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The structure of mimetite, arsenian pyromorphite and hedyphane –a Near Infrared spectroscopic study

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Abstract

Electronic and vibrational spectra of mimetite, arsenianpyromorphite and hedyphane minerals have been analysed and the spectra related to the mimetite and arsenian pyromorphite and hedyphane mineral structure. The chief spectral feature in the electronic spectra at ~10000 cm^{-1} (1.00 μm) with variable band position and intensity results from the ferrous ion. The splitting of Fe(II) band is large in mimetites with a separation of 1415 cm^{-1}. An additional band shown by arsenian pyromorphite at 10735 cm^{-1} (0.93 μm) is assigned to Cu(II) dd-transition. The substitution of Fe(II) causes a blue shift for Cu(II) band in mimetites and the intensity of this band is enhanced at ~11140 cm^{-1} (0.90 μm). The change in colour from brown to orange-yellow relates to the amount of Cu and/or Fe impurities in the mimetite minerals.

The presence of OH-stretching overtones at 7000 cm^{-1} (1.43 μm) is the result of OH substitution for Cl. Phosphate ion bands are produced in arsenian pyromorphite, hedyphane and mimetite-3. Arsenian pyromorphite spectrum is a mixed profile dominated by PO stretching vibrations at 1100-900 cm^{-1}. The spectrum of hedyphane is significant with arsenate bands at 900-700 $cm^{-1}$and weak bands appear on either side of this due to the phosphate ion. The absence of phosphate ion group of bands and the presence of $(AsO_4)^{3-}$ bands near 800 cm^{-1} in selected mimetites is evidence for isomorphic substitution of $(AsO_4)^{3-}$ by $(PO_4)^{3-}$.

Key words: Mimetite; Pyromorphite; Hedyphane; Arsenate; NIR spectroscopy, Vibrational spectroscopy; OH-overtones; Cation/anion substitution effects

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1. Introduction

Arsenic has a diverse chemical behaviour in the natural environment. It has the ability to change oxidation state and bonding configuration that creates rich inorganic and organic compounds. Mimetite is an arsenate mineral, usually forms as a secondary mineral in lead deposits through oxidation of galena and arsenate. Mimetite [$Pb_5(As_4)_3Cl$] forms a chemical series with two other minerals; pyromorphite, $Pb_5(PO_4)_3Cl$ and with vanadinite, $Pb_5(VO_4)_3Cl$. This series differs from other chemical series in which substitution of cations is common, for example; Ca for Mg. In the pyromorphite and mimetite series substitution involves the basic chemical units of the anion groups; Phosphate (PO_4), arsenate (AsO_4) and vanadinite (VO_4). Mimetite is usually found in the form of small hexagonal crystals with colours ranging from pale to bright yellow, orange, yellowish-brown, white, translucent to opaque. Compositional differences and solid solution characteristics of synthetic members of pyromorphite series; pyromorphite, mimetite and vanadinite have been published [1-4]. Spectroscopic studies on mimetite-pyromorphite series are limited [1-4]. This mineral is a member of an isomorphous series having essentially an apatite structure. The compounds form a continuous series, in which Cl, F, and OH substitution occurs [5-7]. The crystal structure of mimetite is hexagonal with space group $P6_3/m$ and its dimorphic relationship with a new mineral species, clinomimetite belongs to monoclinic system (space group $P2_1/m$) [8].The phase transition between the hexagonal system and monoclinic system occurs through shifts of O(3) atom position in the crystal structure of mimetite [9,10]. The study of lead calcium arsenate apatites from Franklin, New Jersey and Langban, Sweden infers additional studies are necessary. In this study, hedyphane was redefined as $Ca_2Pb_3(AsO_4)_3Cl$. The space group is $P6_3/m$ with a = 1.0140 and c= 0.7185 nm and cation ordering in hedyphane is attributed to a preference by atoms with sterically active electron lone pairs, example, Pb(II), for the asymmetrically coordinated 6*h* site. The silent features drawn from tabulation of chemical composition indicate both the ions of phosphate and arsenate are involved [11]. Ca-bearing phosphatian mimetite (honey yellow colour) is composed of Pb (major), in addition, Ca, Cd, Mn, Sb, Fe, As and P in minor amounts. The unit cell parameters are a = 1.0087 and c = 0.7335 nm (space group, $P6_3/m$). X-ray and IR data have shown that it represents a transitional phase in the ternary system mimetite-pyromorphite-turneaureite [12]. Phosphohedyphane, $Ca_2Pb_3(PO_4)_3Cl$, the phosphate analog of hedyphane has been described recently shows the mineral has hexagonal structure (space group, $P6_3/m$, a = 0.9857 and c = 0.7130 nm) and chemical variability[13].

