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# **Raman microscopy of the molybdate minerals koechlinite, iriginite and lindgrenite**

**Ray L. Frost<sup>\*</sup>, Loc Duong and Matt Weier**

Inorganic Materials Research Program, School of Physical and Chemical  
Sciences, Queensland University of Technology, GPO Box 2434, Brisbane  
Queensland 4001, Australia.

## **Abstract:**

A series of molybdate bearing minerals including wulfenite, powellite, lindgrenite and iriginite have been analysed by Raman microscopy. These minerals are closely related and often have related paragenesis. Raman microscopy enables the selection of individual crystals of these minerals for spectroscopic analysis even though several of the minerals can be found in the same matrix because of the paragenetic relationships between the minerals. The molybdenum bearing minerals lindgrenite, iriginite and koechlinite were studied by scanning electron microscopy and compositionally analysed by EDX methods using an electron probe before Raman spectroscopic analyses. The Raman spectra are assigned according to factor group analysis and related to the structure of the minerals. These minerals have characteristically different Raman spectra.

**KEY WORDS:** lindgrenite, iriginite, powellite, wulfenite, molybdate, Raman  
spectroscopy

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<sup>\*</sup> Author to whom correspondence should be addressed (r.frost@qut.edu.au)

## INTRODUCTION

Interest in minerals containing molybdate anions has been ongoing for some considerable time (CANNON & GRIMALDI 1953; FRONDEL 1943; KAMHI 1959; KINGSBURY & HARTLEY 1955; PALACHE 1935; ROCHA & BAPTISTS 1960; SCHALLER 1916; ZEMANN 1956). No doubt because these minerals are of commercial value. Interest in the structure and formation of these minerals has also been forthcoming (DARA & SIDORENKO 1967; KARPOVA et al. 1968; MAKAROV & ANIKINA 1963). Significant advances have been made over time (KRIVOVICHEV & BURNS 2000a; KRIVOVICHEV & BURNS 2000b; KRIVOVICHEV & BURNS 2002; RASTSVETAeva et al. 2000). This interest has been heightened by the use of the molybdate minerals as catalysts (BATIST & LANKHUIJZEN 1973; BATIST et al. 1969; BATIST et al. 1971; GRZYBOWSKA et al. 1972). Many of these minerals have layered structures which can lead to high surface active materials (KRIVOVICHEV & BURNS 2000a; KRIVOVICHEV & BURNS 2000b; KRIVOVICHEV & BURNS 2002; RASTSVETAeva et al. 2000).

Studies of the application of vibrational spectroscopy to these molybdate minerals is not often forthcoming (BODE et al. 1973; GRIFFITH 1970; YUSHKIN & BUSHUEVA 1971). This may be due to the lack of technology at that time or the availability of appropriate specimens. Recently Frost et al. have used vibrational spectroscopic techniques to study groups of related minerals (FROST et al. 2003a; FROST et al. 2002a; FROST et al. 2002b; FROST et al. 2003b; KRISTOF & FROST 2002; MARTENS & FROST 2003; MARTENS et al. 2003). Raman spectroscopy

has proven a powerful technique for studying closely related minerals, particularly where the minerals can be found associated with each other through paragenesis. In this paper we report the vibrational spectra of selected molybdate minerals namely lindgrenite ( $\text{Cu}_3(\text{MO}_4)_2(\text{OH})_2$ ), iriginite ( $\text{UO}_2\text{Mo}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ ) and koechlinite ( $\text{BiMoO}_6$ ) and relate their Raman spectra to the mineral structure. A comparison of the spectra to more common molybdate bearing minerals such as wulfenite and powellite are made.

### **Minerals:**

The following minerals were obtained from the South Australian Museum and have been characterized. The minerals were checked for phase composition using X-ray diffraction and for chemical composition using the electron probe.

Lindgrenite sample G16506 originated from Pinal Co., Arizona, USA

Lindgrenite sample M21019 originated from Broken Hill, NSW, Australia

Lindgrenite - Chuquicamata, Antofagasta Province, Chile.

Lindgrenite - Superior Mine, Globe-Miami District, Gila County, Arizona

Iriginite - Hervey's Range Deposit, 55 Km W. of Townsville, Queensland, Australia.

Koechlinite G17196 originated from Horni, Czechoslovakia

Koechlinite M47373 originated from Pittong, Victoria, Australia

Molybdoformacite M42867 originated from Eagle Eye Mine, New Water, Arizona.

Wulfenite and powellite originated from Dundas, Tasmania, Australia.

Some lindgrenite and iriginite samples were obtained from The Mineral Research Company. The selection of minerals from these related phases for Raman

spectroscopic analysis must be undertaken with care. Often the crystals are found together in the same specimen.

