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**Raman spectroscopy of the phase related basic copper arsenate minerals:  
olivenite, cornwallite, cornubite and clinoclase**

**Ray L. Frost<sup>1\*</sup>, Wayde N. Martens<sup>1</sup> and Peter A. Williams<sup>2</sup>**

<sup>1</sup>Centre for Instrumental and Developmental Chemistry, Queensland University of Technology,  
GPO Box 2434, Brisbane Queensland 4001, Australia.

<sup>2</sup>Centre for Industrial and Process Mineralogy, School of Science, Food and Horticulture,  
University of Western Sydney, Locked Bag 1797, Penrith South DC NSW 1797, Australia.

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**The Raman spectra of olivenite, cornwallite and its diamorph cornubite and clinoclase have been obtained at 298 and 77K using a combination of a thermal stage and Raman microscopy. The vibrational spectra of minerals are different, in line with differences in crystal structure and composition. Some similarity in the Raman spectra of the hydroxyl-stretching region exists, particularly at 298 K. Two hydroxyl-stretching frequencies are observed for each mineral with the bands for clinoclase being well separated. Characteristic differences in the OH deformation regions are observed. Differences are also observed in the arsenate stretching and deformation regions. The OAsO bending modes are identified. The application of Raman microscopy to the study of closely related mineral phases has enabled their molecular characterisation using their Raman spectrum, thus enabling the rapid identification of phases in complex mixtures of secondary copper arsenates from the oxidized zones of base metal ore bodies.**

**Key Words-** copper, arsenate, olivenite, cornwallite, cornubite, clinoclase thermal stage, Raman spectroscopy

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

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## INTRODUCTION

There exists a number of dark emerald green copper arsenate minerals, including olivenite  $[\text{Cu}_2(\text{AsO}_4)_2(\text{OH})]$ ,<sup>1</sup> Olivenite is the most common secondary mineral of the oxidised zone of hydrothermal deposits monoclinic, space group  $P2_1/n$ . Minerals related to this mineral in the phase fields of copper and arsenate are the minerals Cornwallite  $[\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4]$  and clinoclase  $[\text{Cu}_3(\text{AsO}_4)(\text{OH})]$ . Each of these minerals occurs in the oxidized zones of copper deposits and olivenite is by far the commonest.<sup>1</sup> Cornwallite, a rare secondary mineral is monoclinic, space group  $P2_1/a$  and clinoclase, a rare secondary mineral, is also monoclinic, space group  $P2_1/a$ . The relative stabilities of the basic copper arsenates have been determined using estimated chemical parameters and experimentally determined solubility products are available.<sup>2,3</sup> Normal anhydrous copper(II) arsenate is known as the naturally occurring species lammerite  $[\text{Cu}_3(\text{AsO}_4)_2]$ , but it is very rare<sup>4</sup>. The more basic stoichiometries occupy fields at higher pH as expected. Olivenite is the stable phase under chemical conditions intermediate to those that serve to stabilize cornwallite and clinoclase and paragenetic relationships have been explored.<sup>4</sup> Olivenite is often found with cornwallite or clinoclase but not together.

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion ( $\nu_1$ ) is observed at  $810\text{ cm}^{-1}$  and coincides with the position of the asymmetric stretching mode ( $\nu_3$ ). The symmetric bending mode ( $\nu_2$ ) is observed at  $342\text{ cm}^{-1}$  and the out-of-plane bending modes ( $\nu_4$ ) is observed at  $398\text{ cm}^{-1}$ . Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of spectra of arsenates including the basic copper arsenates olivenite and euchroite.<sup>5</sup> The effect of the arsenate ion in a crystal will be to remove the degeneracy and allow splitting of the bands according to factor group analysis. The  $\nu_1$  and  $\nu_3$  bands of olivenite and euchroite were observed at  $860, 828, 790\text{ cm}^{-1}$  and  $830$  and  $770\text{ cm}^{-1}$  respectively. The bending modes were found at  $493$  and  $452\text{ cm}^{-1}$  for olivenite and at  $475$  and  $410$

cm<sup>-1</sup> for euchroite. No  $\nu_2$  bands were shown. This is no doubt related to the fact the bands are found below 400 cm<sup>-1</sup>, which makes the measurement by infrared spectroscopy difficult. Two OH stretching vibrations were observed at 3580 and 3440 cm<sup>-1</sup> for olivenite. A number of bands were listed which were unassigned.