Minerals containing phosphate, arsenate and vanadinate anions have the general formulae $A_m[XO_4]_pZ_{q.x}H_2O$ and $A_mB_m[XO_4]_pZ_{q.x}H_2O$ where $[XO_4]$ is $[PO_4]$, $[AsO_4]$ and $[VO_4]$; Z is OH, F, Cl, O; A and B-metals. Mineral species are formed by the interaction of cations with phosphate, arsenate and vanadinate. Indeed minerals may contain mixed anionic species. Also many of these minerals may contain mixed cationic species. Many of these minerals contain Fe and also other metals like Ca, Al, Mn, Cu, etc [14]. Farmer reported infrared bands for pyromorphite at 1030 and 970 cm^{-1} assigned to phosphate mode, ν_3, anti-symmetric stretching vibrations and at 572 and 542 cm^{-1} for ν_4, bending modes [15]. The infrared spectrum of mimetite is different form pyromorphite, displacing bands at 815, 803 and 783 cm^{-1} attributed to

arsenate ν_3, antisymmetric stretching vibrations and at 415 and 383 cm^{-1} assigned to arsenate ν_4 bending modes [15]. The free ion, AsO_4^{3-} has four vibrational modes and are observed by IR and Raman at 810 cm^{-1} (ν_1); ν_2 at 342 cm^{-1}; ν_3 at 810 cm^{-1} and ν_4 at 398 cm^{-1}[16]. For vanadinites, Ross reported ν_3-bands at 800 and 736 cm^{-1}, and the ν_4 modes at 419, 380 and 322 cm^{-1} [16]. Gadsen also investigated the infrared spectrum of the mimetite [17]. The ν_3 mode is reported to occur in the range, 700 to 900 cm^{-1} and the ν_4 mode between 300 and 410 cm^{-1}. Griffith reported the Raman spectrum of mimetite [18]. Levitt and Condrate reported the infrared and Raman spectra of lead apatite powdered minerals [6].

Earlier papers were limited to the mid-infrared absorption data on apatite, pyromorphite, mimetite and vanadinite [19,20]. Some other studies of Raman and IR spectra of calcium and lead apatites including mimetite show no detailed analysis [6,21,22]. The Raman and IR spectra of single crystals of pyromorphite, vanadinite, and mimetite were recorded and focused mainly on coordinate analysis and force constants of the three minerals that include the assignments of the vibrational frequencies [23]. For mimetite, this paper shows the ν_1 mode observed at 816 cm^{-1}, the ν_3 vibrations at 809 and 787 cm^{-1}, the ν_2 at 414, 390 and 335 cm^{-1} and ν_4 at 424, 373 and 314 cm^{-1}. None of these reports include NIR spectroscopy. There has been almost no research carried out on NIR spectroscopy of the mimetite and pyromorphite series.

In the present work we analysed spectroscopically selected mimetite minerals, arsenianpyromorphite and hedyphane minerals and the spectra are related to the structure of the minerals.

2. Experimental

2.1. Minerals

The minerals used in this work, their formula and origin are listed in Table 1. The phase purity of the minerals was checked by X-ray diffraction and the chemical composition by EDX measurements.

2.2. Near-infrared (NIR) 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 cm^{-1} (0.77-2.50 μm) by the co-addition of 64 scans at a spectral resolution of 8 cm^{-1}. A mirror velocity of 1.266 m sec^{-1} was used. The spectra were transformed using the Kubelka-Munk algorithm to provide spectra for comparison with published absorption spectra. Spectral manipulations, such as baseline correction, smoothing and normalisation, were performed using the software package GRAMS (Galactic Industries Corporation, NH, USA).

2.3. 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^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) 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 Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

3. Results and discussion

3.1. Near-infrared (NIR) spectroscopy

Spectral studies have not been made to examine the effect of cation substitution and its symmetry in any of these minerals. The most common electronic process in minerals results from transition metals and iron is usually suspected in minerals either as a major or minor impurity. The electronic spectra of complex ferrous silicates have been interpreted by crystal field theory and attributed peaks in the 11000-9000 cm^{-1} (0.91-1.11 μm) region to Fe^{2+} ion [24]. Results are given from electronic and vibrational spectra and are explained in terms of the structure of cations and anions in the minerals of mimetite, arsenianpyromorphite and hedyphane.

