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# A Raman and infrared spectroscopic study of the uranyl silicates –weeksite, soddyite and haiweeite

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## Abstract

Raman spectroscopy has been used to study the molecular structure of a series of selected uranyl silicate minerals including weeksite  $K_2[(UO_2)_2(Si_5O_{13})] \cdot H_2O$ , soddyite  $[(UO_2)_2SiO_4 \cdot 2H_2O]$  and haiweeite  $Ca[(UO_2)_2(Si_5O_{12}(OH)_2)(H_2O)_3]$  with  $UO_2^{2+}/SiO_2$  molar ratio 2:1 or 2:5. Raman spectra clearly show well resolved bands in the 750 to 800  $cm^{-1}$  region and in the 950 to 1000  $cm^{-1}$  region assigned to the  $\nu_1$  modes of the  $(UO_2)^{2+}$  units and to the  $(SiO_4)^{4-}$  tetrahedra. For example soddyite is characterised by Raman bands at 828.0, 808.6, 801.8  $cm^{-1}$  ( $UO_2^{2+}$  ( $\nu_1$ )), 909.6 and 898.0  $cm^{-1}$  ( $UO_2^{2+}$  ( $\nu_3$ )), 268.2  $cm^{-1}$  and 257.8 and 246.9  $cm^{-1}$  are assigned to the  $\nu_2$  ( $\delta$ ) ( $UO_2^{2+}$ ). Coincidences of the  $\nu_1$  ( $UO_2^{2+}$ ) and the  $\nu_1$  ( $SiO_4^{4-}$ ) is expected. Bands at 1082.2, 1071.2, 1036.3, 995.1, 966.3  $cm^{-1}$  are attributed to the  $\nu_3$  ( $SiO_4^{4-}$ ). Sets of Raman bands in the 200 to 300  $cm^{-1}$  region are assigned to  $\nu_2$   $\delta$  ( $UO_2^{2+}$ ) and UO ligand vibrations. Multiple bands indicate the non-equivalence of the UO bonds and the lifting of the degeneracy of  $\nu_2$   $\delta$  ( $UO_2^{2+}$ ) vibrations. The  $(SiO_4)^{4-}$  tetrahedral are characterized by bands in the 470 to 550  $cm^{-1}$  and in the 390 to 420  $cm^{-1}$  region. These bands are attributed to the  $\nu_4$  and  $\nu_2$  ( $SiO_4^{4-}$ ) bending modes. The minerals show characteristic OH stretching bands in the 2900 to 3500  $cm^{-1}$  and 3600 to 3700  $cm^{-1}$ .

**Key words:** uranyl silicate minerals, weeksite, haiweeite, soddyite, infrared and Raman spectroscopy

## Introduction

According to Burns (2001), uranyl silicates are common constituents of the oxidized portions of uranium deposits and typically form as a result of their alteration of uraninite [1, 2]. They are important for understanding the genesis of uranium deposits, as well as fluid-rock interaction during the hydration-oxidation weathering of uranium deposits or the mine and mill tailings that result from resource utilization. Uranyl silicates are also significant to the disposal of nuclear waste.

Uranyl silicates are likely to be abundant in a geological repository for nuclear waste under moist oxidizing conditions, owing to the alteration of spent nuclear fuel

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and borosilicate waste glass. An understanding of the structures of uranyl silicates may be a key to understanding the long-term performance of a geological repository for nuclear waste [3]. It is likely that uranyl compounds forming due to alteration of nuclear waste incorporate radionuclides into their crystal structures [2, 4, 5].

Nine uranyl silicate minerals (uranophane, sklodowskite, cuprosklodowskite, boltwoodite, sodium boltwoodite, kasolite, oursinite and swamboite) have been classified as members of the uranophane group on the basis of the  $\text{UO}_2^{2+}/\text{SiO}_2$  molar ratio being 1:1 and a similar uranophane anion sheet topology [6-11].  $\beta$ -uranophane is a polymorph of uranophane ( $\alpha$ -uranophane), and the details of their structural connectivities differ substantially [10-12]. Soddyite is characterized by the  $\text{UO}_2^{2+}/\text{SiO}_2$  molar ratio 2:1 and framework crystal structure [13, 14]. The crystal structure of  $\text{Na}_2(\text{UO}_2)_2\text{SiO}_4\text{F}_2$  is structurally related to soddyite [15]. The molar ratio  $\text{UO}_2^{2+}/\text{SiO}_2$  2:5 was found in the crystal structures of weeksite [3], haiweeite [1], coutinhoite [16] and probably also in some not approved uranyl silicate minerals from Russia [17]. Some synthetic framework uranyl silicates were also described [18-21].

Čejka reviewed all available data on infrared spectra of uranyl silicate minerals and their synthetic analogues [22] (Čejka 1999 and many references therein). Biwer et al. (1990) shortly described the only available Raman spectra of uranophane, sodium boltwoodite, weeksite and soddyite without any detailed interpretation [23]. Plesko et al. (1992) presented infrared vibrational characterization and synthesis of a family of hydrous alkali uranyl silicates and hydrous uranyl silicate minerals [24]. However, their interpretation is questionable. Chernorukov's team prepared monovalent and divalent uranyl silicates and presented their properties inclusive interpretation of the infrared spectra [25-33]. As shown by Čejka (1999), some infrared spectra of uranyl silicate minerals including their assignment have been published but only very few of Raman spectra of these minerals without any detailed attribution are available [22]. Some discrepancies in the IR spectra of uranyl silicate minerals published by various authors can be observed caused probably by ill-defined minerals, different IR spectrophotometers used for the measurements, and incorrect crystallochemical formulas used for the interpretation. In this paper, the Raman and IR spectra of uranyl silicate minerals are interpreted respecting the newest single crystal structures of individual minerals, accepted and approved chemical formulas, and crystallochemical application of uranyl anion sheet topology established by Burns [6, 9, 11, 12].

Akhmanova et al. (1963) proved the position of silanol, SiOH, vibrations in  $(\text{SiO}_3\text{OH})^{3-}$  ions in the IR spectrum of minerals [34, 35]. This was supported by Plyusnina (1977) [36] and for the uranyl silicate minerals by Gevorkyan [37-39], Čejka and Urbanec [40], and Čejka [22]. Vochten et al. (1997) confirmed this observation in the IR spectrum of natural and synthetic boltwoodite and synthetic uranophane and sklodowskite [41, 42]. On this basis, Burns inferred the presence of SiOH in the single crystal structure of boltwoodite. Nyfeler and Armbruster (1998) discussed silanol groups in minerals and inorganic compounds [43]. Chernorukov et al. (see above for details) also assigned some bands in the IR spectra of synthetic uranyl silicates to silanol groups [25-33].