### **Electron Probe microanalysis**

The scanning electron microscope (SEM) used to study the minerals was the FEI Quanta 200 SEM. The SEM was fitted with an EDAX thin-window X-ray detector. Samples examined under SEM consisted of small selected mineral chips mounted with double-sided carbon tape on aluminium stubs. The surface of samples was coated with a thin layer of carbon in a high vacuum coater to provide a good conductive surface. Elemental analyses were carried out with a qualitative energy dispersive X-ray microanalysis at 25kV and 10mm working distance.

### **Raman microprobe spectroscopy**

The crystals of the molybdate minerals were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, which is 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 Spectra-Physics model 127 Nd-Yag laser (785 nm) and acquired at a nominal resolution of  $2\text{ cm}^{-1}$  in the range between 100 and  $4000\text{ cm}^{-1}$ . 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 incident radiation was scrambled to avoid polarisation effects.

Spectralcalc software package GRAMS. 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 regression coefficient of  $R^2$  greater than 0.995.

## RESULTS AND DISCUSSION

### *Electron microscopy.*

The electron micrograph images of iriginite and lindgrenite are shown in **Figures 1 and 2**. Iriginite is a canary yellow colour and is ortho rhombic. Figure 1 shows the crystal patterns of iriginite and the growth of fan-like crystals from a common point. The mineral can be related to other  $UO_2$  bearing minerals including deloryite ( $Cu_4(UO_2)(MoO_4)_2(OH)_5$ ), calcurmolite ( $Ca(UO_2)_3(MoO_4)_3(OH)_2 \cdot 8H_2O$ ), and tengchongite ( $CaO \cdot 6(UO_3)_2(MoO_3)12H_2O$ ). Lindgrenite is more closely related to minerals such as szeniscite ( $Cu_3MoO_4(OH)_4$ ) and cuprotungstite ( $Cu_2WO_4(OH)_2$ ). Lindgrenite is green to olive-green in appearance and is monoclinic. In order to check The composition of the minerals for Raman spectroscopy, electron probe analyses were undertaken. These analyses are shown in **Figures 3 and 4** for iriginite and lindgrenite. The iriginite sample contained uranium and molybdenum only with

traces of iron which was not in the background analyses. The iriginite sample analysed as pure iriginite ( $\text{UO}_2\text{Mo}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ ). Likewise the lindgrenite and koechlinite analysed as the pure phases lindgrenite ( $\text{Cu}_3(\text{MO}_4)_2(\text{OH})_2$ ) and koechlinite ( $\text{BiMoO}_6$ ).

## Theory

Minerals with a scheelite structure like wulfenite have site group  $S_4$  and space group  $C_{4h}^6$ . The crystal structure resembles that of zircon and therefore the  $\text{WO}_4$  and  $\text{MoO}_4$  groups should show four bands only in the Raman spectra, two components each of  $\nu_3$  and  $\nu_4$ . The scheelite structure has been shown to be one of the few for which the correlation splitting of the internal modes has been observed. This results in  $\nu_1: A_g(\text{R}) + B_u(\text{inactive})$ ,  $\nu_2: A_g + B_g(\text{R}) + A_u(\text{ir}) + B_u$ ,  $\nu_3, \nu_4: B_g + E_g(\text{R}) + A_u(\text{ir}) + E_u(\text{ir})$  (CRANE et al. 2002).

## Raman microscopy

The Raman spectra at 298 K for selected molybdate minerals listed above are shown in Figures 5 and 6. Figure 5 shows the spectrum in the  $\text{MoO}_2$  stretching region and Figure 6 in the low wavenumber region. The results of the spectroscopic analyses are reported in Table 1. Calculations for the wulfenite structure indicates the following Raman bands  $\nu_1: A_g + B_u(\text{inactive, but activated due to strain})$ ,  $\nu_2: A_g + B_g + B_u$ ,  $\nu_3, \nu_4: B_g + E_g$ , most of which are easily observed for wulfenite (and scheelite). The  $\nu_1(A_g)$  band is observed at  $871 \text{ cm}^{-1}$  and although the corresponding  $\nu_1(B_u)$  vibration should be inactive a minor band is observed around  $858 \text{ cm}^{-1}$ . It may be possible that this

band is visible as a weak band due to strain in the crystal causing activation of this band. This band for synthetic powellite is observed in the infrared spectrum at 819  $\text{cm}^{-1}$  (BROWN et al. 1970). For powellite the bands are observed at 879 and 847  $\text{cm}^{-1}$ . Interestingly Farmer reported the  $\nu_1(A_g)$  band in the Raman spectrum for synthetic powellite at 880  $\text{cm}^{-1}$  and for wulfenite at 872  $\text{cm}^{-1}$  (FARMER 1974).

