

# Using Raman spectroscopy to identify mixite minerals

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## Abstract:

Raman spectroscopy has been used to identify whether or not a selection of minerals labelled as mixites (formula  $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ ) are correctly marked. Of the four samples, two samples are shown to be potentially mixites because of the presence of the characteristic Raman spectra of  $(\text{AsO}_4)^{3-}$  units and  $(\text{HAsO}_4)^-$  units, characterised by bands at around 803 and 833  $\text{cm}^{-1}$ . Two of the minerals are shown to be predominantly carbonates. Bands are observed at 3473.9 and 3470.3  $\text{cm}^{-1}$  for the two mixite samples. Bands observed in the region 880 to 910  $\text{cm}^{-1}$  and in the 867 to 870  $\text{cm}^{-1}$  region are assigned to the AsO stretching vibrations of  $(\text{HAsO}_4)^{2-}$  and  $(\text{H}_2\text{AsO}_4)^-$  units. Whilst bands at around 803 and 833  $\text{cm}^{-1}$  are assigned to the stretching vibrations of uncomplexed  $(\text{AsO}_4)^{3-}$  units. Intense bands at 473.7 and 475.4  $\text{cm}^{-1}$  are assigned to the  $\nu_4$  bending mode of  $\text{AsO}_4$  units. Bands observed at around 386.5, 395.3 and 423.1  $\text{cm}^{-1}$  are assigned to the  $\nu_2$  bending modes of the  $\text{HAsO}_4$  (434 and 400  $\text{cm}^{-1}$ ) and the  $\text{AsO}_4$  groups (324  $\text{cm}^{-1}$ ). Raman spectroscopy lends itself to the identification of minerals on host matrices and is especially useful for the identification of mixites.

**Key words-** agardite, analytical detection, mixite, petersite, identification, Raman spectroscopy

## INTRODUCTION

Mixite is the mineral of formula  $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$  and is related to agardites. Mixites are secondary minerals associated with Bi bearing ores. The minerals are white or yellow-green through to blue green and are acicular or needle like crystal formation. The minerals are often found with bismutite ( $\text{Bi}_2(\text{CO}_3)_2\text{O}_2$ ), smaltite, atelestite ( $\text{BiO}(\text{OH})(\text{AsO}_4)$ ), erythrite, malachite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ) and barite. Agardite is a member of the mixite group,  $\text{ACu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$  for the fully hydrated formula, with (A = lanthanide<sup>3+</sup>). Mixite (A = Bi), goudeyite (A = Al), zalesiite (A = Ca, with protonation of the lattice for charge compensation) and petersite-(Y), the phosphate analogue of agardite-(Y) are recognized isomorphous species in the group. Of the many possible rare earth congeners constituting the

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agardite group, only agardite-(Y) and agardite-(La) are recognized as distinct species by the IMA. [1] Others have been reported in the literature [2-7] but their species status remains unresolved. It should be noted that formulae given above refer to ideal, end-member compositions; extensive solid solution in the A site and involving P for As is known for naturally occurring material. Water in the lattice is for the most part thought to be zeolitic in nature, as evidenced by single-crystal X-ray structure determinations. [8-10] The crystal structures of natural mixite and agardite compounds reveal a microporous framework structure [4, 8] with a framework similar to that of zeolites. [10] Dietrich et al. [11] originally proposed that the water in agardite was zeolitic. As such these minerals may have potential for catalytic applications.

The mixite group consists of secondary minerals formed through crystallisation from aqueous solution. The conditions under which this crystallisation takes place, particularly relating to anion and cation concentrations, pH, temperature and kinetics of crystallisation, determines the particular mineral that is formed. Recently, Raman spectroscopy has been used to gain an understanding of many properties of secondary minerals. [12-18] In particular, Raman spectroscopy has been used to determine paragenetic relationships between many closely related phases. In this paper we report the Raman spectroscopic analysis of a set of selected mixite minerals.

### ***Raman microprobe spectroscopy***

The crystals of the mixites were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a thermo-electrically cooled Charge Coupled Device (CCD) detector. 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. The crystals were oriented to provide maximum intensity. All crystal orientations were used to obtain the spectra. Power at the sample was measured as 1 mW.

The Galactic software package GRAMS was used for data analysis. 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 carried out 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 regression coefficient of  $R^2$  greater than 0.995.