In this paper, Raman and infrared spectra of soddyite, weeksite, and haiweeite are studied. As a part of our on-going research into the use of vibrational

spectroscopy in particular Raman spectroscopy to assist in the elucidation of the structures of minerals especially secondary minerals, we report the Raman and infrared spectra of some uranyl silicate minerals in particular weeksite, soddyite and haiweeite. These spectra are then related to the recently known mineral structures.

## Experimental

### Minerals

The minerals used in this study and their origin are reported in Table 1. Where possible the chemical composition was checked by EDAX measurements and the phase purity by powder X-ray diffraction.

### Raman microprobe spectroscopy

The crystals of uranyl silicate mineral was 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  $2\text{ cm}^{-1}$  in the range between 100 and  $4000\text{ cm}^{-1}$ . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the  $520.5\text{ cm}^{-1}$  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 liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the techniques which have been applied to the study of uranyl compounds have been published by the authors [44-50].

### 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  $4000\text{--}525\text{ cm}^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of  $4\text{ cm}^{-1}$  and a mirror velocity of  $0.6329\text{ cm/s}$ . Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

## Results and discussion

The ideal linear uranyl group,  $(\text{UO}_2)^{2+}$ , with point group symmetry  $D_{\infty h}$  has four normal vibrations, but only three fundamentals: the Raman active symmetric stretching vibration  $\nu_1$  ( $900\text{--}700\text{ cm}^{-1}$ ), the doubly degenerate IR active bending vibration  $\nu_2$  ( $\delta$ ) ( $350\text{--}180\text{ cm}^{-1}$ ), and the antisymmetric IR active stretching vibration  $\nu_3$  ( $1000\text{--}850\text{ cm}^{-1}$ ). The decrease of uranyl group symmetry  $D_{\infty h} \Rightarrow C_{\infty v}$  results in the IR activation of the  $\nu_1$   $(\text{UO}_2)^{2+}$ , similarly, the change in symmetry  $D_{\infty h} \Rightarrow C_{2v}$  adds the splitting of the doubly degenerate  $\nu_2$   $(\text{UO}_2)^{2+}$ . The former one is due to the presence of nonequivalent bonds in uranyl,  $(\text{O-U-O})^{2+}$ , the latter one in the linearity loss, i.e.  $(\text{O-U-O})^{2+}$  angle deformation. The  $\nu_1$  and  $\nu_3$   $(\text{UO}_2)^{2+}$  may also split in two or more components. This may be influenced especially because of the presence of

symmetrically distinct uranyls in the unit cell and, splitting of degenerate vibrations, and also respecting the factor group analysis.

The ideal  $(\text{SiO}_4)^{4-}$  tetrahedron with point group symmetry  $T_d$  has nine normal vibrations characterized by four fundamental distinguishable modes of vibration: the Raman active symmetric stretching vibration  $\nu_1 (A)$ , ( $819 \text{ cm}^{-1}$ ), the Raman active doubly degenerate bending vibration  $\nu_2 (E)$ , ( $340 \text{ cm}^{-1}$ ), Raman and infrared active triply degenerate antisymmetric stretching vibration  $\nu_3 (F_2)$ , ( $956 \text{ cm}^{-1}$ ), and the Raman and infrared active triply degenerate bending vibration  $\nu_4 (F_2)$ , ( $527 \text{ cm}^{-1}$ ) [51]. The symmetry decrease from  $T_d \Rightarrow C_{3v}$ , which is the case of  $(\text{SiO}_3\text{OH})^{3-}$ , results in IR activation of the  $\nu_1 (A_1)$  and  $\nu_2 (E)$ , and splitting of the both  $\nu_3$  and  $\nu_4$  (both  $A_1 + E$ ). The presence of one proton in the apex of the  $(\text{SiO}_4)^{4-}$  tetrahedron, i. e. formation of  $(\text{SiO}_3\text{OH})^{3-}$ , together with bonding of the remaining three oxygens in the uranyl silicate layers leads to lowering of the  $(\text{SiO}_3\text{OH})^{3-}$  site symmetry to  $C_s$  or  $C_1$ . This symmetry lowering is connected with IR and Raman activation of all vibrations, i.e. the  $\nu_1 (A \text{ or } A)$ , the  $\nu_2$  splits ( $A' + A''$  or  $2A$ ), and further splitting of the  $\nu_3$  and  $\nu_4$  ( $2A + A''$  or  $3A$ ). Number of bands may be enhanced because of the presence of symmetrically distinct  $\text{Si}^{4+}$  in the crystal structure of some uranyl silicate minerals.

According to McMillan (1984), for the framework silicates and silicates with multilayer structures, their formation may be considered as polymerization of  $(\text{SiO}_4)$  tetrahedra by corner-sharing each oxygen with two  $(\text{SiO}_4)$  units [52]. This results in a coupling of the  $\nu_1$  and  $\nu_3$  types of modes. The vibrations follow the frequency order  $\nu_3 (\text{Si-O-Si}) > \nu (\text{Si-O}^-) > \nu_1 (\text{Si-O-Si}) > \delta (\text{Si-O-Si}), \delta (\text{O-Si-O})$ , where  $\nu_3 (\text{Si-O-Si})$  and  $\nu_1 (\text{Si-O-Si})$  refer to the antisymmetric and symmetric stretching modes of Si-O-Si bridges,  $\nu (\text{Si-O}^-)$  represents the stretching (Si-O<sup>-</sup>) bonds,  $\delta (\text{Si-O-Si})$  and  $\delta (\text{O-Si-O})$  refer to the Si-O-Si and O-Si-O bending modes [19, 20]. Spectra of weeksite, haiweeite and coutinhoite will be discussed from this point of view. According to Chernorukov et al. wavenumbers of bands attributed to silanols, Si-OH, are located near  $3200 \text{ cm}^{-1}$  ( $\nu$  SiOH stretching mode),  $1400$  and  $600 \text{ cm}^{-1}$  ( $\delta$  SiOH in-plane and out-of-plane bending mode, respectively) [26, 28]. The most important for the interpretation may be the isolated band observed near  $1400 \text{ cm}^{-1}$  [22]. Similar conclusions were made for double  $(\text{Np}^{6+}\text{O}_2)^{2+}$  and  $(\text{Pu}^{6+}\text{O}_2)^{2+}$  potassium silicates  $\text{K}[(\text{NpO}_2)(\text{SiO}_3\text{OH})] \cdot \text{H}_2\text{O}$  and  $\text{K}[(\text{PuO}_2)(\text{SiO}_3\text{OH})] \cdot \text{H}_2\text{O}$  [53].