The two  $\nu_2$  modes are observed at 319  $\text{cm}^{-1}$  ( $A_g$ ) and 351  $\text{cm}^{-1}$  ( $B_g$ ). Farmer reports these bands at Raman spectra of wulfenite at 321 and 354  $\text{cm}^{-1}$  (FARMER 1974). Three bands were given for synthetic powellite at 404, 394 and 326  $\text{cm}^{-1}$  (FARMER 1974). For the  $\nu_3(E_g)$  Ross reports two values for wulfenite around 748 and 772  $\text{cm}^{-1}$ , which agrees well with the values observed in this study of approximately 745 and 768  $\text{cm}^{-1}$  (BROWN et al. 1970; ROSS 1972). For  $\text{CdMoO}_4$  however only one band has been reported around 759  $\text{cm}^{-1}$ . The corresponding  $\nu_3(B_g)$  is found at 815  $\text{cm}^{-1}$ . The expected  $\nu_4(E_g)$  around 384  $\text{cm}^{-1}$  is absent in the spectrum of natural wulfenite. Two bands were listed at 820 and 770  $\text{cm}^{-1}$  for wulfenite and two bands at 847 and 796  $\text{cm}^{-1}$  for synthetic powellite (BROWN et al. 1970; FARMER 1974). The bands of wulfenite at 351 and 319  $\text{cm}^{-1}$  are assigned as either deformation modes or as  $r(B_g)$  and  $\delta(A_g)$  modes of terminal  $\text{MO}_2$ . these bands are observed at 355 and 320  $\text{cm}^{-1}$  for powellite. The band at 462  $\text{cm}^{-1}$  has an equivalent band in the infrared at 455  $\text{cm}^{-1}$  assigned as  $\delta_{\text{as}}(A_u)$  of the  $(\text{M}_2\text{O}_4)_n$  chain. The equivalent band for powellite is observed at 456  $\text{cm}^{-1}$ . The band at 513  $\text{cm}^{-1}$  for powellite is assigned as  $\nu_{\text{sym}}(B_g)$  of the  $(\text{M}_2\text{O}_4)_n$  chain. The band for powellite at 794  $\text{cm}^{-1}$  is interpreted as an antisymmetric bridging mode associated with the molybdate chain. The bands for wulfenite at 768 and 745  $\text{cm}^{-1}$  are associated with the antisymmetric and symmetric  $A_g$  modes of terminal  $\text{MO}_2$ . Additional bands were observed at 195 and 166  $\text{cm}^{-1}$ ,

assigned as translational modes of Pb-O and MO<sub>4</sub>. Three bands are observed at 196, 159 and 152 cm<sup>-1</sup> for powellite and are assigned to translational modes of Ca-O and MO<sub>4</sub>.

The unit cell of lindgrenite is monoclinic, space group P21/n, with a = 5.613, b = 14.03, c = 5.405 Å, β = 98 Deg23' and contains 2 formula units per unit cell. The structure contains complex chains of joined CuO<sub>4</sub>(OH)<sub>2</sub> octahedra linked into a network by MoO<sub>4</sub> tetrahedra. The average Mo-O distance is 1.75 Å, and Cu-O distances are 2 of 2.43 Å and 4 of 1.96 Å for each Cu atom (CALVERT & BARNES 1957). The crystal structure was refined by Hawthorne (HAWTHORNE & EBY 1985). The structure of lindgrenite consists of strips of edge-sharing CuO<sub>6</sub> (O = unspecified ligand) octahedra that are cross-linked by MoO<sub>4</sub> tetrahedra. Hawthorne and Eby showed that alternate strips were canted at + and – at approximately 25° to (100), the sense of the tilt being along Y. This tilting results in close-packed layers parallel to (100). These layers are modulated along Y with amplitude of approximately 1/6 of a wavelength. These authors report that such modulated layers are common in copper minerals (HAWTHORNE & EBY 1985).

Three samples of lindgrenite from three different localities were analyzed by Raman spectroscopy. Fundamentally the spectra are identical except for some variation in intensity (Figure 5). An intense band is observed at around 932 cm<sup>-1</sup> and is assigned to the ν<sub>1</sub> stretching mode of MoO<sub>4</sub> tetrahedra. Very low intensity bands are observed at around 987 cm<sup>-1</sup> and this band is attributed to the symmetric stretching mode of isomorphous substituted SO<sub>4</sub> units even though no sulphur was determined in the samples by electron probe analyses. The low intensity band at 883 cm<sup>-1</sup> is

attributed to the  $\nu_1(B_u)$  vibration should be inactive in the Raman spectrum but is observed as a low intensity band. It may be possible that this band is visible as a weak band due to strain in the crystal causing activation of this band. The two bands at around 795 and 772  $\text{cm}^{-1}$  are interpreted as antisymmetric and symmetric  $A_g$  modes of terminal  $\text{MO}_2$ . The low wavenumber region of lindgrenite is complex with overlapping bands. The bands at 335 and 354  $\text{cm}^{-1}$  are interpreted as  $\nu_2$  modes with 335  $\text{cm}^{-1}$  ( $A_g$ ) and 354  $\text{cm}^{-1}$  ( $B_g$ ). The bands at 398 and 493  $\text{cm}^{-1}$  are assigned as  $\delta_{\text{as}}(A_u)$  of the  $(\text{M}_2\text{O}_4)_n$  chains. The series of bands between 120 and 210  $\text{cm}^{-1}$  are interpreted as lattice modes and CuO and MoO stretching modes.