## **RESULTS AND DISCUSSION**

Mixite is the mineral of formula  $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$  [7, 19]. Four different vibrating units will contribute to the overall spectral profile, namely the OH units, the water molecules,  $\text{AsO}_4$  groups and the  $\text{HAsO}_4$  groups. The first two vibrating species will contribute to the high wavenumber region whilst the  $\text{AsO}_4$  units will show Raman bands below  $1200 \text{ cm}^{-1}$ . [20] It has been shown that the water can be reversibly lost and the number of water molecules per formula unit can vary up to 3. According to Mereiter and Preisinger (1986) mixites have a microporous framework structure based upon  $(\text{M}^{3+})_{1-x}(\text{M}^{2+})_x\text{Cu}_6(\text{OH})_6(\text{AsO}_4)_{3-x}(\text{AsO}_3\text{OH})_x$ . [19], with vacancies in the A site or substitution by divalent cations being compensated by protonation of the lattice. On the spectroscopic time scale, exchange of protons between water molecules and arsenate ions is also likely. According to this formulation two types of units involving As are found, namely  $\text{AsO}_4$  and  $\text{HAsO}_4$ . Thus two sets of bands involving AsO stretching modes would be expected. Vibrational spectroscopy has been used to study the coordination chemistry of  $(\text{AsO}_4)^{3-}$  ions for some considerable time. [20-25] Vansant et al. showed the frequencies of the  $(\text{AsO}_4)^{3-}$  units of Td symmetry as 818 ( $A_1$ ), 786 (F-stretching), 405 (F-bending) and  $350 \text{ cm}^{-1}$  (E). [23] Vibrational spectroscopic studies have shown that the symmetry of the  $(\text{AsO}_4)^{3-}$  polyhedron are strongly distorted and the  $(\text{AsO}_4)^{3-}$  vibrations are strongly influenced by the protonation, cation presence and water coordination. [22-25] The symmetric stretching vibration of the arsenate anion in aqueous systems ( $\nu_1$ ) is observed at  $810 \text{ cm}^{-1}$  and coincides with the position of the antisymmetric stretching mode ( $\nu_3$ ). [20] The symmetric bending mode ( $\nu_2$ ) is observed at  $342 \text{ cm}^{-1}$  and the ( $\nu_4$ ) bending modes at  $398 \text{ cm}^{-1}$ . Of all the tetrahedral oxyanions, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions.

The Raman spectra of some potential selected mixites in the  $650$  to  $1200 \text{ cm}^{-1}$  region,  $100$  to  $700 \text{ cm}^{-1}$  region,  $2600$  to  $3800 \text{ cm}^{-1}$  region at  $298$  and  $77 \text{ K}$  are shown in Figures 1, 2 and 3 respectively. The results of the Raman spectral analysis are reported in Table 2. Figure 1 displays the spectra for the  $\text{AsO}_4$  and  $\text{HAsO}_4$  stretching region. Clearly the  $298 \text{ K}$  spectra from the Boss Tweed mine and the Majuba Hill mine show peaks in the  $850$  to  $830 \text{ cm}^{-1}$  region which are indicative  $\text{AsO}_4$  bands. The broad bands for the Tooele sample are more indicative of a carbonate. Thus this sample cannot possibly be a mixite. Data for this sample are not reported further. Similarly the sample from Mammoth Mine clearly shows bands at  $1062.1$ ,  $1087.9$ , and  $1097.0 \text{ cm}^{-1}$  which are also assigned to carbonate stretching bands. This spectrum is also that of a carbonate and is bismutite ( $\text{Bi}_2(\text{CO}_3)_2\text{O}_2$ ). The spectra at  $77 \text{ K}$  confirm the  $298 \text{ K}$  spectra. Thus Raman spectroscopy can be used to distinguish potential mixite minerals from other minerals.