The spectra of the samples are presented in three parts: The spectra of electronic part in the high wavenumber region, 12000- 8000 cm^{-1} (0.83-1.25μm) are depicted in Fig. 1. A unique spectral feature with variable band position and intensity observed at ~10000 cm^{-1} (1.00 μm) (Fig. 1) results from the Fe^{2+} ion. This band is a common feature in all the spectra. This broad feature is resolved into two less intense bands in mimetite-1 and mimetite-2 and an additional intense band on high energy side at ~11145 cm^{-1} (0.90 μm). Vibrational spectra in the wavenumber region from 8000 to 6500 cm^{-1} (1.25-1.54 μm) are shown in Fig. 2. A broad band observed in the region, 7500-7000 cm^{-1} (1.33-1.43 μm) is due to overtones of the first fundamental hydroxyl stretching modes observed in the mid-infrared spectra around 3600 cm^{-1} (2.78 μm). The spectra in the low wavenumber region, 6500-4000 cm^{-1} (1.54-2.50 μm) are shown in Fig. 3. The strong feature centred at ~5000 cm^{-1} (2.00 μm) is the result of overtones of OH-stretching bands observed in the lower range of IR spectrum at 3400 cm^{-1}((2.94 μm) The vibrational spectra, in the lower wavenumber region, a complex profile contains a series of multiple sharp bands at wavenumbers < 4600 cm^{-1} (2.17 μm). These sharp series of bands are produced by the combination of vibrational modes of phosphate and or arsenate ions.

3.1a. Electronic spectra: 12000-8000 cm^{-1} (0.83-1.25 μm) region

Divalent cations like Ca^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+} and Cu^{2+} in a complex influence the band positions in the electronic spectrum. The cations also cause shifts for the OH-stretching units, carbonate and arsenate bands both in the near-infrared and IR spectra of the minerals. Spectral properties are related to the structure of minerals. Distinctive band positions are shown in the spectra as depicted in Fig. 1. Mimetite (yellow-orange) and pyromorphite (brown) minerals are differentiated from their electronic spectral features. A vertical line may be drawn across the central portion of the spectral pattern to see an unique spectral feature with variable band position and intensity at ~ 10000 cm^{-1} (1.00 μm) (Fig. 1) resulting from Fe^{2+} ion substitution. This band is a common feature in all the spectra. Burns [24] attributed peaks in cummintonite-grunerites and actinolite in the 11000-9000 cm^{-1} (0.91-1.11 μm) region to Fe^{2+}, while Goldman and Rossman [25] interpreted many of the amphibole spectra claiming that only iron in the M4 site causes the band at 10000 cm^{-1} (1.00 μm). Later it was confirmed the Fe^{2+} band at 10000 cm^{-1} (1.00 μm) for M4 site for the calcic amphibole [26]. The dependence of Fe (II) band with pressure shifts in ferromagnesian olivine has also been analysed [27]. A prominent feature reported for an iron-rich humite is a complex band system in the NIR and is assigned to dd-transitions of Fe^{2+} bands at 10800 and 7600 cm^{-1} (0.93 and1.32 μm) [28].

A broad profile shown (Fig. 1) by mimetite-3 is characterised by a single band at 9890 cm^{-1} (1.01 μm) attributable to Fe(II) ion. This band appears at ~10000 cm^{-1} (1.00 μm) in arsenian pyromorphite splits into two components and are displaced to 10235 and 9760 cm^{-1} (0.98 and 1.02 μm). For mimetite-1 and mimetite-2 samples, the Fe(II) band split into two with a separation of 1415 cm^{-1}. The two bands in mimetite-1 are shown at 9945 and 8530 cm^{-1} (1.00 and 1.17 μm) while they are weak in mimetite-2 at 9915 and 8615 cm^{-1} (1.01 and 1.16 μm). A similar situation was observed from the study of electronic absorption spectra of the orthorhombic olivine-type phosphate minerals of the triphylite-lithiophilite series. All triphylite-lithiophilite spectra showed an intense band system in the NIR around 9400-9100 cm^{-1}(1.06-1.10 μm) is a typical of spin allowed dd-transition in octahedral Fe(II) [29]. Electronic spectrum of Chevreul's salt, $[Cu^{I}{}_2 (SO_3)_2 (SO_3)_2]^{6-}$ consists of two ligand field transitions for Cu(II) at 785 and 1000 nm (12740 and 10000 cm^{-1}) and the isomorphic species present distinct colours. The intense red colour of the Chevreul's salt changes to yellowish-brown, after the substitution of Cu(II) by Fe(II) and the observation of band at 865 nm (11560 cm^{-1}) supports the Fe(II) derivative [30]. Mimetite and pyromorphite minerals are distinguished by means of electronic spectra. An additional weak band in arsenian pyromorphite at 10735 cm^{-1} (0.93 μm) may be assigned to Cu(II) dd-transition. The intensity of this band is enhanced at the cost of Fe(II) in mimetite-1 and mimetite-2 and appeared at ~11140 cm^{-1} (0.90 μm). There is an exception in mimetite-3 in which more iron impurity causes a complex broad band profile. The change of brown colour to orange-yellow relates to the amount of Cu and or Fe impurities in the mimetite minerals. Colour of the minerals may be related to the compositional variations in the minerals.

