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Raman spectroscopic study of pascoite $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 17\text{H}_2\text{O}$

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Abstract

Raman spectroscopy has been used to study the molecular structure of the vanadate mineral pascoite. Pascoite, rauvite and huemulite are examples of simple salts involving the decavanadate anion ($\text{V}_{10}\text{O}_{28}^{6-}$). Decavanadate consists of four distinct $\text{VO}_6$ units which are reflected in Raman bands occurring at higher wavenumbers. The Raman spectrum of pascoite is characterised by two intense bands at 991 and 965 cm$^{-1}$. Raman bands are observed at 991, 965, 958 and 905 cm$^{-1}$ and originate from four distinct $\text{VO}_6$ sites in the mineral structure. In the infrared spectra of pascoite, two wavenumber regions are observed between: 1) 837 and 860, and 2) between 803 and 833 cm$^{-1}$. These bands are assigned to $\nu_3$ antisymmetric stretching modes of ($\text{V}_{10}\text{O}_{28}^{6-}$) or ($\text{V}_5\text{O}_{14}^{3-}$) units. The spectrum is highly complex in the lower wavenumber region, and therefore the assignment of bands is difficult. Bands observed in the 404 to 458 cm$^{-1}$ region are assigned to the $\nu_2$ bending modes of ($\text{V}_{10}\text{O}_{28}^{6-}$) or ($\text{V}_5\text{O}_{14}^{3-}$) units. Raman bands observed in the 530 to 620 cm$^{-1}$ region are assigned to the $\nu_4$ bending modes of ($\text{V}_{10}\text{O}_{28}^{6-}$) or ($\text{V}_5\text{O}_{14}^{3-}$) 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

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INTRODUCTION

Pascoite is a hydrated calcium vanadate and is named after its place of origin Pasco, Peru. The mineral is based upon the decavanadate polyanion [1]. Linking these decavanadate anions gives the unit cationic group \((\text{Ca}_3(\text{H}_2\text{O})_{17})^{6+}\). A picture of the studied mineral is given in Fig. S1 (Supplementary Information). Vanadium in minerals represents the most complicated of systems because of the variable oxidation state of vanadium, as it relates to mineral species and their crystallisation from solution [2-4]. This complication is exacerbated by the range of oxidation states in the natural environment, including the supergene zone. These include \(\text{V}(\text{III})\), \(\text{V}(\text{IV})\), \(\text{V}(\text{V})\). In aqueous \(\text{V}(\text{V})\) solutions at low concentrations, only mononuclear species are present, \(\text{VO}^+\), \(\text{VO}^{\text{OH}_3}\), \(\text{VO}_2^{\text{OH}}\), \(\text{VO}_3^{\text{OH}_2}\) and \(\text{VO}_4^{3-}\). In contrast to this, at higher total \(\text{V}(\text{V})\) concentrations under acid conditions extensive polymerisation of vanadate occurs according to the following equations.

\[
2\text{VO}_4^{3-} + 4\text{H}^+ \leftrightarrow \text{V}_2\text{O}_7^{4+} + 2\text{H}_2\text{O} \quad \text{(pyrovanadate)}
\]

\[
3\text{VO}_4^{3-} + 6\text{H}^+ \leftrightarrow \text{V}_3\text{O}_9^{5+} + 3\text{H}_2\text{O} \quad \text{(metavanadate)}
\]

\[
2\text{V}_2\text{O}_7^{4+} + 4\text{H}^+ \leftrightarrow \text{V}_4\text{O}_{12}^{4+} + 2\text{H}_2\text{O} \quad \text{(metavanadate)}
\]

\[
5\text{V}_4\text{O}_{12}^{4+} + 8\text{H}^+ \leftrightarrow 2\text{V}_{10}\text{O}_{28}^{6-} + 4\text{H}_2\text{O} \quad \text{(decavanadate)}
\]

