Martens, Wayde N., Frost, Ray L., & Williams, Peter (2003) Raman and infrared spectroscopic study of the basic copper chloride minerals: implications for the study of the copper and brass corrosion and "bronze disease". *Neues Jahrbuch für Mineralogie. Abhandlungen*, *178*(2), pp. 197-215.

http://dx.doi.org/10.1127/0077-7757/2003/0178-0197

Raman and infrared spectroscopic study of the basic copper chloride minerals - implications for the study of the copper and brass corrosion and "bronze disease"

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Abstract

The vibrational spectra of both synthetic and natural atacamite and clinoatacamite and are compared with natural paratacamite have been obtained at 298 using a combination of FTIR and Raman microscopy. The vibrational spectra of the minerals are different, in line with differences in crystal structure and composition. The vibrational spectra of paratacamite are different from that of both atacamite and clinoatacamite. Paratacamite is not polymorphic with atacamite but rather is a separate phase. Some similarity in the Raman spectra of the polymorphs exists, particularly in the OH stretching region, but characteristic differences in the OH deformation regions are observed. These differences may be used to characterize the minerals. Differences are also observed in the chloride stretching and deformation regions.

The implication from the study of these minerals is that copper, brass and bronze objects of archaeological, antiquarian and medieval significance can be studied by the use of Raman spectroscopy. Indeed the restoration of these types of articles can be aided by the application of Raman spectroscopy to the study of the degradation products from paintings of antiquity.

Key Words- atacamite, botallackite, claringbullite, clinoatacamite, copper, chloride, infrared spectroscopy, paratacamite, Raman spectroscopy

INTRODUCTION

The interest in the basic copper chloride minerals such as atacamite, paratacamite and clinoatacamite rests with the study of the corrosion products of copper, brass and bronze (ERDOS 1968; HELMI & ISKANDER 1985; METS et al. 1979; OTERO et al. 1994; SCOTT 2000; SELWYN et al. 1996). Indeed the corrosion of bronze was first thought to be of a biological nature and hence was termed "the bronze disease" (SCOTT 2000). X-ray crystallography has shown that the corrosion products of bronze to be of a mineralogical nature. Table 1 shows the crystal structure and lattice parameters for the basic copper chloride minerals. Both bottalackite and clinoatacamite are monoclinic whereas atacamite is orthorhombic and paratacamite rhombohedral.

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Further the interest in these minerals stems from the use of the minerals in paintings and decorations of an antiquarian or mediaeval significance (DEI et al. 1998; FONTANA & FABBRI 1957; NAUMOVA & PISAREVA 1994; REIDERER 1974). It has been suggested that such minerals are the breakdown products of the colouring agents such as azurite and malachite, which were in the original paint pigments. Therefore the understanding of the molecular structure and interrelationships of these minerals is of great importance in the conservation of these paint pigments. In fact the understanding of the chemistry of these minerals will assist in the conservation of such works.

Whilst X-ray diffraction has been used to analyse the basic copper chlorides of copper known as atacamite, paratacamite and clinoatacamite (AIRES-BARROS 1970; DE WOLFF 1953; DE WOLFF & KORTLANDT 1954; FEJER et al. 1977; FLEET 1975; GRICE et al. 1996; LEONYUK et al. 2001; MARTINEZ et al. 1966; OSWALD & GUENTER 1971; WELLS 1949) fundamental studies of the vibrational characterisation of these minerals has not been forthcoming. Some infrared studies have been undertaken (AIRES-BARROS 1970; POVARENNYKH 1979; SHARKEY & LEWIN 1972) and no Raman studies have been published to date. The objective of this research is to elucidate the molecular structures of these minerals using vibrational spectroscopic techniques.

EXPERIMENTAL

Synthesis of the basic copper chloride minerals

Atacamite and clinoatacamite were synthesized by the stoichiometric titration of copper(II)chloride with sodium hydroxide. Time is of the essence in the synthesis. The first phase to separate is botallackite, which rapidly recrystallises to atacamite. It the solid phase is allowed to stand in contact with the solution, the phase formed is clinoatacamite.

