Raman and infrared spectroscopy of selected vanadates

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Abstract

Raman and infrared spectroscopy has been used to study the structure of selected vanadates including pascoite, huemulite, barnesite, hewettite, metahewettite, hummerite. Pascoite, rauvite and huemulite are examples of simple salts involving the decavanadates anion $(V_{10}O_{28})^{6-}$. Decavanadate consists of four distinct VO_6 units which are reflected in Raman bands at the higher wavenumbers. The Raman spectra of these minerals are characterised by two intense bands at 991 and 965 cm^{-1}. For pascoite Raman bands are observed at 991, 965, 958 and 905 cm^{-1} and originate from four distinct VO_6 sites. The other minerals namely barnesite, hewettite, metahewettite and hummerite have similar layered structures to the decavanadates but are based upon $(V_5O_{14})^{3-}$ units. Barnesite is characterised by a single Raman band at 1010 cm^{-1}, whilst hummerite has Raman bands at 999 and 962 cm^{-1}. The absence of four distinct bands indicates the overlap of the vibrational modes from two of the VO_6 sites. Metarossite is characterised by a strong band at 953 cm^{-1}. These bands are assigned to ν_1 symmetric stretching modes of $(V_6O_{16})^{2-}$ units and terminal VO_3 units. In the infrared spectra of these minerals, bands are observed in the 837 to 860 and in the 803 to 833 cm^{-1} region. In some of the Raman spectra bands are observed for pascoite, hummerite and metahewettite in similar positions. These bands are assigned to ν_3 antisymmetric stretching of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units. Because of the complexity of the spectra in the low wavenumber region assignation of bands is difficult. Bands are observed in the 404 to 458 cm^{-1} region and are assigned to the ν_2 bending modes of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units. Raman bands are observed in the 530 to 620 cm^{-1} region and are assigned to the ν_4 bending modes of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units. The Raman spectra of the vanadates in the low wavenumber region are complex with multiple overlapping bands which are probably due to VO subunits and MO bonds.

Keywords: pascoite, huemulite, barnesite, hewettite, metahewettite, hummerite, vanadates, Raman spectroscopy, infrared spectroscopy

Introduction

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Vanadium in minerals represents the most complicated of systems because of the variable oxidation state of vanadium, and many of the minerals have been identified around a century ago [1-3]. The presence of vanadium in minerals presents the most complicated systems especially as it relates to mineral species and their crystallisation from solution. This complication is exacerbated by the range of oxidation states in the natural environment, including the supergene zone. These include V(III), V(IV), V(V). Polymerisation of V(V) as $(VO_4)^{3-}$, in more concentrated solutions, gives rise to three types of complex anions. If the pH is between 9 and 13, pyrovanadates [$(V_2O_7)^{4-}$, $(HV_2O_7)^{3-}$, $(H_2V_2O_7)^{2-}$] are formed, in the pH range 5 to 9 metavanadates [$(V_3O_9)^{3-}$, $(V_4O_{12})^{4-}$, $(H_2V_3O_{10})^{3-}$, $(HV_3O_{10})^{4-}$, $(V_5O_{15})^{5-}$,] are predominantly formed, and as solutions become more acidic decavanadates [$(V_{10}O_{28})^{6-}$] are formed. Huemulite ($Na_4MgV_{10}O_{28}.24H_2O$) is a simple salt of the decavanadate isopolyanion $(V_{10}O_{28})^{6-}$ [4] . Other vanadium minerals may precipitate out from solution. These include the so-called hexavandates which are based upon polymeric $(V_6O_{16})^{2-}$ and contain distorted layers of VO_5 and VO_6 polyhedra [5]. A somewhat similar polymeric structure occurs in the formation of $(V_5O_{14})^{3-}$ ions with the vanadium coordination spheres being tetrahedral and square planar. Minerals which correspond to these types of salts are barnesite ($Na_2V_6O16.3H_2O$) , hewettite ($CaV_6O_{16}.9H_2O$) [6-9], metahewettite ($CaV_6O_{16}.H_2O$), hummerite ($KMgV_5O_{14}.8H_2O$) [10].

