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# A Raman spectroscopic study of the basic copper sulphates-implications for copper corrosion and 'bronze disease'

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## Abstract:

The basic copper sulphates are of interest because of their appearance in many environmental situations such as copper pipe corrosion, restoration of brass and bronze objects, leaching from waste mineral dumps and the restoration of frescoes. The Raman spectra of the basic copper sulphate minerals antlerite, brochantite, posnjakite and langite are reported using a Nd-Yag laser operating at an excitation wavelength of 780 nm. In line with their crystal structures, each basic copper sulphate mineral has its own characteristic Raman spectrum, which enables their identification. Except for brochantite multiple bands are observed for the SO stretching vibration. Similarly multiple bands are observed for the antisymmetric SO and OSO bending regions. Hydroxyl deformation modes in the 730 to 790  $\text{cm}^{-1}$  region are observed. The use of the HeNe laser operating at an excitation wavelength of 633 nm enabled the hydroxyl stretching bands of the minerals to be obtained. Antlerite and brochantite are characterised by hydroxyl stretching bands at 3580 and 3488  $\text{cm}^{-1}$ . The minerals posnjakite and langite display Raman hydroxyl-stretching vibrations at 3588 and 3564  $\text{cm}^{-1}$ . The Raman spectra of these two minerals show water OH-stretching bands at 3405, 3372 and 3260  $\text{cm}^{-1}$ . Raman spectroscopy allows the ready identification of these minerals.

**Key Words-** sulphate, corrosion, brochantite, antlerite, Raman spectroscopy

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[Endnote file: brochantite, arthurite, CuSO4](#)

## INTRODUCTION

Studies of the basic copper sulphate minerals have been in existence for some time.<sup>1-3</sup> The minerals in this group are dolerophanite  $\text{Cu}_2\text{OSO}_4$ <sup>2</sup>, antlerite

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$\text{Cu}_3\text{SO}_4(\text{OH})_4$ <sup>4,5</sup>, brochantite  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ <sup>6</sup>, posnjakite  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$ , langite  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ , wroewulfite  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ .<sup>7,8</sup> The principal interest in these minerals is several fold: (a) the study of the restoration of frescoes<sup>8</sup> (b) the studies of the corrosion and restoration of copper and bronze objects<sup>9-14, 15</sup> (c) the corrosion of copper pipes containing reticulated water<sup>16</sup> (d) the formation of these types of minerals in volcanic sublimations.<sup>16,17</sup> (e) the formation of these types of minerals as leachates from slag dumps.<sup>18,19</sup>

Analysis of the corrosion products of bronzes and brasses has been undertaken using X-ray fluorescence spectroscopy.<sup>13</sup> It was found that (a) sulphate patinas composed mainly of brochantite were detected on all sides of the chosen object a mediaeval Lantern. (b) antlerite was detected in about 50% of the samples, and formation of it was considered to have close relation with malignant atmosphere (c) A large amount of chloride patina composed mainly of atacamite were observed on all sides. (d) on the all sides of the Lantern, patinas were observed together with copper oxides composed mainly of cuprous oxide. These minerals resulted from exposure to an aggressive atmosphere over extended time. Recent work by Bouchard using Raman microscopy identified the presence of brochantite and antlerite on the corroded surface of a bronze object.<sup>15</sup> Bouchard showed and was able to distinguish the minerals malachite, azurite, brochantite and antlerite.<sup>15</sup> Other minerals can be formed during copper and lead corrosion. These include nakaurite ( $\text{Cu}_4(\text{SO}_4)_4(\text{CO}_3)(\text{OH})_6 \cdot 48\text{H}_2\text{O}$ ), and the mixed Cu-Pb species such as chenite ( $\text{CuPb}_4(\text{SO}_4)_2(\text{OH})_6$ ), elyite ( $\text{CuPb}_4(\text{SO}_4)(\text{OH})_8$ ), and caledonite ( $\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{OH})_6$ ). Other minerals such as chalcocyanite ( $\text{CuSO}_4$ ) and dolerophanite ( $\text{Cu}_2\text{OSO}_4$ ) will not form in any atmosphere containing moisture.

Synthetic brochantite decomposed when heated at different temperatures was identified by x-ray diffraction analysis and IR spectroscopy.<sup>20</sup> Dolerophanite,  $\text{CuO} \cdot \text{CuSO}_4$ , which is invariably reported to be formed during the thermal decomposition of brochantite, was not formed at any stage of the decomposition in this case. The sequence of decomposition is the following:  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot 3.5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 + x\text{H}_2\text{O}$  at 80-170 °C;  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \rightarrow \text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2 + \text{CuO} + \text{H}_2\text{O}$  at 250-400 °C and  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2 \rightarrow 3\text{CuO} + 2\text{H}_2\text{O} + \text{SO}_2 + 0.5\text{O}_2$  at 610-700 °. It is probable that one mechanism for the corrosion of bronze objects could be the reverse of these reactions.<sup>21</sup> FTIR photoacoustic spectroscopy (FTIR/PAS) proved to be a useful tool for non-destructive testing of copper corrosion layer (patina) formed in the atmosphere. The samples cut from a piece of the roof of the Stockholm City Hall were examined without any additional pretreatment. The components of the patina-brochantite  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , antlerite  $\text{Cu}_3(\text{OH})_4\text{SO}_4$ , and basic cupric carbonate  $\text{Cu}_2\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$  as well as some other minerals were identified.<sup>22</sup>