Water molecules possessing the point group  $C_{2v}$  are characterized by three fundamentals:  $\nu$  OH stretching vibrations ( $\nu_1$  and  $\nu_3 \text{ H}_2\text{O}$ ) ( $\sim 3600 - 2900 \text{ cm}^{-1}$ ), and  $\delta \text{ H}_2\text{O}$  bending vibration ( $1700-1590 \text{ cm}^{-1}$ ). All vibrations are IR and Raman active.  $\text{H}_2\text{O}$  libration modes may occur in the range  $1100-300 \text{ cm}^{-1}$ . Hydroxyl ions,  $(\text{OH})^-$ , (point group symmetry  $C_{\infty v}$ ) are usually indicated by sharp bands between  $3700-3450 \text{ cm}^{-1}$  but sometimes lower if any appreciable amount of hydrogen bonding is involved. The restricted rotational or libration motion of this ion occurs with a wavenumber usually in the  $600-300 \text{ cm}^{-1}$  range. The  $\delta \text{ M-OH}$  bending vibration may occur over a wide range below approximately  $1500 \text{ cm}^{-1}$ .

The Raman spectra of weeksite, soddyite and haiweeite in the  $700$  to  $1050 \text{ cm}^{-1}$  region are shown in Figure 1 and the infrared spectra of weeksite, soddyite and haiweeite in the  $500$  to  $1300 \text{ cm}^{-1}$  region are shown in Figure 2. The results of the band component analyses of the Raman and infrared spectra are reported in Tables 1

and 2 respectively. The Raman spectra of weeksite, soddyite and haiweeite in the low wavenumber region (100 to 600 $\text{cm}^{-1}$ ) are shown in Figure 3. The Raman and infrared spectra of weeksite, soddyite and haiweeite in the hydroxyl stretching region (2800 to 3800 $\text{cm}^{-1}$ ) are shown in Figures 4 and 5 respectively. The infrared spectra of the water HOH bending region are shown in Figure 6.

### *Soddyite*

Soddyite  $[(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}]$  has only one structurally (symmetrically) identical  $\text{U}^{6+}$  and one structurally (symmetrically) identical  $\text{Si}^{4+}$  in its crystal structure,  $Z=8$  [14]. Bands at 904.5 (IR) (Raman 898.0)  $\text{cm}^{-1}$  (soddyite1) and 909.8 and 899.6 (909.6 and 896.8)  $\text{cm}^{-1}$  (soddyite2) are assigned to the  $\nu_3 (\text{UO}_2)^{2+}$  vibrations. The  $\nu_1 (\text{UO}_2)^{2+}$  vibrations may be connected with the bands at 853.2 (?) (844.4, 835.6, 824.0, 810.9)  $\text{cm}^{-1}$ , and 828.0, 808.6, 801.8 (838.3, 828.6, 819.9)  $\text{cm}^{-1}$ , respectively. A coincidences of the  $\nu_1 (\text{UO}_2)^{2+}$  and the  $\nu_1 (\text{SiO}_4)^{4-}$  is supposed and expected. In the Raman spectrum, bands at 268.2  $\text{cm}^{-1}$  and 257.8 and 246.9  $\text{cm}^{-1}$ , respectively, are assigned to the  $\nu_2 (\delta) (\text{UO}_2)^{2+}$ . Bands at 1082.2, 1071.2, 1036.3, 995.1, 966.3 (1248.4, 1124.0, 1048.5, 1035.2, 1004.4)  $\text{cm}^{-1}$ , and 971.0 (1025.5)  $\text{cm}^{-1}$ , respectively, are attributed to the  $\nu_3 (\text{SiO}_4)^{4-}$ . Bands at 879.1, 853.2 (?) (844.4, 835.6, 824.0, 810.9)  $\text{cm}^{-1}$ , and 860.4, 828.0, 808.6 (838.3, 828.6, 819.9)  $\text{cm}^{-1}$ , respectively are connected with the  $\nu_1 (\text{SiO}_4)^{4-}$ . As mentioned above, a coincidence (an overlapping) of the  $\nu_1 (\text{SiO}_4)^{4-}$  and  $\nu_1 (\text{UO}_2)^{2+}$  may be expected in this region. The  $\nu_4 (\text{SiO}_4)^{4-}$  vibrations are located at 686.4, 658.3, 602.5, 538.3 (687.6, 561.6, 531.6, 492.4)  $\text{cm}^{-1}$ , and 615.7, 603.9, 581.3, 539.1 (591.4, 459.4)  $\text{cm}^{-1}$ . Bands observed at lower wavenumbers are related to the  $\nu_2 (\text{SiO}_4)^{4-}$ ,  $\nu_2 (\delta) (\text{UO}_2)^{2+}$ , external modes of  $\text{H}_2\text{O}$ ,  $\nu$  M-O, and lattice vibrations.

Bands at 3559.4, 3458.4, 3244.1, 2957.2, 2952.0, 2921.6, 2854.3  $\text{cm}^{-1}$ , and 3565.1, 3451.3, 3343.7, 3265.0, 2989.6  $\text{cm}^{-1}$ , respectively, are assigned to the  $\nu$  OH. The  $\delta$   $\text{H}_2\text{O}$  vibrations are observed at 1625.2  $\text{cm}^{-1}$ , and 1598.1, 1578.1 (1584.2, 1569.2)  $\text{cm}^{-1}$ , respectively. According to Moll et al. (1995), a band at 1588  $\text{cm}^{-1}$  with a shoulder at 1635  $\text{cm}^{-1}$  [54]. This shoulder should be attributed to the water adsorbed on the sample surface. Bands at 797.6, 711.2 (750.0)  $\text{cm}^{-1}$ , and 801.8 (?), 754.0 (791.0)  $\text{cm}^{-1}$  may be attributed to the  $\text{H}_2\text{O}$  libration modes. The presence of strong to weak hydrogen bonding networks in the crystal structures of soddyite samples studied was inferred [55].