The infrared spectra of selected minerals containing pentavalent vanadium have been published by Farmer [11]. There are four vibrations for $(VO_4)^{3-}$, namely the A_1 symmetric stretching mode observed at around 824 cm^{-1}, the E bending mode in the region between 305 and 345 cm^{-1}, the F_2 antisymmetric stretching mode between 780 and 855 cm^{-1} and the F_2 bending mode between 340 and 345 cm^{-1}. The F_2 modes are both Raman and infrared active whereas the A_1 and E modes are Raman active only. Farmer reported the infrared spectrum of the vanadium containing mineral pucherite. The ν_1 symmetric stretching modes were observed at 825 and 808 cm^{-1}, the ν_2 bending modes at 475, 423 and 405 cm^{-1} and the ν_4 bending modes at 610 cm^{-1}. Frederickson and Hausen made infrared spectra-structure correlation study of compounds containing vanadium and oxygen [12]. Among the compound studied were the polyvanadates including hummerite, metahewettite and pascoite. These authors stated that these minerals are the decavanadates and can be distinguished from the hexavanadates by having only one intense band in the infrared spectrum of the V-O stretching region near 975 cm^{-1} as opposed to two bands for the hexavalent vanadates[12]. Significant work has been undertaken on the Raman spectroscopy of vanadates as catalysts [13-18]. Recently Frost et al reported the vibrational spectroscopy of simple vanadate containing minerals [19, 20]. The Raman band at 844 cm^{-1}, assigned to the ν_1 symmetric (VO_4^-) stretching mode for descloizite, is shifted to 814 cm^{-1} for mottramite. The ν_3 mode of descloizite is observed as a single band at 777 cm^{-1} but this mode is more complex for mottramite with three bands observed in the 77K spectrum at 811, 785 and 767 cm^{-1}. The bending mode (ν_2) is observed at 437 cm^{-1} for descloizite and at 426 cm^{-1} for mottramite . The free vanadate ion has tetrahedral T_d symmetry. Ross reports the free aqueous vanadate ion as having a ν_1 (A_1) mode at 874 cm^{-1}, the ν_2 mode of E symmetry at 345 cm^{-1}, the ν_3 mode of F_2 symmetry at 855 cm^{-1} and the ν_4 mode also of F_2 symmetry at 345 cm^{-1}. For perfect T_d symmetry the first two modes are Raman active/infrared inactive and the last two modes both Raman and infrared active. The presence of a cation in the aqueous vanadate solution as an ion pair reduces this symmetry. In minerals the

(VO_4^-) units will not be in tetrahedral symmetry but will depend upon the VO_5 and VO_6 coordination sites.

As part of our on-going studies of the vibrational spectroscopy of minerals particularly secondary minerals, we report the Raman and infrared spectra of selected vanadium containing minerals including pascoite, huemulite, barnesite, hewettite, metahewettite and hummerite. The Raman spectra are then related to the mineral structure.

Experimental

Minerals

The minerals are listed in the table below and were checked where possible for phase purity by X-ray diffraction.

Mineral	Formula	Place of origin
Barnesite	$Na_2V_6O_{16}.3H_2O$	Cactus Rat Mine, Thompson district, Grand County, Utah, USA
Hewettite	$CaV_6O_{16}.9H_2O$	Parco #8 Mine, Yellow cat District. Thompson, Grand County, Utah, USA
Metahewettite	$CaV_6O_{16}.H_2O$	Parco #8 Mine, Yellow cat District. Thompson, Grand County, Utah, USA
Huemulite	$Na_4MgV_{10}O_{28}.24H_2O$	The Fish, Eureka County, Nevada, USA
Hummerite	$KMgV_5O_{14}.8H_2O$	Hummer Mine, Paradox valley. Montrose County, Colarado, USA
Pascoite	$Ca_3V_{10}O_{28}.17H_2O$	La Sal District, San Juan County, Utah, USA
Rossite	$CaV_2O_6.4H_2O$	Burro Mine, Slick Rock, San Miguel County, Colarado, USA
Metarossite	$CaV_2O_6.2H_2O$	Burro Mine, Slick Rock, San Miguel County, Colarado, USA

Raman microprobe spectroscopy

The crystals of the vanadate minerals were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and 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 HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident

excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Spectra at controlled temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published by the authors [19, 21-25]. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Infrared absorption 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 to 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.