Recently the authors have applied Raman spectroscopy for the study of minerals containing oxyanions including the elucidation of the structure of the basic copper phosphate and sulphate minerals.<sup>23</sup> The single crystal Raman spectra of azurite and malachite have been obtained.<sup>24</sup> The Raman spectra of the isomorphous series descloizite [ $\text{PbZn}(\text{VO}_4)(\text{OH})$ ] and mottramite [ $\text{PbCu}(\text{VO}_4)(\text{OH})$ ] were obtained at 298 and 77 K.<sup>25</sup> Raman spectroscopy has also been used to study the mixed anionic mineral chillagite.<sup>26</sup> Further the molecular structure of some naturally

occurring pseudo-alums has been determined.<sup>27,28</sup> Recently the Raman spectroscopy of the vivianite phosphates and sulphates has been undertaken. Raman spectroscopy has proven extremely powerful at studying hydrated (such as the vivianite minerals), hydroxylated (basic copper sulphates and phosphates) sulphated (natural alums) minerals. It seems apparent that few if any Raman studies have been undertaken on these basic copper sulphate minerals.

## EXPERIMENTAL

### Minerals:

Langite	sample D4379	from Cornwall, United Kingdom
Brochantite	sample D20320	from Chuquicamata, Chile
Brochantite	sample D28957	from Bisbee, Arizona, USA
Antlerite	sample M33489	from Antlerite, Chuquicamata, Chile.
Posnjakite	sample M27302	from Drakewalls adit, near Gunnislake, Cornwall, UK

The samples were phase analyzed using X-ray diffraction and the compositions checked using EDX measurements.

### Raman microprobe spectroscopy

The crystals of the copper sulphate minerals were placed and orientated on the stage of an Olympus BHS 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 Nd-Yag laser (780 nm) at a resolution of 2 cm<sup>-1</sup> in the range between 100 and 4000 cm<sup>-1</sup>. It should be noted that the limitations of the detector prevent the collection of data at wavenumbers above 3000 cm<sup>-1</sup> Raman shift. Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm<sup>-1</sup> line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled.

Spectroscopic 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 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.

## RESULTS AND DISCUSSION

The basic copper sulphates are difficult to determine by Raman spectroscopy as the colour of the minerals is blue to blue-green. The use of the Nd-Yag laser operating at 780 nm excitation enables better band separation in the low wavenumber

region but has the disadvantage that the detector limitations mean that the high wavenumber region cannot be measured. Raman spectra using very low power (<1 mW) with slight defocusing of the laser beam enables successful spectra to be recorded. If too high a power is used the samples undergo change in the laser beam.

The mineral dolerophanite ( $\text{Cu}_2\text{OSO}_4$ ) is an extremely rare mineral and is only formed during the oxidation of copper in air in the presence of the oxides of sulphur. It is formed as a volcanic sublimate. This mineral is not formed in aqueous environments. The other basic copper sulphates are all formed as secondary minerals in oxidised zones and can form as the result of corrosion of copper, brass and bronzes. The formation of the individual phases depends on the pH and the activity of the sulphate anion. Tenorite ( $\text{CuO}$ ) is the stable phase at high pH and in the pH range 4 to 6 pH units, brochantite is stable and if the pH is lowered to < 4, then antlerite is formed. Under acid conditions (<2.5 pH units) chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) is the stable phase.

The Raman spectroscopy of the aqueous sulphate tetrahedral oxyanion yields the  $\nu_1$  vibration at  $981\text{ cm}^{-1}$ , the  $\nu_2$  mode at  $451\text{ cm}^{-1}$ , the  $\nu_3$  mode at  $1104\text{ cm}^{-1}$  and the  $\nu_4$  mode at  $613\text{ cm}^{-1}$ . The mineral chalcantite has been thoroughly investigated.<sup>29-32</sup> The Raman spectrum of the mineral chalcantite shows a single symmetric stretching mode at  $984.7\text{ cm}^{-1}$ . Two  $\nu_2$  modes are observed at 463 and  $445\text{ cm}^{-1}$  and three  $\nu_3$  modes at 1173, 1146 and  $1100\text{ cm}^{-1}$ . The  $\nu_4$  mode is observed as a single band at  $610\text{ cm}^{-1}$ . A complex set of overlapping bands is observed in the low wavenumber region with broad bands observed at 257, 244, 210 136 and  $126\text{ cm}^{-1}$ . The Raman spectra of the minerals antlerite, brochantite, posnjakite and langite for the five spectral regions are shown in **Figures 1-5** and the results of the spectral analysis reported in **Table 1**. The SO symmetric stretching modes for the four basic copper sulphate minerals are observed at 985, 990, 972 and  $974\text{ cm}^{-1}$ . Only the mineral brochantite has a single band in this region. Michel Bouchard reported the  $\nu_1$  mode for brochantite and antlerite at 975 and  $989\text{ cm}^{-1}$ .<sup>15</sup> The value for antlerite is in good agreement with this work but not the value for brochantite. The value listed by Bouchard corresponds more closely with our value obtained for langite. The Raman spectrum of antlerite shows bands at 990, 985 and  $902\text{ cm}^{-1}$ ; whilst posnjakite has bands at 972 and  $905\text{ cm}^{-1}$ . Langite Raman spectrum shows complexity with overlapping bands observed at 982, 974 and  $911\text{ cm}^{-1}$ . It should also be noted that each of the minerals displays a band(s) at around  $1906\text{ cm}^{-1}$ . This band is attributed to the first overtone of the  $\nu_1$  symmetric stretching vibration. Two bands are observed for langite at 1911 and  $1906\text{ cm}^{-1}$ .