Analysis of samples

Atacamite (nice dark green nodules of small acicular crystals) originated from Mt. Gunson South Australia. Another sample of atacamite was sourced from Atacama, Chile. Paratacamite (small dark green crystals with gaspeite) came from Widgiemooltha Western Australia. The minerals were analysed for phase purity by X-ray diffraction and also for chemical composition by electron probe analysis.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer 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.

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 cm^{-1} 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).

Spectroscopic manipulations such as baseline adjustment, smoothing and normalization 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 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

The minerals such as atacamite paratacamite, clinoatacamite and botallackite are polymorphous. The free energy of formation of the minerals is such that the order of stability is clinoatacamite > paratacamite > 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 paratacamite 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.

There are quite a number of routes for the synthesis of the minerals: (a) direct precipitation through titration of $CuCl_2.2H_2O$ with sodium hydroxide (b) addition of base to metallic copper in contact with copper chloride with or without sodium chloride (c) replacement of malachite or brochantite immersed in copper chloride solutions. These latter two methods are no doubt related to the corrosion of bronze and copper artefacts and to the deterioration of ancient pigments in wall paintings. In the synthesis of atacamite and related minerals, the first phase to separate from the precipitation route is botallackite. This phase is difficult to isolate with purity. The second phase to precipitate in a time sequence is atacamite and if the mineral is allowed to stand for significant periods of time then paratacamite is formed and if further time is allowed such that the mineral is in contact with the solution clinoatacamite is formed. The phases may be isolated by judicious selection of the reaction conditions and the removal of solids, which may give rise to further reactions. In the degradation of the paintings of mediaeval or antiquarian significance the chemical reactions may follow such a sequence through the paintings becoming wet or moist, drying out and repeating of this sequence over extended periods of time.

Hydroxyl stretching and deformation vibrations.

In this work atacamite, paratacamite and clinoatacamite were synthesised by the precipitation method. Figure 1 displays the XRD patterns for the natural atacamite and the synthesised atacamite and clinoatacamite. Other phases were synthesised but were not of a single-phase purity. The infrared spectrum of Eriochalite, atacamite, paratacamite and clinoatacamite are shown in Figure 2. The results of the band deconvolutions of the infrared and Raman spectra of these minerals are reported in Table I. The starting material in the reaction sequence is the mineral eriochalite ($CuCl_2.2H_2O$). The infrared spectrum of this mineral shows hydroxyl stretching bands at 3462, 3352, 3260 and 3157 cm^{-1}. The Raman spectrum of this mineral (Figure 3a) shows a single intense band at 3365 cm^{-1} with two bands of quite low intensity at 3471 and 3160 cm^{-1}. The spectra indicate that there are two types of water molecules at two different distances from the copper atom. This results in two sets of bands with antisymmetric and symmetric stretching modes. The antisymmetric stretching modes are observed as the intense bands at 3462 and 3352 cm^{-1}. The symmetric stretching mode is observed as a band at 3365 cm^{-1}.

The first phase formed of high purity in the reaction sequence is atacamite and the infrared spectrum is shown in Figure 2 and the Raman spectrum in Figure 3a. The Raman spectra of the synthetic and natural atacamites are compared in this latter figure. The synthetic atacamite infrared spectrum shows prominent bands at 3436, 3325, 3276 and 3205 cm^{-1}. In contrast, the Raman spectrum of the synthetic atacamite shows bands at 3434, 3352 and 3320 cm^{-1}. The spectrum of the natural sample shows band at 3435, 3352 and 3332 cm^{-1}. There is excellent agreement between the infrared and Raman spectrum of the synthetic and natural atacamites. The difference rests with the widths of the bands. The widths of the bands of the natural sample (as full widths at half maximum) at 3435, 3351 and 3332 cm^{-1} are 8.1, 11.4 and 13.6 cm^{-1}. In comparison, the widths of the bands at 3434, 3352 and 3320 cm^{-1} are 46.7, 34.7 and 44.9 cm^{-1}. The significance of these results is that the narrow band widths of the natural sample is an indication of high crystallinity and the wide bandwidths of the synthetic sample show the synthetic sample to be disordered and not well crystallised. This is to be expected. Such broad bands might be expected for the atacamite minerals found as the corrosion products of copper and bronzes.

