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Raman spectroscopic study of the uranyl phosphate mineral dewindtite

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Abstract

Raman spectra of two uranyl mineral dewindtite samples are presented and interpreted. Observed bands are attributed to the stretching and bending vibrations of $(\text{UO}_2)^{2+}$ and $(\text{PO}_4)^{3-}$ units and water molecules. Hydrogen bonding network in dewindtite crystal structure is shortly mentioned. U-O bond lengths in uranyls are calculated with empirical relations and wavenumbers of the $(\text{UO}_2)^{2+}$ stretching vibrations. These calculations are in agreement with the X-ray single crystal structure data.

Key words: dewindtite, uranyl, phosphate, mineral, Raman spectroscopy, U-O bond length, molecular water, hydrogen bonding

Introduction

Dewindtite is a rare secondary uranyl mineral formed by alteration of uraninite or earlier-formed secondary uranium minerals¹. Dewindtite was described by Schoep²⁻⁵ from the locality Shinkolobwe, Shaba, Democratic Republic of Congo in association with torbernite, parsonsite, dumontite and uraninite. Later, it was described at other localities and associations¹ Anthony et al.¹ write that the type material may be found in the Royal Museum of Central Africa, Tervuren, Belgium and Natural History Museum, Paris, France. However, the dewindtite type specimen disappeared during last months of the World War II with the Schoep's collection. Piret et al.⁶ found a cotype from Shinkolobwe in the collections of Museum in Tervuren. These authors published an X-ray single crystal structure analysis of this specimen. According to these authors, the formula of dewindtite should be $3\text{PbO} \cdot 6\text{UO}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 13\text{H}_2\text{O}$ or $\text{Pb}_3[\text{H}(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2]_2 \cdot 12\text{H}_2\text{O}$. X-ray powder diffraction patterns, orthorhombic unit cell parameters and number of molecules in the unit cell of dewindtite are close to those of e.g. phosphuranylite and yingjiangite, and also renardite. Matkovskii et al.⁷ published wavenumbers of the $(\text{UO}_2)^{2+}$ stretching vibrations of dewindtite and renardite. The Infrared spectrum of renardite without any interpretation has been published⁸.

After a long detailed discussion, renardite has been stated identical to dewindtite and its name has been discredited⁹⁻¹². According to Deliens et al.¹², renardite is a mixture of phosphuranylite and dewindtite and is not a unique mineral species. However, Sejkora et al.¹³ recently proved on the basis of all available analytical data that dewindtite and renardite are in fact compositionally different and

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are in no way identical. There is therefore no reason for discrediting renardite as a mineral species in the mineralogical system. It may be assumed that relations in PbO - UO₃ - PO₄ - H₂O minerals are similar to those in PbO - UO₃ - H₂O minerals, because of the same radiogenic origin of Pb, but they are compositionally more complex. Some compositional variability may be therefore expected. The phosphuranylite-type of the uranyl sheet anion topology is very similar in various dewindtite samples, but differences may be observed in the interlayer^{14,15}.

The crystal structure of dewindtite consists of [H(UO₂)₃O₂(PO₄)₂]³ⁿ⁻_n layers, parallel to (001), connected by Pb²⁺ oxygens which form distorted bi-capped trigonal prisms⁶. Dewindtite contains the phosphuranylite-type sheet with two symmetrically distinct Pb sites in the interlayer. Each Pb²⁺ cation is coordinated by eight ligands that correspond to uranyl oxygens of adjacent sheets and interlayer water molecules. The Pb cations and water molecules in the interlayer are disordered. The interlayer contains also three symmetrically distinct water molecules that are hydrogen bonded into the structure^{14,15}.

The aim of this paper, which is the part of the Raman and infrared study of secondary minerals including the uranyl minerals, is to present and discuss the Raman spectra of dewindtite and to relate the results with those from the X-ray single crystal structure analysis of dewindtite⁶. Raman spectrum of dewindtite is published in this paper for the first time.

Experimental

The mineral dewindtite

Two dewindtite samples were studied: (a) m44969 (Ranger U Mine - UO₃ 60.1 w.%, P₂O₅ 9.64 w.%, PbO 22.9 w.%, H₂O ~7.05 w.% ; (b) Shinkolobwe Mine, Shaba, Democratic Republic of Congo - UO₃ 55.8 w.%, P₂O₅ 10.6 w.%, PbO 26.2 w.%, H₂O 6.7 w.%). The Ranger U Mine sample is compositionally close to the dewindtite sample studied by Piret et al., while the Shinkolobwe Mine sample to one of the samples described by Schoep [5]. X-ray powder patterns and unit cell parameters of the two samples, however, are practically identical. It is noted that there are many uranium bearing sites in Australia which show the presence of dewindtite including Mt Painter (South Australia) and the Ranger Uranium Mines 1 and 3 (Jabiru, Northern territory, Australia).