The mineral iriginite is orthorhombic of space group Pca21 (SEREZHKIN et al. 1973; SEREZHKIN et al. 1981). Metal atoms form octahedrons  $[\text{MoO}(\text{H}_2\text{O})\text{O}_4]$ , which are connected by tops and sides and give an infinite zig-zag chain of composition  $[\text{Mo}_2\text{O}_7(\text{H}_2\text{O})_2]$ , distributed parallel to period c (SEREZHKIN et al. 1973). In its structure, the uranyl ions (U-O 1.75 and 1.77 Å) are bound by endless zigzag chains of  $\text{MoO}_5(\text{H}_2\text{O})$  octahedrons (with the Mo-O distance 1.69-2.43 Å) into a layer in which the coordination of polyhedrons of U atoms is represented by pentagonal bipyramids of  $(\text{UO}_2)\text{O}_5$  (SEREZHKIN et al. 1981). The Raman spectrum of iriginite will reflect the two vibrating units namely  $(\text{UO}_2)$  and  $(\text{MO}_4)$ . Previous studies have shown that the two UO bonds in the  $\text{UO}_2$  units are not equivalent (CEJKA 1999; CEJKA et al. 1984; CEJKA et al. 1985). This gives rise to two UO stretching bands. In the Raman spectrum of iriginite two closely overlapping bands are observed at 826 and 818  $\text{cm}^{-1}$  and are attributed to these two UO stretching vibrations. This doubling of the UO symmetric stretching vibrations is also reflected in the  $\text{UO}_2$  antisymmetric stretching region where two bands are observed at 965 and

950  $\text{cm}^{-1}$  (CEJKA et al. 1984). The band at 888  $\text{cm}^{-1}$  is therefore assigned to the  $\nu_1$  symmetric stretching vibration of the  $\text{MO}_4$  units. Two comparatively intense bands are observed at 246 and 198  $\text{cm}^{-1}$  and are assigned to the bending modes of the  $\text{UO}_2$  units (CEJKA et al. 1984). The bands at 337 and 301  $\text{cm}^{-1}$  are assigned to the  $\nu_2$  bending modes of the  $\text{MO}_4$  units. The  $\nu_3(B_g)$  vibration is located around 693  $\text{cm}^{-1}$ , whereas the  $\nu_3(E_g)$  is found at 668  $\text{cm}^{-1}$ . The bands observed at 487, 457 and 413  $\text{cm}^{-1}$  are attributed to  $\nu_4(E_g)$  modes.

The crystal structure of koechlinite has been under review for some time (ZEMANN 1954; ZEMANN 1956) and refinement of the crystal structure has been made (VAN DEN ELZEN & RIECK 1973).  $\text{Bi}_2\text{MoO}_6$  is orthorhombic, space group  $\text{Pca}2_1$  (THEOBALD et al. 1984). Complex oxides and oxyhalides of Bi have a pseudo-tetragonal symmetry. Deviations from tetragonal symmetry are due to  $\text{MoO}_6$  octahedra tilts. Further distortions are revealed by octahedra rotations and displacement of Mo atoms from the centres of octahedra (THEOBALD et al. 1984). The Raman spectrum of koechlinite shows an intense band at 797  $\text{cm}^{-1}$  assigned to the  $\nu_1$  symmetric stretching vibration of  $\text{MoO}_4$  units. The band at 843  $\text{cm}^{-1}$  may be assigned to the  $\nu_3$  antisymmetric vibration. The Raman spectrum of the koechlinite sample from Pittong, Victoria, Australia may contain impurities chiefly of bismoclite ( $\text{BiOCl}$ ). These impurities make the interpretation of the Raman spectrum difficult.

For completeness the Raman data for molybdoformacite ( $\text{Pb}_2\text{Cu}[(\text{As,P})\text{O}_4][\text{Mo,Cr}\text{O}_4](\text{OH})$ ) is included. This mineral is related to the formacite-vauquelinite series by substitution of  $\text{MoO}_4$  units for the  $\text{CrO}_4$  units in the structure. These minerals may contain  $\text{AsO}_4$  and/or  $\text{PO}_4$  units. The Raman spectrum

shows an intense band at  $855\text{ cm}^{-1}$  which may be assigned to the  $\text{MoO}_4$  stretching vibrations. Low intensity bands are observed at  $938$  and  $835\text{ cm}^{-1}$  which are likely to be the symmetric stretching vibrations of the  $\text{PO}_4$  and  $\text{AsO}_4$  units. The bands at  $713$  and  $665$  are attributable to the  $\text{MoO}_2$  end groups. The bands at  $320\text{ cm}^{-1}$  is attributed to the  $\nu_2\text{ MoO}_4$  bending modes and the bands at  $387$  and  $355\text{ cm}^{-1}$  to the  $\nu_4\text{ MoO}_4$  bending modes. Low wavenumber bands for molybdoformacite are observed at  $278$ ,  $226$ ,  $196$ ,  $159$  and  $152\text{ cm}^{-1}$ .

