



COVER SHEET

Frost, Ray and Martens, Wayde and Kloprogge, Theo and Williams, Peter (2002) Raman spectroscopy of the basic copper chloride minerals atacamite and paratacamite - implications for the study of copper, brass and bronze objects of archeological significance. *Journal of Raman Spectroscopy* 33(10):pp. 801-806.

Accessed from <http://eprints.qut.edu.au>

Copyright 2002 Publisher

Raman spectroscopy of the basic copper chloride minerals atacamite and paratacamite - implications for the study of copper, brass and bronze objects of archeological significance

Ray L. Frost[•], Wayde Martens, J. Theo Kloprogge and Peter A. Williams^{*}

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

^{*}School of Science, Food and Horticulture, University of Western Sydney, Locked Bag 1797, Penrith South DC NSW 1797, Australia

Abstract

Raman spectra of the basic copper chloride minerals atacamite and paratacamite have been obtained at 298 and 77K using a Raman microprobe in combination with a thermal stage. Four distinct regions involved with hydroxyl stretching, hydroxyl deformation, CuO stretching and CuCl stretching and bending have been identified. The implication from the study is that Raman spectroscopy can be a useful tool for identifying corrosion products of copper, brass and bronze objects of archaeological or antiquarian significance. In addition, the technique may be a useful aid in the restoration degraded pigment products from old paintings.

Key Words- basic copper chloride, atacamite, paratacamite, Raman spectroscopy, infrared spectroscopy

[•] Author for correspondence (r.frost@qut.edu.au)

INTRODUCTION

A group of basic copper(II) chloride minerals of stoichiometry $\text{Cu}_2\text{Cl}(\text{OH})_3$, comprising botallackite, atacamite, paratacamite and clinoatacamite, has been known for some time,¹⁻⁶ although certain details of their structural relationships have been elucidated only recently.⁷ One important applied aspect of these minerals rests with their discovery in wall paintings from antiquity (for example, during the restoration of the fourteenth to fifteenth century wall painting of San Antonio Abate in the church of San Pietro at Quaracchi near Florence, Italy) and the need to take them into account in the preservation of such works of art.⁸ The minerals were also found in the corrosion products of the cooking stove of Ramises II;⁹ species identified included atacamite, paratacamite, calumetite, $\text{Cu}(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$, malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, and, minor azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. While these minerals are frequently found in pigments of ancient paintings,¹⁰ they are suggested to result from the breakdown of original paint pigments such as malachite and azurite as well.¹¹ Such minerals were also important in the cosmetics of the ancient Egyptians.¹² Atacamite has also been found on copper plates from the eighteenth century,¹³ and are well-known in the corrosion products of bronze statues¹⁴ and copper pipes.^{15,16} Atacamite and paratacamite are sometimes found in the volcanic fumaroles,^{5,17} aside from their usual association with the oxidized zones of base metal orebodies.¹⁸

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. Such is also the case in the structure of paratacamite, although the structural links between octahedra are different. This is of some significance in the interpretation of the vibrational spectra (see below). 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 2.12 Å 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.^{7,21,22} Again it is noted that all OH positions are structurally constrained as in atacamite and analogous situations are present in the structures of botallackite and clinoatacamite.^{7,23}

Few papers have been published on the vibrational spectroscopy of these minerals.^{11,24-26} This may be because many of the bands relating to the CuCl and CuO vibrations occur below 400 cm^{-1} and are therefore not easily measured. Further techniques such as infrared reflectance spectroscopy are also limited by cut-off at even higher frequencies. Raman spectroscopy lends itself to the study of these types of minerals and to the best of our knowledge no Raman spectroscopic study of these minerals has appeared. We have thus been prompted to undertake such a study especially in view of the fact that Raman spectroscopy has already been applied to the study of the degradation products in paintings of antiquity.^{8,10,26,27}

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. Nickeloan paratacamite (small dark green crystals associated with gaspéite, NiCO_3) from Widgiemooltha, Western Australia,²² was purchased from BK Minerals, Brisbane, Australia (<http://www.bkminerals.gil.com.au/>). The minerals were analysed for phase purity by powder X-ray diffraction methods and for chemical composition using SEM EDAX techniques.

