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Raman spectroscopy of selected copper minerals of significance in corrosion

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Endnote file: brochantite, atacamite, arthurite, pseudomalachite, ata-TD

Abstract:

The Raman spectroscopy of selected minerals of the corrosion products has been measured including nantokite, eriochalcite, claringbullite, atacamite, paratacamite, clinoatacamite and brochantite and related minerals. The free energy of formation shows that each mineral is stable relative to copper metal. The mineral, which is formed in copper corrosion, depends on the kinetics and conditions of the reaction. Raman spectroscopy clearly identifies each mineral by its characteristic Raman spectrum. The Raman spectrum is related to the mineral structure and bands are assigned to CuCl stretching and bending modes and to SO stretching modes. Clinoatacamite is identified as the polymorph of atacamite and not paratacamite. Paratacamite is a separate mineral with a similar but different structure to that of atacamite.

Key Words: atacamite, clinoatacamite, paratacamite, brochantite, nantokite, eriochalcite, Raman microscopy,

1. Introduction

The interest in copper minerals formed in many environmental situations is high. Indeed many copper minerals may be formed through products of corrosion [1-4]. Corrosion of copper, brass and bronze objects often is titled 'bronze disease' and this corrosion depends upon the conditions of the corrosion such as corrosion in air, corrosion in water, pH and presence of the corroding anion. If chloride is present as in seawater then a range of complex minerals such as connellite or buttgenbachite may form [5, 6]. If sulphate is present then minerals such as anterlite, brochantite or langite may form [7-13]. Important in all of this work is the remediation of copper, brass and bronze objects of medieval or archaeological significance [4]. The question arises as to whether simple thermal treatment may reverse some of the corrosion [14].

Many copper minerals have been used as the basic colouring agents in paintings and frescoes [15-18] and the breakdown products of these pigments can lead to different copper compounds which discolour the original artefact. Perhaps in the case of statues this may be a desired effect to obtain a range of 'stained' green colorants [16, 19-27]. Another environmental aspect of the use of copper piping in an environment sense is the transportation of drinking water and often minerals are formed in the pipes either through corrosion or simply as deposits [1, 28]. Equally well is the formation of copper compounds formed through the leaching of old mine sites, waste dumps, tailings dams and the like [29, 30] [31, 32].

Often databases of the Raman and infrared spectra of minerals of pigments, minerals, and pigment media are established to enable the ready identification of minerals used in the painting of frescoes, paintings and bronze objects [33]. It is important is to have analytical techniques which readily identify the environmental breakdown products [33-35]. Raman spectroscopy is an ideal technique for the study for the investigation of works of art and the degradation products because it is extremely reliable, sensitive, specific and is non-destructive. In this paper the Raman spectra of selected minerals of copper are reported including the chlorides and sulphates. The relationship to related mineral phases is also characterised.

2. Experimental

2.1 Minerals

Atacamite (dark green nodules of small acicular crystals) from Mt Gunson, South Australia and as isolated crystal groups from Atacama, Chile were obtained from the collection of the School of Natural Resources of the Queensland University of Technology. Nickelean paratacamite (small dark green crystals associated with gaspéite, NiCO_3) from Widgiemooltha, Western Australia, was purchased from BK Minerals, Brisbane, Australia (<http://www.bkminerals.gil.com.au/>). Nantokite and eriochalcite were obtained from the Main Lode, Great Australia mine, Cloncurry, Queensland. Eriochalite originated from Atacama, Chile. To obtain pure non-hydrated nantokite, the rock is broken open and the colourless to white mineral, which looks exactly like quartz is obtained. This newly exposed mineral is then analysed immediately.

Minerals were also obtained from the museum collections of several Australian museums.

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 minerals were analysed for phase purity by powder X-ray diffraction methods and for chemical composition using SEM EDAX techniques.

2.2 Raman microprobe spectroscopy

The crystals of the copper minerals were placed and orientated 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 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 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

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.