## CONCLUSIONS

The molybdenum bearing minerals lindgrenite, iriginite and koechlinite were studied by scanning electron microscopy and compositionally analysed by EDX methods using an electron probe before Raman spectroscopic analyses. Raman spectroscopy has been used to characterise a series of molybdate containing minerals including lindgrenite, iriginite and koechlinite and a comparison is made with the Raman spectrum of the more common minerals wulfenite and powellite. The Raman spectra are assigned according to factor group analysis and related to the structure of the minerals. These minerals have characteristically different Raman spectra.

The mineral iriginite is characterised by bands assigned to the vibrations of the  $\text{UO}_2$  units. These units provide intense Raman bands at  $965$ ,  $950$  and  $826$  and  $818\text{ cm}^{-1}$ . These bands are attributed to the antisymmetric and symmetric stretching modes of the  $\text{UO}_2$  units respectively. Bands at  $888$ ,  $693$ ,  $668$ ,  $413$ ,  $373$  and  $337\text{ cm}^{-1}$  are attributed to vibrations of the  $\text{MoO}_4$  units. The bands at  $693$  and  $668\text{ cm}^{-1}$  are attributed to antisymmetric and symmetric  $A_g$  modes of terminal  $\text{MO}_2$  units. Similar

bands are observed at 797 and 773  $\text{cm}^{-1}$  for koechlinite and 798 and 775  $\text{cm}^{-1}$  for lindgrenite. It is probable that some of the bands in the low wavenumber region are attributable to the bending modes of these  $\text{MO}_2$  units.

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**Table 1 Raman spectroscopic analysis of wulfenite, powellite, lindgrenite, iriginite and koechlinite**

wulfenite	wulfenite	powellite	powellite	lindgrenite	lindgrenite	lindgrenite	iriginite	koechlinite	koechlinite	molybdoformacite
	(FARMER 1974)		(FARMER 1974)	G16506	M21019	MinResCo	MinResCo	M47373	G17196	M42867
				982		987				
871	872	879	880	929	932	933	965	843	845	
858	820	847	847	883	887	902	950			855
				837	839	886	888			
						839	826			
							818			
768	770	794	796	795	798	798	693	797	793	
745				772	775		668	773		713
								715	718	665
								685		

		513		493	496	500	487		625	
462	384	456		398	399	412	457	401	529	387
351	354	403	394	354	342	400	413	349	449	355
319		392		335	335	361	373		393	320
						339	337		353	
	321	324	326	300	313	313	301	321	320	
	296	267		284	302	303	246	293	269	
					287	287		281		278
					251	253		268		226
195				210	217	215	198	228	204	196
				198	190	205		195		
				188						
166				167	171	172	164	154	155	159
				155	158	159		141		152