In the crystal structure of atacamite there are four near hydroxyl groups at distances of 1.94, 2.00, 2.04 and 2.07Å and one hydroxyl group further distant at 2.36Å (SHARKEY & LEWIN 1972). Thus there are five distinct hydroxyl units in atacamite. In this wok we observe four bands in the infrared spectrum and three in the Raman spectrum. It is probable that two or bands might overlap as a result of accidental degeneracy. This means there should be five distinct vibrational bands and the intensity of the bands might be attributed to the number of the types of OH units in the crystal structure. The band at around 3430 cm^{-1} in both the Raman and the infrared spectra is attributed to the hydroxyl unit which is furtherest distant from the Cu atom. Thus this band is assigned to the hydroxyl unit, which is 2.36Å from the Cu atom. The band at 3410 cm^{-1} appears to be infrared active-Raman inactive is attributed to the 2.07Å Cu distant Cu atom. The band at 3349 cm^{-1} in the Raman spectrum is infrared inactive may be assigned to the 2.04Å Cu distant hydroxyl unit. The band at 3330 cm^{-1} in both the Raman and infrared spectra is ascribed to the 2.00Å Cu distant hydroxyl unit. The band at 3208 cm^{-1} may be assigned to the hydroxyl unit, which is 1.94Å from the Cu. This band appears to be infrared active-Raman-inactive.

In paratacamite the crystal structure was obtained by reiterative refinement (SHARKEY & LEWIN 1972). Two types of hydroxyl units are observed, those close to copper at around 2.0Å from the copper and those which are further distant at around 2.36Å. The infrared spectrum of paratacamite displays bands at 3531, 3480, 3397, 3331, 3274 and 3239 cm^{-1}. 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}. Thus there are six bands observed in both the infrared and in the Raman spectra. The band at 3395 cm^{-1} is common to both the Raman and infrared spectra. Sharkey and Lewin observed infrared bands for paratacamite at 3420, 3330 and 3280 cm^{-1} (SHARKEY & LEWIN 1972). These bands appear to correspond more closely with that of atacamite than paratacamite. These researchers also synthesised the atacamite type minerals. 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 the results of Raman spectroscopy suggest that the four near OH units are of equal distances from the copper. The ratio of intensities of the two bands at 3395 and 3364 cm^{-1} are 3.44. The expected intensity ratio is 4:1. Thus the band observed at 3395 cm^{-1} is attributed to the near OH units and the band at 3364 cm^{-1} to the far OH units.

The synthetic paratacamite has different spectral features to that of the natural sample. The synthetic and natural samples are not the same. This is not unexpected. According to Grice et al., paratacamite has the same layer composition and topology as clinoatacamite (GRICE et al. 1996). It is the interlayer isolated $\{Cu(OH)_6\}$ octahedron that differs between the two minerals. In the clinoatacamite structure, the interlayer octahedron exhibits a JT distortion but in paratacamite one $\{Cu(OH)_6\}$ is axially compressed whereas the other is a regular octahedron. Such a conclusion was also made by Eby and Hawthorne (EBY & HAWTHORNE 1993; JAMBOUR et al. 1996). All paratacamite crystals studied to date have significant amounts of either Zn or Ni (often > 6%). Zinc also has a six-fold coordination site with regular octahedron geometry. Thus paratacamite as has been suggested needs to be redefined. It is probable that it is not a polymorph of $Cu_4(OH)_6Cl_2$ but is rather a distinct phase $Cu_3(Cu,Zn)(OH)_6Cl_2$. Thus the paratacamite structure would have the Zn ordered at a regular octahedral site. Jambour et al. showed that only 2 % of Zn was required to stabilise the paratacamite rhombohedral structure. In this work we used the paratacamite sample from Widgiemooltha Western Australia, which contains Ni. This is the same paratacamite used by Fleet in his X-ray crystallographic study of paratacamite. Thus in this work the synthetic paratacamite is a mixture of clinoatacamite, and the other polymorphs.