3. Results and discussion

3.1 Free energy of formation of common corrosion products of copper.

The sequence of copper corrosion is likely to follow a number of reactions depending upon the chemistry. The following are possible:

1. $\text{Cu} + 1/2\text{O}_2 \rightarrow \text{CuO}$ (mineral is tenorite)
 $\Delta(G^0)_f = -128.8 \text{ kJ/mole}$
2. $\text{Cu} + 1/2\text{Cl}_2 \rightarrow \text{CuCl}$ (mineral is nantokite)
 $\Delta(G^0)_f = -119.7 \text{ kJ/mole}$
3. $\text{Cu} + \text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (mineral is eriochalcite)
 $\Delta(G^0)_f = -655.9 \text{ kJ/mole}$
4. $3\text{CuO} + 2\text{H}_2\text{O} + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ (mineral is brochantite)
 $\Delta(G^0)_f = -1817.7 \text{ kJ/mole}$
5. $3\text{CuO} + 2\text{H}_2\text{O} + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ (mineral is langite)
 $\Delta(G^0)_f = -2044.1 \text{ kJ/mole}$
6. $3\text{CuO} + 2\text{H}_2\text{O} + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ (mineral is eriochalcite)
 $\Delta(G^0)_f = -1879.8 \text{ kJ/mole}$
7. $2\text{CuO} + \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Cl}(\text{OH})_3$ (mineral is atacamite)
 $\Delta(G^0)_f = -1339.2 \text{ kJ/mole}$
8. $2\text{CuO} + \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Cl}(\text{OH})_3$ (mineral is botallackite)
 $\Delta(G^0)_f = -1322.6 \text{ kJ/mole}$
9. $2\text{CuO} + \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Cl}(\text{OH})_3$ (mineral is clinoatacamite)

$$\Delta(G^0)_f = -1341.8 \text{ kJ/mole}$$

The free energy of formation of the common corrosion products of copper is listed above [36]. The data is extracted from the work of Viellard. All the free energies of formation of the corrosion products are negative and thus all these reactions are spontaneous. The free energy of formation is in the order langite > eriochalcite > brochantite > clinoatacamite > atacamite > botallackite > eriochalcite > tenorite > nantokite. What the thermodynamic data shows is that the more stable phase out of botallackite, atacamite and clinoatacamite series is clinoatacamite and the corrosion of copper in the presence of chloride ions will lead to clinoatacamite. The other phases are intermediates in the series of reactions with the end product being clinoatacamite. Many reports are made of a mineral paratacamite. However this is a separate phase and is not a polymorph of atacamite. The question is why is brochantite the principal corrosion phase rather than langite. This may be related too the conditions of the corrosion and the kinetics of the reaction rather than the basic fundamental thermodynamic parameters.

3.2 polymorphism of atacamite and minerals related to brochantite.

It must be kept in mind that minerals such as brochantite and atacamite are polymorphic. The polymorphs of atacamite are botallackite and clinoatacamite. The minerals related to brochantite are antlerite, posnjakite, langite and wroewulfite. Some confusion exists over the compound $(\text{Cu}_2\text{Cl}(\text{OH})_3)$, which is labelled as paratacamite. Paratacamite is not a polymorph of atacamite but is a separate compound and is formed when Ni, Co or Zn replaces some of the Cu. Paratacamite $((\text{CuM})_2\text{Cl}(\text{OH})_3)$ where M may be Zn, Ni, Co, is rhombohedral, space group $R\bar{3}$ with a well-developed substructure of apparent space group $R\bar{3}m$.²⁰ Of the four crystallographically independent Cu atoms in paratacamite, three have the usual Jahn-Teller distorted octahedral (4+2) coordination geometry, but the fourth is regularly octahedral, with six equivalent Cu-OH bonds some 2.12Å in length. It is now thought that substitution of Zn(II) or Ni(II) at this site is necessary to stabilize the paratacamite structure in preference to that of the polymorph clinoatacamite. Atacamite is orthorhombic, space group $Pnma$, with two crystallographically independent Cu and hydroxyl O atoms in the asymmetric unit.^{6,19} Both Cu(II) ions display characteristically Jahn-Teller distorted octahedral (4+2) coordination geometry; Cu(1) is bonded to 4 OH groups and 2 Cl atoms and Cu(2) to 5 OH groups and 1 Cl atom. The octahedra are edge-linked so that both independent OH groups bridge three Cu ions. Thus the H atoms in both OH groups are structurally constrained to occupy unique positions.