Raman microprobe spectroscopy

The crystals of dewindtite were 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. Previous studies by the authors provide more

details of the experimental technique¹⁶⁻²². Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published elsewhere by the authors^{23,24}.

It should be noted that because of the very small amount of sample supplied on loan from the museum, it was not possible to run the infrared spectra of some of the samples. This does show a major advantage of Raman spectroscopy in the study of uranium minerals is the ability to study very small amounts of mineral. This is especially important in view of the health and safety issues associated with radioactive materials.

Spectral 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 Lorentz-Gauss 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. Further details of the band fitting protocols have been published (JRS in press).

Results and discussion

In the crystal structure of dewindtite, there are two symmetrically distinct U^{6+} as uranyl pentagonal, UO_2O_5 , and uranyl hexagonal, UO_2O_6 , polyhedra, and one symmetrically distinct P^{5+} in phosphate polyhedra, PO_4 , and four molecules in the unit cell.^{6,14,15} Because of symmetry lowering of uranyl and phosphate polyhedra in the structure of dewindtite, splitting of doubly ($\nu_2(UO_2)^{2+}$ and $\nu_2(PO_4)^{3-}$) and triply degenerate vibrations (ν_3 and $\nu_4(PO_4)^{3-}$) are expected in the Raman spectra. It is assumed that the uranyl and phosphate groups are in identical crystal symmetry environments. Based upon the work of Burns, this is not unreasonable^{14,15,25}. If however the repeat units are not identical then the spectroscopy of the Dewindtite samples would prove more complex. Raman spectra of dewindtite from The Ranger Uranium Mine (Australia) and The Shinolobwe Mine (Congo) at 298 and 77 K between 700 and 950 cm^{-1} , 100 and 700 cm^{-1} , 950 and 1200 cm^{-1} , 2800 and 3800 cm^{-1} are shown in Figures 1-4 respectively.

Raman bands, located in the region from 785 to 910 cm^{-1} are attributed to the $(UO_2)^{2+}$ stretching vibrations (Figure 1). Application of some empirical relations enables the calculation of U-O bond lengths in uranyls using the wavenumbers of the uranyl stretching vibrations [see for example Cejka²⁶]. According to two empirical relations by Bartlett and Cooney²⁷ the ν_1 symmetric and ν_3 antisymmetric uranyl stretching vibrations may be used ($R_{U-O} = 106.5\nu_1^{-2/3} + 0.575 \text{ \AA}$; $R_{U-O} = 91.41\nu_3^{-2/3} + 0.804 \text{ \AA}$). Table 2 reports the relationship between the band positions and the UO bond lengths based upon the above empirical relationships. The table shows the bond

distances are almost identical for both of the dewindtite minerals. Bands close to 860 cm^{-1} may be due to the libration modes of water molecules. The number of observed bands corresponds to two symmetrically distinct uranyls in the structure of dewindtite, four molecules in the dewindtite unit cell and FGA. U-O bond lengths in uranyls inferred from X-ray single crystal structure analysis of dewindtite for UO_2O_5 pentagonal polyhedra are 1.78(3) and 1.79(3) Å and for UO_2O_6 hexagonal polyhedra 1.92(5) and 1.80(5) Å [5]. These values are in agreement with those calculated from the wavenumbers of the $(\text{UO}_2)^{2+}$ stretching vibrations. Recent calculation of bond-valence parameters for UO_2O_6 and UO_2O_5 uranyl polyhedra on the basis of U-O (uranyl) and U-O (ligand) bond lengths inferred from the crystal structure of dewindtite^{6,8} proves the values 5.344 and 6.177 valence units, respectively. The U^{6+} in hexagonal dipyramidal coordination polyhedra is highly undersaturated. The U-O bond lengths published for UO_2O_6 in dewindtite (U-O in uranyl 1.92(5) and 1.80(5) Å, on average 1.86 Å and in $\text{U-O}_{\text{ligand}}$ 2.60(2), 2.60(2), 2.63(20), 2.63(2), 2.35(4) and 2.28(4) Å, on average 2.515 Å⁶ differ from the average values 1.78(3) and 2.47(4) Å for UO_2O_6 ^{14,15,28} and may probably be revised. On the other hand, the U-O bond lengths in uranyls calculated in this paper using the wavenumbers of the $(\text{UO}_2)^{2+}$ stretching vibrations are in agreement with Burns's conclusions.²⁸