The Raman spectra of the antisymmetric stretching region are shown in **Figure 2**. The intensity of the bands compared with that of the symmetric stretching region has been amplified some 20 times. In this spectral region each mineral has its own characteristic spectrum. The two minerals posnjakite and langite show considerable complexity whilst antlerite and brochantite show some similarity, which is not unexpected since their stoichiometry is similar. The Raman spectrum of chalcantite has the most intense band in this spectral region centred at  $1146\text{ cm}^{-1}$ . The Raman spectrum of antlerite shows bands at 1173, 1134 and  $1078\text{ cm}^{-1}$  with the latter band being the most intense. Bouchard reported bands for antlerite at 1171, 1133, and  $1078\text{ cm}^{-1}$  in excellent agreement with the data reported in table 1.<sup>15</sup> A broad band centred on  $1266\text{ cm}^{-1}$  is also observed for each of the minerals. The Raman spectrum

of brochantite displays bands at 1173, 1135 and 1078  $\text{cm}^{-1}$ . Michel Bouchard reported bands for brochantite at 1125, 1098, and 1078  $\text{cm}^{-1}$ .<sup>15</sup> The values are at variance with the data reported in this work. The Raman spectra of posnjakite and langite are very different from that of the former two minerals with a complex set of overlapping bands. The Raman spectrum of posnjakite shows bands at 1147, 1153, 1132, 1105 and 1078  $\text{cm}^{-1}$  in the antisymmetric stretching region. In addition, bands are also observed at 1271 and 1251  $\text{cm}^{-1}$ . A further band is observed at around 1370  $\text{cm}^{-1}$ . This band is common to all the spectra of these basic copper sulphate minerals. The band is of very low intensity for antlerite, brochantite and chalcantite. One possibility of the assignment of this band is to a combination band. Raman bands for langite are observed at 1266, 1172, 1149, 1128, 1102 and 1076  $\text{cm}^{-1}$ .

The Raman spectra of the  $\nu_2$  mode of the basic copper sulphate minerals are shown in [Figure 3](#). The complexity of the antisymmetric stretching region is reflected in the spectra of this bending region. The spectra of antlerite and brochantite are similar as are those for posnjakite and langite in this spectral region. The antlerite Raman spectrum shows bands at 485, 469, 440 and 415  $\text{cm}^{-1}$  with the latter band having the most intensity. Bouchard reported bands for antlerite at 483, 470, 444 and 416  $\text{cm}^{-1}$  in excellent agreement with our data.<sup>15</sup> Raman spectra of brochantite are similar except that additional bands at 517 and 501  $\text{cm}^{-1}$  are observed. The Raman spectra of posnjakite show bands at 511, 482, 447, 422, 386 and 363  $\text{cm}^{-1}$ . This complex set of bands in this region is also observed for langite with bands observed at 507, 481, 449, 420, 391  $\text{cm}^{-1}$ . The observation of additional bands over and above that which would be predicted for the sulphate anion (a single band at 451  $\text{cm}^{-1}$ ), may be attributed to a number of factors including symmetry reduction, local stress in the crystals and crystal orientation effects. The hydroxyl group of one antlerite or brochantite unit hydrogen bonds to the sulphate of an adjacent molecule.<sup>33</sup> In the case of posnjakite and langite, both the hydroxyl groups and water molecules hydrogen bond to the sulphate anion. This is the principal reason for the observation of the number of bands in the bending region.