Two Raman bands may be observed in the region  $880$  to  $910 \text{ cm}^{-1}$  and in the  $867$  to  $870 \text{ cm}^{-1}$  region. These are assigned to the AsO stretching vibrations of  $(\text{HAsO}_4)^{2-}$  and  $(\text{H}_2\text{AsO}_4)^-$  units. [22, 23] According to Myeni et al. (see Myeni table 3) the band at around  $915 \text{ cm}^{-1}$  corresponds to the antisymmetric stretching vibration of protonated  $(\text{AsO}_4)^{3-}$  units and the band at around  $880 \text{ cm}^{-1}$  to the symmetric stretching vibration of the protonated  $(\text{AsO}_4)^{3-}$  units. [24, 25] The position of the bands indicate a  $C_{2v}$  symmetry of the  $(\text{HAsO}_4)^-$  anion. For the two mixites no band was observed in the  $867$  to  $870 \text{ cm}^{-1}$  region. This suggests there are no  $(\text{H}_2\text{AsO}_4)^-$  units in the sample. For the Boss sample two bands are observed at  $880.6$  and  $851.8 \text{ cm}^{-1}$  with band widths of  $30.1$  and  $35.9 \text{ cm}^{-1}$ . These bands shift to  $878.8$  and  $910.4$

$\text{cm}^{-1}$  at 77 K with band widths of 36.3 and 24.9  $\text{cm}^{-1}$ . For the Majuba sample only a single band was found at 909.7  $\text{cm}^{-1}$  in the 298 K spectrum. No bands were found in the spectrum of the Mammoth sample in this region. Two bands are found at around 803 and 833  $\text{cm}^{-1}$ . These are assigned to the stretching vibrations of uncomplexed  $(\text{AsO}_4)^{3-}$  units. The bands correspond to the antisymmetric (803  $\text{cm}^{-1}$ ) and symmetric (833  $\text{cm}^{-1}$ ) stretching vibrations of  $(\text{AsO}_4)^{3-}$  units of  $T_d$  symmetry. [24, 25] In the case of the Boss mineral, the first band is found at 805.1  $\text{cm}^{-1}$  and for the Majuba mineral at 809.8  $\text{cm}^{-1}$ . The bands shift to 806.6 and 809.2  $\text{cm}^{-1}$  in the 77 K spectrum. Two bands are found at 830.8  $\text{cm}^{-1}$  and 851.8  $\text{cm}^{-1}$  for the Boss mineral and at 831.5 and 854.3  $\text{cm}^{-1}$  for the Majuba mineral.

A number of bands are observed in the 350 to 550  $\text{cm}^{-1}$  region (Figure 2). A band is observed at around 539  $\text{cm}^{-1}$  which is cation sensitive. One possible assignment is that the band is the  $\nu_4$  bending mode of  $(\text{HAsO}_4)^-$  units. Such a band position was not observed in the work of Vansant et al. [22, 23] and was not reported as was any of the bending modes in the work of Myeni et al. [24, 25] Theoretical studies have shown such bond distances are dependent upon the type of arsenate unit in the structure. [24, 25] (see for example Table 2 in the Myeni reference). Such bond distances are cation sensitive for example the As-O bond distance is 1.62 Å for  $\text{Al-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$ , 1.65 Å for  $\text{Mg-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$ , 1.66 Å for  $\text{CdO}_2\text{-AsO}_2(\text{H}_2\text{O})_4$  and 1.64 Å for  $\text{Cd-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$ . Such cationic sensitivity is expected to be translated to the bending modes of the  $(\text{HAsO}_4)^-$  units. Vansant et al showed the potential energy distributions for  $(\text{AsO}_4)^{3-}$ ,  $(\text{HAsO}_4)^{2-}$  and  $(\text{H}_2\text{AsO}_4)^-$  units. [22] These distributions were then used to calculate the attribution of the vibrational modes. [22]

Intense bands are observed at 473.7 and 475.4  $\text{cm}^{-1}$  (Boss), 475.1 (Majuba) and are assigned to the  $\nu_4$  antisymmetric bending mode of  $\text{AsO}_4$  units. An additional band is observed around 458.4  $\text{cm}^{-1}$  (Boss); 459.5 (Majuba). Three bands are observed at around 386.5, 395.3 and 423.1  $\text{cm}^{-1}$  and are of similar intensities. These are assigned to the  $\nu_2$  bending modes of the  $\text{HAsO}_4$  (423.1 and 395.3  $\text{cm}^{-1}$ ) and the  $\text{AsO}_4$  groups (386.5  $\text{cm}^{-1}$ ). For the Majuba sample two bands are observed at 393.2 and 422.7  $\text{cm}^{-1}$ . These bands shift to 394.4 and 424.0  $\text{cm}^{-1}$  at 77 K. The spectral pattern in the 350 to 550  $\text{cm}^{-1}$  region is very similar for the Boss and Majuba samples and appears to be characteristic of the Raman spectrum of the mixite minerals.

