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Raman spectroscopic study of the tellurite minerals: mackayite and quetzalcoatlite

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Abstract

Tellurites may be subdivided according to formula and structure. There are five groups based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3).xH_2O$, (c) $A_2(XO_3)_3.xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Raman spectroscopy has been used to study mackayite and quetzalcoatlite are examples of tellurites containing OH units. Raman bands for mackayite observed at 732, 782 and 579, 635 cm^{-1} are assigned to the ν_1 $(Te_2O_5)^{2-}$ symmetric stretching and ν_3 $(Te_2O_5)^{2-}$ antisymmetric stretching modes. The Raman spectral profile of quetzalcoatlite is more complex with a considerable number of overlapping bands. Two bands may be resolved at 719 and 754 cm^{-1} which may be attributed to ν_1 $(Te_2O_5)^{2-}$ symmetric stretching mode. The two Raman bands of quetzalcoatlite at 602 and 606 cm^{-1} are accounted for by the ν_3 $(Te_2O_5)^{2-}$ antisymmetric stretching mode. Raman bands for mackayite, observed at (306, 349, 379) and (424, 436 cm^{-1}) are assigned to the $(Te_2O_5)^{2-}$ ν_2 (A_1) bending mode and ν_4 (E) bending modes. This research shows that Raman spectroscopy may be applied to tellurite minerals successfully.

Keywords: tellurite, tellurate, Raman spectroscopy, mackayite, quetzalcoatlite, cliffordite, rajite, denningite

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1. Introduction

Selenites and tellurites may be subdivided according to formula and structure [1]. There are five groups based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3).xH_2O$, (c) $A_2(XO_3)_3.xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Of the selenites molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are minerals of type (b) mandarino is an example of type (c). There are no known examples of selenite minerals with formula (d) and (e). Tellurite minerals which belong to type (a) are fairbankite, balyakinite, plumbotellurite, mocktezumite, magnolite and smirnite and tellurite minerals which are type (b) include graemite, teineite and chaloalite. Zemmanite and emmonsite are examples of group (c). Rajite and denningite are examples of tellurite minerals of type (d). Tellurite minerals such as spiroffite, winstanleyite, carlfreisite and pingguite are examples of type (e). Another type of tellurite mineral are those with hydroxyl units in the structure. Included are the minerals mackayite $Fe^{3+}(OH)(Te^{4+})_2O_5$ and quetzalcoatlite $Zn_6Cu_3(TeO_6)(OH)(Ag_xPb_yCl_{x+2y})$. Further information may be obtained by consulting the web site <http://www.mindat.org/dana.php?a=34>.

The mineral mackayite $Fe^{3+}(OH)(Te^{4+})_2O_5$ is a zeolite-like tellurite with a negatively charged framework of [2-4]. Such minerals have large open channels of 8.28 Å parallel to [0001] [5]. The mineral, and related compounds, have been synthesised [6-8]. Substitution of Zn by other cations such as Mn^{2+} can occur [9, 10]. A related mineral is quetzalcoatlite $Zn_6Cu_3(TeO_6)(OH)(Ag_xPb_yCl_{x+2y})$ [11, 12]. Mackayite $Cu^{2+}(Te_2O_5)_2$, is found in the tellurium rich deposits of Mexico [13-15]. The other pyrotellurite related mineral is mackayite $Fe^{3+}(Te^{4+})_2O_5(OH)$ [2-4, 16]. According to Anthony et al. [17] some uncertainty exists as to the formula of this mineral. The importance of these tellurium bearing minerals is their open framework structures with negatively charged surfaces and zeolitic pores [18]. Other related tellurite minerals are cliffordite $UTe_3^{4+}O_9$ [19, 20] and keystoneite $Mg_{0.5}[Ni^{2+}Fe^{3+}(TeO_3)_3]_4.5H_2O$ [21, 22].

Raman spectroscopy has proven very useful for the study of minerals [23-31]. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with many minerals [32-34]. Some previous studies have been undertaken by the authors, using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions. The aim of this paper is to present Raman and infrared spectra of natural selected tellurites and to discuss the spectra from a structural point of view. It is part of systematic studies on the vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

2. Experimental

Minerals

The mineral mackayite originated from the Moctezuma mine, New Mexico. The mineral quetzalcoatlite originated from Moctezuma mine, New Mexico. The compositions have been reported by Anthony et al. (mackayite on page 416 and quetzalcoatlite page 573) [35]. For comparison a spectrum from the RRUFF database was also used [<http://rruff.info/mackayite/display=default/>]. The mineral originated from Lone Pine mine, Lone Pine Hill area, Wilcox District, Catron County, New Mexico, USA.