Clinoatacamite is monoclinic of space group $P2_1/n$. This structure is transformable to a pseudorhombohedral cell approximating that of paratacamite. The structure of clinoatacamite is based upon layers of partially occupied edge sharing partially distorted $\{Cu(OH)_4Cl_2]$ octahedra, which are parallel to the (101) plane. The adjacent layers of octahedra are offset such that the vacant sites in one sheet align with the occupied sheets of the adjacent neighbouring sheet. (GRICE et al. 1996) The layers are linked by individual distorted {Cu(OH)6] octahedra. These distorted octahedra mean that the CuO bond differences will be different. Bond distances for the CuO bonds are 1.934, 1.975, 1.999 and 2.015Å. The bond distances depend upon the polyhedral unit and other CuO bond distances of 2.288, 2.05 and 1.991 are observed. Each of these hydroxyl units is hydrogen bonded to the adjacent Cl atoms at distances of between 3.04 to 3.09Å. The CuCl bond distances are 2.766Å. The implication from the crystal structure is that a significant number of hydroxyl stretching bands should be observed. Since there are nine different CuOH bond distances, it could be predicted that 9 bands should be observed, providing there is no overlap of the bands.

The infrared spectrum of clinoatacamite displays bands at 3440, 3359, 3300, 3252 and 3139 cm^{-1} (Figure 2). Five bands are observed. Several of the bands are broad and may be composed of component bands. In the Raman spectrum of synthetic clinoatacamite bands are observed at 3475, 3443, 3357 and 3314 cm^{-1}.

Hydroxyl deformation vibrations.

Important in this work is the identification of the hydroxyl deformation modes. Normally with the other basic copper minerals of sulphate, phosphate or arsenate, the symmetric stretching vibrations of the SO, PO and AsO modes are so intense that the hydroxyl deformation modes are masked by these intense stretching bands (FROST et al. 2002). By using the basic copper chloride minerals, the CuCl vibrations are observed at wavenumbers less than 500 cm^{-1}, and as a consequence a clear window between 500 and 1500 cm^{-1} is enabled for the observation of the hydroxyl deformation modes. The infrared spectra of the hydroxyl deformation modes of atacamite and clinoatacamite are shown in Figure 4. The natural atacamite displays infrared bands at 982, 945, 914, 891, 867, 845, 819, 794, 754 and 697 cm^{-1}. The bands for the synthetic atacamite are in identical positions confirming the X-ray diffraction results for the correct synthesis of the atacamite phase. In the Raman spectrum of the hydroxyl deformation region of atacamite (Figure 5) Raman bands are identified at 972, 907, 862 843 and 817 cm^{-1}. The results of the Raman spectra of the synthetic atacamite are in quite good agreement with those of the natural sample. What is quite striking is the Raman spectrum of the paratacamite (Figure 5). 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.

CuCl and CuO vibrations.

The infrared spectra of the CuCl vibrations were not obtained as the use of the diamond ATR cell has a spectral limit of 500 cm^{-1}. Raman spectra of the low wavenumber region of atacamite, paratacamite and clinoatacamite are shown in Figure 6. A band, which is common to the atacamite phases, is observed at 511 cm^{-1} and is assigned to the CuO stretching vibration. This band is slightly shifted in paratacamite and is observed at 501 cm^{-1}. The position of this band for paratacamite is in harmony with the concept that paratacamite is not a dimorph of atacamite. Intense bands are also observed at around 148 cm^{-1}. This band is attributed to the OCuO bending modes.

In the low wavenumber region of atacamite Raman bands are observed at 385 and 353 cm^{-1} (Figure 6). These bands are attributed to the CuCl stretching vibrations. In the crystal structure of atacamite The Cl is at 2.75Å from the Cu atom. Only one CuCl bond is observed in the crystallographic data, as all Cl's are equivalent. In this work we observe two distinct Raman bands, which are attributed to the CuCl vibrations. This means that at least on a molecular scale the CuCl bonds are not equivalent and that two distinct bond distances for the CuCl should be observed. Raman spectroscopy shows here the need for further refinement of the crystal structure of atacamite. These two bands in paratacamite are observed at 404 and 367 cm^{-1}. The bands here are in similar positions as for that of atacamite. This simply means that the CuCl or Cu(Zn or Ni) bond distances are similar in atacamite and paratacamite. These bands as for atacamite are assigned to CuCl stretching vibrations. Again two distinct CuCl vibrations are observed which brings into question the X-ray crystallographic data since Raman spectroscopy shows the non-equivalence of the CuCl vibrations. 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.