The Raman spectrum of the  $\nu_4$  mode is displayed in [Figure 4](#). The Raman spectra of the mineral phases for this region are different, and each phase has its own characteristic spectrum. For antlerite four Raman bands are observed at 651, 629, 606 and 600  $\text{cm}^{-1}$ . Bands at 630 and 604  $\text{cm}^{-1}$  were found by Bouchard for antlerite.<sup>15</sup> In contrast, chalcantite showed only a single band at 610  $\text{cm}^{-1}$ . The Raman spectrum of brochantite shows bands at 629, 608 and 600  $\text{cm}^{-1}$ . Bands were observed for brochantite by Bouchard at 621, 611 and 599  $\text{cm}^{-1}$ .<sup>15</sup> The Raman spectrum of posnjakite shows bands at 621, 609 and 596  $\text{cm}^{-1}$  and langite at 621, 609 and 596  $\text{cm}^{-1}$ . Whilst the bands for posnjakite and langite are in similar positions, the intensity of the bands varies considerably, although this may be a crystal orientation effect. In each of the spectra sets of bands are observed in the 730 to 790  $\text{cm}^{-1}$  region. Each of the four minerals contains hydroxyls in the unit cell and consequently both stretching and deformation modes of this unit should be observed. It is suggested that the bands in this region are due to the hydroxyl deformation modes. Antlerite Raman spectrum shows two bands at 786 and 759  $\text{cm}^{-1}$ , brochantite at 786, 770 and 749  $\text{cm}^{-1}$ , posnjakite at 734  $\text{cm}^{-1}$ , and langite at 773 and 732  $\text{cm}^{-1}$ . M. Bouchard observed bands at 785 and 770  $\text{cm}^{-1}$  for antlerite and at 785, 770, 730  $\text{cm}^{-1}$  for brochantite.<sup>15</sup> The Raman spectra of the low wavenumber region are shown in [Figure 5](#). As for the low wavenumber region of chalcantite, complexity and overlap of bands in this spectral

region is in evidence. The similarity in this spectral region between antlerite and brochantite is evident as is the similarity between posnjakite and langite. Bands in this region are difficult to assign except to comment that the sets of bands are characteristic of basic copper sulphates. Bands have been observed for antlerite at 340, 298, 265, 249, 230, 217, 172, 148 and 125  $\text{cm}^{-1}$ .<sup>15</sup>

The mineral antlerite has four hydroxyl units in the structure. Brochantite has six OH units and therefore Raman spectroscopy enables the spectra of these units to be obtained. Both antlerite and brochantite have hydroxyl stretching bands at 3580 and 3480  $\text{cm}^{-1}$  as is shown in **Figure 6**. Posnjakite and langite are hydrated forms of brochantite and hence additional bands in their spectra over and above those observed in the spectra of antlerite and brochantite are attributable to water OH stretching bands. Bands are observed at 3405, 3372 and 3262  $\text{cm}^{-1}$  and are assigned to these water vibrations. Two hydroxyl OH stretching bands are observed at 3588 and 3564  $\text{cm}^{-1}$ . Bouchard reported the Raman spectrum of brochantite and observed bands at 3562 and 3585  $\text{cm}^{-1}$ .<sup>15</sup> However in the spectrum reported by Bouchard for brochantite additional bands were observed at 3370 and 3400  $\text{cm}^{-1}$ .<sup>15</sup> The spectrum corresponds to that of langite. The Raman spectrum reported for antlerite shows hydroxyl stretching bands at 3488 and 3580  $\text{cm}^{-1}$ . These values are in good agreement with the data reported in Table 1 for the mineral antlerite.

## Conclusions

Raman spectroscopy has enabled the identification of the basic copper sulphate minerals. Each phase has its own characteristic Raman spectrum enabling identification. Raman spectroscopy allows the hydroxyl unit OH stretching vibrations of the four minerals to be obtained and the water OH stretching vibrations of posnjakite and langite to be observed. The significance of this work rests with the identification of these phases on the surfaces of the corroded products of copper, brass and bronze. It is probable that copper corrodes to tenorite  $\{\text{Cu(II)O}\}$  phase, which may then react to form antlerite or brochantite. In moist atmospheres brochantite will change to posnjakite or langite depending on the pH and sulphate concentrations. However langite is meta-stable with respect to brochantite and so the latter will be the phase observed in the corrosion products of copper, brass and bronze.