Results and discussion

The Raman and infrared spectra of a series of selected vanadium containing minerals are shown in Figures 1 and 2. The results of the band component analysis of the Raman spectra are reported in Table 1. Three distinct bands are observed in the Raman spectrum of pascoite at 991, 965 and 958 cm^{-1} with bandwidths (FWHM) of 9.6, 11.8 and 8.9 cm^{-1}. The band at 958 cm^{-1} appears as a shoulder on the 965 cm^{-1} band. In contrast the infrared spectrum shows three overlapping bands at 1025, 987 and 945 cm^{-1}. The published infrared spectra gave bands at 975 and 960 cm^{-1} [12]. These bands are attributed to ν_1 symmetric stretching modes of the V=O bonds of the $(V_6O_{16})^{2-}$ units. The bands originate from four distinct VO_6 sites. The bands correspond to terminal V=O bond vibrations. According to Frederickson and Hausen, decavanadates can be distinguished from hexavanadates by having only one band in the infrared spectrum in the V-O stretching region near 975 cm^{-1} as opposed to two bands for hexavanadates. In the infrared spectrum of pascoite in this work three bands are observed which are broad with bandwidths of 56.0, 15.8, 37.9 cm^{-1}. In the transmission infrared spectrum of pascoite given by Frederickson and Hausen three bands are observed [12]. Pascoite and huemulite are decavanadates containing the polyanion $(V_{10}O_{28})^{6-}$. In contrast, two distinctly sharp bands are observed for hummerite at 999 and 962 cm^{-1} with bandwidths of 6.6 and 9.9 cm^{-1} respectively. In the infrared spectrum of hummerite given by Frederickson and Hausen two bands were shown at around 975 and 960 cm^{-1} with the former as a shoulder on the latter band [12]. In our infrared spectrum only a single band was observed at 952 cm^{-1}. The band is broad with a bandwidth of 41.6 cm^{-1}. A low intensity band is observed as a slight shoulder at 982 cm^{-1}. Hummerite is an example of a mineral containing the $(V_5O_{14})^{3-}$ anion. For hummerite two distinct bands are present at 999 and 962 cm^{-1} with corresponding infrared bands at 982 and 952 cm^{-1}. The absence of four distinct bands for hummerite suggests that there is a probable overlap of the vibrations of two of the four VO_6 sites. Pascoite former has multiple bands around 975 cm^{-1} and the latter only a single band at 952 cm^{-1}. In the Raman spectrum there are two sharp bands for both minerals. It would appear that the 'rule' suggested by Frederickson and Hausen for distinguishing between hexa and decavanadates is invalid. A mineral which also contains the decavanadate ion is the uranyl vanadate mineral rauvite. The Raman spectrum of such a mineral is more complex because of the potential overlap of bands from both the uranyl and vanadate units.

The Raman spectrum of metahewettite shows two intense bands at 994 and 954 cm^{-1}. The bands are sharp with bandwidths of 10.6 and 11.0 cm^{-1} respectively. The infrared spectrum shows a complex set of overlapping bands with curve resolved peaks at 1031, 998, 962 and 957 cm^{-1}. These bands are significantly broader than the Raman peaks with bandwidths of 43.9, 20.7, 19.3 cm^{-1}. Frederickson and Hausen reported the transmission infrared spectrum of metahewettite and two well separated peaks at 1000 and 970 cm^{-1} were observed. Metahewettite fits into the group of minerals which includes barnesite. In the Raman spectrum of barnesite, a single sharp band is observed at 1010 cm^{-1} with a bandwidth of 4.2 cm^{-1}. The observation of a single Raman band for barnesite suggests that the four VO_6 units overlap with all bands being coincident. The infrared spectrum of barnesite was not reported by Frederickson and Hausen. In the infrared spectrum of barnesite three overlapping bands are observed at 1099, 999 and 960 cm^{-1}. Barnesite is a mineral containing the $(V_5O_{14})^{3-}$ anion, which is made up of tetrahedral and square pyramidal vanadium coordination spheres. It is clear from the Raman and infrared data there are two distinct sites in barnesite. In the Raman spectrum of metarossite, an intense band is observed at 953 cm^{-1} with a second less intense band at 933 cm^{-1}. In the infrared spectrum of metarossite, a complex set of bands is observed with infrared bands found at 956, 935 and 912 cm^{-1} with bandwidths of 31.8, 19.5, and 29.8 cm^{-1}. Metarossite is an example of a metavanadate mineral. Metavanadates minerals are characterised by infinite chains of tetrahedra apically linked or by trigonal bipyramids which share edges. The Raman spectra when combined with the infrared spectra suggest there arte three distinct sites in metahewettite. Rossite, metarossite and munirite fit into this type of category. The single crystal X-ray study of metarossite contains linked trigonal bipyramids with double chains which are in turn linked by Ca^{2+} ions in square antiprismatic coordination.