### *Weeksite and related minerals*

Weeksite is given by  $\text{K}_2[(\text{UO}_2)_2(\text{Si}_5\text{O}_{13})] \cdot \text{H}_2\text{O}$  ( $Z=16$ ) and haiweeite, by the formula  $\text{Ca}[(\text{UO}_2)_2(\text{Si}_5\text{O}_{12}(\text{OH})_2)(\text{H}_2\text{O})_3]$ , ( $Z=4$ ). The published IR spectrum of coutinhoite,  $\text{Th}_{0.5}[(\text{UO}_2)_2(\text{Si}_5\text{O}_{13})] \cdot 1-3.5 \text{H}_2\text{O}$  ( $Z=16$ ) is also included [16]. Simplified formulas are used for weeksite [3] haiweeite [12] and coutinhoite [16].

Absorption bands in the IR spectra of weeksite at 916.1, 903.2 and most probably also at 861.5  $\text{cm}^{-1}$ , weeksite(2) at 910.8 and 861.7  $\text{cm}^{-1}$ , haiweeite at 908.5 and 877.3  $\text{cm}^{-1}$ , and coutinhoite at 907  $\text{cm}^{-1}$  were assigned to the  $\nu_3 (\text{UO}_2)^{2+}$ . Two bands at 919.6 and 886.9  $\text{cm}^{-1}$  observed in the Raman spectrum of haiweeite were also

attributed to the  $\nu_3$  ( $\text{UO}_2$ )<sup>2+</sup>. No bands related to this vibration were observed in Raman spectra of both weeksite samples. In Raman spectra, absorption bands at 813.7, 810.2 and 800.2  $\text{cm}^{-1}$  (weeksite(1)), 812.7, 808.7 and 796.7  $\text{cm}^{-1}$  (weeksite (2)), and 807.7 and 799.7  $\text{cm}^{-1}$  (haiweeite) are assigned to the  $\nu_1$  ( $\text{UO}_2$ )<sup>2+</sup> vibrations. In Raman spectra, bands at 266.2 and 264.0  $\text{cm}^{-1}$  (weeksite (1) and weeksite (2), respectively), and 264.0 and 260.4  $\text{cm}^{-1}$  (haiweeite) may be attributed to the  $\nu_2$  ( $\delta$ ) ( $\text{UO}_2$ )<sup>2+</sup>. The number of some of these vibrations is enhanced. This is supported by the number of symmetrically distinct  $\text{U}^{6+}$  in the crystal structures of weeksite (4) and haiweeite (2), number of molecules in the unit cell (weeksite 16, haiweeite 4) and FGA.

Absorption bands in the IR spectra at 1172.7, 1170.4, 11010.2, 1044.2, 1020.8, 982.3 and 952.8 (Raman 1154.5, 1008.0, 961.6 and 939.6)  $\text{cm}^{-1}$  (weeksite (1)), 1174.6, 1122.5, 1067.5, 1043.1, 985.0, 975.7 (1163.0, 1148.4, 1007.7, 960.7, 938.9)  $\text{cm}^{-1}$  (weeksite(2)), 1224.5, 1164.9, 1090.5, 1037.4, 978.4 (1163.0, 1148.4, 1007.7, 960.7, 938.9)  $\text{cm}^{-1}$  (haiweeite), and 1102, 1061 and 988  $\text{cm}^{-1}$  (coutinhoite) are assigned to the  $\nu_3$  (Si-O-Si) and  $\nu$  (Si-O) vibrations, those at 784.2, 743.5, 697.7, 635.6 and 613.9 (765.3, 744, 573.9)  $\text{cm}^{-1}$  (weeksite(1)), 784.0, 741.2, 636.2, 621.3, 590.9 (771.6, 748.3, 744.2, 573.9)  $\text{cm}^{-1}$  (weeksite (2)), 784.9, 748.2, 710.5, 621.7 (756.1, 724.4, 588.9) (haiweeite), 788, 698, 639, 585  $\text{cm}^{-1}$  (coutinhoite) the  $\nu_1$  (Si-O-Si), and those at 524.6 (521.4, 479.7)  $\text{cm}^{-1}$  (weeksite (1)), 532.9 (517.9, 480.0) (weeksite (2)), (473.4, 418.4)  $\text{cm}^{-1}$  (haiweeite), and 535, 452, 415  $\text{cm}^{-1}$  (coutinhoite) to the  $\delta$  (Si-O-Si) and probably also  $\nu$  ( $\text{U-O}_{\text{ligand}}$ ). Bands at lower wavenumbers may be attributed to the  $\delta$  (Si-O-Si),  $\delta$  (O-Si-O),  $\delta$  ( $\text{UO}_2$ )<sup>2+</sup>,  $\nu$  (M-O) (molecular deformation and lattice modes?). These conclusions may be supported by the presence of ten symmetrically distinct  $\text{Si}^{4+}$  in weeksite and four symmetrically distinct  $\text{Si}^{4+}$  in haiweeite. According to Atencio et al. (2004), coutinhoite is probably isostructural with weeksite.

All three minerals contain molecular water. In the IR spectra, absorption bands assigned to the  $\nu$  OH vibrations were observed in the range 3605.7-2942.5  $\text{cm}^{-1}$  (weeksite (1)), 3605.3-2848.9  $\text{cm}^{-1}$  (weeksite (2)), 3581.5-3233.1  $\text{cm}^{-1}$  (haiweeite), and 3609, 3535, 3468 and 3242  $\text{cm}^{-1}$  (coutinhoite). The  $\delta$   $\text{H}_2\text{O}$  vibrations were observed at 1653.8 and 1622.7 (1637.6)  $\text{cm}^{-1}$  (weeksite (1)), 1652.7 and 1622.4 (1638.7)  $\text{cm}^{-1}$  (weeksite (2)), 1636.7  $\text{cm}^{-1}$  (haiweeite), and 1627  $\text{cm}^{-1}$  (coutinhoite). According to Libowitzky (1999), strong to very weak hydrogen bonding networks should be arranged in the crystal structure of all three minerals. Bands at 1468.3  $\text{cm}^{-1}$  (weeksite (1)), 1442.5  $\text{cm}^{-1}$  (weeksite (2)), 1423.1  $\text{cm}^{-1}$  (haiweeite), and 1434, 1403 and 1386  $\text{cm}^{-1}$  (coutinhoite) may indicate the presence of silanols, Si-OH, in the crystal structure of all three minerals, however, this agrees only with the crystal structure of haiweeite.

## Conclusions

Raman spectroscopy has enabled the characteristic spectra of a suite of uranyl silicates of the 2:1 group to be obtained. These spectra are characteristic of the particular mineral being studied. The application of Raman spectroscopy enabled excellent band separation with no overlap of bands due to different vibrating units as

is found with infrared spectroscopy. This separation enabled definitive assignment of the bands.