The Raman spectra of the OH stretching region are shown in Figure 3. For a mixite of formula  $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$  there should be two types of OH units: firstly one from the OH units and the second from the interlamellar water. A band is observed at 3473.9  $\text{cm}^{-1}$  (Boss) and 3470.3  $\text{cm}^{-1}$  (Majuba) with bandwidths of 37.5  $\text{cm}^{-1}$  and 34.2  $\text{cm}^{-1}$ . This band is attributed to the OH stretching vibration of the hydroxyl units. A second band is observed at 3428.4  $\text{cm}^{-1}$  (Boss) and 3444.0  $\text{cm}^{-1}$  (Majuba) and may also be assigned to OH stretching vibrations. This suggests two non-equivalent OH units in the mixite crystal structure. An intense broad band is found at 3386.7  $\text{cm}^{-1}$  (298 K) and at 3394.2  $\text{cm}^{-1}$  (77 K) for Boss mineral and at 3412.3  $\text{cm}^{-1}$  (298 K) and 3402.7  $\text{cm}^{-1}$  (77 K) for the Majuba sample. These bands are assigned to the interlamellar water in the mixite structure. It should be noted that Mammoth sample shows an intense band at 3359.5  $\text{cm}^{-1}$  which may also be attributed to a water stretching band.

Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances [26-29]. Libowitzky based upon the hydroxyl stretching frequencies as determined by infrared spectroscopy, showed that a regression function can be employed relating the above correlations with regression coefficients better than 0.96 [30]. The function is  $\nu_1 = 3592 - 304 \times 10^9 \exp(-d(\text{O-O})/0.1321) \text{ cm}^{-1}$ . If the assumption is made that the wavenumber of the OH stretching vibrations can be used instead of the infrared band, then estimations of the hydrogen bond distances can be made. The H-bond distance for the OH units are 2.819 Å (3428.4  $\text{cm}^{-1}$ ) and 2.862 Å (3473.9  $\text{cm}^{-1}$ ) and the H-bond distances of the water are 2.784 (3377.6  $\text{cm}^{-1}$ ) and 2.789 Å (3386.7  $\text{cm}^{-1}$ ). There are two distinct hydrogen bond distances namely around 2.78 Å and 2.86 Å. The water is more strongly hydrogen bonded than the OH units. The water is hydrogen bonded to other water molecules and may also coordinate the  $\text{AsO}_4$  units atom.

## CONCLUSIONS

Mixites are an uncommon secondary mineral found in the oxidised zone of copper deposits. The minerals contain bismuth and are often mixed with other bismuth based minerals such as malachite, bismuthite and atelestite. These minerals are all carbonate based. Since Raman spectroscopy can readily distinguish between carbonates and arsenates, the technique lends itself to the ready identification of mixites.

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**Table 1 Table of the selected mixite minerals**

<b>Mineral</b>	<b>Formula</b>	<b>Location</b>	<b>Referent</b>
Mixite	$\text{Cu}_6\text{Bi}(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$	Boss Tweed Mine, Tintic District, Juab Vounty, Utah	Boss
Mixite?		Conichalcite Central Pit, Gold Hill, Tooele County, Utah	Tooele
Mixite		Tin Stope, Majuba Hill, Pershing Co., Nevada	Majuba
Mixite?		Mammoth Mine, Tintic District, Utah	Mammoth