The stability of the basic copper arsenate minerals is related to their redox potential and phase fields exist for the related minerals olivenite, cornubite, clinoclase and cornwallite. The mineral structure of olivenite is monoclinic, pseudo-orthorhombic with point group  $2/m$ <sup>6,7</sup>. The mineral has a space group of  $P2_1/n$ . Cornwallite is monoclinic with point group:  $2/m$  and space group  $P2_1/a$ <sup>6,8</sup>. Clinoclase is also monoclinic with point group  $2/m$  and space group  $P2_1/a$ <sup>6,9,10</sup>. Thus the structure of these three phase related minerals are related and should provide related spectra, which should only differ in terms of the intensity of the bands according to the relative mole ratios of Cu/As/OH.

Whilst the infrared spectra of some minerals have been forthcoming, few comprehensive studies of related minerals such as the basic copper arsenates have been undertaken<sup>11-13</sup>. No spectroscopic investigation of these phase related minerals has been undertaken. The structural investigation of some arsenates and the nature of the hydrogen bond in these structures have been reported<sup>14</sup>. It was found that the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion<sup>14</sup>. These minerals selected in this study were fundamentally unrelated. Indeed few Raman studies have been undertaken<sup>15-17</sup>. Recently Raman spectroscopy has proven most useful for the study of minerals which have phase relationships<sup>18-21</sup>. As part of a comprehensive study of the molecular structure of minerals containing oxyanions using IR and Raman spectroscopy, we report the Raman properties of the abovenamed basic copper arsenate phases.

## **EXPERIMENTAL**

### **The mineral samples**

The sample of cornubite from the Daly mine, Flinders Ranges, South Australia was obtained from the collections of the Mineralogy Section, Museum Victoria,

Melbourne, Victoria, Australia (specimen M37793). Cornwallite and olivenite from the Penberthy Croft mine, St Hilary, Cornwall, UK, were supplied by Mr John Betterton. Samples of olivenite and clinoclase from the Tin Stope, Majuba Hill mine, Utah, USA, were purchased from the Mineralogical Research Company. All were checked for purity by powder X-ray diffraction and by SEM and microprobe methods. Negligible amounts of phosphorus or transition metals other than copper were found in the samples used for this spectroscopic study.

### **Raman microprobe spectroscopy**

Crystals of the minerals were orientated on a polished metal surface on the stage of an Olympus BHSM microscope equipped with 10x and 50x objectives. For ludjibaite and reichenbachite, crystals on matrix were placed directly under the microscope. The microscope is 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 Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of  $2\text{ cm}^{-1}$  between 100 and  $4000\text{ cm}^{-1}$ . Repeated acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio in the spectra, which were calibrated using the  $520.5\text{ cm}^{-1}$  line of a silicon wafer. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

Spectroscopic manipulations such as baseline adjustment, smoothing and normalization were performed using the Spectralcalc 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 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 correlations of  $r^2$  greater than 0.995.

## THEORY

### FACTOR GROUP ANALYSIS OF OLIVENITE

Point group	Site group	Crystal
AsO <sub>4</sub>		
T <sub>d</sub>	C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
A <sub>1</sub> E 2T <sub>2</sub>	9A	9A <sub>g</sub> 9A <sub>u</sub> 9B <sub>g</sub> 9B <sub>u</sub>
Cu(I)OH		
C <sub>s</sub>	C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
3A'	3A	3A <sub>g</sub> 3A <sub>u</sub> 3B <sub>g</sub> 3B <sub>u</sub>

**Table 1 Factor group analysis of the arsenate ion and Cu(I)OH in olivenite**

The factor group analysis predicts 36 vibrations for the arsenate ion represented by  $\Gamma = 9A_g + 9A_u + 9B_g + 9B_u$ . For the factor group analysis for the prediction of the Raman spectra, we must use a value of  $Z = 4$ <sup>22</sup>. The reason for this is that there are four arsenate ions from 4 adjacent ions with the oxygens of these arsenate ions in any individual unit cell. The AsO<sub>4</sub> splitting should be the same for clinoclase and cornwallite but will have different lattice vibrations due to different splitting patterns and different bond lengths. Thus the vibrational modes for the arsenate ion in olivenite is given by:  $\Gamma = 9A_g + 9A_u + 9B_g + 9B_u$ . Thus there should be 18 Raman active modes for the arsenate ion for olivenite.