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## References

1. Fowles, G. *J. Chem. Soc.* 1926: 1845.
2. Richmond, WE, Wolfe, CW. *Am. Mineral* 1940; **25**: 606.

3. Ungemach, H. *Bull. soc. franc. mineral.* 1924; **47**: 124.
4. Finney, JJ, Araki, T. *Nature* 1963; **197**: 70.
5. Araki, T. *Mineral. J. (Tokyo)* 1961; **3**: 233.
6. Helliwell, M, Smith, JV. *Acta Crystallographica, Section C: Crystal Structure Communications* 1997; **C53**: 1369.
7. Dunn, PJ, Rouse, RC, Nelen, JA. *Mineral. Mag.* 1975; **40**: 1.
8. Bersani, D, Antonioli, G, Lottici, PP, Fornari, L, Castrichini, M. *Proceedings of SPIE-The International Society for Optical Engineering* 2001; **4402**: 221.
9. Kratschmer, A, Odnevall Wallinder, I, Leygraf, C. *Corrosion Science* 2002; **44**: 425.
10. Livingston, RA. *Environ. Sci. Technol.* 1991; **25**: 1400.
11. Lobnig, R, Frankenthal, RP, Jankoski, CA, Siconolfi, DJ, Sinclair, JD, Unger, M, Stratmann, M. *Proceedings - Electrochemical Society* 1999; **99-29**: 97.
12. Mankowski, g, Duthil, JP, Giusti, A. *Corrosion Science* 1997; **39**: 27.
13. Matsuda, S, Aoki, S, Kawanobe, W. *Hozon Kagaku* 1997; **36**: 1.
14. Nord, AG, Mattsson, E, Tronner, K. *Neues Jahrbuch fuer Mineralogie, Monatshefte* 1998: 265.
15. Bouchard-Abouchacra, M. *Phd Thesis* 2001.
16. Vergasova, LP, Filatov, SK, Serafimova, EK, Semenova, TF. *Dokl. Akad. Nauk SSSR* 1988; **300**: 1197.
17. Vergasova, LP, Filatov, SK, Serafimova, EK, Starova, GL. *Dokl. Akad. Nauk SSSR* 1984; **275**: 714.
18. Wappler, G, Tischendorf, G. *Z. Geol. Wiss.* 1980; **8**: 1397.
19. Ruesenberg, KA, Paulis, P. *Aufschluss* 1996; **47**: 267.
20. Prasad, SVS, Rao, VS. *J. Therm. Anal.* 1985; **30**: 603.
21. Tanaka, H, Kawano, M, Koga, N. *Thermochim. Acta* 1991; **182**: 281.
22. Salnick, AO, Faubel, W. *Appl. Spectrosc.* 1995; **49**: 1516.
23. Frost, RL, Williams, PA, Martens, W, Kloprogge, JT, Leverett, P. *Journal of Raman Spectroscopy* 2002; **33**: 260.
24. Frost, RL, Martens, WN, Rintoul, L, Mahmutagic, E, Kloprogge, JT. *Journal of Raman Spectroscopy* 2002; **33**: 252.
25. Frost, RL, Kristof, J, Horvath, E, Kloprogge, JT. *Langmuir* 2001; **17**: 3216.
26. Crane, M, Frost, RL, Williams, PA, Kloprogge, JT. *Journal of Raman Spectroscopy* 2002; **33**: 62.
27. Kloprogge, JT, Van Veen, JAR, Booij, E, Frost, RL. *Clays Clay Miner.* 2001; **49**: 183.
28. Frost, RL, Kloprogge, JT, Williams, PA, Leverett, P. *Journal of Raman Spectroscopy* 2000; **31**: 1083.
29. Degen, IA, Newman, GA. *Spectrochim. Acta, Part A* 1993; **49A**: 859.
30. Liu, D, Ullman, FG. *J. Raman Spectrosc.* 1991; **22**: 525.
31. Berger, J. *C. R. Acad. Sci., Ser. B* 1970; **270**: 815.
32. Berger, J. *J. Raman Spectrosc.* 1976; **5**: 103.
33. Libowitzky, E. *Monatshefte fur Chemie* 1999; **130**: 1047.



Antlerite Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	Brochantite Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub>	Posnjakite Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub> .H <sub>2</sub> O	Langite Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub> .2H <sub>2</sub> O	Suggested assignment
Chile	Chile	UK	UK	
3580	3580	3588	3587	OH stretch
	3501	3564	3564	
3488	3489	3405	3405	
		3372	3372	
		3262	3260	
1905	1906	1906	1911 1906	First overtone of SO <sub>4</sub> symmetric stretch
1266	1265	1271 1251	1266	SO <sub>4</sub> antisymmetric stretch
1173	1173	1147	1172	
1148	1135	1153	1149	
1135		1132	1128	
		1105	1102	
1079	1078	1078	1076	
990	990		982	SO <sub>4</sub> symmetric stretch
985		972	974	
902		905	911	
786	786		773	OH deformation modes
759	770 749	734	732	
651	629			
629	608	621	621	
606	600	609	609	
600		596	596	
	517			

485	501	511	507	
469	482	482	481	
440	467			
415	442	447	449	
	415	422	420	
		386	391	
		363		
335	340			
330	330	317	317	
295	295		273	
265	265		258	
259	247	241	241	
	238	225	226	
	228			
	213			
169	172	195	194	
151	149	175	183	
146	141	168	175	
141	124	140	167	
131			155	
			147	
			139	
			130	
			118	

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**Figure 1 Raman spectra of the SO symmetric stretching region of (a) antlerite (b) brochantite (c) posnjakite (d) langite.**

**Figure 2 Raman spectra of the SO anti-symmetric stretching region of (a) antlerite (b) brochantite (c) posnjakite (d) langite.**

**Figure 3 Raman spectra of the 350 to 550  $\text{cm}^{-1}$  region of (a) antlerite (b) brochantite (c) posnjakite (d) langite.**

**Figure 4 Raman spectra of the 550 to 850  $\text{cm}^{-1}$  region of (a) antlerite (b) brochantite (c) posnjakite (d) langite.**

**Figure 5 Raman spectra of the 100 to 350  $\text{cm}^{-1}$  region of (a) antlerite (b) brochantite (c) posnjakite (d) langite.**

**Figure 6 Raman spectra of the hydroxyl-stretching region of (a) antlerite (b) brochantite (c) posnjakite (d) langite.**

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**Table 1 Raman spectral analysis of antlerite, brochantite, posnjakite and langite.**