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## References

- [1]. P. C. Burns, *Can. Miner.* 39 (2001) 1153.
- [2]. P. C. Burns, R. C. Ewing and M. L. Miller, *J. Nuc. Mat.* 245 (1997) 1.
- [3]. J. M. Jackson and P. C. Burns, *Can. Miner.* 39 (2001) 187.
- [4]. P. C. Burns, K. M. Deely and S. Skanthakumar, *Radiochim. Acta* 92 (2004) 151.
- [5]. P. C. Burns, *Can. Miner.* 36 (1998) 1069.
- [6]. P. C. Burns, R. Finch and Editors, *Uranium: Mineralogy, Geochemistry and the Environment. (Proceedings of a Short Course held 22-23 October 1999 in Golden, Colorado.) [In: Rev. Mineral., 1999; 38], 1999.*
- [7]. P. C. Burns and F. C. Hill, *Can. Miner.* 38 (2000) 163.
- [8]. P. C. Burns and K. M. Deely, *Can. Miner.* 40 (2002) 1579.
- [9]. P. C. Burns, *Materials Research Society Symposium Proceedings* 802 (2004) 89.
- [10]. P. C. Burns, R. C. Ewing and F. C. Hawthorne, *Can. Miner.* 35 (1997) 1551.
- [11]. P. C. Burns, M. L. Miller and R. C. Ewing, *Can. Miner.* 34 (1996) 845.
- [12]. P. C. Burns, *Revs in Miner.* 38 (1999) 23.
- [13]. P. C. Burns, *J. Nuc. Mat.* 265 (1999) 218.
- [14]. F. Demartin, C. M. Gramaccioli and T. Pilati, *Acta Cryst.*, C48 (1992) 1.
- [15]. N. Blaton, R. Vochten, O. M. Peeters and K. Van Springel, *Neues Jahr. Miner.* (1999) 253.
- [16]. D. Atencio, F. M. S. Carvalho and P. A. Matioli, *Am. Miner.* 89 (2004) 721.
- [17]. G. A. Sidorenko, N. V. Chukanov and I. S. Naumova, *Mineralogicheskii Zh.* 23 (2001) 55.
- [18]. Y. Huang, Z. Jiang and W. Schwieger, *Micro. Mesoporous Mat.* 26 (1998) 215.
- [19]. Y. Huang, Z. Jiang and W. Schwieger, *Can. J. Chem.* 77 (1999) 495.
- [20]. Y. Huang, Z. Jiang and W. Schwieger, *Chem. Mats* 11 (1999) 1210.
- [21]. J. Huang, X. Wang and A. J. Jacobson, *J. Mat. Chem.* 13 (2003) 191.
- [22]. J. Cejka, *Revs in Miner.* 38 (1999) 521.
- [23]. B. M. Biwer, W. L. Ebert and J. K. Bates, *J. Nuc. Mat.* 175 (1990) 188.
- [24]. E. P. Plesko, B. E. Scheetz and W. B. White, *Am. Miner.* 77 (1992) 431.
- [25]. N. G. Chernorukov and V. E. Kortikov, *Zhu. Neorganicheskoi Khimii* 45 (2000) 1949.
- [26]. N. G. Chernorukov and V. E. Kortikov, *Radiochem. (Moscow)(Translation of Radiokhimiya)* 42 (2000) 446.
- [27]. N. G. Chernorukov and V. E. Kortikov, *Zh. Neorganicheskoi Khimii* 45 (2000) 1110.
- [28]. N. G. Chernorukov and V. E. Kortikov, *Russian J. Gen. Chem.* 71 (2001) 1669.
- [29]. N. G. Chernorukov and V. E. Kortikov, *Zh. Neorganicheskoi Khimii* 46 (2001) 1949.
- [30]. N. G. Chernorukov and V. E. Kortikov, *Radiochem.* 43 (2001) 229.
- [31]. N. G. Chernorukov and V. E. Kortikov, *Zh. Neorganicheskoi Khimii* 46 (2001) 222.
- [32]. N. G. Chernorukov and V. E. Kortikov, *Radiochem.* 44 (2002) 446.
- [33]. N. G. Chernorukov and V. E. Kortikov, *Zh. Neorganicheskoi Khimii* 47 (2002) 232.

- [34]. M. V. Akhmanova and L. L. Leonova, Tr. Mineralog. Muzeya, Akad. Nauk SSSR No. 14 (1963) 3.
- [35]. M. V. Akhmanova, A. V. Karyakin and G. B. Yukhnevich, Geokhimiya 6 (1963) 581.
- [36]. I. I. Plyusnina, *Infrared Spectra of Minerals*, 1977.
- [37]. S. V. Gevork'yan and A. S. Povarennykh, Mineralogicheskii Zhurnal 2 (1980) 29.
- [38]. S. V. Gevork'yan, A. O. Matkovskii, A. S. Povarennykh and G. A. Sidorenko, Mineralogicheskii Zhurnal 1 (1979) 78.
- [39]. S. V. Gevork'yan, A. S. Povarennykh, S. I. Ignatov and E. A. Il'chenko, Miner. Zhurnal 3 (1981) 3.
- [40]. J. Cejka, Jr., A. Muck and J. Cejka, Neues Jahr. Miner. (1985) 115.
- [41]. R. Vochten, N. Blaton, O. Peeters, K. Van Springel and L. Van Haverbeke, Can. Min. 35 (1997) 735.
- [42]. R. Vochten, N. Blaton and O. Peeters, Neues Jahr. Miner. (1997) 569.
- [43]. D. Nyfeler and T. Armbruster, Am. Miner. 83 (1998) 119.
- [44]. R. L. Frost, Spectrochim. Acta. 60 (2004) 1469.
- [45]. R. L. Frost and M. Weier, Spectrochim. acta. 60 (2004) 2399.
- [46]. R. L. Frost, Spectrochim. Acta, 60A (2004) 1469.
- [47]. R. L. Frost, O. Carmody, K. L. Erickson, M. L. Weier and J. Cejka, J. Molec. Struc. 703 (2004) 47.
- [48]. R. L. Frost, D. A. Henry and K. Erickson, J. Raman Spec. 35 (2004) 255.
- [49]. R. L. Frost and M. L. Weier, J. Raman Spec. 35 (2004) 299.
- [50]. R. L. Frost, M. L. Weier and M. O. Adebajo, Thermochim. Acta 419 (2004) 119.
- [51]. K. Nakamoto, J. Wiley & Sons, New York, 484 pp. (1986).
- [52]. P. Mcmillan, Amer. Miner. 69 (1984) 622.
- [53]. G. B. Andreev, A. M. Fedoseev, V. P. Perminov and N. A. Budantseva, Radiochem. 45 (2003) 488.
- [54]. H. Moll, W. Matz, G. Schuster, E. Brendler, G. Bernhard and H. Nitsche, J. Nuc. Mat. 227 (1995) 40.
- [55]. E. Libowitzky, Monatshefte fuer Chemie 130 (1999) 1047.