In the Raman and Raman spectra of minerals such as pascoite, bands are observed in the 775 to 875 cm^{-1} region. In contrast to the bands assigned to the symmetric stretching modes, these bands tend to be broad. In the Raman spectrum of pascoite two bands are observed at 837 and 815 cm^{-1} with bandwidths of 26.3 and 40.1 cm^{-1}. In the published infrared spectrum of pascoite two bands were observed at 840 and 805 cm^{-1}[12]. An additional quite broad band was observed at 750 cm^{-1} [12]. In our infrared spectrum of pascoite, four overlapping bands are observed at 845, 812, 775 and 743 cm^{-1}. These bands are attributed to the ν_3 antisymmetric stretching modes of $(V_6O_{16})^{2-}$ units. The Raman spectrum of hummerite displays bands in similar positions with bands observed at 833 and 817 cm^{-1} with bandwidths of 19.8 and 45.0 cm^{-1}. In the published infrared spectrum of Frederickson and Hausen, three bands were observed at 845, 800 and 750 cm^{-1}. In our infrared spectrum we observe bands at 837, 803, 741 and 685 cm^{-1}. These bands are in good agreement with the published data. These bands are attributed to the ν_3 antisymmetric stretching modes. The Raman spectrum of metahewettite shows a different pattern in this region with a single band observed at 878 cm^{-1} with bandwidth of 13.0 cm^{-1}. A second very intense Raman band is observed at 692 cm^{-1} with a bandwidth of 45.2 cm^{-1}. An intense infrared band was observed at 740 cm^{-1} by Frederickson and Hausen. In our infrared spectrum bands were observed at 736 and 687 cm^{-1}. In the Raman spectrum of barnesite, three low intensity bands are observed at 761, 728, 683 and 670 cm^{-1}. In the infrared spectrum bands are observed at 794, 775, 692 and 667 cm^{-1}. These bands are assigned to the ν_3 antisymmetric stretching of $(V_5O_{14})^{3-}$ units. The Raman

spectrum of metarossite shows bands at 750 and 704 cm^{-1}. Infrared bands are found at 860, 833 and 785 cm^{-1}. These bands are ascribed to the ν_3 antisymmetric stretching vibrations.

The Raman spectrum of the free vanadate ion shows the ν_2 mode of E symmetry at 345 cm^{-1} and the ν_4 mode also of F_2 symmetry at 345 cm^{-1}. The bending mode (ν_2) was observed at 437 cm^{-1} and 426 cm^{-1} for descloizite and mottramite. The Raman spectra of pascoite, hummerite, barnesite, metarossite and metahewettite all show bands in the 404 to 470 cm^{-1} region. These bands are assigned to the (ν_2) bending modes. A band is observed in the 530 to 546 cm^{-1} region of these vanadates and is ascribed to the ν_4 bending mode. The Raman spectra in the 200 to 345 cm^{-1} region are complex to say the least and consist of several overlapping bands. The question arises as to the significance of these bands. One possibility is that the bands are from the ν_4 bending modes. Another possibility is that the bands are due to subunits such as the V_2O_2 units. Band assignment in this region is realistically not possible. Bands below 240 cm^{-1} are attributed to MO bonds and lattice vibrations.

Conclusions

Raman spectroscopy has enabled a review of the vibrational spectroscopy of the vanadate minerals. This technique has the advantages of obtaining the spectra of the minerals with no sample preparation; the minerals can be measured in situ on the host matrix; and spectra below 400 cm^{-1} can be readily measured. Bands attributed to the stretching and bending modes of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units have been assigned. In summary (a) terminal V=O bonds occur in the 900 to 1000 cm^{-1} region; (b) Bridging V-O-V bonds vibrate in the ~500 and 700 cm^{-1} region as symmetric and antisymmetric stretching modes respectively;. V-O bending modes occur in the 300 to 400 cm^{-1} region. The decavanadate ion consists of four distinct distorted VO_6 units which are observed as V=O bonds at the highest wavenumbers.