**Table 2 Results of the Raman spectra of three mixites (Boss, Majuba, Mammoth)**

Boss 298K			Boss 77K			Majuba 298K			Majuba 77K			Mammoth 298K			Mammoth 77K		
Center	FWHM	%	Center	FWHM	%	Center	FWHM	%	Center	FWHM	%	Center	FWHM	%	Center	FWHM	%
<b>3473.9</b>	37.5	1.4	<b>3471.8</b>	35.1	0.7	<b>3470.3</b>	34.2	1.1	<b>3470.9</b>	50.1	1.5	<b>3575.8</b>	76.8	0.4			
<b>3428.4</b>	45.3	1.5				<b>3444.0</b>	65.2	0.7									
<b>3386.7</b>	233.2	16.9	<b>3394.2</b>	176.5	14.0	<b>3412.3</b>	213.0	9.2	<b>3402.7</b>	128.3	5.2	<b>3380.3</b>	46.1	5.8	<b>3379.8</b>	36.6	3.2
<b>3377.6</b>	80.9	3.8										<b>3359.5</b>	236.6	28.9	<b>3324.1</b>	268.4	24.3
												<b>1678.4</b>	48.0	0.6			
									<b>1596.0</b>	90.2	14.5	<b>1639.7</b>	21.0	0.5			
			<b>1559.7</b>	145.5	4.9				<b>1530.0</b>	45.6	2.0	<b>1522.5</b>	18.9	0.4			
									<b>1483.6</b>	60.4	7.8	<b>1493.0</b>	28.0	15.4	<b>1494.2</b>	27.1	10.3
									<b>1430.9</b>	45.7	3.1	<b>1460.0</b>	25.2	0.7	<b>1461.2</b>	11.5	0.6
			<b>1391.5</b>	183.7	2.5				<b>1429.4</b>	70.4	0.4	<b>1429.4</b>	70.4	0.4			
									<b>1358.3</b>	111.1	8.2	<b>1368.3</b>	21.1	1.7	<b>1370.4</b>	21.3	2.6
												<b>1097.0</b>	17.5	4.5	<b>1096.7</b>	15.1	7.8
												<b>1087.9</b>	24.6	1.5			
												<b>1062.1</b>	35.4	7.3	<b>1066.0</b>	42.1	8.8
<b>1044.1</b>	22.0	0.3	<b>1045.4</b>	14.5	0.1	<b>1055.0</b>	69.0	0.4									
<b>1014.7</b>	4.5	0.1															
<b>988.2</b>	47.6	2.5	<b>992.8</b>	25.7	0.5	<b>986.0</b>	63.0	2.9				<b>988.0</b>	32.7	0.4			
<b>909.9</b>	35.9	1.1	<b>910.4</b>	24.9	1.0	<b>909.7</b>	29.5	1.1	<b>915.9</b>	45.0	1.4						
<b>880.6</b>	30.1	2.0	<b>878.8</b>	36.3	3.5												
						<b>864.6</b>	60.3	11.9									
<b>851.8</b>	18.8	22.2	<b>853.0</b>	16.7	12.5	<b>854.3</b>	19.9	37.4	<b>856.0</b>	14.4	11.0						
									<b>844.5</b>	61.6	27.2						
<b>830.8</b>	25.3	9.6	<b>835.2</b>	41.8	26.6	<b>831.5</b>	17.2	1.3									
<b>808.0</b>	19.3	4.2				<b>809.8</b>	24.4	8.1	<b>809.2</b>	13.1	1.0	<b>818.6</b>	5.7	0.1			
<b>805.1</b>	61.7	3.7	<b>806.6</b>	23.6	5.3												
			<b>783.5</b>	56.3	1.3												
												<b>750.5</b>	19.5	1.2			