**Table 1 Sample details**

<b>Mineral</b>	<b>Formula</b>	<b>Locale</b>	<b>#</b>
Weeksite	$K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$	Anderson's Mine, Yavapai Co. Arizona, USA	M33365
Haiweeite	$Ca(UO_2)_2[Si_5O_{12}(OH)_2] \cdot 4.5H_2O$	Teofild Otoni, Minas Gerais, Brazil	M44481
Soddyite	$(UO_2)_2SiO_4 \cdot 2H_2O$	Katanga, Congo, Zaire	M27299

<b>m33365 Weekiste</b>			<b>m27299 soddyite</b>			<b>m44481 haweite</b>		
<b>Center</b>	<b>FWHM</b>	<b>%</b>	<b>Center</b>	<b>FWHM</b>	<b>%</b>	<b>Center</b>	<b>FWHM</b>	<b>%</b>
<b>3610</b>	46.8	7.2				<b>3606</b>	51.0	3.5
<b>3548</b>	52.0	34.9						
			<b>3516</b>	148.6	22.1			
<b>3497</b>	125.3	35.9				<b>3498</b>	150.8	37.0
			<b>3414</b>	172.1	71.7			
						<b>3375</b>	80.4	3.0
<b>3356</b>	253.7	22.0				<b>3273</b>	369.1	45.3
			<b>3158</b>	185.0	6.1			
						<b>2923</b>	90.7	8.8
						<b>2875</b>	45.6	1.8
						<b>2851</b>	15.7	0.6
<b>1637</b>	54.4	0.6						
			<b>1584</b>	67.8	0.7			
			<b>1569</b>	17.0	0.1			
<b>1154</b>	43.9	1.5				<b>1170</b>	18.1	0.3
						<b>1115</b>	21.5	0.7
						<b>1108</b>	43.6	2.7
						<b>1087</b>	5.3	0.1
			<b>1025</b>	15.0	6.3	<b>1019</b>	15.3	7.0
<b>1008</b>	23.1	5.8				<b>1015</b>	13.1	1.8
<b>962</b>	32.1	0.6						
<b>939</b>	26.6	7.9				<b>936</b>	16.9	6.0
			<b>909</b>	9.8	0.4	<b>919</b>	15.6	2.7
			<b>897</b>	16.9	0.3	<b>887</b>	14.2	0.1
			<b>838</b>	15.5	5.8			
			<b>828</b>	9.4	35.8			
<b>814</b>	15.8	25.1	<b>820</b>	21.6	13.2			
<b>810</b>	14.7	8.9				<b>808</b>	15.1	11.5
<b>800</b>	30.0	17.0	<b>791</b>	111.5	8.4	<b>799</b>	30.7	32.4
<b>765</b>	68.5	6.9				<b>756</b>	28.0	1.1
<b>744</b>	19.4	1.1						
			<b>591</b>	10.5	1.3	<b>724</b>	38.0	1.5
<b>574</b>	27.9	3.8				<b>589</b>	17.0	3.8
<b>521</b>	37.1	1.0						
<b>480</b>	23.3	0.9				<b>473</b>	21.1	1.7
			<b>459</b>	15.5	2.8			
						<b>418</b>	33.4	1.1
<b>349</b>	23.4	3.2	<b>355</b>	18.3	0.6	<b>375</b>	21.3	1.5
<b>333</b>	16.9	1.1						
						<b>317</b>	74.0	3.3
			<b>310</b>	12.6	4.9	<b>307</b>	14.9	1.9
<b>301</b>	29.5	2.3	<b>290</b>	12.5	3.1			
						<b>283</b>	7.5	0.1
<b>266</b>	44.1	4.8				<b>264</b>	17.3	2.3
			<b>258</b>	7.6	0.6	<b>260</b>	67.9	6.8
			<b>247</b>	18.4	1.4			
			<b>229</b>	16.3	1.6	<b>236</b>	15.1	0.3

<b>210.0</b>	27.6	5.2	<b>219.4</b>	13.9	3.2			
			<b>190.9</b>	21.8	4.0	<b>191.7</b>	21.0	8.3
<b>167.5</b>	46.7	1.9	<b>164.5</b>	16.6	4.1			
			<b>129.3</b>	12.1	0.4	<b>148.1</b>	21.9	0.2
<b>112.6</b>	15.3	0.4	<b>111.4</b>	5.5	0.1	<b>108.3</b>	10.8	0.8
			<b>101.9</b>	6.2	0.8			

**Table 2 Raman spectral analysis of the uranyl silicate minerals weeksite, haiweeite, soddyite**

m33365 Weeksite			m27299 soddyite			m44481 haweite		
Center	FWHM	%	Center	FWHM	%	Center	FWHM	%
<b>3605</b>	49.7	1.1				<b>3582</b>	96.5	0.7
<b>3550</b>	81.6	1.4	<b>3565</b>	82.0	2.3			
<b>3494</b>	134.5	1.5				<b>3467</b>	207.1	3.8
<b>3412</b>	214.5	2.8	<b>3451</b>	152.6	5.9			
			<b>3343</b>	119.6	2.4			
			<b>3265</b>	299.9	13.5	<b>3233</b>	440.0	8.8
<b>3205</b>	349.1	7.2	<b>2989</b>	278.1	3.3			
<b>2942</b>	237.8	1.4						
<b>1653</b>	50.3	0.3				<b>1636</b>	57.8	1.1
<b>1622</b>	40.0	1.5	<b>1598</b>	74.0	1.9			
			<b>1578</b>	22.7	1.0			
<b>1468</b>	160.6	0.3				<b>1423</b>	110.0	1.6
						<b>1224</b>	54.0	2.3
<b>1172</b>	17.9	0.1				<b>1164</b>	79.5	8.1
<b>1170</b>	81.3	2.1						
<b>1101</b>	89.4	10.1				<b>1090</b>	68.2	18.3
<b>1044</b>	66.3	9.9				<b>1037</b>	65.4	17.6
<b>1020</b>	23.5	0.5						
<b>982</b>	80.5	22.0	<b>971</b>	33.2	2.0	<b>978</b>	62.0	15.9
<b>952</b>	22.5	0.5						
<b>916</b>	40.9	3.2	<b>909</b>	87.4	25.6	<b>908</b>	44.2	7.6
<b>903</b>	18.1	0.5	<b>899</b>	23.5	2.1			
<b>861</b>	77.2	22.7	<b>860</b>	41.9	13.8	<b>877</b>	42.1	6.0
			<b>828</b>	18.1	3.1			
			<b>808</b>	19.2	2.9	<b>808</b>	47.6	3.5
			<b>801</b>	60.0	8.4			
<b>784</b>	43.7	5.6				<b>784</b>	32.3	3.0
<b>743</b>	59.8	3.2	<b>754</b>	91.9	5.4	<b>748</b>	69.2	1.0
<b>697</b>	25.3	0.3				<b>710</b>	9.8	0.2
<b>635</b>	20.8	0.9						
<b>613</b>	37.1	0.8	<b>615</b>	21.3	3.5	<b>621</b>	26.0	0.3
			<b>603</b>	24.9	1.3			
			<b>581</b>	39.6	1.1			
<b>541</b>	15.5	0.3	<b>539</b>	27.0	0.6			
<b>524</b>	83.5	0.0				<b>524</b>	167.0	0.0