3.1b. Vibrational spectra: 8000-6500 cm^{-1} (1.25-1.54 μm) region

The vibrational absorption characteristics of mimetite and arsenian pyromorphite minerals are shown in Fig. 2. Spectral variations support mineralogical

variations especially in composition. Selected absorption bands were studied at high resolution. The minerals show fine structure particularly in the OH-stretching overtone region near 7000 cm^{-1} (1.43 μm) region [31]. The multi-component bands derived for each profile in spectra enhance the ability to discriminate between the minerals. Arsenian pyromorphite, $Pb_5(PO_4,AsO_4)_3Cl$ exhibits a sharp band at 7070 cm^{-1} (1.41 μm) with four components due to OH-stretching overtones. The observation of OH-stretching overtones implies substitution for Cl by OH. Mimetite samples show variable band positions with more intensity at 7010 and 7215 cm^{-1} (1.43-1.39 μm). The cause for the shifts of bands may be attributed to the presence of Fe and Cu in mimetites and Ca(II) perhaps substitution by Fe(II) and or Cu(II). Vibrational bands for several minerals like turquoise, rosasite, smithsonite, rhodochrosite, alunite, rectorite and jarosite reported in 7200-7000 region (1.39-1.43 μm) [31,32-34].

3.1c. Near-IR spectra: 6500-4000 cm^{-1} (1.54-2.5 μm) region

The overtones of water are observed in the spectra of H_2O-bearing minerals near 5200 cm^{-1} (1.92 μm) [35,36]. Vibrational spectra of the minerals shown in Fig. 3 contain many significant absorption features. A strong feature at ~5000 cm^{-1} (2.00 μm) accompanied by a weak feature at 6100 cm^{-1} (1.64 μm) suggests incorporation of H_2O into the mineral structure. Arsenian pyromorphite band is strong at 5175 cm^{-1} (1.93 μm). For mimetites this band is almost equally strong but displaced differently at 5185, 5190 and 5200 cm^{-1} (1.93, 193, and 1.92 μm) respectively, because, the functional ions and cations are compositionally variant in the isomorphic series. The liquid water band was observed in sedimentary rocks at 1.90 μm (5260 cm^{-1}) [37]. A series of sharp bands are observed in the spectra of the lower wavenumbers. Despite the complexity of the overlapping bands a sequence of bands in each of the spectra can be observed. The sequence for mimetites is observed at ~ 4500, 4400 and 4300 cm^{-1} (2.22, 2.27 and 2.33 μm) in which a single anion (AsO_4) is involved. The sequence of bands in arsenian phosphate and hedyphane becomes much more complicated. The modified features result from the substitution of Pb(II) by Ca(II) and $(AsO_4)^{3-}$ by $(PO_4)^{3-}$ are reflected by the number of overlapping bands which are shifted to lower wavenumbers.

3.2. Mid-IR spectroscopy

In the mid-IR spectral region bands attributable to phosphate and arsenate anions can be observed. These features in the vibrational stretching region of 1300-500 cm^{-1} is shown in the Fig. 4. The spectra of the minerals are complex with the spectral profile in the 900-500 cm^{-1} region. For three mineral samples mimetite-3, arsenian pyromorphite and hedyphane additional bands produced by the phosphate anion are included in the 900 to 1100 cm^{-1} region. Infrared spectra were poorly defined in the 3600 to 1500 cm^{-1} region and they are not included here. Bands are strong in Raman for mimetites and pyromorphites in high wavenumber region, 4000-3000 cm^{-1}as reported by Frost et al. [38, 39] and the assignments of these bands are correlated with NIR data in the present work.