The minerals such as atacamite, clinoatacamite and botallackite are polymorphous. The free energy of formation of the minerals is such that the order of stability is clinoatacamite > atacamite > botallackite. Under ambient conditions paratacamite is said to be the stable phase. This sequence is in fact an example of the Ostwald step rule. This rule states that if a chemical reaction can result in several products then the first phase to form is not the phase with the least amount of free energy of formation but rather the phase with the highest free energy of formation. This phase is closest to the free energy of the original starting material. Thus botallackite is formed first and clinoatacamite last. The chemistry of the Ostwald step

rule may give a guide to the position of the degradation of the paint in the mediaeval paintings. If atacamite is found then the degradation sequence is only part way through the sequence. If clinoatacamite is found then the sequence is close to completion. From a conservation point of view the question may be asked as to whether such a sequence can be reversed. A salient point here is that such sequences cannot be predicted by equilibrium thermodynamic data, particularly with respect to thermochemical data of bulk solids as compared to fine-grained materials with large surface areas as might be found in the original paint pigments used by the mediaeval painters.

The minerals related to brochantite are dolerophanite, antlerite, posnjakite, langite and wroewulfite. The mineral dolerophanite (Cu_2OSO_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. Consequently it is unlikely that the mineral will be formed as a copper corrosion product. 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 latter three minerals can be considered as hydrated forms of brochantite. The formation of the individual phases depends on the pH and the activity of the sulphate anion. Tenorite (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.

3.3 Raman spectra and assignments of the common corrosion products of copper.

The Raman spectra of the copper chloride minerals are shown in **Figure 1**. The results of the spectral analysis are reported in **Table 1**. It may be possible under extremely desiccant conditions for Cu(I)Cl known as nantokite to form as a corrosion product. The Raman spectrum of nantokite in this region shows an extremely intense band at 463 cm^{-1} . This band is assigned to the symmetric stretching mode of nantokite. The second most intense band is observed at 206 cm^{-1} . This band may be assigned to a ClCuCl bending mode. The spectrum of nantokite reported in **Figure 1** for nantokite differs from that reported by Burgio and Clarke [33]. For eriochalcite ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), the strongest bands are observed at 405 and 215 cm^{-1} . These bands as for nantokite are assigned to the CuCl stretch and the Cl-CuCl bending modes. Eriochalcite contains water units. Therefore bands, which are attributable to water, should be in the spectrum. The Raman spectrum of eriochalcite in the hydroxyl-stretching region displays a band at 3367 cm^{-1} and also a water-bending mode at 1620 cm^{-1} is observed in the Raman spectrum. What is not so obvious is the observation of low intensity bands at around 687 cm^{-1} . The bands are present in both the Raman and infrared spectra. The bands in this position are attributed to water librational modes.

Other more rare minerals that may form depending on pH and ion concentrations are the minerals claringbullite, connellite and buttgenschachite. Claringbullite has the formula $\text{Cu}_8\text{Cl}_2(\text{OH})_{14} \cdot \text{H}_2\text{O}$. The mineral will be characterised by CuCl , OH stretching and deformation vibrations. Claringbullite will transform to atacamite and clinoatacamite if the mineral is left in contact with an aqueous environment. Connellite is a mixed chloride-sulphate species and may result if copper is exposed to corrosion by chloride and sulphate anions. The Raman spectrum of

claringbullite displays an intense peak at 511 cm^{-1} , which is attributed to the CuCl stretching vibration. The band is in a similar position to that of nantokite. The band is considerable broader with a bandwidth of 23.8 cm^{-1} (as FWHM) compared with that for nantokite of 8.4 cm^{-1} . This broadness is also reflected in the bands observed around 231 cm^{-1} , which have been assigned for nantokite and eriochalite to the ClCuCl bending modes. A sharp band is observed at 147 cm^{-1} and whilst it is difficult to assign bands in the low wavenumber region, it is considered that this band may be due to an OH---O hydrogen bond stretching vibration. More importantly, three bands are observed in the Raman spectrum of claringbullite at 970 , 906 and 815 cm^{-1} . These three vibrations are attributed to hydroxyl deformation modes.