Protonated analogues are also present in solution. The pyrovanadates, metavanadates and decavanadates are all expressed in a number of mineral structures. Metavanadates, in the solid state, consist of infinite chains of \(\text{VO}_3^-\) composition, \((\text{VO}_3^-)_n\). The chemistry of polymerisation of vanadate in acidic solution is well understood and is reflected in many examples in the mineral kingdom. Depending upon the prevailing redox potential in solution, from which such species crystallise, highly coloured, mixed \(\text{V}(\text{IV},\text{V})\) species are formed, are called vanadium bronzes. Polymerisation of \(\text{V}(\text{V})\) as \((\text{VO}_4)^{3-}\), in more concentrated solutions, gives rise to three types of complex anions. If the pH is between 9 and 13, pyrovanadates \([\ (\text{V}_2\text{O}_7)^{4+}\), \((\text{HV}_2\text{O}_7)^{3+}\), \((\text{H}_2\text{V}_2\text{O}_7)^{2+}\) are formed, in the pH range 5 to 9 metavanadates \([\ (\text{V}_3\text{O}_9)^{5+}\), \((\text{V}_4\text{O}_{12})^{4+}\), \((\text{H}_2\text{V}_3\text{O}_{10})^{3+}\), \((\text{HV}_3\text{O}_{10})^{4+}\), \((\text{V}_5\text{O}_{15})^{5+}\) are predominantly formed, and as solutions become more acidic decavanadates \([\ (\text{V}_{10}\text{O}_{28})^{6-}\) are formed.
As part of our on-going studies of the vibrational spectroscopy of minerals particularly secondary minerals, we report the Raman of the vanadium containing mineral pascoite. The Raman spectra of pascoite are studied and compared with the Raman spectrum of pascoite from the RRUFF data base, where it has been published without any interpretation. The Raman spectra are related to the molecular structure of the mineral pascoite. It is necessary to get a full understanding of this mineral as it is a secondary mineral occurring as a leachate of near-surface vanadium oxides by ground waters and as efflorescences in mine tunnels.

EXPERIMENTAL

Minerals

The pascoite Ca₃V₁₀O₂₈·17H₂O was obtained by one of the authors (AVC) and originated from the Vanadium Queen Mine, San Juan County, Utah, USA. For comparison, a Raman spectrum of pascoite was also downloaded from the RRUFF mineral data base. This mineral originated from Arrowhead Claim, Slick Rock, San Miguel County, Colorado, USA. The spectra from the RRUFF data base is provided in the supplementary information

Raman spectroscopy

The crystals of pascoite 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. Spectra at controlled temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). 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 4000–525 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. The minerals were used as is. No sample preparation was involved.

**RESULTS AND DISCUSSION**

**Background**

The infrared spectra of selected minerals containing pentavalent vanadium have been published by Farmer [5]. 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. Frost *et al.* provided the Raman spectra of pucherite, clinobisvanite, and namibite [6] and have also undertaken studies of uranyl vanadates [7] including carnotite, curienite, francevillite, tyuyamunite and metatyuyamunite. The minerals are characterized by an intense band in the 800-824 cm\(^{-1}\) region, assigned to the \(\nu_1\) symmetric stretching vibrations of the (UO\(_2\))\(^{2+}\) units. Frederickson and Hausen made infrared spectra-structure correlation study of compounds containing vanadium and oxygen [8]. Among the compounds studied were the polyvanadates 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 attributed to the V-O stretch near 975 cm\(^{-1}\), as opposed to two bands for the hexavalent vanadates[8]. Recently Frost *et al.* reported the vibrational spectroscopy of simple vanadate containing minerals [9, 10]. The
Raman band at 844 cm\(^{-1}\), assigned to the \(\nu_1\) symmetric (\(\text{VO}_4^+\)) stretching mode for descloizite, is shifted to 814 cm\(^{-1}\) for mottramite. The \(\nu_3\) 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 (\(\nu_2\)) 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 \(\nu_1\) (A\(_1\)) mode at 874 cm\(^{-1}\), the \(\nu_2\) mode of E symmetry at 345 cm\(^{-1}\), the \(\nu_3\) mode of F\(_2\) symmetry at 855 cm\(^{-1}\) and the \(\nu_4\) 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.