Site group	Crystal
Cu (I)OH, Cu(II), AsO <sub>4</sub>	
C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
15A	<div style="display: flex; flex-direction: column; align-items: center;"> <div style="margin-bottom: 5px;">→ 15A<sub>g</sub></div> <div style="margin-bottom: 5px;">→ 15A<sub>u</sub></div> <div style="margin-bottom: 5px;">→ 15B<sub>g</sub></div> <div>15B<sub>u</sub></div> </div>

**Table 2 Factor group analysis of the lattice modes in olivenite**

$$\Gamma = 14A_g + 13B_g + 14A_u + 13B_u$$

The irreducible representation above predicts that there are 27 Raman active modes for olivenite in the lattice region.

## FACTOR GROUP ANALYSIS OF CORNWALLITE

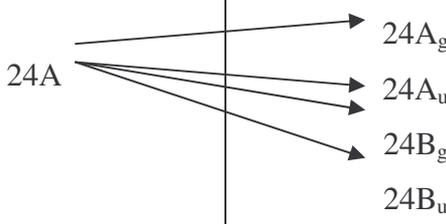
Point group	Site group	Crystal
AsO <sub>4</sub>		
T <sub>d</sub>	C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
A <sub>1</sub> E 2T <sub>2</sub>	9A	9A <sub>g</sub> 9A <sub>u</sub> 9B <sub>g</sub> 9B <sub>u</sub>

**Table 3 Factor group analysis of the arsenate ion in cornwallite**

For cornwallite  $Z = 2$ <sup>23</sup>. This may be compared with cornubite where  $Z = 1$ <sup>24</sup>. Thus the vibrational modes for the arsenate ion in cornwallite are given by:  $\Gamma = 9A_g + 9A_u + 9B_g + 9B_u$ . Thus there should be 18 Raman active modes for the arsenate ion for cornwallite. In Table 3, in going from the point group to the site symmetry of the crystal the rotational modes are no longer present. Even though cornwallite and cornubite have the same chemical formula, the unit lattices are different. Hence different vibrational splitting is predicted.

Site group	Crystal
Cu (I)	
C <sub>i</sub>	C <sub>2h</sub> <sup>5</sup>
3A <sub>u</sub>	3A <sub>u</sub> 3B <sub>u</sub>

**Table 4 Factor group analysis of the lattice modes in cornwallite**

Site group	Crystal
Cu(II), Cu(III),AsO <sub>4</sub> , OH(I) , OH(II)	
C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
24A	

**Table 5 Factor group analysis of the all modes in cornwallite**

$$\Gamma = 23A_g + 22A_u + 26B_g + 25B_u$$

The above analysis predicts that there are 45 Raman active modes. This includes all the lattice vibrational modes

## FACTOR GROUP ANALYSIS OF CORNUBITE

Point group	Site group	Crystal
AsO <sub>4</sub>		
T <sub>d</sub>	C <sub>1</sub>	C <sub>i</sub>
A <sub>1</sub>	9A	9A <sub>g</sub>
E		9A <sub>u</sub>
2T <sub>2</sub>		

**Table 6 Factor group analysis of the arsenate ion in cornubite**

For cornubite  $Z = 1$ <sup>24</sup>. This allows the splitting of the free arsenate vibrations into symmetric and antisymmetric modes. Hence

$\Gamma = 9A_g + 9A_u$ . Thus 9 Raman bands are predicted.

Site group	Crystal
Cu (I)	
C <sub>i</sub>	C <sub>i</sub>
3A <sub>u</sub>	3A <sub>u</sub>

**Table 7 Factor group analysis of the lattice modes in cornubite**

Site group	Crystal
Cu(II), Cu(III), AsO <sub>4</sub> , OH(I), OH(II)	
C <sub>1</sub>	
	24A <sub>g</sub>
24A	24A <sub>u</sub>

### **Table 8 Factor group analysis of the lattice modes in cornubite**

$$\Gamma = 21A_g + 24A_u$$

Cornubite is  $C_i$  and even though it is a polymorph of cornwallite it has a different space group so will have different  $AsO_4$  splitting. Lattice modes will be very distinctly different. The representation predicts 21 Raman active modes including the lattice vibrations.