<b>717.4</b>	94.2	1.1				<b>707.6</b>	55.1	0.4				<b>717.8</b>	12.6	0.8	<b>721.7</b>	66.1	4.1
												<b>704.0</b>	14.1	0.1			
												<b>593.0</b>	17.8	0.5			
						<b>565.3</b>	19.4	0.2				<b>566.8</b>	27.6	0.4			
<b>547.2</b>	36.8	1.2	<b>546.2</b>	55.4	2.8												
<b>531.0</b>	13.5	0.4	<b>531.5</b>	14.7	0.5	<b>530.5</b>	13.7	0.3	<b>531.3</b>	26.0	1.8	<b>529.8</b>	26.8	3.9			
						<b>522.7</b>	61.0	3.4				<b>510.2</b>	21.4	0.8	<b>519.7</b>	52.6	11.9
						<b>490.3</b>	28.3	2.2	<b>492.4</b>	31.2	1.1	<b>495.2</b>	42.7	1.6			
<b>475.4</b>	14.9	6.7	<b>477.1</b>	54.9	10.9												
<b>473.7</b>	62.6	8.7	<b>475.6</b>	11.9	2.4	<b>475.1</b>	18.6	6.3	<b>475.4</b>	16.7	3.3						
<b>458.4</b>	10.3	0.3	<b>459.0</b>	7.5	0.3	<b>459.5</b>	39.2	3.4	<b>458.4</b>	24.9	1.0						
<b>432.5</b>	13.2	0.4															
<b>423.1</b>	16.9	3.6	<b>424.2</b>	18.4	3.0	<b>422.7</b>	20.0	2.7	<b>424.0</b>	18.7	2.5	<b>431.6</b>	16.6	7.0	<b>433.5</b>	10.4	2.6
<b>395.3</b>	14.0	1.8	<b>393.0</b>	21.5	2.3	<b>393.2</b>	22.1	1.5	<b>394.4</b>	17.3	1.9	<b>420.4</b>	24.7	2.9	<b>420.4</b>	29.2	5.7
<b>386.5</b>	24.9	1.9															
<b>334.3</b>	15.6	0.3										<b>347.6</b>	23.5	2.0	<b>345.6</b>	26.6	4.5
<b>319.5</b>	16.6	1.3	<b>321.4</b>	20.2	0.9	<b>314.4</b>	27.7	1.7	<b>318.5</b>	22.2	1.2						
<b>302.5</b>	7.3	0.1															
<b>282.5</b>	14.5	0.4	<b>281.6</b>	15.2	0.5	<b>285.9</b>	27.6	1.0	<b>289.3</b>	20.6	0.4						
												<b>264.0</b>	26.3	4.7	<b>258.5</b>	44.3	10.0
<b>249.0</b>	10.7	0.1				<b>250.9</b>	15.1	0.6									
			<b>243.5</b>	22.8	0.5	<b>241.8</b>	48.4	1.0	<b>244.6</b>	28.7	2.2						
<b>227.8</b>	23.8	1.0	<b>225.2</b>	15.1	0.8	<b>229.9</b>	19.7	0.6	<b>224.9</b>	13.6	0.6	<b>220.5</b>	14.5	1.9	<b>221.6</b>	15.9	2.5
<b>192.0</b>	19.8	0.9	<b>196.6</b>	14.7	1.2	<b>198.9</b>	18.2	0.4	<b>201.0</b>	10.5	0.6	<b>206.8</b>	12.1	0.3			
<b>178.4</b>	9.5	0.2	<b>181.7</b>	13.5	1.0	<b>178.1</b>	9.5	0.1	<b>180.3</b>	9.9	0.5	<b>179.7</b>	12.2	3.0	<b>180.5</b>	9.0	1.4
<b>158.9</b>	5.1	0.0	<b>159.6</b>	6.4	0.1				<b>159.4</b>	6.4	0.1	<b>157.0</b>	7.1	0.2			