Two bands close to 980 and 995 cm^{-1} were attributed to the $\nu_1(\text{PO}_4)^{3-}$ symmetric stretching vibrations. In the case of Shino sample at 77 K only one band at 997 cm^{-1} was observed. Bands in the range 1020 – 1125 cm^{-1} : Ranger sample at 1021, 1033, 1069 and 1117 cm^{-1} (298 K) and 1025, 1037, 1077 and 1121 cm^{-1} (77 K), and Shino sample 1024, 1070 and 1115 (298 K) and 1025, 1039, 1076 and 1123 cm^{-1} (77 K) are attributed to the split triply degenerate $\nu_3(\text{PO}_4)^{3-}$ antisymmetric stretching vibrations. Bands in the range 360-690 cm^{-1} : Ranger sample at 369, 390, 415 and 445 cm^{-1} (298 K), and 362, 376, 395, 419 and 446 cm^{-1} (77 K), and Shino sample 390, 425 and 447 cm^{-1} (298 K), and 391, 423, 448 and 459 cm^{-1} (77 K) are assigned to the split doubly degenerate $\nu_2(\text{PO}_4)^{3-}$ bending vibrations, while those for Ranger sample at 485, 536, 576 and 617 cm^{-1} (298 K), and 492, 540, 577, 616 and 653 cm^{-1} (77 K), and for Shino sample at 485, 535, 577, 615 and 689 cm^{-1} (298 K), and 493, 540, 545 and 580 cm^{-1} (77 K) to the split triply degenerate $\nu_4(\text{PO}_4)^{3-}$ bending vibrations. Bands at wavenumbers lower than 280 cm^{-1} are connected with the split doubly degenerate $\nu_2(\delta)(\text{UO}_2)^{2+}$ bending vibrations and $\delta, \nu(\text{U-O}_{\text{ligand}})$ vibrations.

Bands observed in the region from 3140 to 3670 cm^{-1} are attributed to the ν_{OH} stretching vibrations. Bands in this region are broad (see Table 1). Considerable band narrowing is observed in the 77 K spectra. Their number and wavenumbers prove that a set of symmetrically distinct and structurally nonequivalent water molecules is present in the crystal structure of Dewindtite. A hydrogen-bonding network is arranged including weakly to strongly hydrogen bonded water molecules which are important for the stability of the crystal structure of dewindtite.^{29,30} Bands in the 1600-1650 cm^{-1} region are related to the $\delta \text{H}_2\text{O}$ bending vibrations. Some bands (767, 775 and 783 cm^{-1}) may be connected with libration modes of water molecules. It is noted that in Figure 4, the spectra of the mineral at 77 K in the OH stretching region appears to show some self absorption. The self absorption is observed at 3288 cm^{-1} .

Conclusions

Raman spectra of two samples of the uranyl mineral dewindtite are presented and interpreted with regard to the vibrations of $(\text{UO}_2)^{2+}$, $(\text{PO}_4)^{3-}$ units and water molecules present in the crystal structure of dewindtite. U-O bond lengths in uranyles are calculated using the wavenumbers of the $(\text{UO}_2)^{2+}$ symmetric and antisymmetric stretching vibrations. They are in agreement with the values inferred from the X-ray single crystal structure of dewindtite. The existence of the hydrogen-bonding network in the crystal structure of dewindtite is discussed.