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. 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 acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio in the spectra, which were calibrated using the 520.5 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).

Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrophotometer with a smart endurance, single bounce, diamond ATR cell. Spectra over the 4000 to 525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s .

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 allows specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Hydroxyl stretching

Atacamite has two crystallographically independent hydroxyl groups. Factor group analysis predicts six bands for the hydroxyl-stretching region of which three should be Raman active and three infrared active. Raman spectra of the hydroxyl stretching region of atacamite and paratacamite at 298 and 77 K are shown in **Figure 1**. Results of band component analysis of the spectra are reported in **Table 1**. The Raman spectrum of the Chilean atacamite displays three major bands at 3433 , 3349 and 3328 cm^{-1} with lower intensity components at 3457 , 3365 and 3208 cm^{-1} . These bands may be attributed to the infrared active modes. Atacamite from Mt Gunson, shows bands at 3447 , 3434 , 3349 and 3331 cm^{-1} . Thus there is excellent agreement

between the Raman spectra of the atacamite samples from different origins; slight differences in the spectra may be attributed to preferential orientation of the crystals in the two samples.

Figure 2 shows the infrared spectrum of atacamite and a comparison is made with its Raman spectrum. IR bands are observed at 3430, 3330, 3287 and 3189 cm^{-1} , in excellent agreement with those identified by Sharkey and Lewin,²⁸ although these authors found additional bands at 3457, 3364 and 3208 cm^{-1} . These appear to correspond with some of the Raman-active modes. Bandwidths of the Raman bands at 3433, 3349 and 3328 cm^{-1} are 5.9, 7.6 and 9.9 cm^{-1} , respectively and Raman bands are very sharp compared to the infrared bands; widths of the IR bands at 3430 and 3330 cm^{-1} are 47.9 and 59.5 cm^{-1} and remaining IR bands are broader.

There are two distinct hydroxyl units in atacamite and thus there should be two distinct vibrational bands whose intensity might be attributed to number and type of OH groups in the crystal structure. The band at around 3430 cm^{-1} in both Raman and the infrared spectra can be attributed to the hydroxyl unit that is furthest from the Cu atom (2.36 Å from Cu(2)). Bands at 3410, 3349, 3330 and 3208 cm^{-1} may be attributed to the 2.02 Å Cu-OH groups of lengths 2.02, 2.01, 1.99 and 1.94 Å, respectively, but it is apparent that some of these bands are combination modes by virtue of the symmetry of the structure.

In paratacamite, two types of hydroxyl groups are observed, those around 2.0 Å from the copper and those that are further distant at about 2.36 Å. In the Raman spectrum of paratacamite two intense bands are observed at 3395 and 3364 cm^{-1} with bandwidths of 13.3 and 11.2 cm^{-1} . Low intensity bands are also observed at 3508, 3446, 3341 and 3232 cm^{-1} . IR bands at 3531, 3482, 3398 and 3237 cm^{-1} are observed; the band at 3395 cm^{-1} is common to both Raman and IR spectra. Sharkey and Lewin²⁸ reported IR bands for paratacamite at 3420, 3330 and 3280 cm^{-1} . These appear to correspond more closely with atacamite than paratacamite. It might be expected that the four near hydroxyl units are non-equivalent and are similar to the bond distances observed for atacamite. This is not the case and Raman spectroscopy suggests that the four nearest OH groups are approximately equidistant from Cu. The intensity ratio of the two bands at 3395 and 3364 cm^{-1} is 3.44 and the expected ratio is 4:1. Thus the band at 3395 cm^{-1} is attributed to the nearer OH groups and the band at 3364 cm^{-1} to the more distant ones.