				139	123	142				
				120		126				

## **List of Figures**

**Figure 1 Electron micrograph of iriginite.**

**Figure 2 Electron micrograph of lindgrenite.**

**Figure 3 Electron probe analysis of iriginite.**

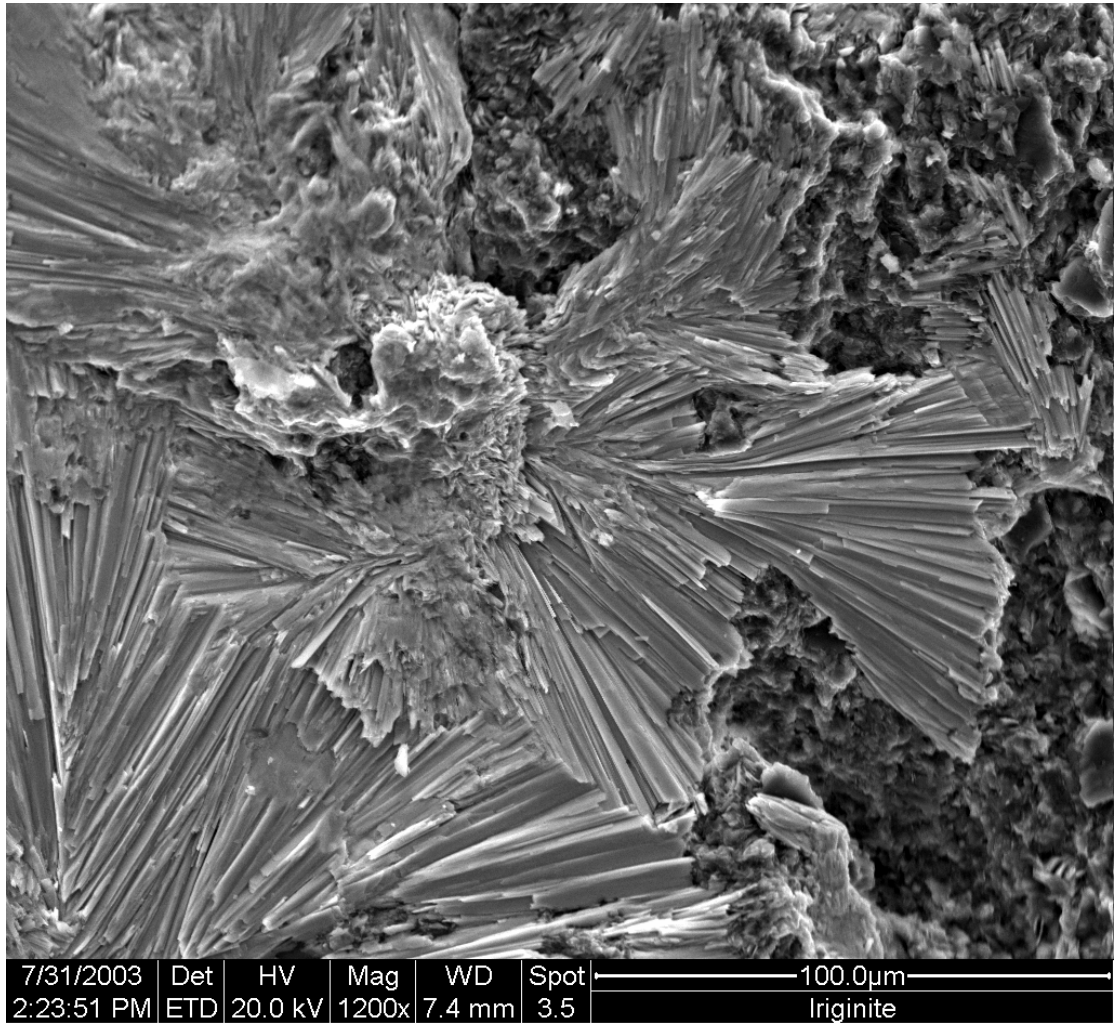
**Figure 4 Electron probe analysis of lindgrenite.**

**Figure 5 Raman spectra of the  $\text{MO}_4$  stretching region of wulfenite, powellite, lindgrenite, iriginite and koechlinite.**

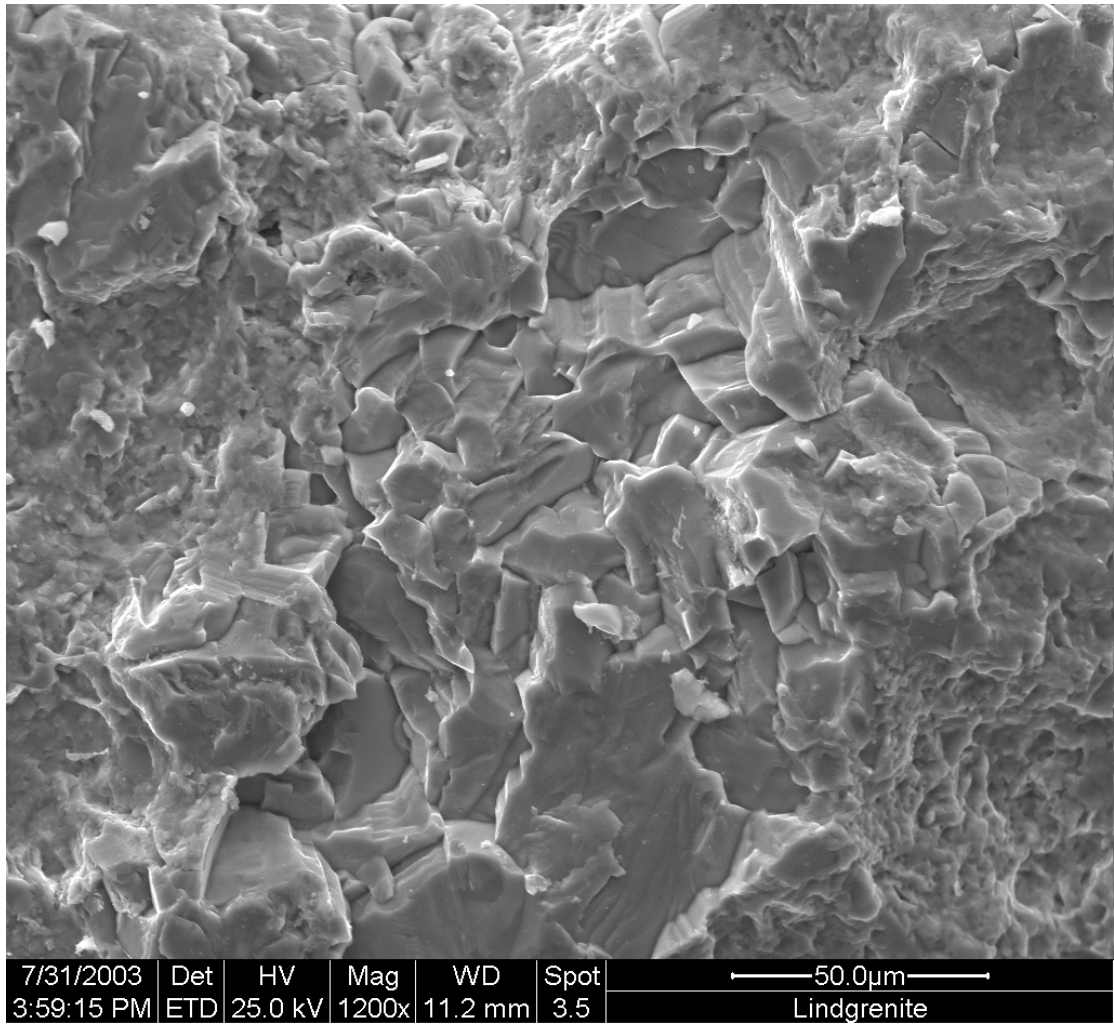
**Figure 6 Raman spectra of the low wavenumber region of  $\text{MO}_4$  of wulfenite, powellite, lindgrenite, iriginite and koechlinite.**

