the data is presented in Table 1.

### 2.2. Near-infrared (NIR) and Mid-infrared spectroscopy

NIR spectra were collected on a Nicolet Nexus FT-IR spectrometer with a Nicolet Near-IR Fibreport accessory (Madison, Wisconsin). A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from 13 000 to 4000  $\text{cm}^{-1}$  (0.77-2.50  $\mu\text{m}$ ) by the co-addition of 64 scans at a spectral resolution of 8  $\text{cm}^{-1}$ . A mirror velocity of 1.266  $\text{m sec}^{-1}$  was used. The spectra were transformed using the Kubelka-Munk algorithm to provide spectra for comparison with published absorption spectra.

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  $\text{cm}^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . 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.

### 3. Results and discussion

#### 3.1. Near-infrared spectroscopy

Most of the minerals produce characteristic bands in the near-infrared region. The minerals may contain transition metals that give rise to absorption features in the 12000-8000  $\text{cm}^{-1}$  (0.83-1.25  $\mu\text{m}$ ) region. Spectra of minerals show several strong bands from 7400 to 400  $\text{cm}^{-1}$  (1.35-25.00  $\mu\text{m}$ ) due to vibrational process. For example, pyromorphites are expected to show bands due to phosphate ion and OH units [1,31,32]. Spectral reflectance properties of these minerals can be utilized for the determination of mineralogy and composition controls in natural systems.

The observed spectra of the samples are divided into three regions: The spectra of electronic part in the high wavenumber region, 12000-8000  $\text{cm}^{-1}$  (0.83-1.25 $\mu\text{m}$ ) display a broad band (Fig. 1). This band is a common feature in all the spectra of pyromorphite minerals studied. Vibrational spectra in the wavenumber region from 8000 to 6500  $\text{cm}^{-1}$  (1.25-1.54  $\mu\text{m}$ ) are here shown in Fig. 2. The broad spectral feature extending from 7400-6500  $\text{cm}^{-1}$  (1.35-1.54  $\mu\text{m}$ ) is ascribed to the overtones of the first fundamental hydroxyl stretching modes observed in the mid-infrared spectra around 3600  $\text{cm}^{-1}$  (2.78  $\mu\text{m}$ ). The spectra in the low wavenumber region, 6500-4000  $\text{cm}^{-1}$  (1.54-2.50  $\mu\text{m}$ ) are shown in Fig. 3. The strong feature centred at 5200  $\text{cm}^{-1}$  (1.92  $\mu\text{m}$ ) is due to the overtones of OH-stretching bands observed in the lower range of IR spectrum at 3400  $\text{cm}^{-1}$  (2.94  $\mu\text{m}$ ). The vibrational spectra, in the extreme lower region, a complex profile contains a series of multiple sharp bands at wavenumbers < 4600  $\text{cm}^{-1}$  (2.17  $\mu\text{m}$ ). These sharp series of bands are produced by the combination of vibrational modes of phosphate and or arsenate ions.

##### 3.1a. Electronic spectral region: 12000-8000 $\text{cm}^{-1}$ (0.83-1.25 $\mu\text{m}$ ) region

The spectral properties of minerals may be correlated with mineralogical and chemical properties. There is a need to maintain a close relation with near-infrared and mid-IR spectroscopy is reason enough here. Analysis could be made on the basis of spectral properties as a function of compositional variations and isomorphous

substitution of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$  in the selected series of pyromorphite minerals. Compositional variation may cause change in colour of these minerals. The difference between green-yellow- and brown-pyromorphites was analysed through NIR and IR spectroscopy.