**Raman Spectroscopy**

The Raman spectra of the vanadium containing mineral pascoite are shown in Fig. 1 and S1. 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 from Utah at 991, 961 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 961 cm\(^{-1}\) band. The Raman spectrum of pascoite from the RRUFF data base (Fig. S2) displays two distinct bands at 953 and 993 cm\(^{-1}\). A broad Raman peak centred at 1080 cm\(^{-1}\). This band is attributed to an impurity in the mineral, possibly silicate. Solid solution involving anionic substitution is ubiquitous in vanadate minerals. Phosphate and arsenate frequently substitute for vanadate in these minerals, albeit to different extents. The vanadate ion, \(\text{VO}_4^{3-}\), is somewhat larger than phosphate and arsenate ions, whose radii are 230 and 237 pm, respectively [11]. Other comparable ions such as silicate may also substitute with charge balance compensation. Thus, many of the formulae of the vanadate minerals conceal more complex compositions for natural materials, although substitution for vanadate is more limited in many cases than is found for mutually soluble phosphate and arsenate analogues and related minerals.
In contrast to the Raman spectrum, the infrared spectrum of the San Juan mineral shows three overlapping bands at 945, 987 and 1030 cm\(^{-1}\) (Fig. 2). Other infrared bands are observed at 746, 816 and 840 cm\(^{-1}\). The published infrared spectra gave bands at 975 and 960 cm\(^{-1}\) [8]. These bands are attributed to \(\nu_1\) symmetric stretching modes of (V\(_6\)O\(_{16}\))\(^{2-}\) units and terminal VO\(_3\) units. 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 at around 975 cm\(^{-1}\) as opposed to two bands for hexavanadates. In the infrared spectrum of pascoite in this work three bands are observed at 945, 987 and 1030 cm\(^{-1}\) 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 were observed [8]. Pascoite and huemulite are decavanadates containing the polyoxyanion (V\(_{10}\)O\(_{28}\))\(^6-\). 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 [8]. 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\(_5\)O\(_{14}\))\(^3-\) anion. Pascoite 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 of questionable validity.

In the Raman spectrum of pascoite (Fig. 3), bands are observed in the 775 to 875 cm\(^{-1}\) region. In the Raman spectrum of pascoite from the RRUFF data base, Raman bands are observed at 542, 695 and 878 cm\(^{-1}\). Considerable differences are observed in this spectral region for the two minerals. In contrast to the bands assigned to the symmetric stretching modes, these Raman bands tend to be broad. In the Raman spectrum of pascoite, two bands are observed at 815 and 841 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\(^{-1}\) [8]. An additional quite broad band was observed at 750 cm\(^{-1}\) [8]. In our infrared spectrum of pascoite, four overlapping bands are observed at 746, 816 and 840 cm\(^{-1}\). These bands are attributed to the \(\nu_3\) antisymmetric stretching modes of (V\(_6\)O\(_{16}\))\(^{2-}\) units.
The Raman spectrum of pascoite in the low wavenumber region is displayed in Fig. 4. Raman bands are observed at 292, 320, 337 and 360 cm$^{-1}$. The Raman spectrum of the RRUFF sample is very different in this spectral region (Fig. S3). Raman bands are observed at 241, 282 and 330 cm$^{-1}$. Additional bands are observed at 406 and 428 cm$^{-1}$ which appear unrelated to the vanadate anion. The bending mode ($\nu_2$) of the vanadate anion was observed at 426 cm$^{-1}$ and 437 cm$^{-1}$ for descloizite and mottramite. The Raman spectrum of the free vanadate ion shows the $\nu_2$ mode of E symmetry at 345 cm$^{-1}$ and the $\nu_4$ mode also of F$_2$ symmetry at 345 cm$^{-1}$. 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 $\nu_4$ bending modes. Another possibility is that the bands are due to subunits such as the V$_2$O$_2$ units. Band assignment in this region is realistically not possible. Bands below 240 cm$^{-1}$ are attributed to MO bonds and lattice vibrations.