## FACTOR GROUP ANALYSIS OF CLINOCLASE

Point group	Site group	Crystal
AsO <sub>4</sub>		
T <sub>d</sub>	C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
A <sub>1</sub> E 2T <sub>2</sub>	9A	9A <sub>g</sub> 9A <sub>u</sub> 9B <sub>g</sub> 9B <sub>u</sub>

**Table 9** Factor group analysis of the arsenate ion in clinoclase

For clinoclase X-ray diffraction predicts  $Z = 4$ . Thus there are arsenate ions per unit cell, thus predicting 36 vibrations. Factor group analysis predicts 36 vibrations represented by  $\Gamma = 9A_g + 9A_u + 9B_g + 9B_u$ . For the factor group analysis for the prediction of the Raman spectra, we must use a value of  $Z = 4^{10}$ . The reason for this is that there are four arsenate ions from 4 adjacent ions with the oxygens of these arsenate ions in any individual unit cell.

Site group	Crystal
Cu (I)OH, Cu(II), Cu(III),AsO <sub>4</sub> , OH(I) , OH(II) , OH(III)	
C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
33A	33A <sub>g</sub> 33A <sub>u</sub> 33B <sub>g</sub> 33B <sub>u</sub>

**Table 10** Factor group analysis of the lattice modes in Clinoclase

$$\Gamma = 32A_g + 31B_g + 32A_u + 31B_u$$

Site group	Crystal
Cu (I)OH, Cu(II), Cu(III),AsO <sub>4</sub> , OH(I) , OH(II) , OH(III)	
C <sub>1</sub>	C <sub>2h</sub> <sup>5</sup>
33A	33A <sub>g</sub> 33A <sub>u</sub> 33B <sub>g</sub> 33B <sub>u</sub>

**Table 11 Factor group analysis of the lattice modes in Clinoclase**

$\Gamma = 32A_g + 31B_g + 32A_u + 31B_u$ . This analysis suggests that there are 63 Raman active modes for the lattice region alone.

## RESULTS and DISCUSSION

### Use of the HeNe 663 nm laser for Raman excitation of minerals

Many of the arsenates and phosphates of copper are highly coloured being either green or bluish green in colour. This means the minerals absorb radiation at the red wavelengths. Often, particularly with arsenates, the incident radiation of the HeNe laser causes the hydroxy arsenate samples to be destroyed. This no doubt is due to the power density whereby all the incident radiation is focused over a micron spot. Successful spectra were obtained by using very low power of the order of 1 mW and defocusing the beam. The consequence of this technique is that spectral data must be collected over a longer period of time.

### Hydroxyl-stretching and deformation vibrations.

The Raman spectra of the hydroxyl-stretching region of olivenite, cornwallite, cornubite and clinoclase are shown in [Figure 1](#). For olivenite the Raman spectrum may be resolved into two overlapping bands centred upon 3464 and 3437  $\text{cm}^{-1}$ . In the spectrum of the hydroxyl-stretching region of cornwallite two partially band-separated peaks are observed at 3411 and 3350  $\text{cm}^{-1}$ . For cornubite two bands are observed at 3324 and 3042  $\text{cm}^{-1}$ . For clinoclase two well separated bands separated peaks are observed at 3559 and 3339  $\text{cm}^{-1}$ . Diffuse reflectance spectroscopy (DRIFT) spectroscopy indicates no band around 1620  $\text{cm}^{-1}$ . Thus no water is present in these minerals. The observation of two hydroxyl-stretching vibrations means that there are two distinct and different hydroxyl units in the basic copper arsenate minerals. The difference between the peak positions of olivenite and cornwallite is related to the strength of the hydrogen bond formed between the hydroxyl unit and an adjacent arsenate unit. This bonding is much stronger in cornwallite as indicated by the lower wavenumber position of the hydroxyl-stretching vibrations. One interpretation is that the higher wavenumber vibration is ascribed to the As-OH vibration and the lower wavenumber hydroxyl stretching frequency to the As-OH $\cdots$ O vibration.