The observation of isomorphic substitution for $(PO_4)^{3-}$ by $(AsO_4)^{3-}$ in mimetites could easily be distinguished on the basis of their spectral properties from the mixed spectra of phosphate and arsenate ions in arsenian pyromorphite. As shown

in the Fig. 4, the spectrum of mimetite-3 is a simple system where arsenate bands are moderately resolved at 887 and 788 cm^{-1} and are identified as ν_1 and ν_3 modes of $(AsO_4)^{3-}$ ion. On either side of this low intensity profiles that contain multiple bands are the cause of partial substitution for $(PO_4)^{3-}$. A series of bands observed on high wavenumbers side of the spectrum at 1095, 1020, 990 and 914 cm^{-1}. The first three bands are assigned to ν_3, antisymmetric mode, and last one at 914 cm^{-1} is attributed to ν_1, the symmetric mode of phosphate ion. Farmer reported infrared bands for pyromorphite at 1030 and 970 cm^{-1} assigned to phosphate mode, ν_3, and antisymmetric stretching vibrations [15]. The range of bands observed for phosphate in other samples are not found in mimite-1 and mimetite-2 spectra but appeared with single broad profile having four component bands near 800 cm^{-1}. In this case $(PO_4)^{3-}$ is almost completely substituted by $(AsO_4)^{3-}$. Mimetite-1 bands are located at 812, 774, 752 and 702 cm^{-1}. Band at 812 cm^{-1} is attributed to ν_1 mode and the last three bands are due to ν_3 mode of AsO_4^{3-} ion. In mimetite-2, these bands are shifted to lower wavenumbers. A similar set of bands with variable band positions and intensity are seen in arsenian pyromorphite and hedyphane. The spectrum of hedyphane is significant with arsenate bands at 900-700 $cm^{-1}$and weak bands appear on either side of this due to the phosphate ion. Arsenian pyromorphite spectrum is also a mixed profile dominated by PO stretching vibrations at 1100-900 cm^{-1}. The effect of anion substitution is noticed in the spectra of mimetites and hedyphane. The substitution of $(PO_4)^{3-}$ for $(AsO_4)^{3-}$ characteristically decreases the vibrational frequencies of ν_3 and ν_1 modes of the $(PO_4)^{3-}$ slightly to lower wavenumbers with respect to arsenian pyromorphite. Investigations of anion substitutions in lead apatites reveal the effect of substitution of Ca^{2+} by Pb^{2+} and $(PO_4)^{3-}$ by $(AsO_4)^{3-}$ and $(VO_4)^{3-}$ in apatites cause a shift of the ν_3 (1082 cm^{-1}) and ν_1 (980 cm^{-1}) [40]. Raman studies show a complexity of band systems for phosphate and arsenate ions in mimetites, pyromorphite and hedyphane in three ranges at ~500-400 cm^{-1}, 400-300 cm^{-1} and 200-100 cm^{-1} assigned to$(PO_4)^{3-}$ and/or $(AsO_4)^3$ bending modes [38, 39]. The low wavenumber region of the mid-IR spectrum (Fig. 4) are very weak from 650-500 cm^{-1} may be attributed to ν_4 bending modes of $(PO_4)^{3-}$. In the spectra in Figure 4, the spectra for mimetites 1 and 2 are due to the $(AsO_4)^{3-}$ ion only. Whereas in Figure 4, the spectra of the other three samples show bands attributable to both $(PO_4)^{3-}$ and $(AsO_4)^{3-}$ anions. Thus the fundamental bands of $(PO_4)^{3-}$ and $(AsO_4)^{3-}$ can be interpreted to identify the minerals. The spectra for mimetites 1 and 2 can be considered as standard. Mimetite 3 is strictly a phosphated mimetite.

Conclusions

The minerals of mimetite, arsenianpyromorphite and hedyphane have been analysed using NIR spectroscopy and the spectra related to the mineral structure.

1. The minerals of mimetite and pyromorphite can be distinguished by means of the electronic spectra.

2. In NIR spectra of the mimetite minerals, a prominent spectral feature observed for ferrous ion is a complex band system at ~10000 cm^{-1} (1.00 μm).