As a result of d-d transitions, characteristic bands appear in the spectral region of  $12000\text{-}8000\text{ cm}^{-1}$  ( $0.83\text{-}1.25\text{ }\mu\text{m}$ ). Iron impurity is common in natural minerals. For example, carbonate minerals contain iron impurity. Report on the NIR spectra of smithsonites show one broad feature near  $9000\text{ cm}^{-1}$  ( $1.11\text{ }\mu\text{m}$ ) related to ferrous ion substituting for  $\text{Zn}^{2+}$  [33]. In the present study, all the samples exhibit a broad feature with band maximum at  $\sim 10000\text{ cm}^{-1}$  ( $1.00\text{ }\mu\text{m}$ ). Even though iron was below the detection limit of EDX analysis, these spectra show a common feature and are a result of Fe(II) impurity (Fig. 1). The use of Fe-, Mn-, and Cu-containing synthetic hydroxyapatite (SHA) as a slow release fertilizer for crops was discussed by Sutter et al., [34]. XRD and SEM analyses were made on synthetic SHA materials bearing Fe-Mn-Cu and transition metal free SHA materials and confirmed apatite structure. The shift in the infrared  $(\text{PO}_4)^{3-}$   $\nu_3$  vibrations suggests that Fe, Mn and Cu are incorporated into the SHA structure [34]. Reports on surface complexation of phosphate rocks (PR) shows, solid-liquid interface reaction between PR and the metals (Pb, Cu and Zn). Phosphate rock has the highest affinity for Pb, followed by Cu and Zn. This research demonstrated that phosphate-induced formation of fluoropyromorphite is primarily responsible for Pb immobilization by phosphate rock, whereas Cu and Zn retention is mainly attributable to the surface adsorption or complexation [35]. The NIR spectrum depicted in Fig. 1 shows a broad band and is resolved into two main components common to all samples. This is a characteristic Fe(II) band observed with a splitting of the order of  $1000\text{ cm}^{-1}$  for iron phosphate minerals, satterlyite and gormanite [36]. Fe(II) band is weak for yellowish-green and green samples where as this band is strong for light green and brown minerals. It appears that intensity of the ferrous ion band is a function of concentration and henceforth the content of Fe increases from green-yellow to brown coloured samples. On the higher wavenumbers side of NIR, a new component band for pyromorphite-3 at  $11590\text{ cm}^{-1}$  ( $0.86\text{ }\mu\text{m}$ ) and another  $10900\text{ cm}^{-1}$  ( $0.92\text{ }\mu\text{m}$ ) band in pyromorphite-5 are observed. The effect of cation substitution is noticed on band positions. That is, Fe(II) band shows significant shift (blue shift) towards higher energy, for light-green and brown coloured samples and the additional band that could be seen clearly in these two samples at  $\sim 11000\text{ cm}^{-1}$  ( $0.91\text{ }\mu\text{m}$ ) is attributable to Cu(II) ion [37-39]. The observation of electronic transition bands from  $12000\text{-}8000\text{ cm}^{-1}$  ( $0.83\text{-}1.25\text{ }\mu\text{m}$ ) region suggests Fe and Cu are incorporated into the pyromorphite structure [34].

### **3.1b. Near-IR spectral region: $7400\text{-}6500\text{ cm}^{-1}$ ( $1.35\text{-}1.54\text{ }\mu\text{m}$ )**

The vibrational spectra of pyromorphite series are shown in Fig. 2. A broad profile extending from  $7300\text{ to }6700\text{ cm}^{-1}$  ( $1.37\text{-}1.49\text{ }\mu\text{m}$ ) is similar in all samples because of their identical structure. The broad band shows a number of component bands that appear differently in all the spectra. This feature enables the characterization of all four pyromorphite minerals. Previous studies on reflectance spectra of some silicates, for example, chrysotile,  $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$  and antigorite,  $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$  show vibrational bands due to OH near  $7200\text{ cm}^{-1}$  ( $1.40\text{ }\mu\text{m}$ )[40]. The appearance of bands in the spectra (Fig. 2) from  $7300\text{ to }6700$

$\text{cm}^{-1}$  (1.37-1.49  $\mu\text{m}$ ) are related to the overtones of the first fundamental OH-stretching vibrational modes observed from IR and Raman spectra of lead chlorophosphate minerals in the range, 3650-3500  $\text{cm}^{-1}$  (2.74-2.86  $\mu\text{m}$ ) [29]. One band with weak intensity registered for pyromorphite-3 at 7380  $\text{cm}^{-1}$  (1.36  $\mu\text{m}$ ) as a shoulder to the main band is assigned to MOH mode where M= Fe or Cu.