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Ranger 298 Centre	FWHM	Ranger 77 Centre	FWHM	Shino 298 Centre	FWHM	Shino 77 Centre	FWHM
3524	84	3526	85	3521	97	3567	32
		3512	25			3519	88
3456	162	3446	96	3442	191	3435	122
3299	310	3319	141	3308	79	3288	27
3297	34	3289	35	3217	257	3277	186
		3178	111			3147	164
1659	20	1659	25	1643	96		
1623	51			1561	122		
1117	26	1121	24	1115	29	1123	24
1069	42	1077	22	1070	47	1076	28
1033	32	1037	31			1039	24
1021	18	1025	11	1024	26	1025	14
994	14	996	10	996	18	997	20
978	34	987	37	981	35		
		909	10	897	41	909	15
868	40			862	28		
857	10	857	6			859	31
831	18	831	12	830	22	834	18
818	8	823	5			821	18
808	18	809	10	805	27	806	24
		805	35				
795	27			788	22	789	15
783	47			775	43		
						767	18
				689	45		
		653	34				
617	21	616	29	615	47		
576	28	577	28	577	28	580	20
						545	105
536	30	540	21	537	52	540	20
485	36	492	26	485	38	493	26
						459	9
445	26	446	26	447	27	448	26
415	33	419	20	425	41	423	25
390	24	395	29	390	37	391	39
		376	10				
369	31	362	10				
274	9	276	10			277	5
260	14	261	14	262	60		
				258	18		
251	61	245	18	244	12	246	6
						243	89
204	37	216	69	210	47	209	40
		210	24	205	28		
170	35			170	36	172	43
		157	13				
143	27	144	17	146	26	146	24
115	19	114	16	116	19	115	20

Table 1 Results of the Raman spectral analysis of dewindtite at 298 and 77 K.

	Dewindite Ranger		Dewindite Shino	
	Wavenumber (cm ⁻¹)	Bond distance (Å)	Wavenumber (cm ⁻¹)	Bond distance (Å)
R _{U-O} /v ₃	909 (77 K)	1.778	909 (77 K)	1.778
	868	1.808	897	1.787
			862	1.813
	857	1.817	859	1.816
		834 (77 K)	1.777	
R _{U-O} /v ₁	831	1.780	830	1.781
	831 (77 K)	1.780	821 (77 K)	1.790
	823	1.788	806 (77 K)	1.805
	818	1.793	805	1.806
	809 (77 K)	1.802		
	806 (77 K)	1.806		
	808	1.803	789 (77 K)	1.822
	795	1.816	788	1.823

Table 2 Relationship between the band positions of the antisymmetric and symmetric stretching modes and the UO bond distances.

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Figure 1 Raman spectra of dewindtite from The Ranger Uranium Mine (Australia) and The Shinolobwe Mine (Congo) between 700 and 950 cm^{-1} .

Figure 2 Raman spectra of dewindtite from The Ranger Uranium Mine (Australia) and The Shinolobwe Mine (Congo) between 100 and 700 cm^{-1} .

Figure 3 Raman spectra of dewindtite from The Ranger Uranium Mine (Australia) and The Shinolobwe Mine (Congo) between 950 and 1200 cm^{-1} .

Figure 4 Raman spectra of dewindtite from The Ranger Uranium Mine (Australia) and The Shinolobwe Mine (Congo) between 2800 and 3800 cm^{-1} .

List of Tables

Table 1 Results of the Raman spectral analysis of dewindtite at 298 and 77 K.

Table 2 Relationship between the band positions of the antisymmetric and symmetric stretching modes and the UO bond distances.