Acknowledgements

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Table 1 Results of the Raman and infrared spectral analysis of pascoite, hummerite, barnesite, metarossite and metahewettite.

pascoite			hummerite		barnesite		meta rossite		meta hewettite		Suggested assignments
Raman 298 K	IR	IR published [11]	Raman	IR	Raman	IR	Raman	IR	Raman	IR	
	1108					1099				1086	Impurities-Phosphate?
991 965 958	1025 987 945	975 960	999 962	982 952	1010	999 962	953 933	956 935 912	1013 994 954	1031 998 962 957	symmetric stretching of $(V_{10}O_{28})^{6-}$ units and terminal VO_3 units terminal V=O stretches
837 815	845 812	840 805	833 817	837 803			886 871	860 833	878		antisymmetric stretching of $(V_{10}O_{28})^{6-}$ units or $(V_5O_{14})^{3-}$ units
	775 743	750		741 685	761 728 683 670	794 775 692 667	750 704	785	692	736 687	antisymmetric stretching of bridging VOV units
619 584			590		620	596 580					Water librational modes antisymmetric stretching of V_2O_2 units ν_4 bending of VO_3 units
546			532		534		537		530		ν_3 symmetric stretching of VOV units
458			442		492 433 413		474 453 423		470 425 404		bending of VO_3 units

							387				
362 334 317 289 275			360 326 314		341 287 284 260		359 301 279 263		290 280		bending of VO_3 units V-O-V bridging bending modes
235 192 175			254 241 227 208 183 146		248 217 192 153		241 210 196 181 161		240 188 154 140		M-O and lattice modes

List of Figures

Figure 1 Raman spectra of pascoite, hummerite, barnesite, metarossite and metahewettite in the 700 to 1050 cm^{-1} region.

Figure 2 Infrared spectra of pascoite, hummerite, barnesite, metarossite and metahewettite in the 600 to 1200 cm^{-1} region.

Figure 3 Raman spectra of pascoite, hummerite, barnesite, metarossite and metahewettite in the 100 to 600 cm^{-1} region.

List of Tables

Table 1 Results of the Raman and infrared spectral analysis of pascoite, hummerite, barnesite, metarossite and metahewettite.

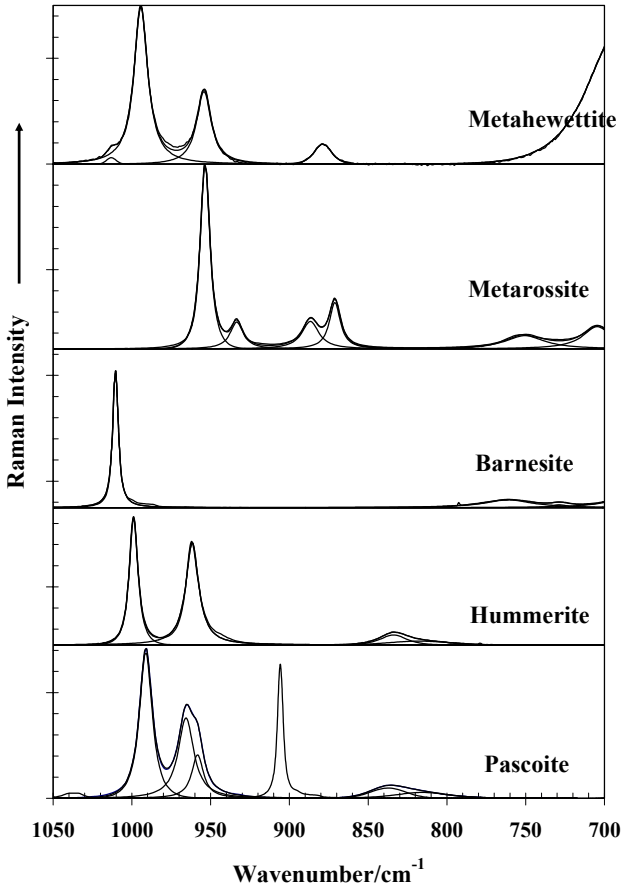
Metahewettite
Metarossite
Barnesite
Hummerite
Pascoite
Raman Intensity
1050
1000
950
900
850
800
750
700
Wavenumber/cm-1