The Raman spectra of the hydroxyl stretching region at 77 K were obtained and although the spectra suffer from a lack of scattering due to the low energy of excitation, bands can be easily observed although suffer from a lack of signal to noise. The Raman spectrum of the hydroxyl-stretching region of olivenite at 77K shows two partially separated bands at 3468 and 3441  $\text{cm}^{-1}$ . Interestingly the bands have shifted to higher wavenumbers upon cooling to liquid nitrogen temperature. This suggests a weakening of the hydrogen bonding upon cooling. A similar result is observed for the other two minerals. Cornwallite displays two partially resolved hydroxyl-stretching bands at 3415 and 3369  $\text{cm}^{-1}$  at 77 K and clinoclase displays two well resolved and very narrow bands at 3557 and 3339  $\text{cm}^{-1}$  at 77 K. The widths of these latter two bands were 7.6 and 9.3  $\text{cm}^{-1}$  respectively. It was not possible to obtain quality Raman spectrum of the hydroxyl-stretching region of cornwallite.

In the Raman spectra of the AsO stretching vibrations, an additional low intensity band may be observed in each of the spectra in the high wavenumber region. These bands occur at 957, 962 and 981  $\text{cm}^{-1}$  and are broad. The bands are observed at 960, 967, 962 and 989  $\text{cm}^{-1}$  for olivenite, cornwallite, cornubite and clinoclase respectively. These bands are attributed to the hydroxyl deformation modes of the OH unit coordinated to the Cu atom.

### **Arsenate vibrations**

The free arsenate ion has tetrahedral symmetry and thus should have four bands of which two are infrared active with theoretical values of  $\nu_3$  ( $F_2$ ) 887  $\text{cm}^{-1}$  and  $\nu_4$  ( $F_2$ ) 463  $\text{cm}^{-1}$  <sup>14,17</sup>. The Raman active modes are observed at 837 ( $A_1$ ) and 349 ( $E$ )  $\text{cm}^{-1}$  <sup>17</sup>. Upon coordination of the arsenate ion to the copper atom, then the symmetry of the arsenate ion reduces to  $C_{3v}$  and may further reduce to  $C_{2v}$ . The implication is that all bands will be both infrared and Raman active.

**Figure 2** displays the Raman spectra of the AsO stretching vibration. For each mineral two bands are observed in the 298 K spectra. Olivenite shows two bands at 853 and 820  $\text{cm}^{-1}$ ; Cornwallite at 859 and 806  $\text{cm}^{-1}$ , cornubite at 815 and 780  $\text{cm}^{-1}$  and clinoclase at 823 and 771  $\text{cm}^{-1}$ . By scale expansion of the Y-axis for olivenite,

additional very weak bands are observed at 880 and 790  $\text{cm}^{-1}$ . The most intense band is assigned to the  $\nu_1(\text{A}_1)$  symmetric stretching vibration. This assignment differs from that described by Sumin de Portilla <sup>14</sup>. In this work, the  $\nu_3(\text{F}_2)$  mode was described as splitting into four components at 870, 830, 800 and 750  $\text{cm}^{-1}$ . Farmer suggested that the  $\nu_1$  and  $\nu_3$  modes overlapped and were to be found at the same frequency <sup>5</sup>. Whilst this is highly unusual, we suggest that the two vibrations at 853 and 820  $\text{cm}^{-1}$  are the AsO symmetric and antisymmetric stretching vibrations respectively. Griffith reported the Raman spectrum of olivenite <sup>17</sup>. Raman bands were found at 880 ( $\text{A}^1$ ), 856 ( $\text{B}_{2u}$ ), 810 ( $\text{A}^1$ ) and 790 ( $\text{B}_{2u}$ )  $\text{cm}^{-1}$ . The observation of the bands 853 and 820  $\text{cm}^{-1}$  is in good agreement with the data published by Griffith. Bands at 880 and 790  $\text{cm}^{-1}$  are in excellent agreement with the data of Griffith. The most intense bands in the Raman spectra are the bands at 853 and 810  $\text{cm}^{-1}$ . Factor group analysis suggests that there should be one active Raman band and one active infrared band in this region. The two vibrations result from a loss of site symmetry. The difference in intensity is related to the number of  $\text{AsO}_4$  units involved in this site symmetry reduction. Thus the other two infrared bands observed at 800 and 750  $\text{cm}^{-1}$  for olivenite are the corresponding  $\nu_3$  vibrations. The second band observed at 806 and 771  $\text{cm}^{-1}$  is more intense for cornwallite and clinoclase. The AsO stretching vibration for olivenite and cornwallite are in similar band positions, suggesting a similar molecular structure. For cornubite two bands are observed at 815 and 780  $\text{cm}^{-1}$ .