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**Table 1 Raman spectroscopic analysis of wulfenite, powellite, lindgrenite, iriginite and koechlinite**

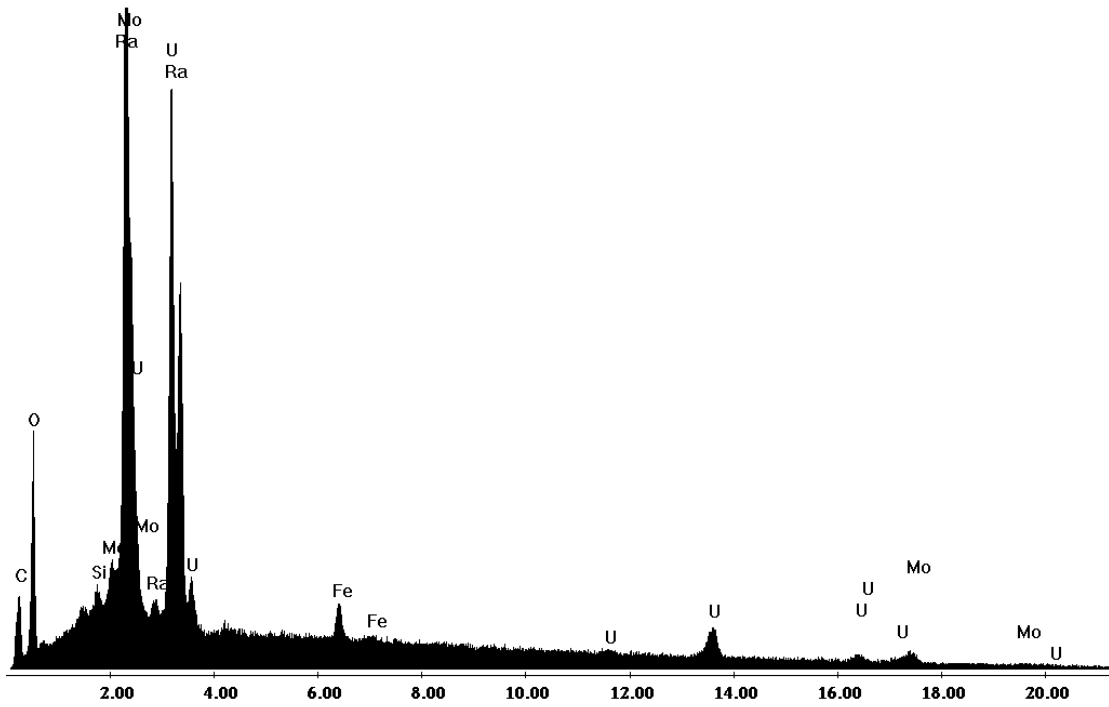