Raman microprobe spectroscopy

The crystals of mackayite or quetzalcoatlite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives as 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.

Infrared 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 128 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.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ 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 Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

Farmer [36] states that very little research has been undertaken on selenates/selenites or tellurates/tellurites. No minerals with the selenate ion SeO_4^{2-} have been discovered and reported [37]. The tellurite ion should show a maximum of six bands. The free ion will have C_{3v} symmetry and four modes, $2A_1$ and $2E$. Farmer based upon the work of Siebert [38, 39] defines the spectrum of $(\text{TeO}_4)^{2-}$ as $\nu_1 (A_1)$ 758 cm^{-1} , $\nu_2 (A_1)$ 364 cm^{-1} , $\nu_3 (E)$ 703 cm^{-1} and $\nu_4 (E)$ 326 cm^{-1} [36]. The comment may be made, that there is very little published on the vibrational spectroscopy of tellurite and/or tellurate minerals, especially the Raman spectroscopy of these minerals. Saltout and Mohammed have published quantum mechanical calculations for TeO_2 glasses [40]. Although a comparison of tellurium oxide glasses with natural mineral crystals is questionable, nevertheless a comparison of the spectral data may be made.

The Raman spectra of mackayite and quetzalcoatlite in the 100 to 1000 cm^{-1} region are displayed in Figure 1. For comparison the Raman spectrum for mackayite extracted from the RRUFF data base is given in Figure 2. Two Raman bands for mackayite observed at 732, 782 and 579, 635 cm^{-1} are assigned to the $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$ symmetric stretching and $\nu_3 (\text{Te}_2\text{O}_5)^{2-}$ antisymmetric stretching modes. Two bands are observed for the mackayite from Lone Pine mine, Wilcox District, Catron County, New Mexico, USA at 733 and 778 cm^{-1} . The values agree well with the bands for mackayite in Figure 1. Two Raman bands are also observed at 579 and 635 cm^{-1} which also agree well with the Raman data for the mackayite from Moctezuma mine, New Mexico. The Raman spectral profile of quetzalcoatlite is more complex with a considerable number of overlapping bands. Two bands may be resolved at 719 and 754 cm^{-1} which may be attributed to $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$ symmetric stretching mode. The two Raman bands of quetzalcoatlite at 602 and 606 cm^{-1} are accounted for by the $\nu_3 (\text{Te}_2\text{O}_5)^{2-}$ antisymmetric stretching mode.

The infrared spectra of mackayite and quetzalcoatlite are displayed in Figure 3. An intense infrared band for mackayite is observed at 1088 cm^{-1} . Bands were not observed in this position in the Raman spectrum. One possible assignment is to the OH deformation vibrations. The fact that several bands at 1020, 1088, 1166 and 1217 cm^{-1} may be resolved suggests that the OH units are not all identical in the mackayite structure. A similar observation is made for quetzalcoatlite. A complex band profile is observed in the 900 to 1180 cm^{-1} spectral region. Infrared bands observed at 862, 973, 1983 and 1164 cm^{-1} may be assigned to OH deformation bands. The low intensity infrared band of mackayite at 790 cm^{-1} is attributed to the $\nu_1 (\text{Te}_2\text{O}_5)^{2-}$ symmetric stretching mode. This infrared band is observed at 778 cm^{-1} for quetzalcoatlite. The three bands at 602, 630 and 683 cm^{-1} may therefore be assigned to $\nu_3 (\text{Te}_2\text{O}_5)^{2-}$ antisymmetric stretching modes. Two infrared bands at 645 and 694 cm^{-1} for quetzalcoatlite may be assigned to this vibrational mode. In the infrared spectra of both mackayite and quetzalcoatlite a band at around 1637 cm^{-1} is observed and is assigned to the water bending mode. The position of this band is sensitive to the strength of the hydrogen bond of the water. In these spectra the position of the band indicates significantly strong hydrogen bonds. Two possibilities may be offered: firstly water is involved in the tellurite mineral structure and secondly the water is strongly adsorbed on the mineral surface.