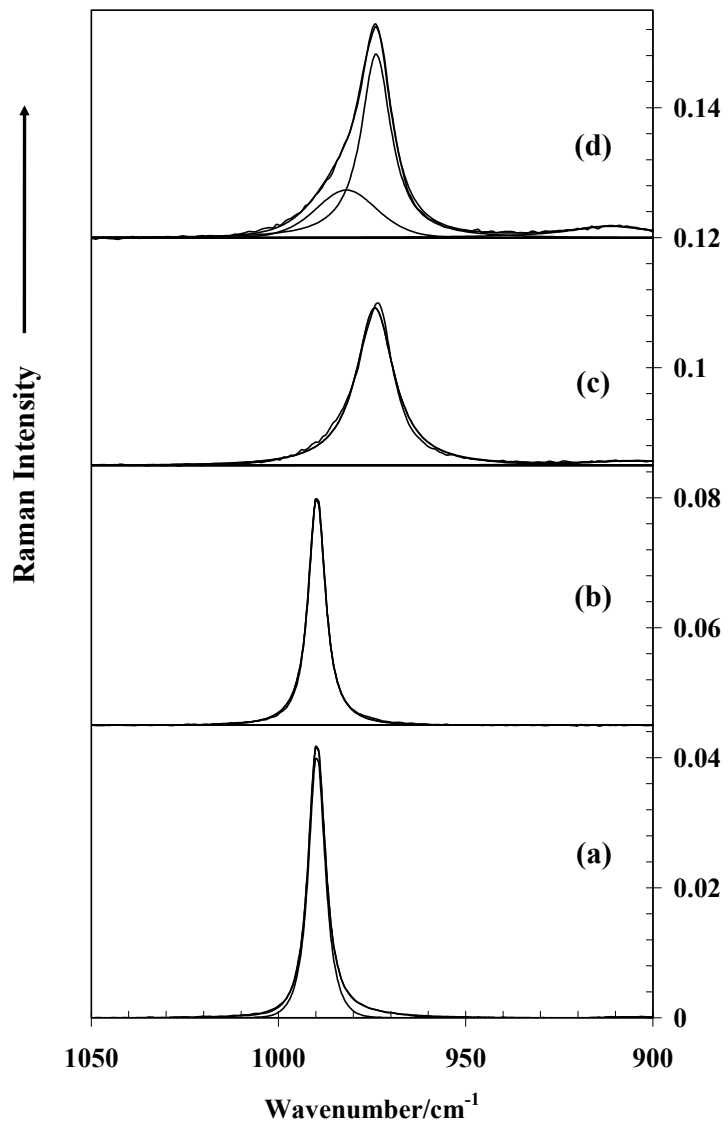


Figure 1

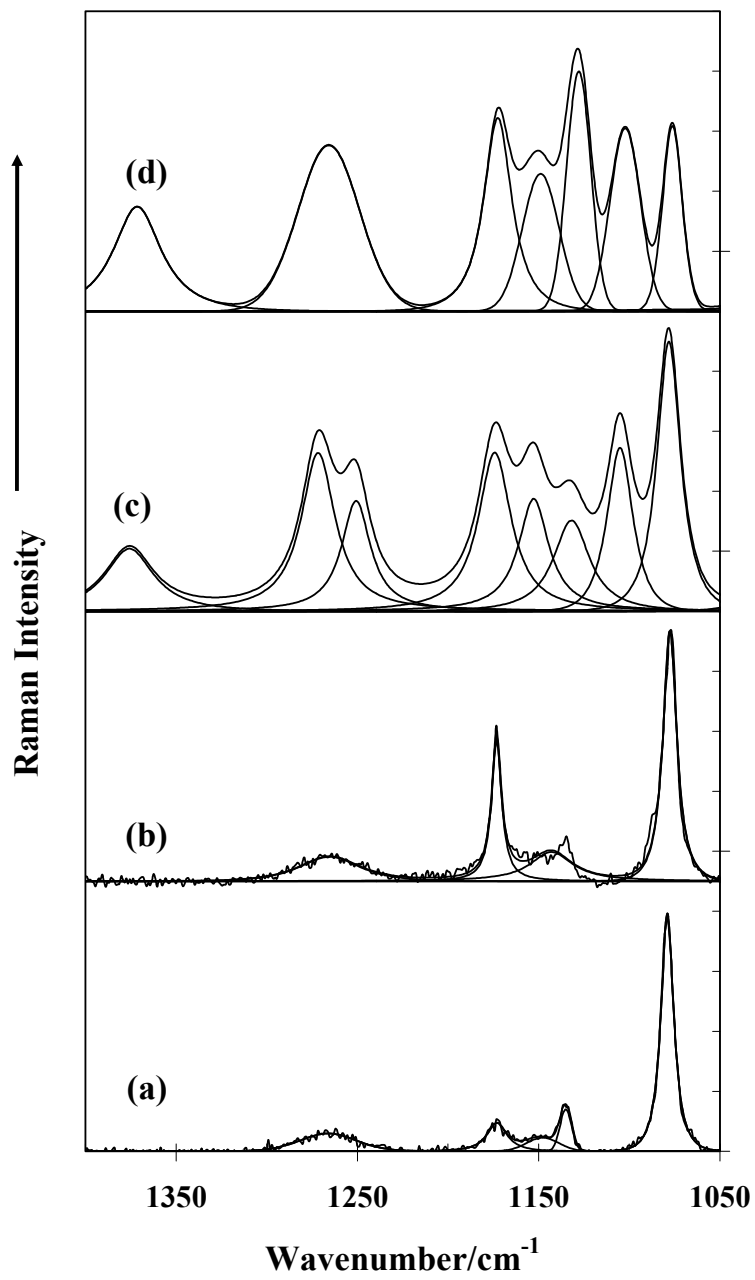