Upon obtaining the spectra at liquid nitrogen temperature, additional bands are resolved. For olivenite an additional band is observed at 840  $\text{cm}^{-1}$  and the 853 and 819  $\text{cm}^{-1}$  bands shift to 855 and 815  $\text{cm}^{-1}$ . This shift indicates one of the AsO bonds is strengthened and the other is weakened upon cooling to 77 K. The very weak bands observed at 880 and 790  $\text{cm}^{-1}$  for olivenite in the 298 K spectra are better band separated and show greater intensity in the 77 K spectrum. The exact same phenomena are observed for cornwallite; the two bands observed at 859 and 806  $\text{cm}^{-1}$  shift to 865 and 802  $\text{cm}^{-1}$  at 77 K. In addition a band is observed at 884  $\text{cm}^{-1}$ . In contrast the Raman spectrum of cornubite at 77K shows four bands at 827, 816, 784 and 766  $\text{cm}^{-1}$ . The observation of four AsO stretching vibrations indicates a further reduction in symmetry upon cooling to 77K. One possibility is that this band is attributable to the antisymmetric stretching vibration. The band is 'hidden' under the symmetric stretching vibration in the 298K spectra and only is observed by obtaining

the spectra at 77 K. By using factor group analysis we attribute these four bands to the  $\nu_3$  ( $B_u$ ),  $\nu_1$  ( $A_g$ ),  $\nu_3$  ( $A_u$ ) and  $\nu_3$  ( $B_g$ ) modes. The Raman spectra of the AsO stretching region of clinoclase shows two bands at 823 and 771  $\text{cm}^{-1}$  and upon obtaining the spectra at 77 K, the bands are observed at 833 and 785  $\text{cm}^{-1}$ . In addition two bands are observed at 884 and 865  $\text{cm}^{-1}$ . The higher wavenumber band in this position was also observed for cornwallite. There is the possibility that this band is an additional symmetric stretching mode observed because of site symmetry reduction. For cornubite at 77 K four bands are observed at 827, 816, 784 and 766  $\text{cm}^{-1}$ . Additional bands over and above that for the 298 K spectra were also observed for the other minerals. For clinoclase additional bands are observed at 876, 851 and 782  $\text{cm}^{-1}$  in the 298 K spectrum. These bands were observed at 884, 856 and 764  $\text{cm}^{-1}$  with an additional band at 844  $\text{cm}^{-1}$ , which is partially resolved.

By obtaining spectra at 77 K, better band separation is obtained resulting in the observation of additional bands. If the assumption is made and it is a good assumption that further symmetry reduction is obtained upon cooling the crystals of the basic copper arsenates to liquid nitrogen temperature then these bands can come from the loss of degeneracy of the  $\nu_3$  vibrational modes. Hence, the bands, which are on the lower wavenumber side of the AsO stretching vibrations, are attributable to the  $\nu_3$  vibrational modes. In the Raman spectrum of olivenite two bands are observed with very different intensities. The higher wavenumber band is in each case more intense than the band at the lower wavenumbers. In each mineral there are more than one arsenate involved in the factor group analysis, hence the existence of symmetric and antisymmetric stretching vibrations can be observed. It is proposed that the band at 820  $\text{cm}^{-1}$  is the antisymmetric stretching mode of the AsO unit. Upon cooling to liquid nitrogen temperature additional bands are observed on the low wavenumber side of the AsO stretching region spectrum.

In terms of factor group analysis the  $A_1$  mode under  $T_d$  symmetry splits into  $A_g$ ,  $A_u$ ,  $B_g$ ,  $B_u$  vibrational modes. Of these two are Raman active and two are infrared active. The Raman active modes are the  $A_g$  and  $B_g$  modes. Thus we predict two bands in the symmetric stretching region for the arsenate ion and we observe two bands. In the spectra reported here the  $B_g$  modes occur at lower wavenumbers than the

$A_g$  modes. Normally the antisymmetric stretching modes occur at higher wavenumbers than the symmetric stretching modes, however sometimes when atoms of large atomic mass are involved, the position of the bands can be the other way around.