Raman bands for mackayite, observed at (306, 349, 379) and (424, 436 cm^{-1}) are assigned to the $(\text{Te}_2\text{O}_5)^{2-}$ ν_2 (A_1) bending mode and ν_4 (E) bending modes respectively (Figure 1). Raman bands for the USA mackayite mineral are observed at 304, 350 and 375 cm^{-1} [ν_2 (A_1) bending mode] and also 424 cm^{-1} [ν_4 (E) bending mode]. The values for the Raman spectra for the two mackayite minerals compare well. The complex Raman spectral profile of quetzalcoatlite makes the identification and consequential band assignment difficult. Two Raman bands at 319 and 364 cm^{-1} for quetzalcoatlite may be assigned to $(\text{Te}_2\text{O}_5)^{2-}$ ν_2 (A_1) bending modes. The two Raman bands at 403 and 477 cm^{-1} are assigned to the $(\text{Te}_2\text{O}_5)^{2-}$ ν_4 (E) bending modes. The two Raman bands for quetzalcoatlite at 108, 148 and 197 cm^{-1} are probably related to Cu/ZnO stretching vibrations. The sharp Raman bands at 124, 150, 177 and 243 cm^{-1} are probably related to the Fe-O-Te vibrations.

In the infrared spectrum of both mackayite and quetzalcoatlite as shown in Figure 4, a complex spectral pattern with multiple overlapping bands is observed. This spectral region is where the water and OH stretching vibrations are observed. The sharp infrared band for mackayite at 3484 cm^{-1} is assigned to the OH stretching vibrations. The two infrared bands for mackayite at 3203 and 3416 cm^{-1} are attributed to water stretching modes. The infrared spectral profile in this spectral region is complex with a series of overlapping bands. The higher wavenumber bands may be assigned to the OH stretching vibrations of the OH units. The infrared bands at 3241 and 3401 cm^{-1} are attributed to water stretching bands. The Raman spectrum of mackayite in the 3100 to 3600 cm^{-1} region is shown in Figure 5. It is noted that the spectrum of mackayite taken from the RRUFF data base is incomplete since it does not report the OH stretching region. It is noted that it was not possible to obtain the Raman spectrum of quetzalcoatlite in this spectral region. This may reflect the disordered nature of this mineral. Three Raman bands for mackayite are observed at 3216, 3285 and 3340 cm^{-1} .

4. Conclusions

Raman spectroscopy has been used to study the tellurite minerals mackayite and quelzalcoatlite, which are minerals of formula type $A_2(X_2O_5)(OH)$ where A is Fe^{3+} , for the mineral mackayite and is or Zn^{2+}, Cu^{2+} for the mineral quelzalcoatlite. Substitution by Zn or Ca may occur which may result in a more complex formula. Raman spectroscopy enables bands to be assigned to the internal vibrations which are characteristic of the $(Te_2O_5)^{2-}$ anion.