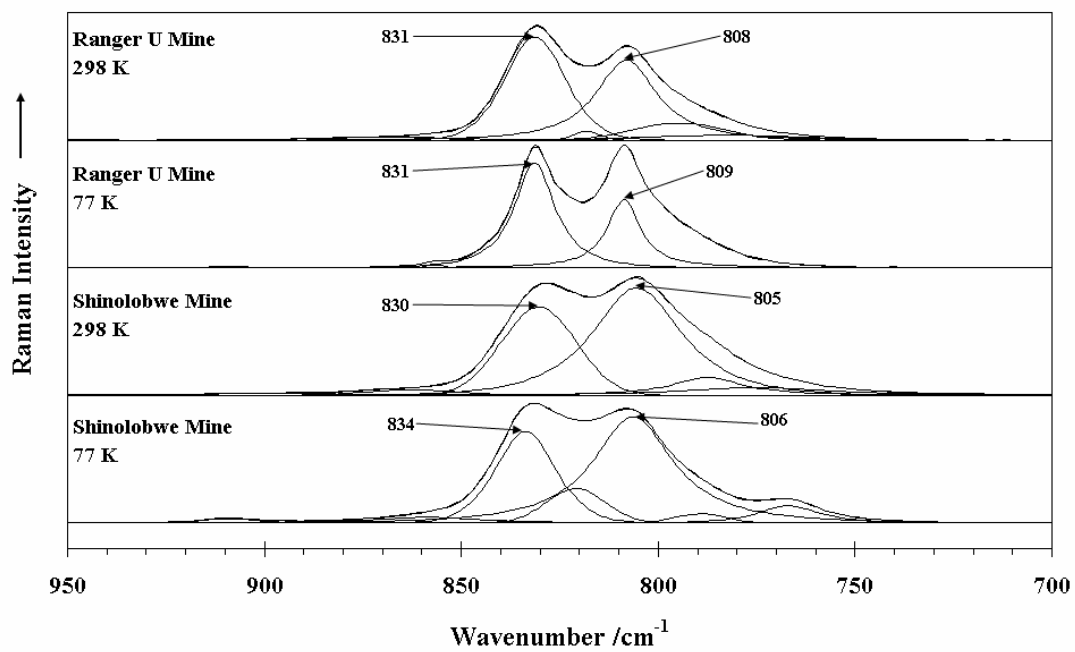


Figure 1

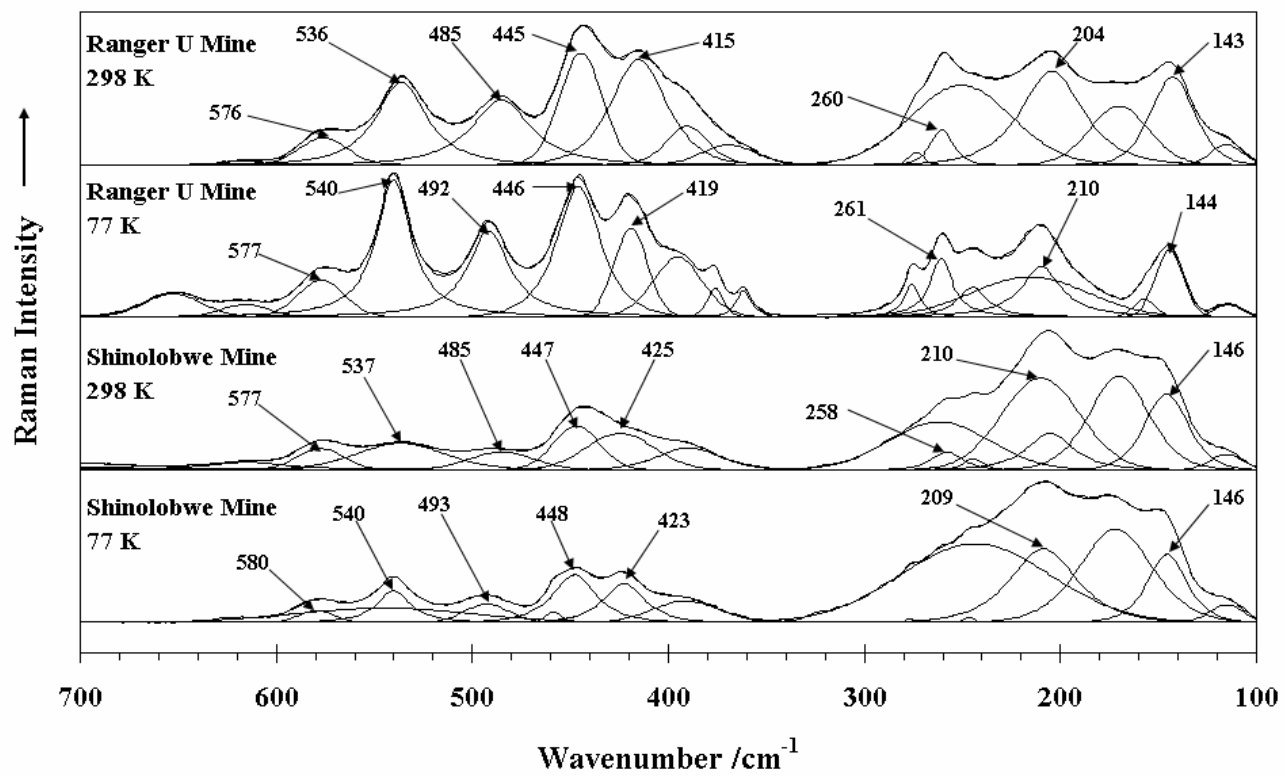


Figure 2