The Raman spectrum in the 1300 to 1800 cm$^{-1}$ region is shown in Fig. 5. A broad band is observed at 1514 cm$^{-1}$ along with a sharp band at 1646 cm$^{-1}$ with a shoulder at 1668 cm$^{-1}$. The first broad band is attributed to an overtone band. The two bands at 1646 and 1668 cm$^{-1}$ are assigned to the bending modes of water. The position of these bands provides evidence for strongly hydrogen bonded water. Water is found in the (Ca$\text{$_3$(H$_2$O)$_{17}$}$)$^{6+}$ units. Based upon Raman spectroscopy it is suggested that two non equivalent water molecules exist in the pascoite mineral structure with slight differences in hydrogen bond lengths. The Raman spectrum of the OH stretching region is shown in Fig. 6. The spectrum is complex with multiple overlapping bands with bands observed at 3125, 3254, 3405, 3466 and 3570 cm$^{-1}$. These bands are attributed to water stretching vibrations. The observation of multiple bands supports the concept of non-equivalent water molecules in the pascoite structure. The position of the water stretching vibrations is a function of the hydrogen bond distances. The bands at 3125 and 3254 cm$^{-1}$ are associated with strong hydrogen bonds and as the wavenumber increases with the other peaks the bond distances become larger.
CONCLUSIONS

The Raman spectra of the vanadate mineral pascoite from the Vanadium Queen Mine, San Juan County, Utah, USA. have been collected and the spectra related to the molecular structure of the mineral. A comparison of the spectra obtained in this work with the Raman spectra of pascoite from the Arrowhead Claim, Slick Rock, San Miguel County, Colorado, USA from the RRUFF data base is made. Bands attributed to the stretching and bending modes of \((V_{10}O_{28})^{6-}\) units or \((V_{5}O_{14})^{3-}\) 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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REFERENCES


Table 1 Results of the Raman and infrared spectral analysis of pascoite [12, 13]

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Fig. 1  Raman spectrum of pascoite from Utah in the 900 to 1100 cm\(^{-1}\) region

Fig. 2  Infrared spectrum of pascoite from Utah in the 600 to 1200 cm\(^{-1}\) region

Fig. 3  Raman spectrum of pascoite from Utah in the 400 to 900 cm\(^{-1}\) region

Fig. 4  Raman spectrum of pascoite from Utah in the 100 to 400 cm\(^{-1}\) region

Fig. 5  Raman spectrum of pascoite from Utah in the 1300 to 1800 cm\(^{-1}\) region

Fig. 6  Raman spectrum of pascoite from Utah in the 2700 to 3700 cm\(^{-1}\) region
Pascoite
Ca$_5$[V$_{10}$O$_{28}$]·17H$_2$O
Utah USA

Fig. 1
Fig. 2

Pnictolite
$\text{Ca_3[V_3O_9]} \cdot 17\text{H}_2\text{O}$
Fig. 3

Puscoite
Ca$_3$[V$_{10}$O$_{28}$]:17H$_2$O
Utah USA
**Pascolite**

Ca$_3$(V$_{10}$O$_{28}$)·17H$_2$O

Utah USA

**Fig. 4**
Fig. 5
Fig. 6

Pascoite
Ca$_3$[V$_{10}$O$_{28}$]·17H$_2$O
Utah USA

Wavenumber/cm$^{-1}$

Raman Intensity

3466  3405  3125
3254
3570