The low wavenumber region of olivenite is complex and it is difficult to separate the Raman bands according to their symmetry. The spectrum of the low wavenumber region of olivenite may be divided into three separate regions: (a) 450 to 650  $\text{cm}^{-1}$  (b) 400 to 450  $\text{cm}^{-1}$  and (c) 400 to 250  $\text{cm}^{-1}$ . It is proposed that these three regions define the (a)  $\nu_4$  modes (b)  $\nu_2$  modes and (c) AsO stretching and bending and lattice modes. The  $\nu_2$  bending vibration should be common to all three spectra and should be intense. Thus the band at 350  $\text{cm}^{-1}$  for olivenite, 340  $\text{cm}^{-1}$  for cornwallite and at 380  $\text{cm}^{-1}$  is assigned to the  $\nu_2$  symmetric bending vibration. The observation of this mode below 400  $\text{cm}^{-1}$  has been predicted but not reported<sup>5</sup>. Our results differ from those of Griffith who reported bands at 324 and 310  $\text{cm}^{-1}$  for the bending modes of olivenite<sup>17</sup>.

In the Raman spectrum of olivenite, a series of bands are observed at 632, 590, 554 and 513  $\text{cm}^{-1}$ . These bands are attributed to the  $\nu_4$  mode of arsenate. Infrared bands were observed by Sumin de Portilla at 492, 452 and 400  $\text{cm}^{-1}$  with a fourth component predicted to be below 400  $\text{cm}^{-1}$ . No comparison can be made between the infrared data and these Raman results although a closer comparison with the Raman results for this spectral region of cornwallite exists. The Raman spectrum of cornwallite displays bands at 603, 536, 509, 446 and 416  $\text{cm}^{-1}$ . For clinoclase Raman bands are observed at 607, 539, 508, 482 and 460  $\text{cm}^{-1}$ , which are more in harmony with the Raman data for olivenite. Reduction in site symmetry would be the cause of additional bands in this region. A band at 545  $\text{cm}^{-1}$  was observed in the infrared spectrum of olivenite and it was suggested that this was a CuO stretching vibration<sup>14</sup>. However a band in this position seems too high for this type of vibration. We propose that the bands in these positions are attributable to the  $\nu_4$  vibrational modes and the number of bands is due to the loss of degeneracy.

Upon collecting the spectral data at 77 K, bands for olivenite are observed at 631, 595, 550, 526, 514 and 497  $\text{cm}^{-1}$ . These bands have narrowed considerably but are in the same or similar positions to the values for the 298 K spectra. For cornwallite at 77 K, bands were observed at 606, 542, 512, 454, 449, 436 and 422  $\text{cm}^{-1}$ . It should be noted that the spectra for cornwallite at 298 and 77 K, appear to be different in terms of intensity. This may be due to having a different orientation of the crystals on the thermal stage. The band positions are however identical. Raman bands for clinoclase at 77 K are observed at 619, 616, 515, 488, 478, 462, 442 and 398  $\text{cm}^{-1}$ . The spectra for clinoclase at 298 and 77 K are in good agreement.

With vibrational spectroscopic studies of these minerals, two questions arise (a) the position of the hydroxyl deformation vibration and (b) the position of the  $\nu_2$  band. Because of the atomic mass of As, it is predicted that the bending modes will be below 400  $\text{cm}^{-1}$ . Thus the region from around 270 to around 360  $\text{cm}^{-1}$  is the region where this vibration is to be observed. In the Raman spectrum of olivenite we observe three bands at 350, 346 and 335  $\text{cm}^{-1}$  and we assign these bands to the  $\nu_2$  bending modes. Bands were observed at 363, 349 and 337  $\text{cm}^{-1}$  in the spectrum collected at 77 K. For cornwallite, three bands are observed at 363, 347 and 330  $\text{cm}^{-1}$  in the 298 K spectrum and at 368, 347 and 337  $\text{cm}^{-1}$  in the 77 K spectrum. These results are consistent with those of olivenite. For clinoclase bands are observed at 348, 318 and 308  $\text{cm}^{-1}$  in the 298 K spectrum and at 351, 310, 320 and 300  $\text{cm}^{-1}$  in the 77 K spectrum.

