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Raman spectroscopic study of pascoite $Ca_3V_{10}O_{28}\cdot 17H_2O$

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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 $(V_{10}O_{28})^{6-}$. Decavanadate consists of four distinct 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 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 ν_3 antisymmetric stretching modes of $(V_{10}O_{28})^{6-}$ or $(V_5O_{14})^{3-}$ 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 ν_2 bending modes of $(V_{10}O_{28})^{6-}$ or $(V_5O_{14})^{3-}$ units. Raman bands observed in the 530–620 cm^{-1} region are assigned to the ν_4 bending modes of $(V_{10}O_{28})^{6-}$ 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.

1. 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 $(Ca_3(H_2O)_{17})^{6+}$. 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 V(III), V(IV), V(V). In aqueous V(V) solutions at low concentrations, only mononuclear species are present, $VO_2{}^+$, $VO(OH)_3$, $VO_2(OH)_2{}^-$, VO_3OH^{2-} and $VO_4{}^{3-}$. In contrast to this, at higher total V(V) concentrations under acid conditions extensive polymerisation of vanadate occurs according to the following equations:

$$2VO_4{}^{3-} + 4H^+ \leftrightarrow V_2O_7{}^{4-} + 2H_2O \quad \text{(pyrovanadate)}$$

$$3VO_4{}^{3-} + 6H^+ \leftrightarrow V_3O_9{}^{3-} + 3H_2O \quad \text{(metavanadate)}$$

$$2V_2O_7{}^{4-} + 4H^+ \leftrightarrow V_4O_{12}{}^{4-} + 2H_2O \quad \text{(metavanadate)}$$

$$5V_4O_{12}{}^{4-} + 8H^+ \leftrightarrow 2V_{10}O_{28}{}^{6-} + 4H_2O \quad \text{(decavanadate)}$$

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 $VO_3{}^-$ composition, $(VO_3{}^-)_n$. 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 V(IV,V) species are formed, are called vanadium bronzes. 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 5–9 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.

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

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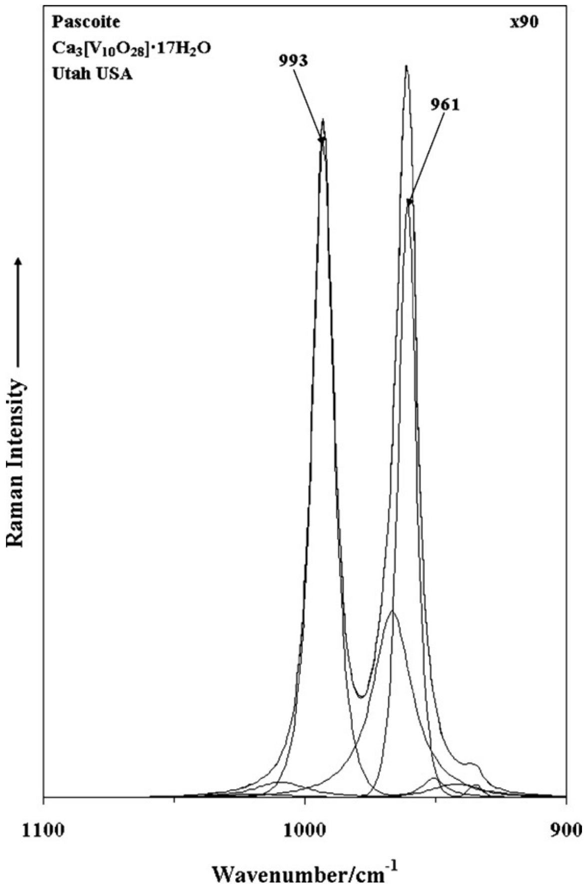

Fig. 1. Raman spectrum of pascoite from Utah in the 900–1100 cm^{-1} region.

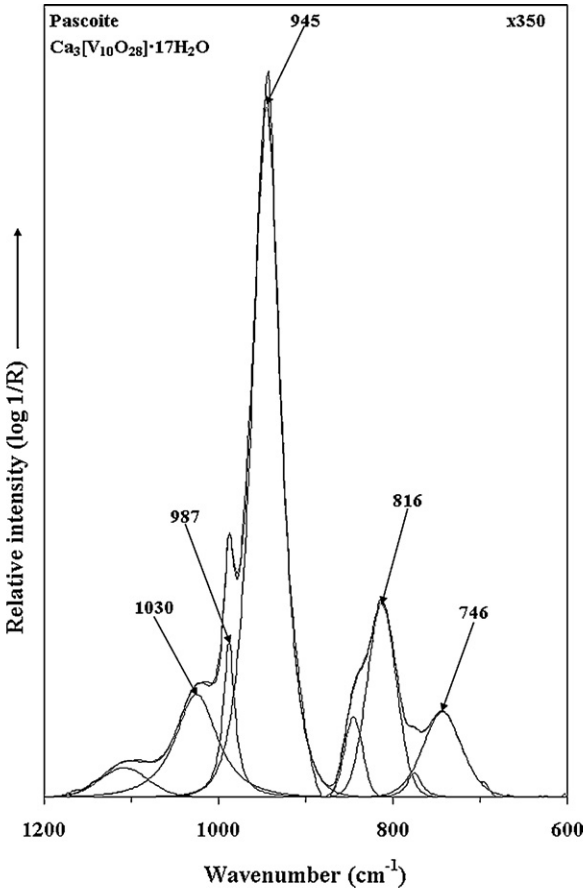

Fig. 2. Infrared spectrum of pascoite from Utah in the 600–1200 cm^{-1} region.

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.

2. Experimental

2.1. Minerals

The pascoite originated from $Ca_3V_{10}O_{28}{\cdot}17H_2O$ 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.

2.2. Raman spectroscopy

The crystals of pascoite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10× and 50× 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).

2.3. 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.

3. Results and discussion

3.1. 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,