4. For arsenian pyromorphite, an additional feature observed at 10735 cm^{-1} (0.93 μm) is assigned to the Cu(II) dd-transition. The intensity of this band is enhanced at the expense of Fe(II) in mimetite-1 and mimetite-2 and appeared at higher wavenumbers at ~11140 cm^{-1} (0.90 μm).

5. The cause of colour in mimetites (brown through to orange to yellow) depends on the impurities of Fe and or Cu.

6. The variation of spectral properties is related to the compositional variations in the minerals.

7. The minerals show fine structure particularly in OH-stretching fundamental overtone region and the PO_4/AsO_4 stretching region. The multi-component bands derived for each profile in vibrational spectra enhance the ability to discriminate between the minerals. The presence of OH-stretching overtones at 7000 cm^{-1} (1.43 μm) is the effect of Cl substitution by OH.

8. The observation of isomorphic substitution of $(AsO_4)^{3-}$ by $(PO_4)^{3-}$ in mimetites could easily be distinguished on the basis of their spectral properties from the mixed spectra of phosphate and arsenate ions in arsenian pyromorphite.

9. The range of bands observed for phosphate in other samples are not observed in the spectra of mimite-1 and mimetite-2 but appeared with a single broad profile having four component bands near 800 cm^{-1} attributed to the presence of the arsenate ion.

10. The observation of single profile in the mid-IR with four component bands due to $(AsO_4)^{3-}$ ion near 800 cm^{-1} in mimetite-1 and mimetite-2 is evidence for isomorphic substitution of $(PO_4)^{3-}$ by $(AsO_4)^{3-}$.

11. The substitution of $(PO_4)^{3-}$ for $(AsO_4)^{3-}$ characteristically decreases the vibrational wavenumbers of ν_3 and ν_1 modes of the $(PO_4)^{3-}$ slightly to lower wavenumbers when compared with the spectra of arsenian pyromorphite.

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Code	Mineral	Colour	Formula	Origin
Mime-1	Mimetite	Yellow	$Pb_5(AsO_4)_3Cl$	Tsumeb, Namibia, South Africa
Mime-2	Mimetite	Orange	$Pb_5(AsO_4)_3Cl$	Geronimo Mine, Yuma Co., Arizona, USA
Mime-3	Mimetite	Black	$Pb_5(AsO_4)_3Cl$	Mount Bonnie Mine, Northern Territory, Australia
Pyro-8	Arsenian Pyromorphite	Light brown	$Pb_5(PO_4,AsO_4)_3Cl$	Bunker Hill Mine, Kellogg, Idaho, USA
Hedy-1	Hedyphane	Grey white	$Pb_3Ca_2(AsO_4)_3Cl$	Puttapa Mine, Beltana, South Australia

Table 1 Table of the minerals, their origin and formula

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Table 1 Table of the minerals, their origin and formula

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Figure 1 Near-IR spectra of mimetite (samples 1,2,3) and arsenian pyromorphite in the 8000-12000 cm^{-1} region.

Figure 2 Near-IR spectra of mimetite (samples 1 and 2) and arsenian pyromorphite in the 6500-8000 cm^{-1} region.

Figure 3 Near-IR spectra of mimetite (samples 1,2,3), hedyphane and arsenian pyromorphite in the 4000-6500 cm^{-1} region.

Figure 4 Mid-IR spectra of mimetite (samples 1,2,3), hedyphane and arsenian pyromorphite in the 500-1300 cm^{-1} region.