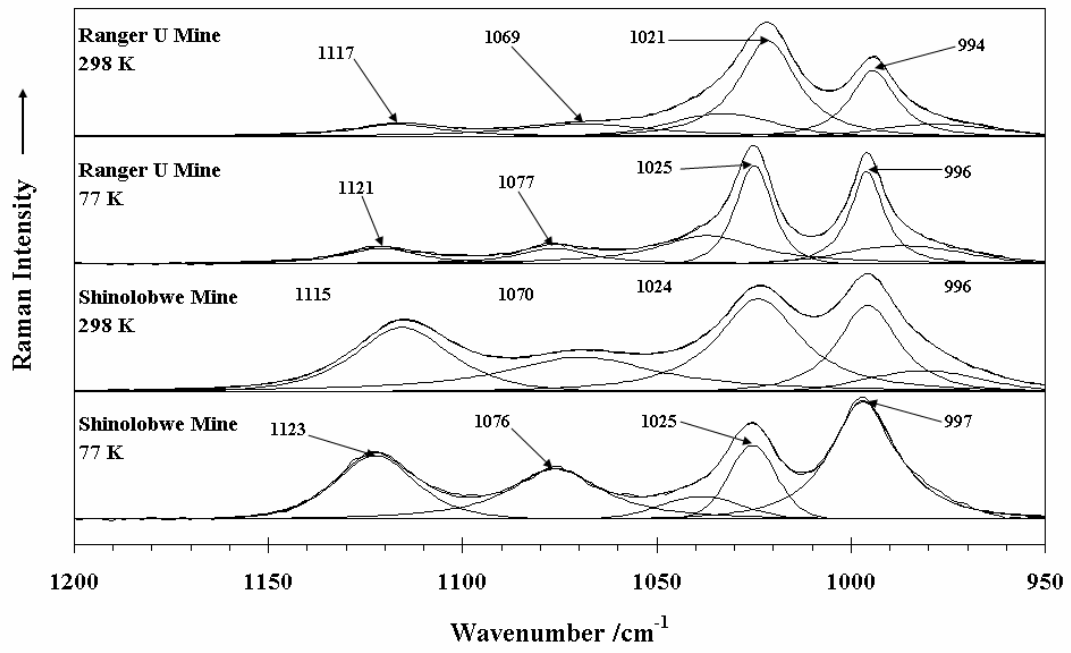


Figure 3

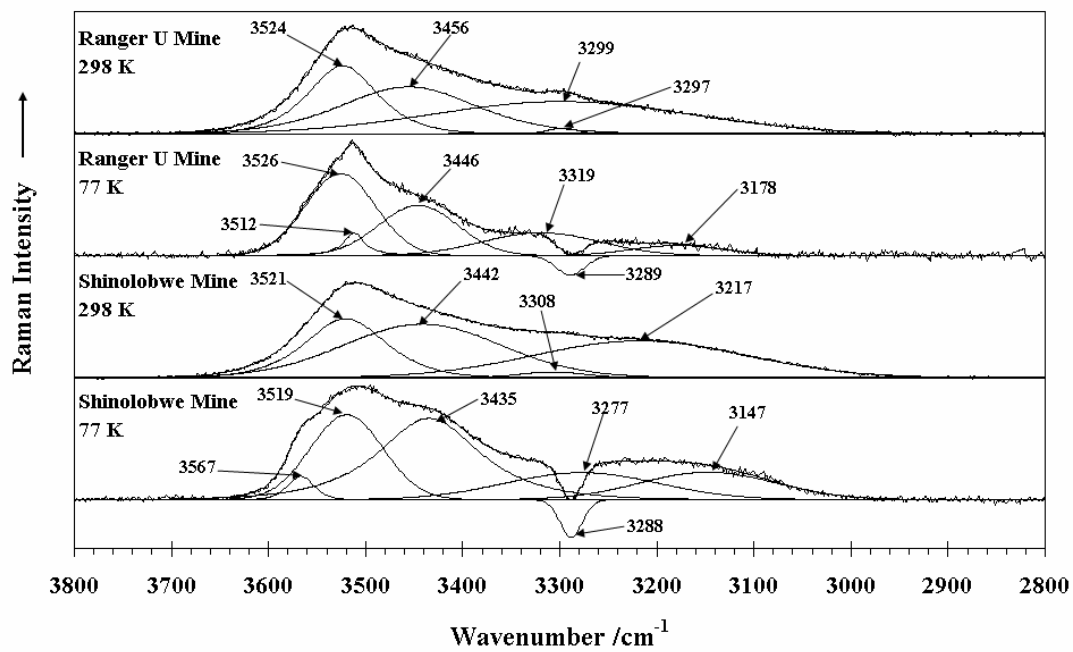


Figure 4