RAMAN SPECTROSCOPY OF SELECTED VANADATES

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Abstract: This study reports on vibrational spectroscopy work of selected vanadium containing minerals including pascoite, huemulite, barnesite, hewettite, metahewettite and hummerite. The Raman and IR spectra are then related to the mineral structure.

Raman and infrared spectroscopy has been used to study the structure of selected vanadates including pascoite, huemulite, barnesite, hewettite, metahewettite, hummerite [1-7]. 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.

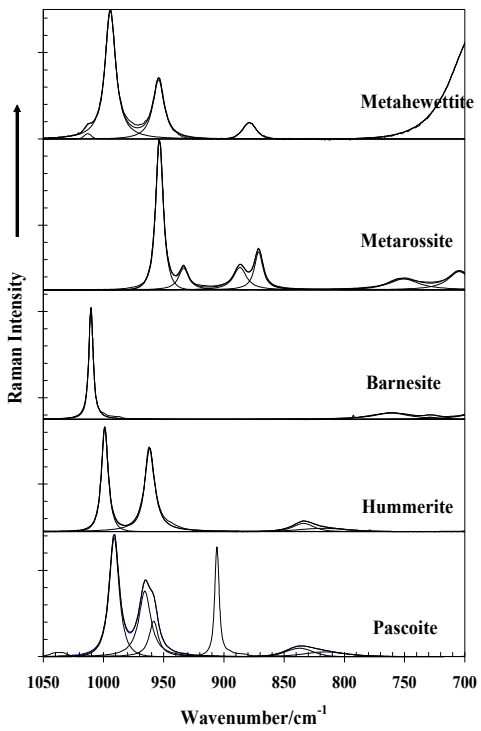

Fig 1. Raman spectra of pascoite, hummerite, barnesite, metarossite and metahewettite in the 700 to 1050 cm^{-1} region.

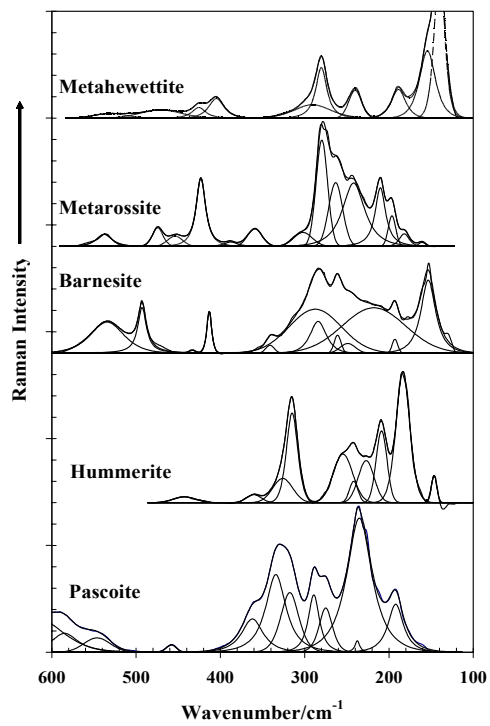

Fig 2. Raman spectra of pascoite, hummerite, barnesite, metarossite and metahewettite in the 600 to 100 cm^{-1} region.

In the infrared spectra of these minerals, bands are observed in the 837 to 860 and in the 803 to 833 cm^{-1} regions. 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. Due to 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. Raman spectroscopy enables the identification of these decavanadates minerals with each mineral having its own characteristic spectrum. Raman spectroscopy has the advantages that there is no sample preparation other than the orientation of the sample in the incident beam, and crystals of the minerals can be measured *in situ*.

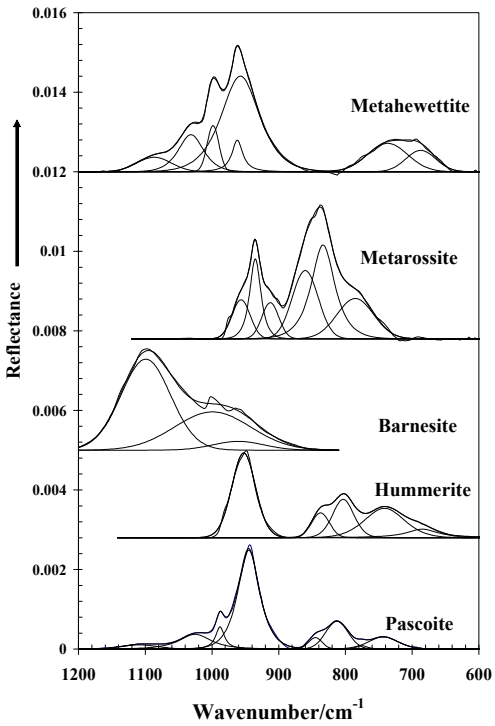

Fig 3. Infrared spectra of pascoite, hummerite, barnesite, metarossite and metahewettite in the 600 to 1200 cm^{-1} region.

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