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References

- [1] J.D. Dana, Dana's Manual of Mineralogy, by W. E. Ford. 22nd edition, 2006 Wiley, London.
- [2] C. Frondel, F.H. Pough, *Am. Min.* 29 (1944) 211-225.
- [3] F. Pertlik, A. Gieren, *Neues Jahr.Min.* (1977) 145-154.
- [4] F. Pertlik, *Anz. Oester. Akad. Wissen.* (1968) 332-333.
- [5] J.A. Mandarino, E. Matzat, S.J. Williams, *Can. Min.* 14, Pt. 3 (1976) 387-390.
- [6] R. Miletich, *Monat. Chem.* 126 (1995) 417-.
- [7] M. Wildner, *Min. Petr.* 48 (1993) 215-225.
- [8] N.S. Bhuvanesh, P.S. Halasyamani, *Inorg Chem.* 40 (2001) 1404-1405.
- [9] H. Hori, Y. Dogane, M. Nakata, *Chig. Ken.* 44 (1996) 261-265.
- [10] M. Wildner, K. Langer, *Phys. Chem.Min.* 20 (1994) 460-468.
- [11] P.C. Burns, J.J. Pluth, J.V. Smith, P. Eng, I. Steele, R.M. Housley, *Am. Min.* 85 (2000) 604-607.
- [12] S.A. Williams, *Min. Mag.* 39 (1973) 261-263.
- [13] H. Zenzai, H. Nishii, M. Nakata, *Chig. Ken.* 54 (2005) 131-136.
- [14] S.A. Williams, *Min. Mag.* 43 (1979) 91-92.
- [15] R.V. Gaines, *Univ. Nacl. Autonoma Mex., Inst. Geol. Bol.* 75 (1965) 1-15.
- [16] F. Pertlik, *Tsch. Min. Petro. Mitt.* 13 (1969) 219-232.
- [17] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, *Handbook of Mineralogy, Volume V, Borates, Carbonates, Sulfates., Mineral Data Publishing, Tuscon, Arizona, U. S. A., 2003.*
- [18] J. Li, E. Makovicky, *Neues Jahr.Min.* 176 (2001) 269-297.
- [19] R. Fischer, M. Schlatti, J. Zemann, *Anz. Oester. Akad. Wissen.* 5 (1969) 93-94.
- [20] R.V. Gaines, *Am. Min.* 54 (1969) 697-701.
- [21] A.C. Roberts, T.S. Ercit, A.J. Criddle, G.C. Jones, R.S. Williams, F.F. Cureton, II, M.C. Jensen, *Min. Mag.* 58 (1994) 417-424.
- [22] A.C. Roberts, M. Bonardi, J.D. Grice, T.S. Ercit, W.W. Pinch, *Can. Min.* 27 (1989) 129-131.
- [23] R.L. Frost, J. Cejka, G. Ayoko, *J. Raman Spec.* 39 (2008) 495-502.
- [24] R.L. Frost, J. Cejka, G.A. Ayoko, M.J. Dickfos, *J. Raman Spec.* 39 (2008) 374-379.
- [25] R.L. Frost, J. Cejka, M.J. Dickfos, *J. Raman Spec.* 39 (2008) 779-785.
- [26] R.L. Frost, M.J. Dickfos, J. Cejka, *J. Raman Spec.* 39 (2008) 582-586.
- [27] R.L. Frost, M.C. Hales, D.L. Wain, *J. Raman Spec.* 39 (2008) 108-114.
- [28] R.L. Frost, E.C. Keefe, *J. Raman Spec.* in press (2008).
- [29] R.L. Frost, A. Locke, W.N. Martens, *J. Raman Spec.* 39 (2008) 901-908.
- [30] R.L. Frost, B.J. Reddy, M.J. Dickfos, *J. Raman Spec.* 39 (2008) 909-913.
- [31] S.J. Palmer, R.L. Frost, G. Ayoko, T. Nguyen, *J. Raman Spec.* 39 (2008) 395-401.
- [32] R.L. Frost, M.J. Dickfos, *J. Raman Spec.* 38 (2007) 1516-1522.
- [33] R.L. Frost, S.J. Palmer, J.M. Bouzaid, B.J. Reddy, *J. Raman Spec.* 38 (2007) 68-77.
- [34] R.L. Frost, M.L. Weier, P.A. Williams, P. Leverett, J.T. Kloprogge, *J. Raman Spec.* 38 (2007) 574-583.
- [35] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, *Handbook of Mineralogy, Mineral Data Publishing, Tuscon, Arizona, USA, 2000.*

- [36] V.C. Farmer, Editor, Mineralogical Society Monograph 4: The Infrared Spectra of Minerals, 1974.
- [37] V.C. Farmer, Mineralogical Society Monograph 4: The Infrared Spectra of Minerals, 1974.
- [38] H. Siebert, Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie (Anorganische und Allgemeine Chemie in Einzeldarstellungen, Bd. 7) (Application of Vibrational Spectroscopy in Inorganic Chemistry (Monographs in Inorganic and General Chemistry, Vol. 7)), 1966.
- [39] H. Siebert, Z. anorg. u. allgem. Chem. 301 (1959) 161-170.
- [40] I. Shaltout, A. Mohamed Tarek, Spectrochim. Act. 67 (2007) 450-454.

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Figure 2 Raman spectrum of mackayite in the 100 to 1000 cm^{-1} region taken from the RRUFF data base.