Figure 2

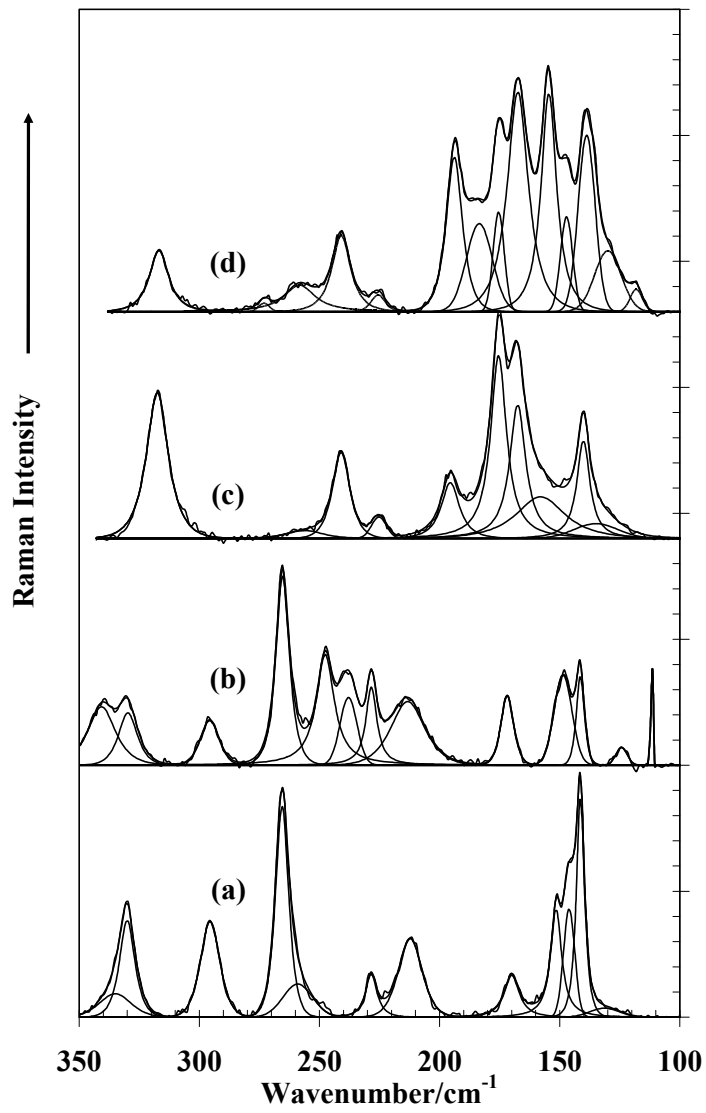
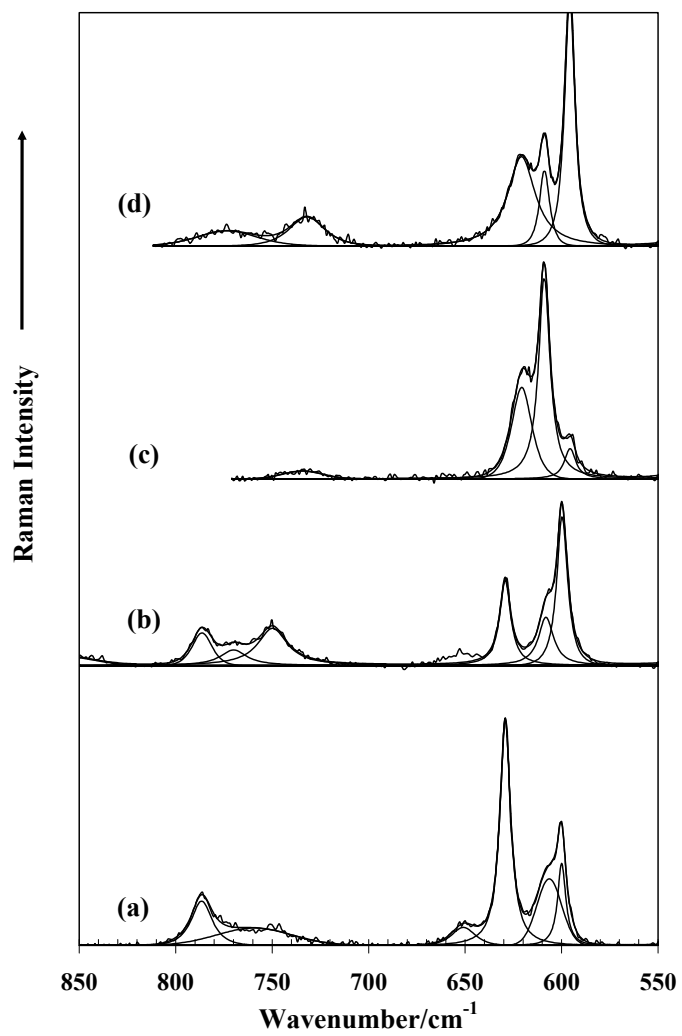