Raman spectra were measured at 77 K to confirm the results of the 298K spectra, to provide increased band separation and to enhance the peak heights of low intensity bands. Reducing the temperature to 77 K caused a shift in band positions to lower frequencies. For example, for the Mt Gunson atacamite, the bands observed 3437, 3434, 3349 and 3331 cm^{-1} shifted to 3435, 3432, 3342 and 3325 cm^{-1} , respectively. This shift is constant for the different bands and is attributed to the strengthening of the Cu-OH bond. This shift to lower wavenumbers of the OH vibration indicates a shortening of the OH bonds. In addition, the intensity of the OH stretching bands at 3325 and 3318 cm^{-1} increased. It is apparent that by obtaining the spectra at liquid nitrogen temperature, further differentiation of the hydroxyl units is observed. The additional band at 3318 cm^{-1} is probably an additional combination mode. Similar results are observed for paratacamite. Bands at 3446, 3395, 3364 and 3341 cm^{-1} shift to 3445, 3393, 3358 and 3330 cm^{-1} , respectively. Bandwidths of the two bands 3432 and 3342 cm^{-1} for atacamite are 3.7 and 4.3 cm^{-1} . Similarly the bandwidths of the bands at 3392 and 3357 cm^{-1} for paratacamite decrease to 8.1 and 7.3 cm^{-1} at 77 K.

Hydroxyl deformation region

Identification of the hydroxyl deformation modes is an important aspect of this study. Normally, as with other basic sulphate, phosphate or arsenate copper minerals, symmetric SO, PO and AsO stretching modes are so intense that the hydroxyl deformation modes are masked.²⁹ In the basic copper chloride minerals, CuCl vibrations are observed at frequencies less than 500 cm^{-1} . As a consequence a clear window between 500 and 1500 cm^{-1} is made for the observation of hydroxyl deformation modes. Raman spectra of this region are shown in **Figure 3** and data reported in **Table 1**.

For the Chilean 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 the Chilean atacamite. Bands are observed in identical positions for the Mt Gunson atacamite sample. In our infrared spectra we observed bands at 984 , 945 , 913 , 890 , 869 , 844 and 820 cm^{-1} . Sharkey and Lewin²⁸ 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 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.

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 Lewin²⁸ 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. Upon cooling the paratacamite sample to 77K , these modes are observed at 981 , 950 , 897 and 737 cm^{-1} . This observation is in excellent harmony with the shifts of the hydroxyl-stretching modes to lower frequencies upon cooling the sample to 77 K .

Copper-oxygen vibrations

The lower wavenumber region where CuO and CuCl vibrations are expected is shown in **Figure 4**. The most intense band in this region occurs at around 511 cm^{-1} for atacamite. 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} . **Figure 5** displays the deconvolution of this region. 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} .²⁸ At 77K , increased peak heights for the bands in the low wavenumber region are observed through band narrowing. In spectra of Mt Gunson atacamite bands at 77 K are observed at 606 , 588 , 516 , 505 and 455 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. 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.

Copper chloride vibrations

In the low frequency region of atacamite Raman bands are observed at 385 and 353 cm^{-1} (Figure 6). These bands shift to 392 and 358 cm^{-1} at 77K and are attributed to Cu-Cl stretching vibrations. In the crystal structure of atacamite Cl is some 2.78 Å from Cu(1) and 2.75Å from Cu(2), in accord with the spectroscopic data. Similarly, two such bands are observed at 404 and 367 cm^{-1} for paratacamite and shift to 409 and 371 cm^{-1} at 77K. Four separate Cu-Cl bond lengths are identified in the structure and some overlap is apparent in this case.