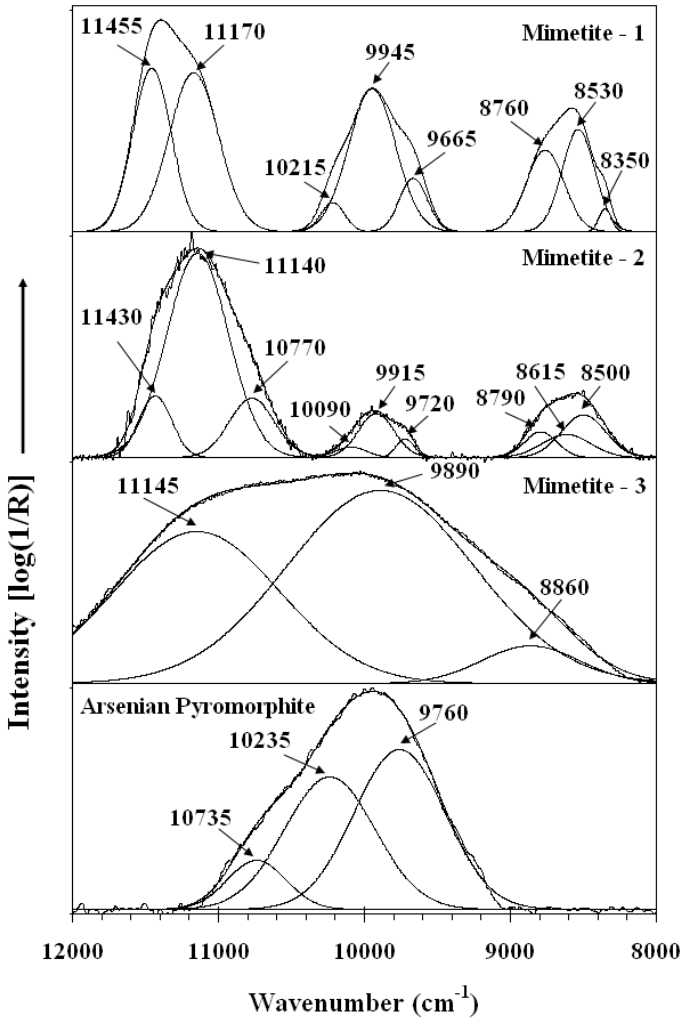
11455
11170
9945
8760
8530
9665
10215
8350
Mimetite - 1
11140
Mimetite - 2
11430
10770
9915
8615
8500
8790
10090
9720
9890
11145
Mimetite - 3
8860
Arsenian Pyromorphite
9760
10235
10735
Intensity [log(1/R)]
12000
11000
10000
9000
8000
Wavenumber (cm-1)

Figure 1

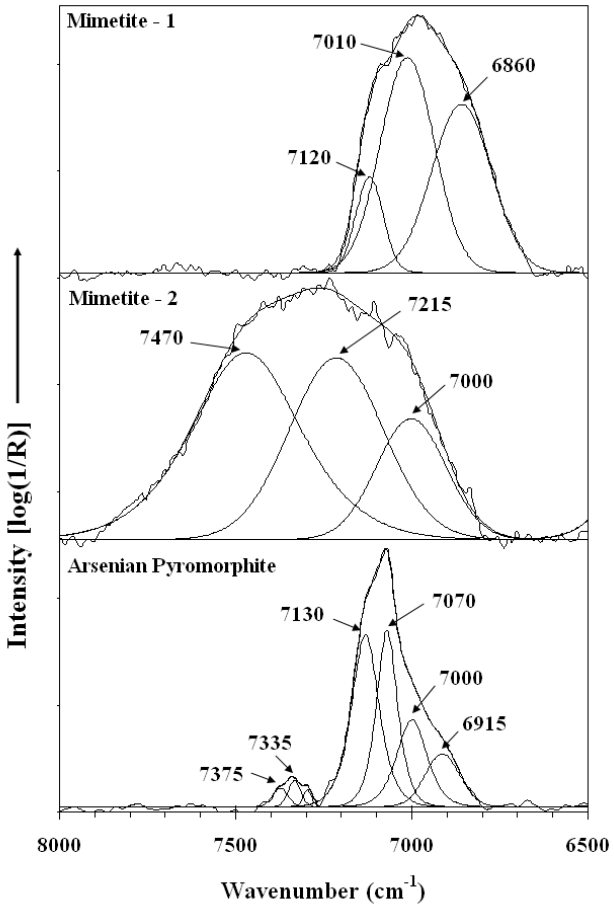
Mimetite - 1
7010
6860
7120
Mimetite - 2
7215
7470
7000
Arsenian Pyromorphite
7130
7070
7000
6915
7335
7375
Intensity [log(1/R)]
8000
7500
7000
6500
Wavenumber (cm-1)