### **3.1c. Near-IR spectral region: 6500-4000 $\text{cm}^{-1}$ (1.54-2.50 $\mu\text{m}$ )**

Fig. 3 shows, a strong feature centred at 5200  $\text{cm}^{-1}$  (1.92  $\mu\text{m}$ ) due to the overtones of OH-stretching bands observed in the lower range of IR spectrum at about 3400  $\text{cm}^{-1}$  (2.94  $\mu\text{m}$ ). Hunt and Salisbury reported liquid water bands in sedimentary rocks at 1.90  $\mu\text{m}$  (5260  $\text{cm}^{-1}$ ) [41]. For rosasite group minerals, strong bands around 5300  $\text{cm}^{-1}$  (1.89  $\mu\text{m}$ ) were attributed to water-OH vibrations [39]. For all the minerals of pyromorphite, the strong band with multiple components located at 5100  $\text{cm}^{-1}$  (1.96  $\mu\text{m}$ ) is the contribution of water-OH overtones of the bonded water OH-stretching bands observed in Raman spectra of pyromorphites, over the range, 3450-3200  $\text{cm}^{-1}$  [30]. The complexity of bands recorded from 4700-4000  $\text{cm}^{-1}$  (2.13-2.50  $\mu\text{m}$ ) results mostly from overtones and/or combinational tones of the fundamental vibrations of phosphate ion, arsenate ions and/or a combination of arsenate and phosphate ions. There are three main bands with variable positions and intensities and are observed around the wavenumbers, 4500, 4300 and 4200  $\text{cm}^{-1}$  (2.22, 2.33 and 2.38  $\mu\text{m}$ ). For pyromorphite-1 and Pyromorphite-3 (yellowish green and light green samples) the bands are resolved into three sharp peaks but their intensities are quite different and the peaks are shifted to lower wavenumbers in the later sample (pyromorphite-3). The complexity of bands increased in the case of other samples (green and brown). These features are accounted for by the isomorphic substitution of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$  and also the presence phosphate ion.

### **3.2. Mid- IR spectroscopy**

The vibrational stretching region of the series of selected pyromorphite minerals is shown in the Fig. 4. The spectra of the minerals include a strong feature due to  $(\text{PO}_4)^{3-}$  ion from 1200 to 900  $\text{cm}^{-1}$  and a relatively weak intensity band centred at  $\sim 800 \text{ cm}^{-1}$ . The lead chlorophosphate minerals also exhibit sharp bands near 600  $\text{cm}^{-1}$ . The hydroxyl stretching region of the minerals was poorly resolved in the infrared spectra and is not included. Strong bands could be observed in Raman for pyromorphite, in the high wavenumber region of 4000-3000  $\text{cm}^{-1}$  [30] and the data is compared here with NIR results.

The spectra of the minerals examined in the mid-infrared region are shown in Fig. 4. This figure includes the infrared spectra of calcian pyromorphite. Phosphate mineral structure is based on the  $\text{PO}_4$  tetrahedron. The  $(\text{PO}_4)^{3-}$  ion produces dominant spectral features at  $\sim 1000 \text{ cm}^{-1}$ . A series of bands are well resolved in pyromorphite-1 at 1017, 961 and 894 and 777  $\text{cm}^{-1}$ . The first two bands are assigned to  $\nu_3$ , the antisymmetric stretching mode. Farmer published infrared bands for pyromorphite at 1030 and 970  $\text{cm}^{-1}$  assigned to phosphate mode,  $\nu_3$ , anti-symmetric stretching vibrations [19]. The observation of the band at 894  $\text{cm}^{-1}$  is an indication of reduction in symmetry for phosphate ion and is attributed to the symmetric mode,  $\nu_1$ . In other cases the  $\nu_3$  and  $\nu_1$  modes are in almost similar positions but some variation in intensity is observed. A single broad band is conspicuous at 777  $\text{cm}^{-1}$  in

Pyromorphite-1. In the case of pyromorphite-2 this band is clearly resolved into three components at 844, 794 and 740  $\text{cm}^{-1}$ . The cause of multiple bands is the result of isomorphic substitution of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$ . Pyromorphite-5 also discloses three bands nearly in the same region at 859, 791 and 716  $\text{cm}^{-1}$ . These bands are assigned to the  $(\text{AsO}_4)^{3-}$   $\nu_1$  symmetric stretching mode. The infrared spectrum of the calcian pyromorphite includes the spectra of both the phosphate and arsenate anions. Clearly the spectrum of the arsenate anion is present proving the partial replacement of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$ . Multiple  $(\text{AsO}_4)^{3-}$  stretching vibrations are observed at 778, 752 and 692  $\text{cm}^{-1}$ . The report of Raman spectra also shows bands for pyromorphite-2 at 824 and 802  $\text{cm}^{-1}$  and 851 and 826  $\text{cm}^{-1}$  in pyromorphite-5 and are assigned to the symmetric stretching mode,  $\nu_1$  of arsenate ion [30]. The presence of  $(\text{AsO}_4)^{3-}$  is significant in pyromorphite-2 and pyromorphite-5. The single broad band at 777  $\text{cm}^{-1}$  in pyromorphite-1 implies partial substitution for  $(\text{PO}_4)^{3-}$  is not effected.  $(\text{AsO}_4)^{3-}$  substitution for this mineral is quite small. However, the appearance of three bands in pyromorphite-3 at 885, 802 and 722  $\text{cm}^{-1}$  is an indication of  $(\text{AsO}_4)^{3-}$  substitution for  $(\text{PO}_4)^{3-}$ . It is interesting to note a common feature with a weak band at 658-678  $\text{cm}^{-1}$  and one spectacular doublet near 570  $\text{cm}^{-1}$  is seen in all the minerals of pyromorphite. Levitt and Condrate [21] and Bhatnagar [42] reported two bands at 542 and 572  $\text{cm}^{-1}$ . Henceforth the bands in the low wavenumber range, 700-500  $\text{cm}^{-1}$  are assigned to  $\nu_4$   $(\text{PO}_4)^{3-}$  bending modes.