CONCLUSION

This research has used vibrational spectroscopy to characterise the molecular structure of the mineral phases of $Cu_2(OH)_3Cl$ namely atacamite and clinoatacamite. This molecular structure has been related to the crystal structure of the minerals. The infrared and Raman spectra of paratacamite is sufficiently different from those of these phases to prove that the paratacamite is not dimorphous with atacamite or clinoatacamite but rather is a separate phase in line with the conclusions of X-ray diffraction. A significant number of hydroxyl stretching and deformation modes are observed for each of the minerals, which readily may be sued for the identification of the basic copper chloride minerals. Bands attributable to the CuO, OCuO bending and CuCl stretching modes were identified.

This research has serious implications for the analysis of bronzes, brasses and copper objects of archaeological, medieval and antiquarian significance. This work has shown the ease with which the basic oxy chlorides of copper may be determined using Raman spectroscopy. Hence degraded pigments, paintings and corroded bronze, copper and brass statues may be readily examined for corrosion products using Raman spectroscopy.

ACKNOWLEDGMENTS

The financial and infra-structure support of the Queensland University of Technology Centre for Instrumental and Developmental Chemistry is gratefully acknowledged. The Australian research Council (ARC) is thanked for funding.

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TABLE 1 Crystallographic data for the basic copper(II) chlorides of composition $Cu_2Cl(OH)_3$.

mineral	class	space group	a/Å	b/Å	c/Å	β/º	Z	Ref.
Botallackite	monoclinic	$P2_1/m$	5.717(1)	6.126(1)	5.636(1)	93.07(1)	2	1
Atacamite	orthorhombic	*Pnma*	6.030(2)	6.865(2)	9.120(2)		4	2
paratacamite	rhombohedral	$R\bar{3}$	13.654(5)		14.041(6)		24	3
clinoatacamite	monoclinic	$P2_1/n$	6.157(2)	6.814(3)	9.105(5)		4	4

1. (HAWTHORNE 1985)
2. (PARISE & HYDE 1986)
3. (FLEET 1975)
4. (GRICE et al. 1996)

Table I. Results of the vibrational spectra of the $Cu_3(OH)_2Cl$ minerals.

Eriochalite $CuCl_2.2H_2O$		Atacamite $Cu_2Cl(OH)_3$ (synthetic)		Atacamite $Cu_2Cl(OH)_3$ (Mt Gunson)		Paratacamite $Cu_2Cl(OH)_3$ (synthetic)	Paratacamite $Cu_2Cl(OH)_3$		Clinoatacamite $Cu_2Cl(OH)_3$ (synthetic)		Suggested assignment
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Infrared	Raman	Infrared	Raman	
3462	3471	3507	3434	3436	3435		3531	3508	3440	3475	Hydroxyl stretching
3352	3365	3433	3352	3325	3351	3442	3480	3446	3359	3443	
3260		3406	3320	3276	3332	3358	3397	3395	3300	3357	
3157	3160	3359		3203		3307	3331	3364	3252	3314	
		3322				3289	3274	3341	3139		
		3269				3237	3239	3232			
					1009			942	984	969	Hydroxyl deformation
		987	974	982	972	986		890	921	927	
		950		945		921			904	892	
		915	909	914	907	905			891	866	
		896		891		891			861	799	
		850	854	867	862	862			821		
				845	843	822			804		
		819	816	819	817						
		784	785	794							
				754				732			
		701		697							
						578					
682	688			601			592				Water libration
	662			584	585		589				
								513	577	576	CuO stretch
			511		511			501		511	
								474			
	405		447		448					445	CuCl stretch
	387		400		411			404		420	
					386			367		364	

			359 323		353						
	274 234		277 248		264 238 213			277 243		256	
	214 119		174 150 124		184 148 138 119			148 124		206 193 183 165 142 118	ClCuCl bends

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