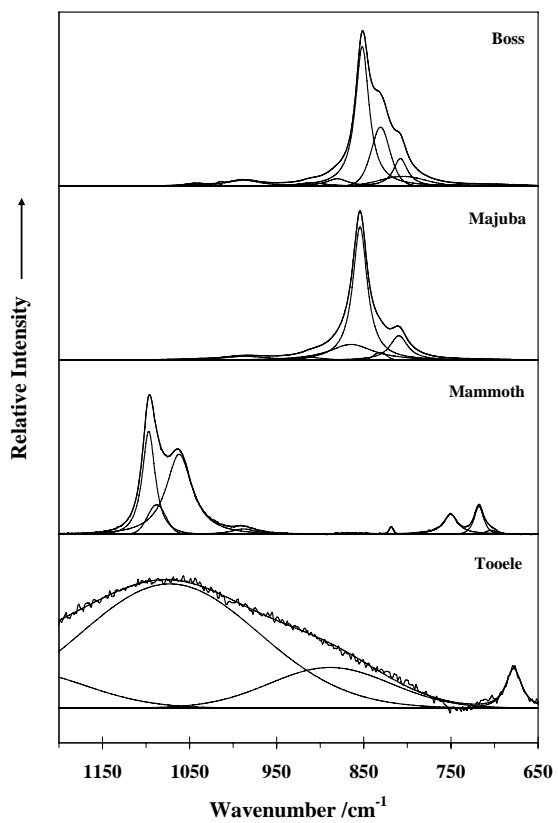
### **List of Figures**

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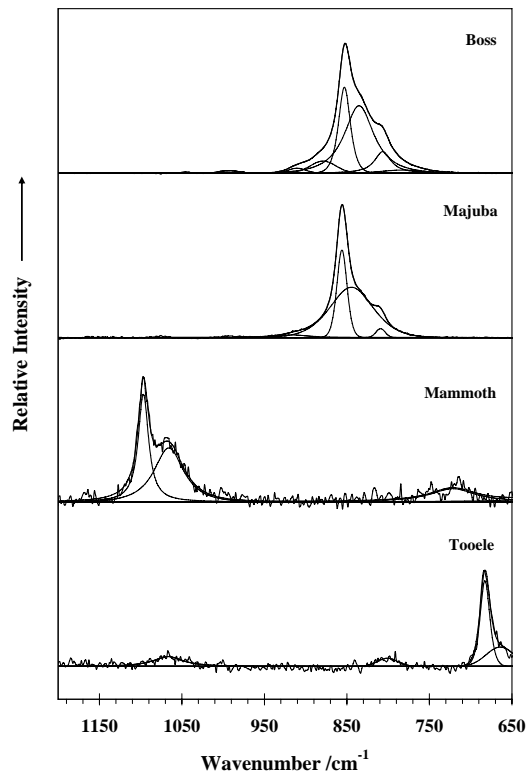
### **List of Tables**

**Table 1 Table of the selected mixite minerals**

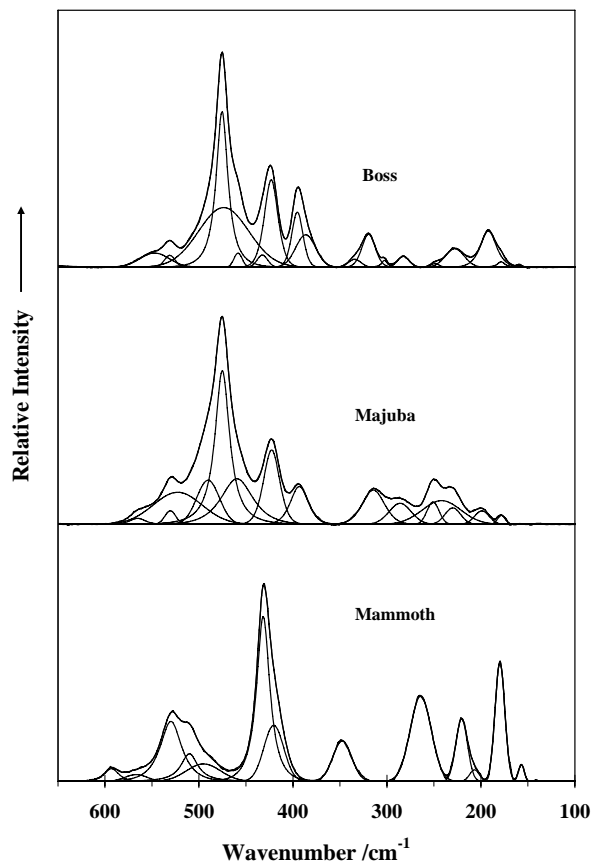
**Table 2 Results of the Raman spectra of three mixites (Boss, Majuba, Mammoth)**