Figure 1

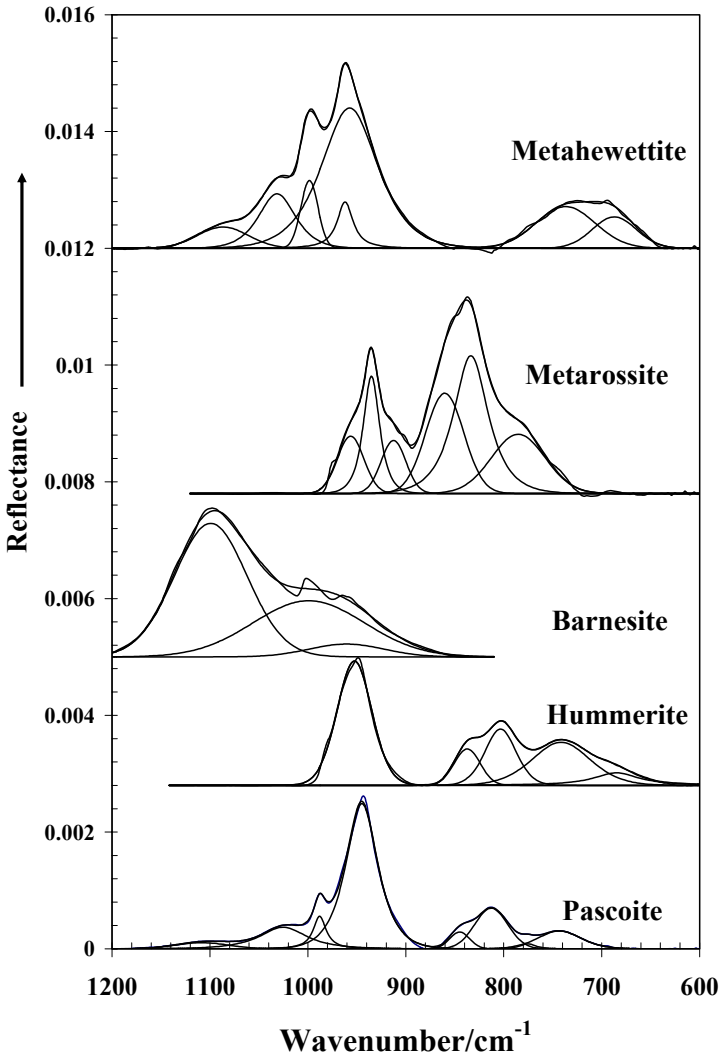
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Reflectance
Metahewettite
Metarossite
Barnesite
Hummerite
Pascoite
1200
1100
1000
900
800
700
600
Wavenumber/cm-1

Figure 2

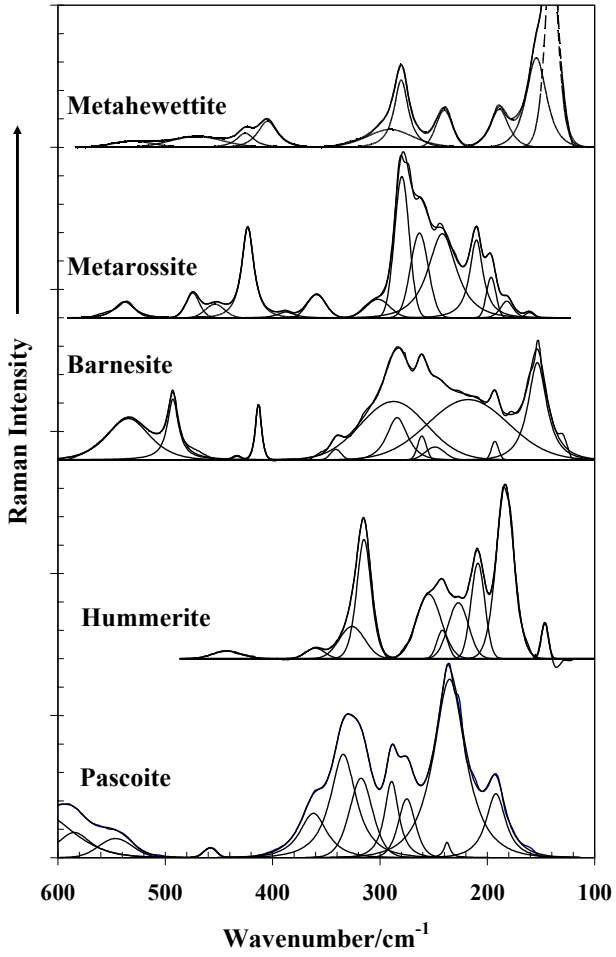
Metahewettite
Metarossite
Barnesite
Hummerite
Pascoite
Raman Intensity
600
500
400
300
200
100
Wavenumber/cm-1

Figure 3