The most intense band in this region occurs at around 511 cm^{-1} for atacamite (Figure 2). Bands are also observed at 601 , 586 , 450 cm^{-1} . The 511 cm^{-1} band may be resolved into two components at 513 and 501 cm^{-1} . These bands are assigned to CuO stretching vibrations. These values are in agreement with Brillouin zone centre vibrations predicted by ab-initio calculations of phonon spectra. Since there are five CuOH stretching vibrations based upon different Cu-OH bond lengths, there should be at least five CuO stretching vibrations and we do observe five bands in this region. Published infrared data gave infrared bands at 598 , 515 , 483 and 445 cm^{-1} . The second most intense band in the atacamite spectra is observed at around 150 cm^{-1} . This is assigned to OCuO bending modes.

For atacamite sample, three intense Raman bands are observed at 974 , 912 and 819 cm^{-1} with the latter having a strong shoulder at 827 cm^{-1} . Bands of much lower intensity are observed at 987 , 957 , 864 and 845 cm^{-1} . Thus there are eight hydroxyl deformation modes observed in the Raman spectrum of atacamite. In infrared spectra bands at 984 , 945 , 913 , 890 , 869 , 844 and 820 cm^{-1} are observed. Sharkey and Lewin [14] observed bands at 987 , 974 , 957 and 912 cm^{-1} and also at 864 , 845 , 827 and 819 cm^{-1} . Although they did not assign these bands, there is good agreement between the two sets of infrared data. It should also be noted that the atacamite samples these authors used were synthetic. The fact that we observed six distinct hydroxyl stretching vibrations in the Raman spectra of the hydroxyl-stretching region implies that six bands should also be observed in the hydroxyl deformation region. Eight bands are observed. This suggests that in the hydroxyl-stretching region, accidental degeneracy is occurring because of overlap. We note too the fact that several of these bands must be combination modes.

In the structure of paratacamite many different Cu-OH bond lengths are identified. Raman bands attributed to Cu-O for paratacamite are observed at 513 , 501 and 474 cm^{-1} and thus accidental degeneracy is a feature of this region of the spectrum. For paratacamite two intense bands are observed at 150 and 125 cm^{-1} . The first is assigned to OCuO bending modes. For paratacamite, Raman bands are observed at 942 , 890 and 732 cm^{-1} attributed to hydroxyl deformation modes. In the infrared spectrum of paratacamite we observed bands at 1099 , 1003 , 862 , 751 and 666 cm^{-1} . In contrast Sharkey and Lewin [14] observed bands at 987 , 926 , 915 , 900 , 865 and 830 cm^{-1} . As suggested previously these bands appear to correspond more closely with those of atacamite.

What is quite striking is the Raman spectrum of the paratacamite (Figure 2). The spectrum is very different from that of either atacamite or clinoatacamite. A

single intense band is observed at 942 cm^{-1} with lower intensity bands at 890 and 732 cm^{-1} . Thus the results of the Raman spectrum of both the hydroxyl stretching and deformation regions of the paratacamite support the results of the single crystal X-ray diffraction in that paratacamite is not dimorphic with atacamite but rather is a separate phase. In contrast clinoatacamite displays bands attributable to the hydroxyl deformation modes at $984, 921, 904, 891, 861, 821$ and 804 cm^{-1} in the infrared spectrum and at $969, 927, 892, 866$ and 799 cm^{-1} in the Raman spectrum. For clinoatacamite, strong Raman bands are observed at 367 cm^{-1} with other bands observed at 445 and 420 cm^{-1} . It is probable that these three bands are all attributable to CuCl stretching vibrations. The spectrum of paratacamite reported in this work differs from that previously reported. It should be noted that the spectrum reported by Bergio and Clarke for paratacamite is the spectrum of clinoatacamite [33]. The spectrum of atacamite reported by these authors is identical to the spectrum reported in this work.