Figure 3 Infrared spectrum of mackayite and quetzalcoalite in the 550 to 1600 cm^{-1} range

Figure 4 Infrared spectrum of mackayite and quetzalcoalite in the 2700 to 3700 cm^{-1} range

Figure 5 Raman spectrum of mackayite and quetzalcoalite in the 3100 to 3600 cm^{-1} range

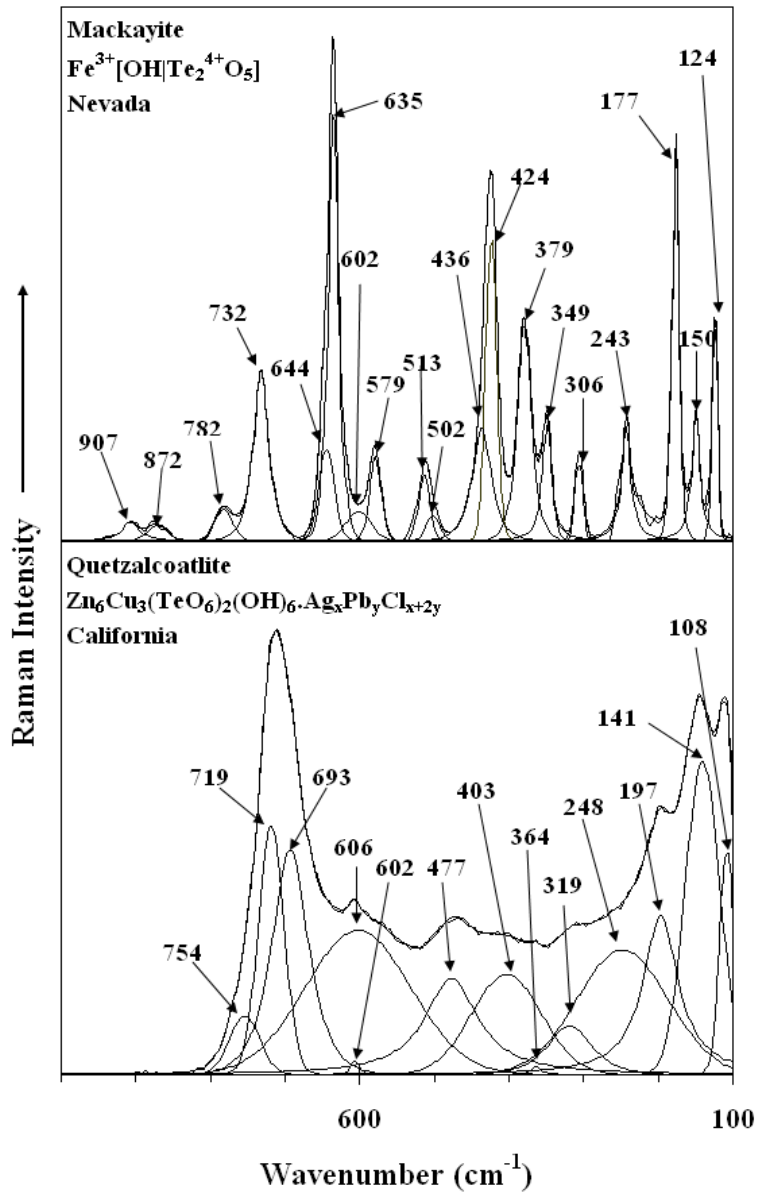


Figure 1

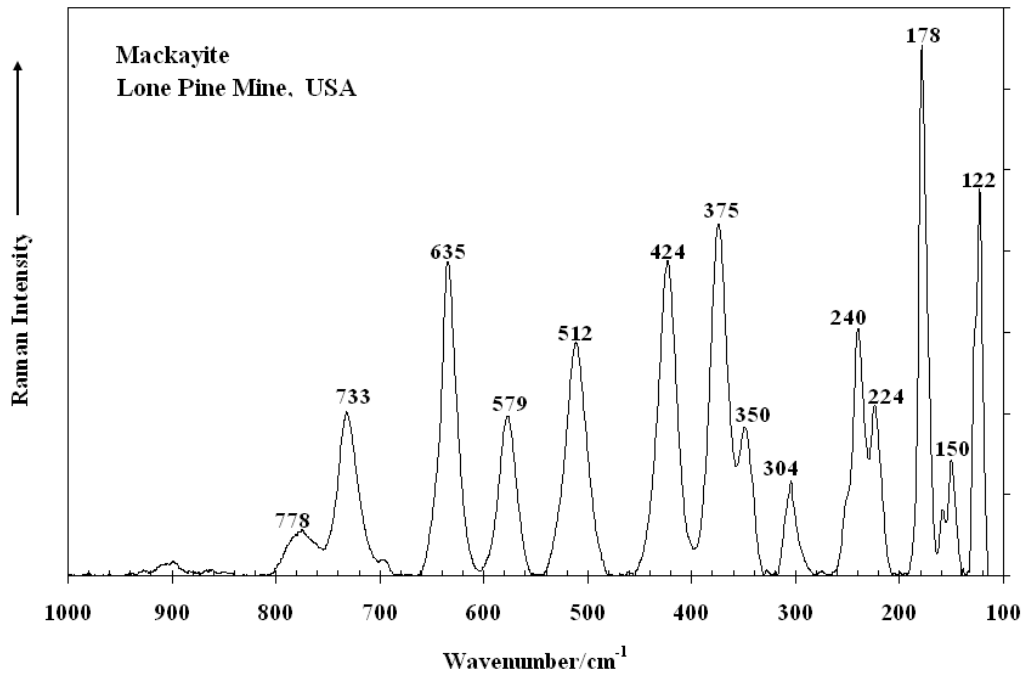