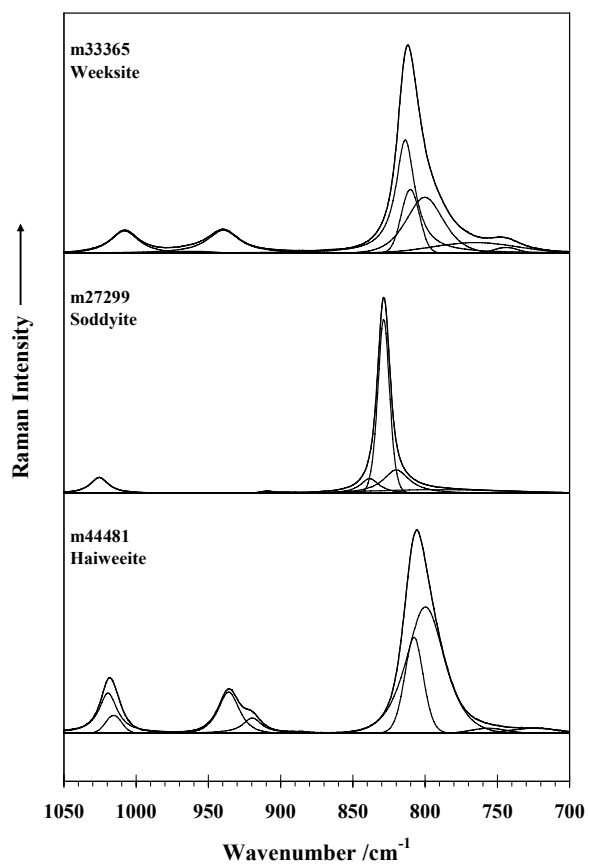
**Table 3 Infrared spectral analysis of the uranyl silicate minerals weeksite, haiweeite, soddyite**

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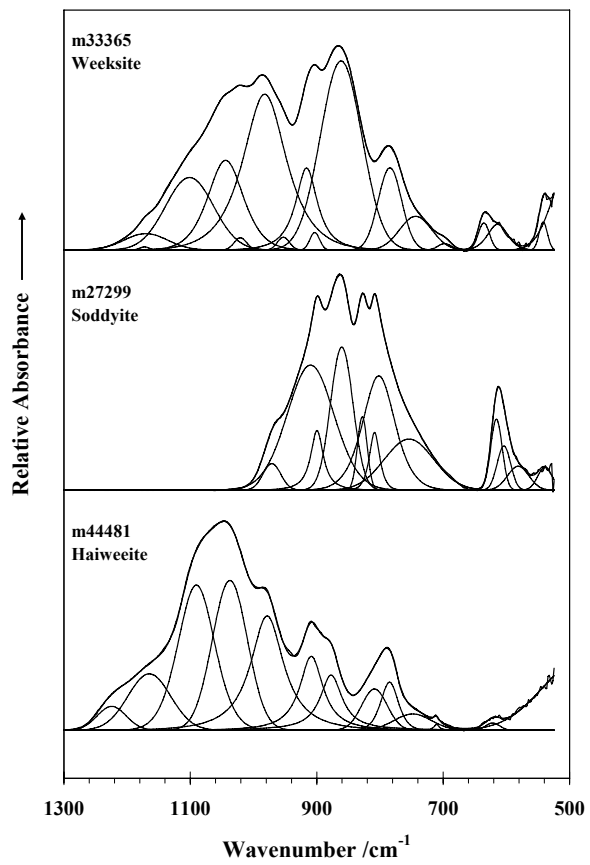
- Figure 1** Raman spectra of weeksite, soddyite and haiweeite in the 700 to 1050  $\text{cm}^{-1}$  region
- Figure 2** infrared spectra of weeksite, soddyite and haiweeite in the 500 to 1300  $\text{cm}^{-1}$  region
- Figure 3** Raman spectra of weeksite, soddyite and haiweeite in the low wavenumber region (100 to 600 $\text{cm}^{-1}$ ).
- Figure 4** Raman spectra of weeksite, soddyite and haiweeite in the hydroxyl stretching region (2800 to 3800 $\text{cm}^{-1}$ ).
- Figure 5** Infrared spectra of weeksite, soddyite and haiweeite in the hydroxyl stretching region (2800 to 3800 $\text{cm}^{-1}$ ).
- Figure 6** Infrared spectra of weeksite, soddyite and haiweeite in the water HOH bending region (1500 to 1800 $\text{cm}^{-1}$ ).