Figure 3



**Figure 4**

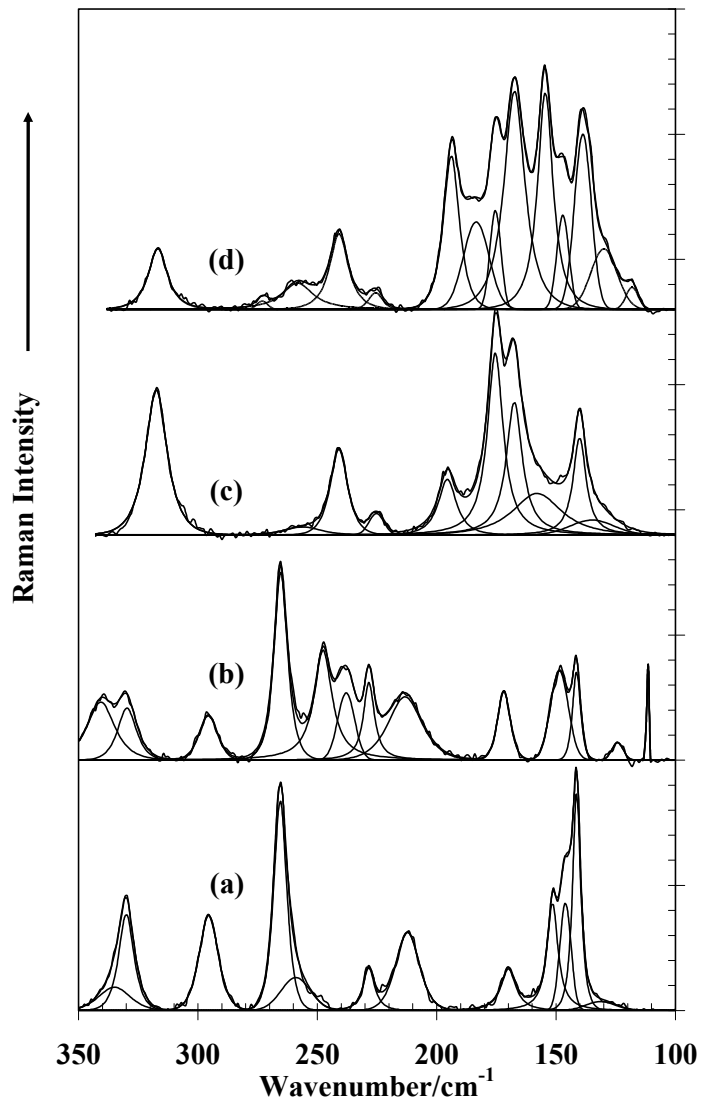


Figure 5



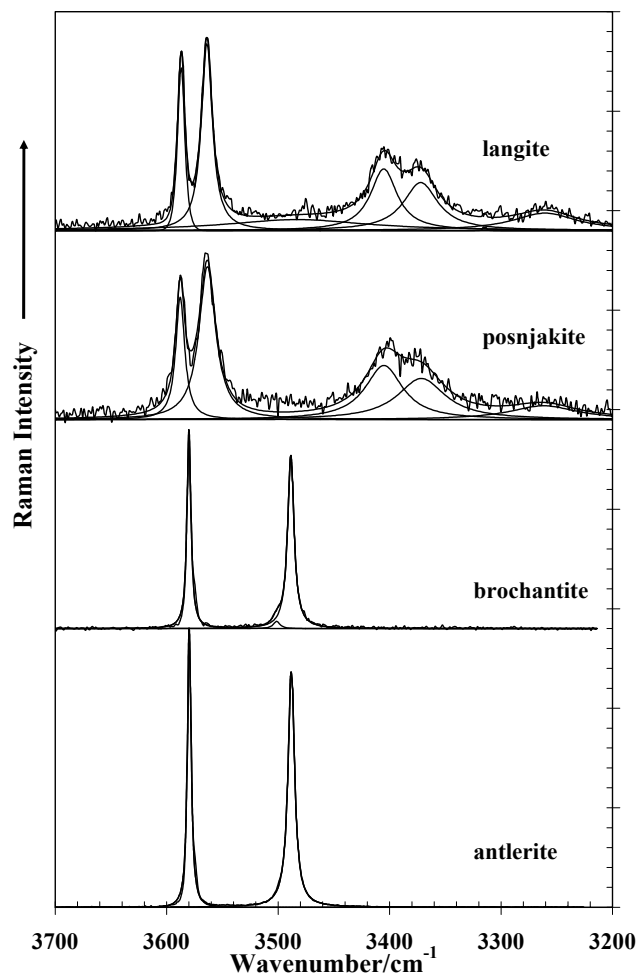


Figure 6