**Figure 1**



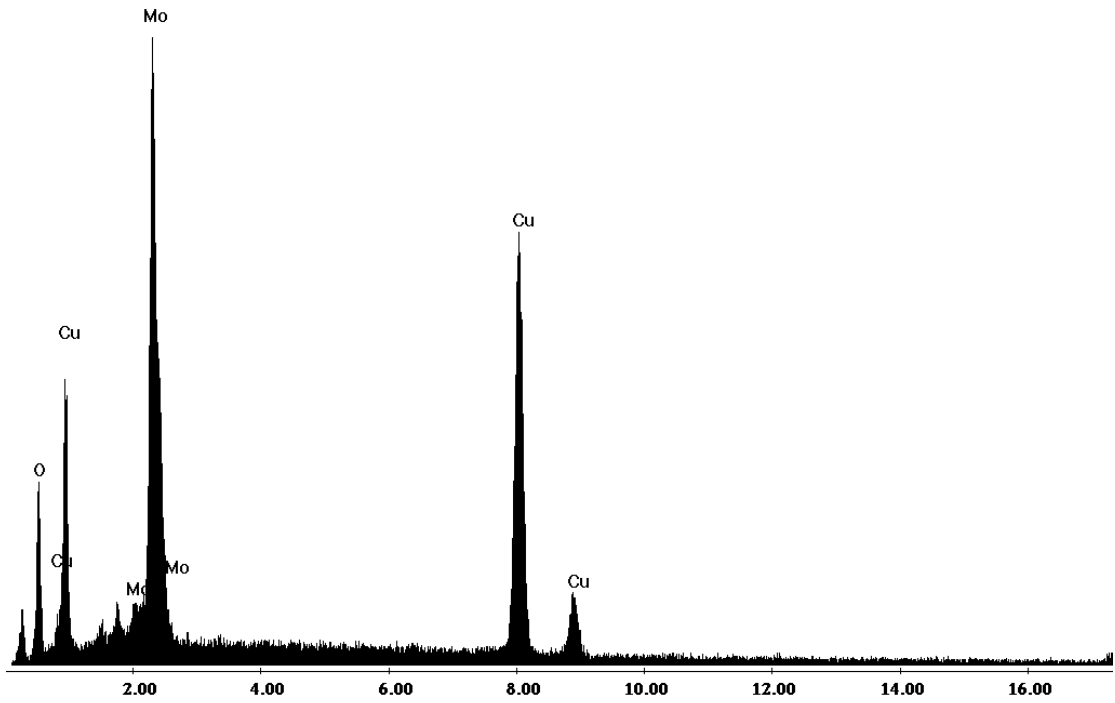
**Figure 2**

Label A: Irriginite

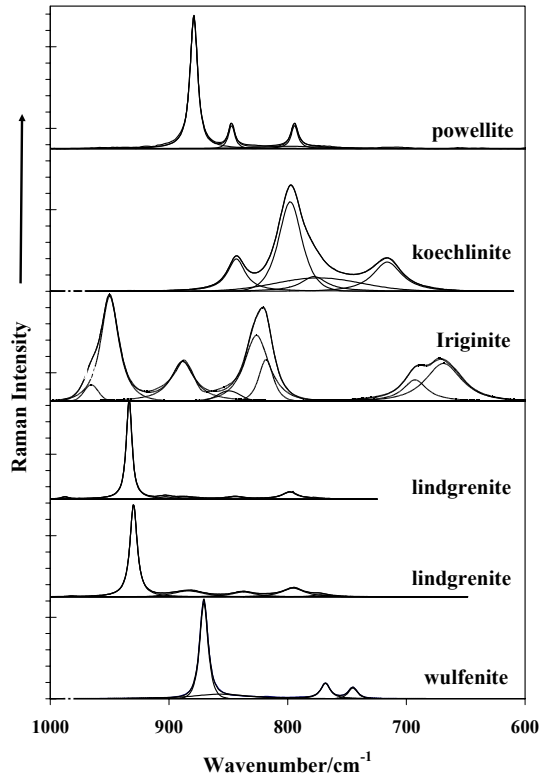


**Figure 3**

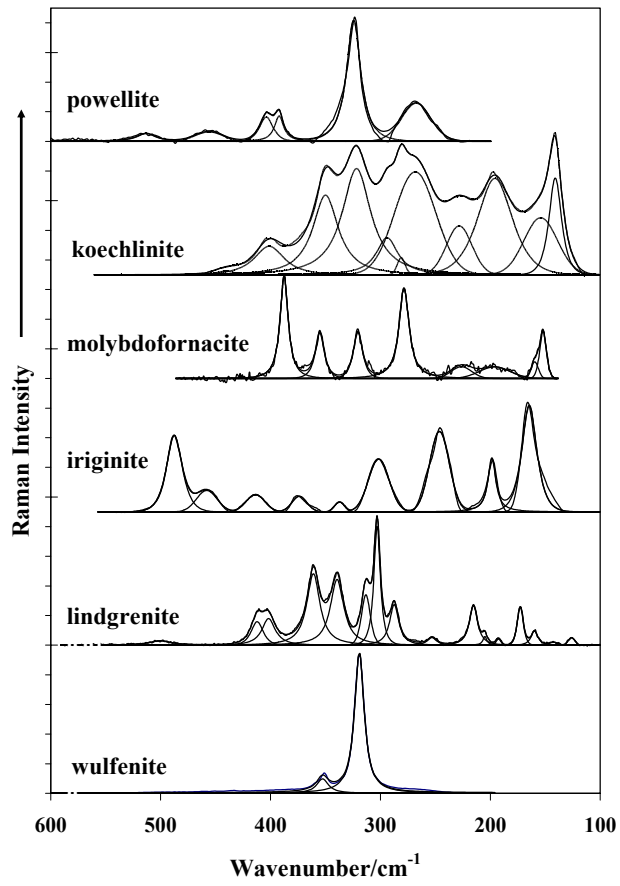
Label A: Lind1



**Figure 4**



**Figure 5**



**Figure 6**