The Raman spectrum of the low wavenumber region of brochantite and related minerals is displayed in **Figure 3**. The Raman spectra of the mineral phases for this region are different from the afore-mentioned corroded copper phases, and each basic copper sulphate phase has its own characteristic spectrum. For antlerite four Raman bands are observed at $651, 629, 606$ and 600 cm^{-1} . In contrast, chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) showed only a single band at 610 cm^{-1} . The Raman spectrum of brochantite shows bands at $629, 608$ and 600 cm^{-1} . The Raman spectrum of posnjakite shows bands at $621, 609$ and 596 cm^{-1} and langite at $621, 609$ and 596 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 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 cm^{-1} , brochantite at $786, 770$ and 749 cm^{-1} , posnjakite at 734 cm^{-1} , and langite at 773 and 732 cm^{-1} . The spectrum reported here of brochantite is in good agreement with that reported by Burgio and Clarke [33].

4. Conclusions

This paper reports the Raman spectra and band assignments of some common and not so common phases of corroded copper. The work shows that paratacamite is not polymorphic with atacamite and is a separate phase. The mineral formed at the end of the corrosion of copper in the presence of chloride ion is clinoatacamite. The first phase, which is formed is tenorite or nantokite, which may rapidly change to the other phases through a sequence of reactions to the final phase: clinoatacamite. This work exemplifies the power of Raman spectroscopy in the rapid identification of the corroded copper mineral phases. Each mineral has its own characteristic spectrum and although several minerals are quite closely structurally related, each mineral can be identified by its Raman spectrum. From the point of view of the establishment of a data base of minerals of the Raman spectra of minerals in relation to pigments, minerals, pigment media and varnishes, it is important to have not only the correct spectra but also the correct identification of the mineral phase.

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Nantokite CuCl	Eriochalite CuCl ₂ ·2H ₂ O	Atacamite Cu ₂ Cl(OH) ₃	Paratacamite (Cu,Zn,Ni,Co) ₂ Cl(OH) ₃	Clinoatacamite Cu ₂ Cl(OH) ₃	Antlerite Cu ₃ (SO ₄)(OH) ₄	Brochantite Cu ₄ (SO ₄)(OH) ₆	Posnjakite Cu ₄ (SO ₄)(OH) ₆ ·H ₂ O	Langite Cu ₄ (SO ₄)(OH) ₆ · 2H ₂ O
	3462 3367 3317 3176	3457 3433 3365 3349 3328 3208	3508 3446 3395 3364 3341 3232	3475 3443 3357 3314	3580 3488	3580 3501 3489	3588 3564 3405 3372 3262	3587 3564 3405 3372 3260
	1620	1804 1738			1905	1906	1906	1911 1906
1230 1218 1156 1079 1064		1672			1266 1173 1148 1135 1079	1265 1173 1135 1078	1271 1251 1147 1153 1132 1105 1078	1266 1172 1149 1128 1102 1076
		987 974 957 912	942 890	969 927 892 866 799	990 985 902	990	972 905	982 974 911
804 794	690 672	864 845 827 819	732	576 511	786 759	786 770 749	734	773 732
692 510 463	405 390	601 586 511 (vs) 451	513 501 474	445 420 364	651 629 606 600	629 608 600	621 609 596	621 609 596

403 393 356	247 234 215	412 393 362	404 367	256	485 469 440 415	517 501 482 467 442 415	511 482 447 422 386 363	507 481 449 420 391
262		267 240 217	277 243	206 193	335 330 295	340 330 295	317	317 273
207	117	160 149 138 120	148 124	183 165 142 118	265 259	265 247 238 228 213	241 225	258 241 226
					169 151 146 141 131	172 149 141 124	195 175 168 140	194 183 175 167 155 147 139 130 118