Figure 2

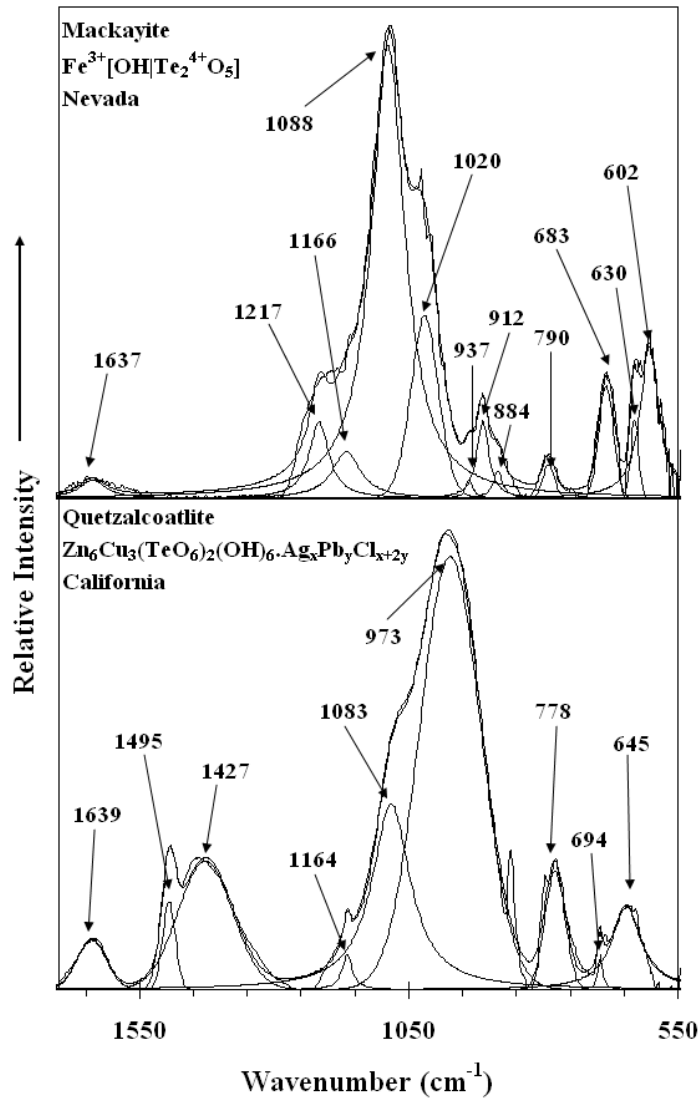


Figure 3

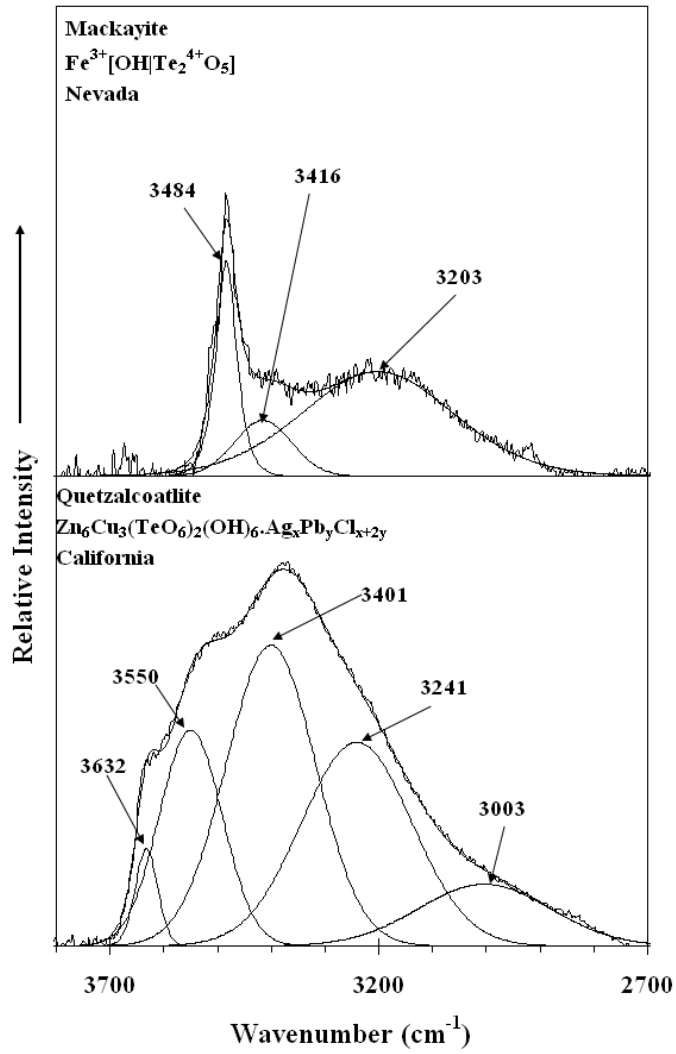


Figure 4

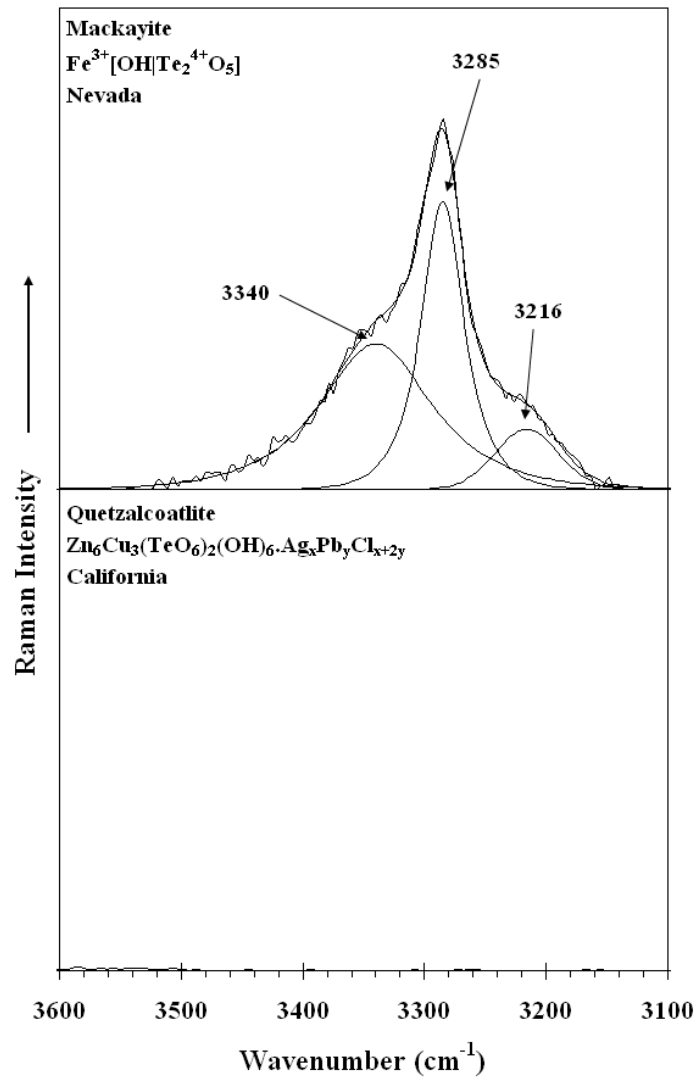


Figure 5