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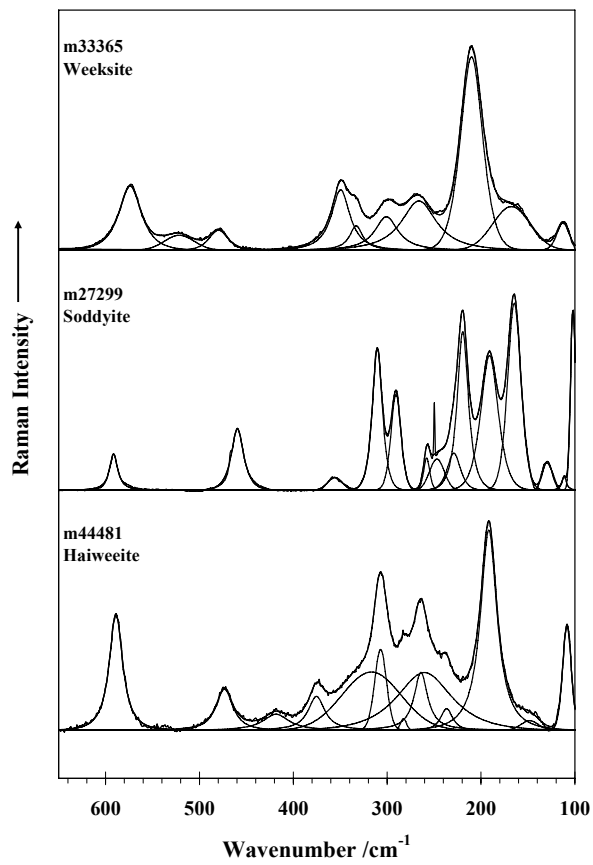
- Table 1** Sample details
- Table 2** Raman spectral analysis of the uranyl silicate minerals weeksite, haiweeite, soddyite
- Table 3** Infrared spectral analysis of the uranyl silicate minerals weeksite, haiweeite, soddyite



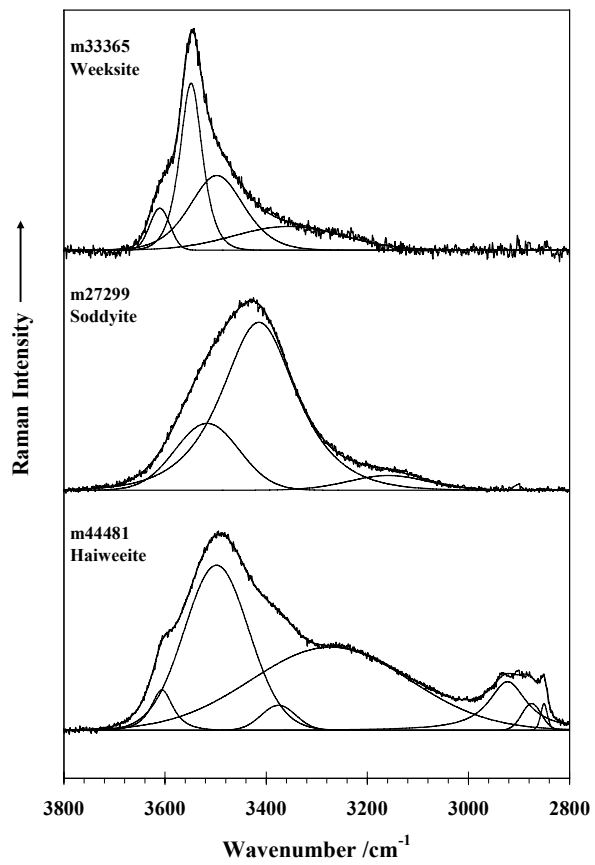
**Figure 1**



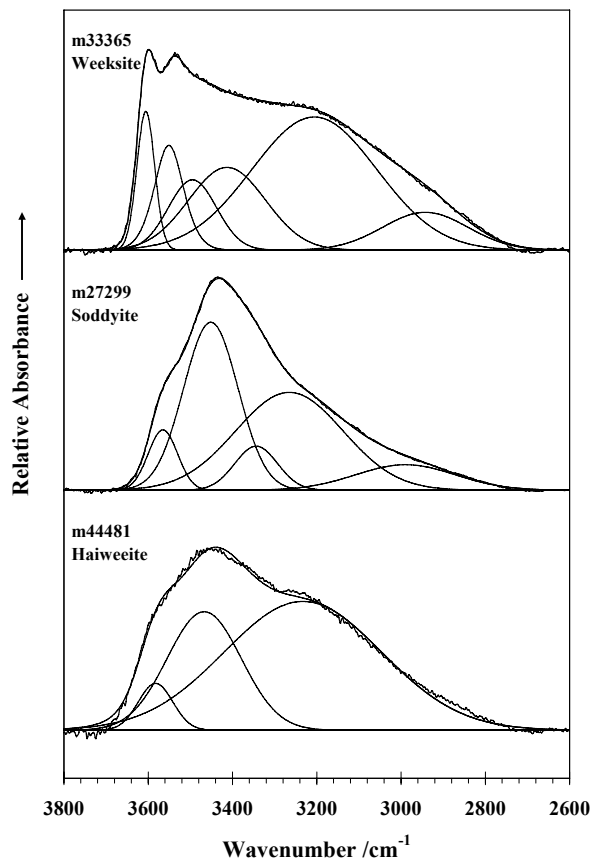
**Figure 2**



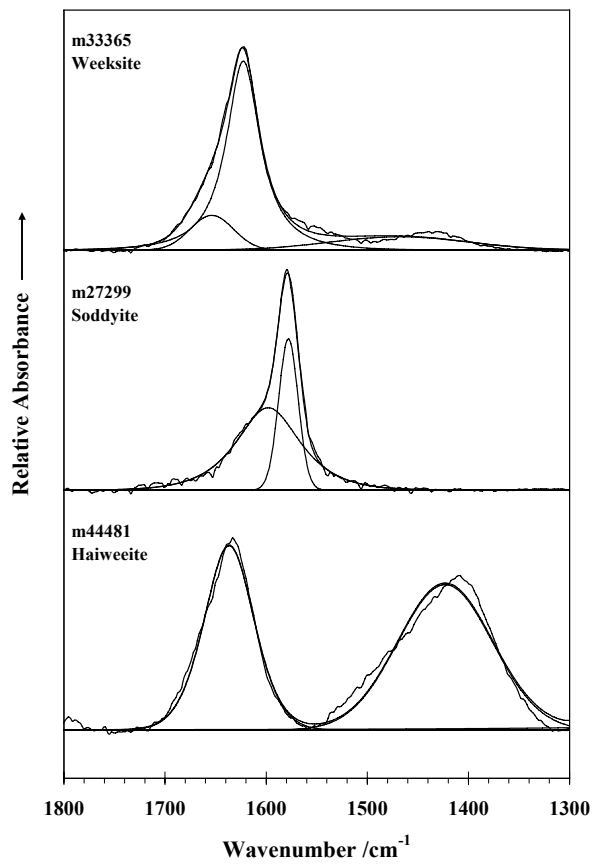
**Figure 3**



**Figure 4**



**Figure 5**



**Figure 6**