#### 4. Conclusions

A series of selected pyromorphite minerals of Australian origin were analysed using a combination of near-IR and mid-IR spectroscopy as a function composition. The difference between green-yellow- and brown-pyromorphites is distinguished using these techniques. The intensity of the near-IR bands attributed to the ferrous ion increases from green-yellow to brown in the selected pyromorphites. The observation of electronic transition bands from 12000-8000  $\text{cm}^{-1}$  (0.83-1.25  $\mu\text{m}$ ) region suggests Fe and Cu are incorporated into the pyromorphite structure. Iron is most frequently found in minerals as impurity and is readily determined through NIR spectroscopy in pyromorphite.

The effect of band shifts on cation substitution has been observed both in electronic and vibrational spectra. The complexity of bands in the region, 4700-4000  $\text{cm}^{-1}$  (2.13-2.50  $\mu\text{m}$ ) results mostly from overtones and/or combinational overtones of the fundamental vibrations of phosphate and arsenate ions. The presence of bands due to these overtones of the first fundamental OH vibrational modes from 7300 to 6700  $\text{cm}^{-1}$  (1.37-1.49  $\mu\text{m}$ ) and the contribution of water-OH vibrations through a strong absorption feature at 5100  $\text{cm}^{-1}$  (1.96  $\mu\text{m}$ ) confirms OH<sup>-</sup> substitution for Cl<sup>-</sup>

A single broad band (777  $\text{cm}^{-1}$ ) in pyromorphite-1 implies partial substitution for  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$  is almost negligible. The cause of multiple bands near 800  $\text{cm}^{-1}$  is the result of isomorphic substitution of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$ . The presence of  $(\text{AsO}_4)^{3-}$  is significant in pyromorphite-2 and pyromorphite-5. The infrared spectrum of the calcian pyromorphite includes the spectra of both the phosphate and arsenate anions. Clearly the spectrum of the arsenate anion is present proving the partial replacement of  $(\text{PO}_4)^{3-}$  by  $(\text{AsO}_4)^{3-}$ . The minerals of pyromorphite can be regarded as a known mixed complex of phosphate and arsenate ions. Studies on

pyromorphite series of minerals are useful for the development of inorganic barrier coatings on lead water pipes.

Investigations and interpretations are necessary for strengthening the knowledge on the geochemistry and mineralogy of the phosphate minerals (in Australia): Minerals include the pyromorphite series; pyromorphite, mimetite and vanadinite. This demand extends further because in many cases phosphates may be used as indicators for the discovery of metal ore bodies.

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<b>Code</b>	<b>Mineral</b>	<b>Colour</b>	<b>Formula</b>	<b>Arsenate substitution</b>	<b>%PbO</b>	<b>%P<sub>2</sub>O<sub>5</sub></b>	<b>%As<sub>2</sub>O<sub>5</sub></b>	<b>%Cl</b>	<b>Origin</b>
Pyromorphite-1	Pyromorphite	Yellowish green	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl		82.3	16.1	0.1	2.7	Mount Isa, QLD, Australia
Pyromorphite-2	Pyromorphite	Green	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	AsO <sub>4</sub>	Not measured				Brown's Prospect, Rum Jungle Northern Territory, Australia
Pyromorphite-3	Pyromorphite	Light green	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl		82.2	14.7	-	2.6	Tennant Creek, Northern Territory, Australia
Pyromorphite-5	Pyromorphite	Brown	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	AsO <sub>4</sub>	82.9	12.6	4.5	2.7	Broken Hill, NSW, Australia
Pyromorphite-7	Calcian pyromorphite	Greenish yellow	(Ca,Pb) <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	Not determined					Block 14 Mine, Broken Hill, NSW, Australia