CONCLUSIONS

Raman spectroscopy has been used to probe the molecular structure of atacamite and paratacamite. The Raman spectra of atacamite and paratacamite are different. Raman spectroscopy confirms that paratacamite is not a polymorph of atacamite but is a separate mineral with a different structure. The polymorphs of atacamite are clinoatacamite and botallackite. Hence it is most unlikely that paratacamite is a product of the corrosion of copper, bronze or brass.

Raman spectra are conveniently divided into sections according to the type of vibration in the structure. Thus bands were assigned to hydroxyl stretching, hydroxyl deformation, CuO stretching and CuCl stretching modes. Combination bands are present in some cases. The observation of CuO and CuCl bands is significant as they are often hidden beneath vibrations arising from oxyanions in other basic copper minerals. This research has implications for the analysis of bronzes, brasses and copper objects of archaeological, medieval and antiquarian significance. The study has shown the ease with which the basic hydroxy-chlorides of copper may be determined using Raman spectroscopy. Hence degraded pigments and paintings, and corroded bronzes or copper and brass objects may be readily examined for corrosion products using Raman spectroscopy, because of the widespread occurrence of these phases in them. Finally, in this connection, it is noted that the spectroscopic method is non-destructive.

Acknowledgments

The financial and infrastructure support of the Queensland University of Technology Centre for Instrumental and Developmental Chemistry is gratefully acknowledged. The School of Natural Resources of the Queensland University of Technology is thanked for the supply of the atacamite specimens used in this study. The Australian research Council (ARC) is thanked for funding.

REFERENCES

1. Brasseur, H, Toussaint, J. *Bull. Soc. roy. Sci. Liege* 1942; **11**: 555.
2. de Wolff, PM, Kortlandt, D. *Appl. Sci. Research* 1954; **3B**: 400.
3. de Wolff, PM. *Acta Cryst.* 1953; **6**: 359.
4. Frondel, C. *Mineralog. Mag.* 1950; **29**: 34.

5. Lacroix, A. *Bull. Soc. franç. Min.* 1907; **30**: 219.
6. Wells, AF. *Acta Cryst.* 1949; **2**: 175.
7. Grice, JD, Szymański, JT, Jambor, JL. *Can. Min.* 1996; **34**: 73.
8. Dei, L, Ahle, A, Baglioni, P, Dini, D, Ferroni, E. *Stud. Conserv.* 1998; **43**: 80.
9. Helmi, FM, Iskander, NY. *Stud. Conserv.* 1985; **30**: 23.
10. Kuchitsu, N, Kuroki, N, Inokuchi, S, Mitsuishi, S. *Hozon Kagaku* 1999; **38**:108.
11. Scott, DA. *Stud. Conserv.* 2000; **45**: 39.
12. Reiderer, J. *Archaeometry* 1974; **16**: 102.
13. Otero, E, Bastidas, JM, Lopez, W, Fierro, JLG. *Werkst. Korros.* 1994; **45**: 387.
14. Selwyn, LS, Binnie, NE, Poitras, J, Laver, ME, Downham, DA. *Stud. Conserv.* 1996; **41**: 205.
15. Erdos, E. *Werkst. Korros.* 1968; **19**: 385.
16. Nunez, L, Haces, C, Gonzalez, E, Echague, M. *Rev. CENIC, Cienc. Quim.* 1998; **29**: 21.
17. Naboko, SI, Glavatskikh, SF. *Vulkanol. Seismol.* 1983: 3.
18. Williams, PA. 1990; *Oxide Zone Geochemistry*; Ellis Horwood, Chichester.
19. Parise, JB, Hyde, BG. *Acta Crystallogr.* 1986; **C42**: 1277.
20. Fleet, ME. *Acta Crystallogr.* 1975; **B31**: 183.
21. Jambor, JL, Dutrizac, JE, Roberts, AC, Grice, JD, Szymański. JL. *Can. Min.* 1996; **34**: 61.
22. Nickel, EH, Clout, JFM, Gartrell, BJ. *Mineral.Rec.* 1994; **25**: 283, 302.
23. Hawthorne, FC. *Min Mag.* 1985; **49**: 87.
24. Fontana, P, Fabbri, G. *Boll. sci. fac. chim. ind. Bologna* 1957; **15**: 109.
25. Hunt, GR, Salisbury, JW, Lenhoff, CJ. *Mod. Geol.* 1972; **3**: 121.
26. Povarennykh, AS. *Konst. Svoistva Miner.* 1979; **13**: 78.
27. Naumova, MM, Pisareva, SA. *Stud. Conserv.* 1994; **39**: 277.
28. Sharkey, JB, Lewin, SZ. *Thermochimica Acta* 1972; **3**: 189.
29. Frost, RL, Williams, PA, Martens, W, Kloprogge, JT, Leverett, P. *J. Raman Spectrosc.* 2002; **33**: 252