Figure 2

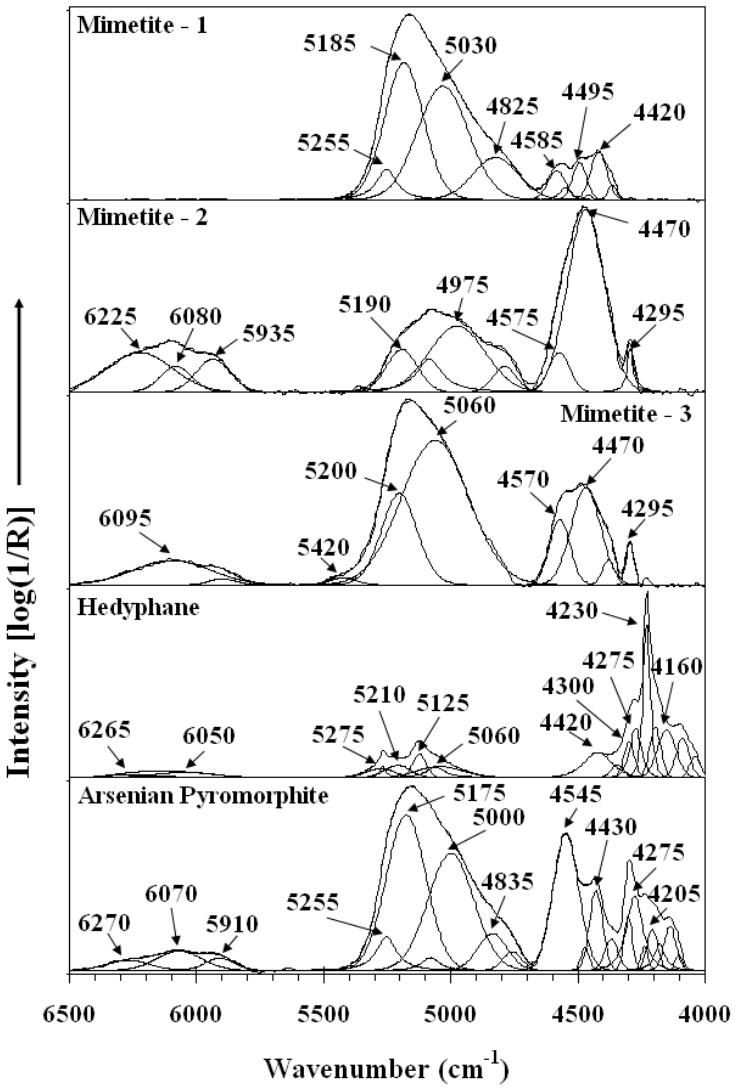
Mimetite - 1
5185
5030
4825
4495
4420
5255
4585
Mimetite - 2
4470
4975
6225
6080
5190
4575
4295
5935
Mimetite - 3
5060
4470
5200
4570
6095
4295
5420
Hedyphane
4230
4275
4160
5210
5125
4300
6265
6050
5275
5060
4420
Arsenian Pyromorphite
5175
4545
5000
4430
4275
4835
6070
5255
4205
6270
5910
Intensity [log(1/R)]
6500
6000
5500
5000
4500
4000
Wavenumber (cm-1)

Figure 3

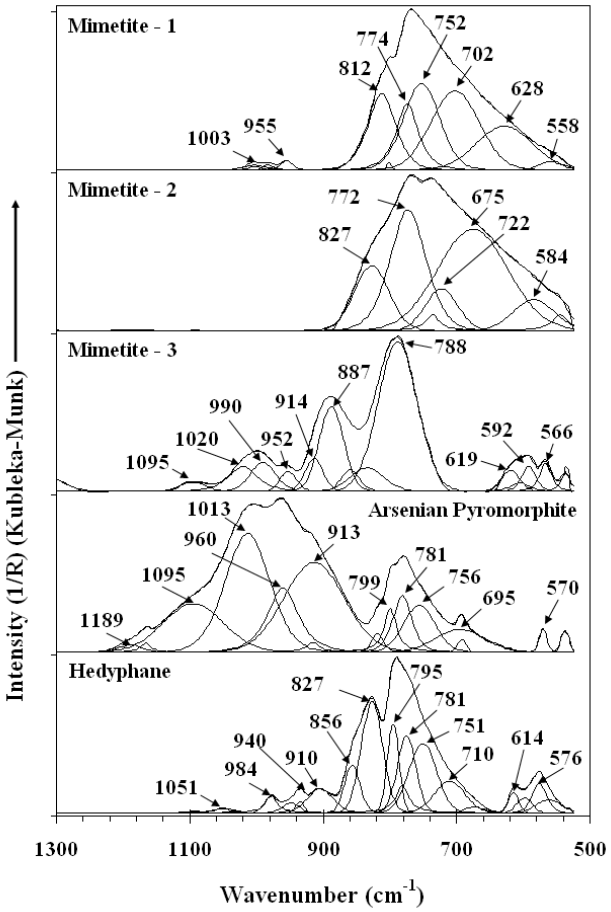

Figure 4 Mid IR spectra