**Table 1 Table of the pyromorphite minerals used in this work and their origin**



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**Table 1 Table of the pyromorphite minerals used in this work and their origin**

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**Figure 2 Near-IR spectra of pyromorphite (samples 1,2,3 and 5) and arsenian pyromorphite in the 6500-8000  $\text{cm}^{-1}$  region.**

**Figure 3 Near-IR spectra of pyromorphite (samples 1,2,3 and 5) pyromorphite in the 4000-6500  $\text{cm}^{-1}$  region.**

**Figure 4 Mid-IR spectra of pyromorphite (samples 1,2,3 and 5) and calcian pyromorphite in the 500-1300  $\text{cm}^{-1}$  region.**



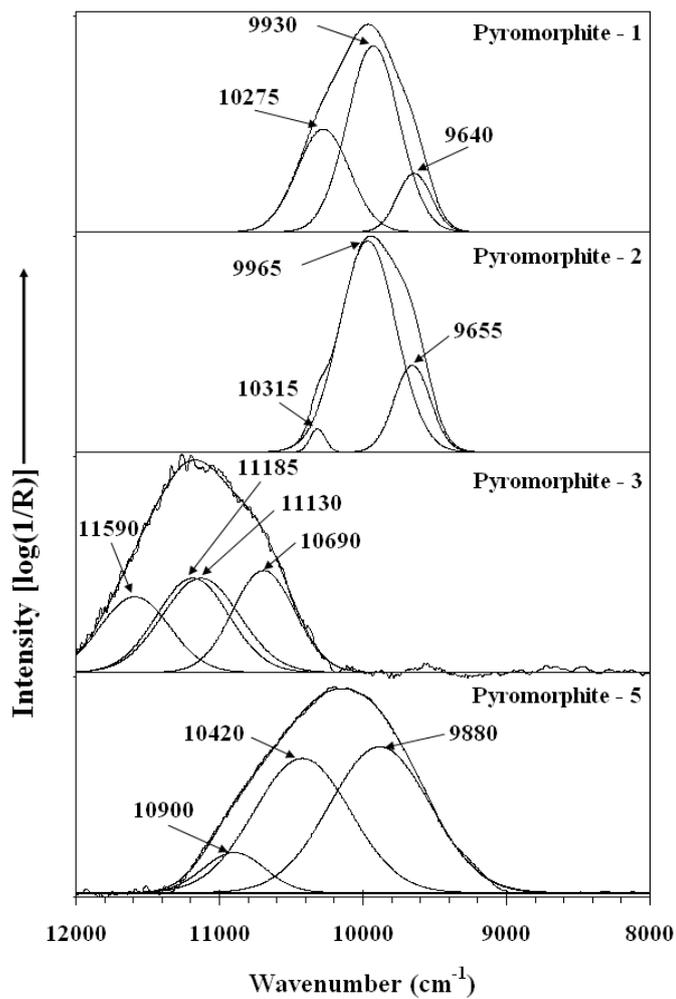


Figure 1

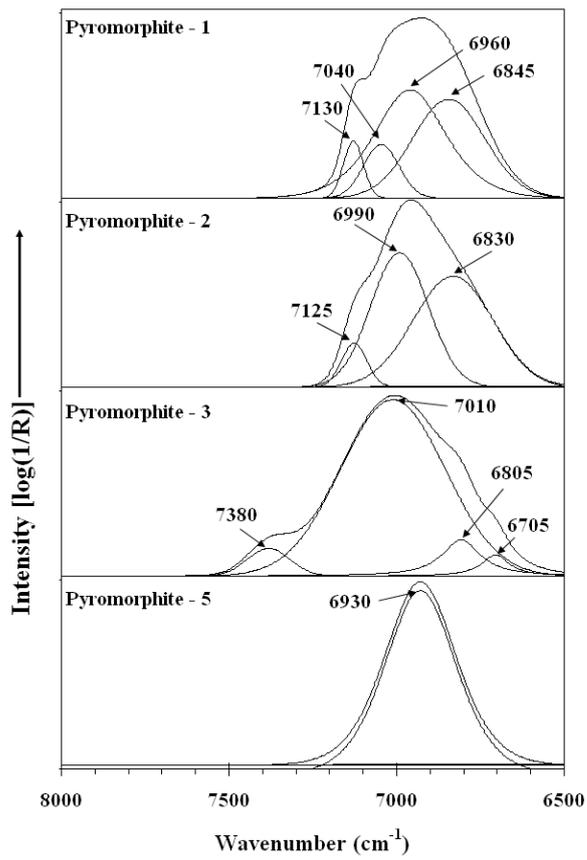
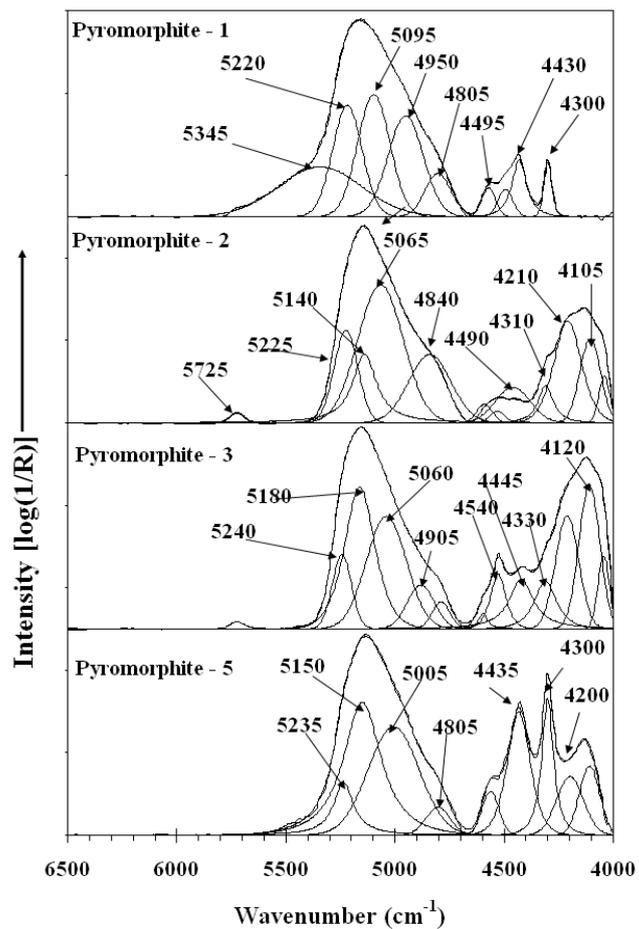
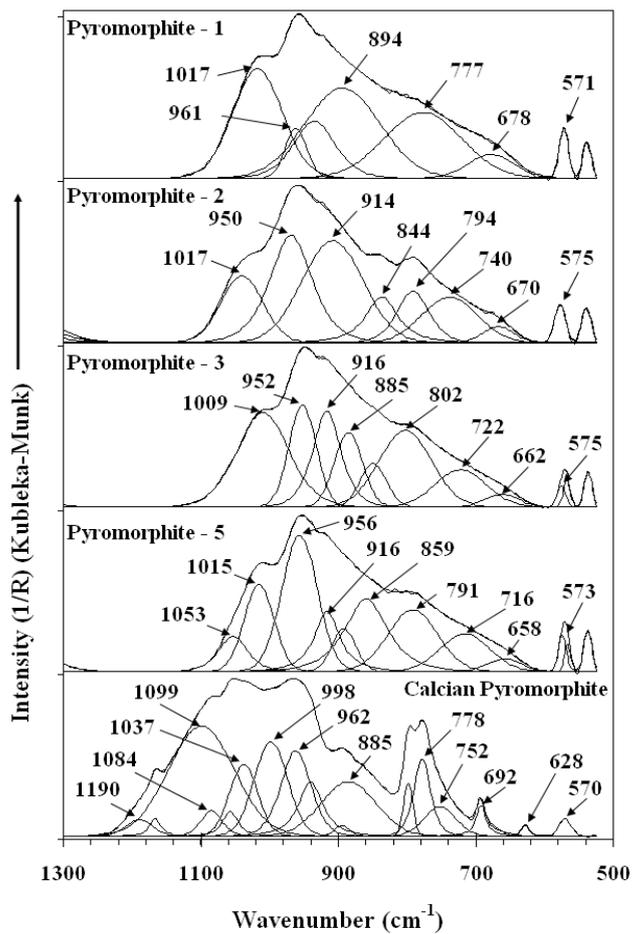


Figure 2



**Figure 3**



**Figure 4 Mid IR spectra**