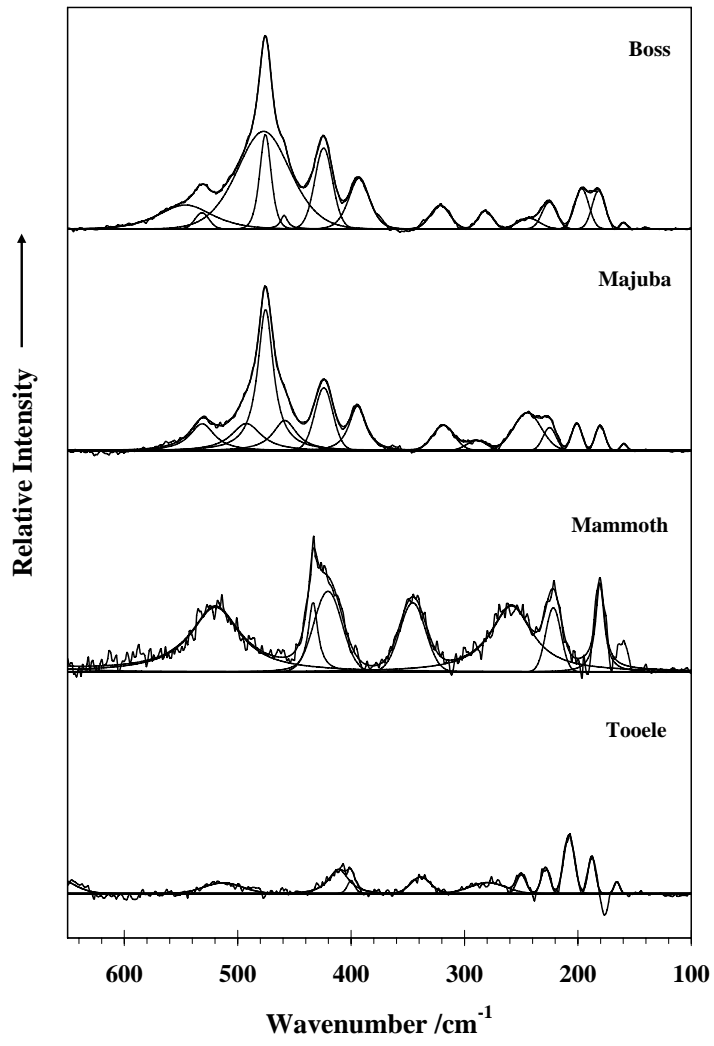
**Figure 1a**



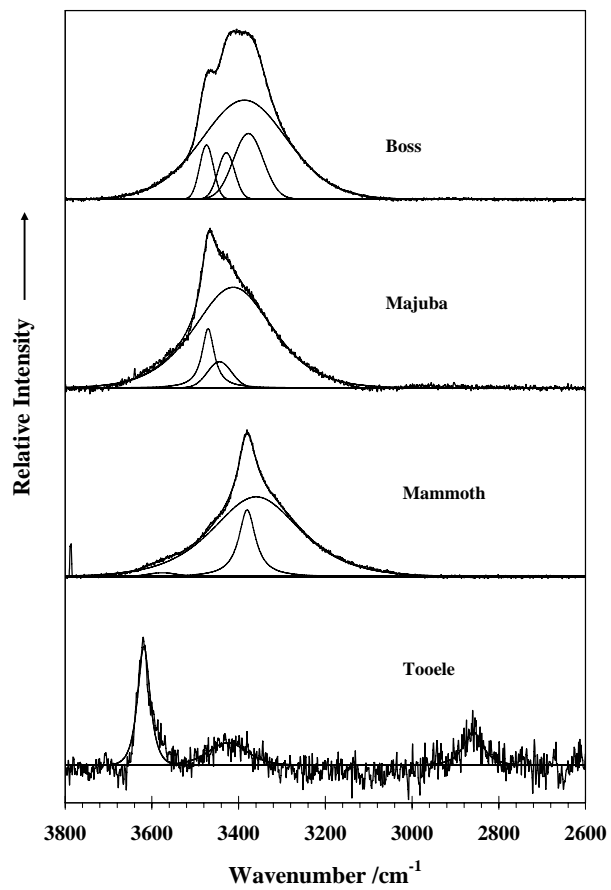
**Figure 1b 77 K**



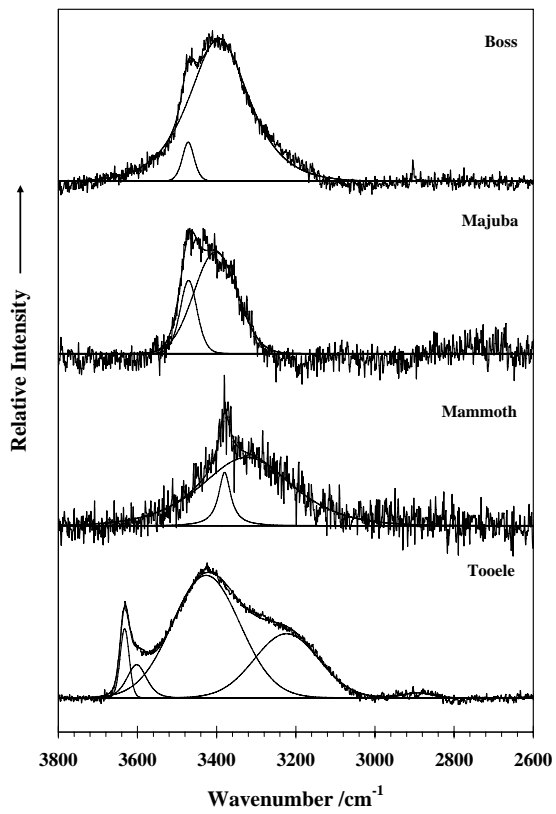
**Figure 2a**



**Figure 2b**



**Figure 3a**



**Figure 3b**