Table 1 Results of the Raman and infrared spectra of atacamite and paratacamite.

Atacamite Sample 1 (Atacama, Chile)		Atacamite Sample 2 (Mt. Gunson South Australia)	Atacamite	Atacamite Sample 2 (Mt. Gunson South Australia)		Paratacamite	Paratacamite		
Raman		Infrared This work	Infrared ²³	Raman		Infrared ²³	Raman		Suggested assignment
298 K	77 K	298 K	298 K	298 K	77 K	298 K	298 K	77 K	
3457	3452	3588	3457	3437	3435		3508		Hydroxyl stretching of individual OH units
3433	3435	3436	3433	3434	3432	3420	3446	3445	
3365	3360	3410	3349		3342		3395	3393	
3349	3342			3349	3325		3364	3358	
3328	3325	3330	3328	3331		3330	3341	3330	
3208	3205	3287	3208		3318	3280	3232	3321	
		3208							
		3067							
1804	1804		1804						Overtones
1738	1738		1738						
1672	1672		1672						Water HOH bending

987 974 957 912	990 978 959 918	984 945 913 890	987 974 957 912	979 973 908	980 920 918	987 926 915 900	942 890	981 950 897	Hydroxyl deformation
864 845 827 819	864 845 827 819	869 844 820	864 845 827 819	864 844 818	871 851 829 825	865 830	732	737	Hydroxyl deformation
601 586 511 (vs) 451	598 515 483 445	608 590 566	598 515 483 445	585 511 448	606 588 516 455		513 501 474	506 484 478	CuO stretching
412 393 362	410		410	385 353	392 358		404 367	421 412 409 371 321	CuCl stretching
267 240 217				238 216 184	247 224 190		277 243	283 181	Lattice modes
160 149 138 120	150 140 122			148 137 118	151 140 121		148 124	150 144 125	OCuO bending

List of Figures

Figure 1 Raman spectra of the hydroxyl stretching region of (a) atacamite from Atacama (Chile) (b) atacamite from Mt Gunson (South Australia) at 298 and (c) 77 K (d) paratacamite at 298 and (e) 77 K.

Figure 2 Comparison of the Raman and Infrared spectrum of the hydroxyl stretching region of atacamite from Mt Gunson.

Figure 3 Raman spectra of the hydroxyl deformation region of (a) atacamite from Atacama (Chile) (b) atacamite from Mt Gunson (South Australia) at 298 and (c) 77 K (d) paratacamite at 298 and (e) 77 K.

Figure 4 Raman spectra of the low wavenumber region of (a) atacamite from Atacama (Chile) (b) atacamite from Mt Gunson (South Australia) at 298 and (c) 77 K (d) paratacamite at 298 and (e) 77 K.

Figure 5 Raman spectra and band deconvolutions of the 650 to 400 cm^{-1} region of the Chilean and South Australian atacamites.

Figure 6 Raman spectra and band deconvolutions of the 450 to 200 cm^{-1} region of the Chilean and South Australian atacamites.

List of Tables

Table 1 Results of the Raman and infrared spectra of atacamite and paratacamite.