In the low wavenumber region of each of these basic copper arsenates, intense Raman bands may be observed. For olivenite strong bands are observed at 310 and 286  $\text{cm}^{-1}$  in the 298 K spectrum and at 310 and 285  $\text{cm}^{-1}$  in the 77 K spectrum. We therefore assign the vibration at 285  $\text{cm}^{-1}$  to CuO stretching vibration. A second low intensity band is observed at 285  $\text{cm}^{-1}$ . This may be a second CuO stretching vibration. According to the factor group analysis there should be 27 Raman active modes in the lattice region. We observe 15 bands down to 100  $\text{cm}^{-1}$ , which is the position where the filters cut in. It is likely the other bands may be below 100  $\text{cm}^{-1}$ . Two CuO vibrations exist because there are two types of units namely OH and  $\text{AsO}_4$  units coordinating to the copper. In cornwallite, these two bands are observed at 306 and 275  $\text{cm}^{-1}$  at 298 K and at 310 and 284  $\text{cm}^{-1}$  at 77 K. For clinoclase an intense

band is observed at 252 and 248  $\text{cm}^{-1}$  in the 298 and 77 K spectra respectively. Intense bands are also observed at 219 and 151  $\text{cm}^{-1}$  for olivenite, 198 and 172  $\text{cm}^{-1}$  for cornwallite and at 189 and 185  $\text{cm}^{-1}$  for clinoclase. Bands in similar positions are observed in the 77 K spectra. One possibility of assignment of these bands is to the OCuO bending modes.

## CONCLUSIONS

Raman spectra of the basic copper arsenate minerals have been collected using a very low powered HeNe laser as the excitation radiation. The beam was slightly defocused to prevent the destruction of the samples due to self-absorption of the incident beam and consequential damage to the mineral. Spectra at 77 K were obtained using a thermal stage. The Raman spectra of olivenite, cornwallite, cornubite and clinoclase at 298 and 77 K are reported. A comparison with published infrared data made. This work clearly demonstrates the power of Raman spectroscopy as compared to infrared spectroscopy in determining the vibrational spectrum of these basic hydroxy copper arsenates. More particularly the Raman spectra were obtained using a Raman microscope. The Raman spectra were clearly resolved and better band separation was obtained by collecting spectral data at 77K. factor group analysis was undertaken but differences in the predicted and the number of band found occurred. Such differences were attributed to reduction in site symmetry in the case of the arsenate ion and in bands occurring below 100  $\text{cm}^{-1}$  for the lattice region.

The application of Raman microscopy to the study of closely related mineral phases has enabled their molecular characterisation using their Raman spectrum thus enabling the rapid identification of phases in complex mixtures of secondary copper arsenates from the oxidized zones of base metal ore bodies.

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**Table 1 Results of the Raman spectroscopic analysis of olivenite, cornwallite and clinoclase.**

Olivenite				Cornwallite		Clinoclase		Cornubite		Suggested Assignments
Raman 298 K /cm <sup>-1</sup>	Raman 77 K /cm <sup>-1</sup>	Published data <sup>14,17</sup> /cm <sup>-1</sup> Infrared	Published data <sup>14,17</sup> /cm <sup>-1</sup> Raman	Raman 298 K /cm <sup>-1</sup>	Raman 77 K /cm <sup>-1</sup>	Raman 298 K /cm <sup>-1</sup>	Raman 77 K /cm <sup>-1</sup>	Raman 298 K /cm <sup>-1</sup>	Raman 77 K /cm <sup>-1</sup>	
3464 3437	3468 3441	3580 <sup>14</sup> 3440		3411 3350	3415 3369	3559 3339	3557 3339	3324 3042	3313 2993	OH stretches
957	960	950 <sup>14</sup>		962	967	983	989	962	967	OH deforms
853  819	855 840 815	860 828 790	880 <sup>17</sup> 856 790	877 859 806 763	884 865 802	850 832 783	884 865 833 785	815 780	827 816 784 766	v <sub>1</sub> & v <sub>3</sub>
360 346 335	363 349 337		324 310	363 347 330	368 347 337	348 318 308	351 320 310 300			v <sub>2</sub>
		1082 1037 938		1087				1051	1059	Overtones or impurity

632 590 554	631 595 550 526	638 600 545		603 536 509	606 542 512 454	607 508 539 482	619 616 515 488 478	525 496 440 398 365	531 499 441 399 368	v <sub>4</sub>
513 496 421	514 497 453 423 382 361 348	492 452 400	464 410	446 416	449 436 422	460 438	462 442 398			
310 286	311 285			306 275	311 275	306	310	327 301	330 303	
282 231	262 227			273 242 226 197	279 246 203	295 247 231	298 260 251 237 219	259 249 211	261 251 224 212	CuO stretch OCuO and lattice modes
219 205 182 174 154 150 119	220 185 173 157 151 125			171 148 130	169 160 137	185 171 160 136	188 178 171 139	168 151	169 153	lattice modes

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