Is chrysocolla (Cu,Al)$_2$H$_2$Si$_2$O$_5$(OH)$_4$·nH$_2$O related to spertiniite Cu(OH)$_2$?

- a vibrational spectroscopic study

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ABSTRACT

Chrysocolla (Cu, Al)$_2$H$_2$Si$_2$O$_5$(OH)$_4$·nH$_2$O is a hydrated copper hydroxy silicate and is commonly known as a semi-precious jewel. The mineral has an ill defined structure but is said to be orthorhombic, although this remains unproven. Thus, one of the few methods of studying the molecular structure of chrysocolla is to use vibrational spectroscopy.

Chrysocolla is a colloidal mineral. The question arises as to whether chrysocolla is a colloidal system of spertiniite and amorphous silica. The main question addressed by this study is whether chrysocolla is (1) a mesoscopic assemblage of spertiniite, Cu(OH)$_2$, silica, and water, (2) represents a colloidal gel or (3) is composed of microcrystals with a distinct structure.

Considerable variation in the vibrational spectra is observed between chrysocolla samples. The Raman spectrum of chrysocolla is characterised by an intense band at 3624 cm$^{-1}$ assigned to the OH stretching vibrations. Intense Raman bands found at 674, 931 and 1058 cm$^{-1}$ are assigned to SiO$_3$ vibrations. The Raman spectrum of spertiniite does not correspond to the spectrum of chrysocolla and it is concluded that the two minerals are not related. The spectra of chrysocolla correspond to a copper silicate colloidal gel.

Keywords: chrysocolla, silicate, spertiniite, Raman spectroscopy, planchéite, shattuckite

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Introduction

Chrysocolla is a hydrated hydroxy silicate of copper and aluminium of formula \((\text{Cu, Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot n\text{H}_2\text{O}\) [1]. It is one of a number of copper silicates [2]. There are a significant number of silicate minerals which have copper as the main cation. These include kinoite \(\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10}(\text{OH})_4\), chrysocolla \((\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot n\text{H}_2\text{O}\), dioptase \(\text{CuSiO}_3\cdot \text{H}_2\text{O}\), planchéite \(\text{Cu}_8\text{Si}_8\text{O}_{22}(\text{OH})_4\cdot \text{H}_2\text{O}\), shattuckite \(\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2\cdot \text{whelanite}\), \(\text{Ca}_5\text{Cu}_2(\text{OH})_2\text{CO}_3\cdot \text{Si}_6\text{O}_{17}\cdot 4\text{H}_2\text{O}\), ajoite \((\text{K,Na})\text{Cu}_7\text{AlSi}_9\text{O}_{24}(\text{OH})_6\cdot 3\text{H}_2\text{O}\), apachite \(\text{Cu}_9\text{Si}_{10}\text{O}_{29}\cdot 11\text{H}_2\text{O}\), papagoite \(\text{CaCuAlSi}_2\text{O}_6(\text{OH})_3\). Apart from chrysocolla which appears as a normally amorphous mineral, all of these copper silicate minerals are crystalline; however the crystallinity may vary between the minerals. All of the minerals contain either hydroxy units or water units or both. These water and OH units are important for the stability of the minerals. Chrysocolla is a common mineral found in the oxidised zone of copper bearing ores [3]. It is found in many sites worldwide [3] and is found in quite a few localities in Australia; for example it is known from the Chillagoe mining district in Northern Queensland [4]. The mineral is also found at Cloncurry and Broken Hill, Australia, from the Burra Burra Mine, S.A. and also the Kara Mine, Tasmania. Chrysocolla is also used as a gemstone despite its softness and difficulty to work as a gem mineral. The mineral is used as a semi-precious jewel.

Details of the mineral chrysocolla have been published (page 142) [5]. The chemical composition of the chrysocolla from Inspiration mine has been reported [6]. Sun reported that this chrysocolla is not a definite chemical compound but a hydrogel containing mainly \(\text{SiO}_4\), \(\text{CuO}\) and \(\text{H}_2\text{O}\), and minor amounts of \(\text{Al}_2\text{O}_3\), \(\text{CaO}\) and \(\text{MgO}\). A cryptocrystalline phase is present in the chrysocolla, but its composition is ill-defined. Such a proposition fits well with the more recent studies which suggest chrysocolla is a colloidal gel. The name chrysocolla is often used for any massive, globular, glassy, blue to green copper-bearing silicate minerals which have not been specifically identified. Multiple analyses of different compositions have been offered over the years. Chrysocolla is usually X-ray amorphous with crystallites too small to give a crystal's diffraction pattern. The mineral is associated with copper oxides and carbonates rather than other copper silicate minerals such as planchéite, shattuckite and dioptase. Crane et al. proposed that chrysocolla is formed by the reaction of copper hydroxy carbonate with siliceous acid according to the reaction [4]:

\[
\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s}) + 3\text{H}_4\text{SiO}_4(\text{aq}) \rightarrow 3\text{CuSiO}_3\cdot \text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{l}) + 2\text{CO}_2(\text{g})
\]
Such a reaction will be controlled by the amount of dissolved silica, the pH and the partial pressure of CO₂. Crane et al. suggested that the reaction involved azurite but (according to their own phase diagram), the other pseudomorph malachite is more likely to be involved in the chemical reaction. The reaction and phase stability diagram proposed by Crane et al. explains why chrysocolla is more likely to be found with carbonates and oxides rather than other copper silicates. Crane et al. [4] postulated a phase stability diagram which showed the phase field of chrysocolla relative to malachite as a function of the partial pressure of carbon dioxide and the concentration of dissolved silica. The formula written above for chrysocolla is the end member formula. The formula may be reduced to CuH₂SiO₄·nH₂O or CuSiO₃·nH₂O [7]. This latter formulation is identical to that of diopside CuSiO₃·H₂O. However diopside is a highly crystalline monocyclosilicate with a ring periodicity of six. The crystal structure of diopside is well established [8-11]. Some thermogravimetric studies of chrysocolla have been undertaken and support the reduced formula above [12].

Chrysocolla is of an uncertain structure but is possibly orthorhombic with a non-determined point group [13, 14]. Chrysocolla has a distinctive X-ray diffraction pattern (ICDD Powder Diffraction file No. 27-188) which differs from that of spertiniite (ICDD Powder Diffraction File No. 35-505), and the unit cell dimensions of each are very different. Van Oosterwyck-Gastuche and Grégoire [15] suggested a chain structure for fibrous microcrystals from 0.5 to 3 microns long and 60–70 nm across, with corresponding idealized formula of Cu₂H₂(Si₂O₅)(OH)₄·nH₂O. This formulation is supported by the work of Chukrov et al. [16] and a number of analyses of chrysocolla containing small amounts of other metals such as Al³⁺ substituting for Cu²⁺, with charge compensation for Al³⁺ being maintained by variation of the number of protons present [17, 18]. Chukrov and Anosov [19] compared the structure of chrysocolla with that of montmorillonite. Chukrov et al. [20] also described chrysocolla as a cupric halloysite. Allophane is often associated with chrysocolla in some of the Arizona Cu-bearing mineral localities, and it is also found with chrysocolla in other worldwide deposits where the two minerals are found together. The allophane from Cu-bearing deposits is often tinted blue-green, which suggests that there is some kind of relationship. Allophane has been found associated with chrysocolla from the Tynagh Mine in Southern Ireland.

Recent studies have brought into question whether chrysocolla is a mineral at all, but rather is a mesoscopic assemblage of dominantly spertiniite Cu(OH)₂, water and amorphous silica
[21, 22]. Farges et al. [23] supported this concept showing that chrysocolla is an assemblage using XAFS and $\mu$-XAFS spectroscopy. The results suggest that the local structure around Cu is similar to that in Cu(OH)$_2$ (spertiniite). The structure of chrysocolla may resemble that of planchéite which consists of brucite-like (CuO$_2$) layers with pyroxene-type (SiO$_3$)$_n$ chains joined to their surfaces. Such structural analyses, however, do not present a vibrational spectroscopic analysis of chrysocolla. Chrysocolla presents no long range structural order, thus vibrational spectroscopy is a suitable tool for the study of the molecular structure.

Raman spectroscopy has proven very useful for the study of minerals. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing copper and silicate groups. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman and infrared spectra of chrysocolla and to relate the spectra to the molecular structure of the mineral. A comparison of the spectra of chrysocolla with spertiniite is made. The main question addressed by this study is whether chrysocolla is (1) a mesoscopic assemblage of spertiniite, Cu(OH)$_2$, silica, and water, (2) represents a colloidal gel or (3) is composed of microcrystals with a distinct structure.

**Experimental**

**Minerals**

The minerals were supplied by the Mineralogical Research Company. Three mineral samples were used in this study: (a) Kaluruluka Mine, Katanga Provence, Democratic Republic of Congo (b) Inspiration Mine, Globe-Miami District, Gila County, Arizona (c) Copper Stope, Majuba Hill, Perishing County, Nevada. The first two chrysocolla samples are identical to that used by Fargas et al. in their research [23]. The spectroscopic analyses of other chrysocolla samples were obtained but are not reported in this work.

**X-ray diffraction**

The synthetic goethite and Al-substituted goethite were prepared as pressed powders and mounted in stainless steel sample holders. The powder X-ray diffraction (XRD) patterns were
recorded on a Philips PANalytical X’Pert PRO diffractometer using Cu Kα radiation operating at 40 kV and 40 mA. XRD diffraction patterns were taken in the range of 10-70° at a scan speed of 2° min⁻¹ with 0.5° divergence slit size. Phase identification was carried out by comparison with XRD patterns included in the Inorganic Crystal Structure Database (ICSD).

Raman spectroscopy

Samples of chrysocolla were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm⁻¹ and a precision of ± 1 cm⁻¹ in the range between 200 and 4000 cm⁻¹. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. Care was taken to use low laser power to prevent damage to the sample. A power density of 0.1 mW at the sample was used. No deterioration of the mineral was observed. It is noted that spectra of chrysocolla are given in the RRUFF data base [http://rruff.info/chrysocolla/display=default/R050053]. However the spectra suffer from a lack of signal to noise.

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 4000–525 cm⁻¹ range were obtained by the co-addition of 128 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package that 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 Lorentzian-Gaussian cross-product
function with the minimum number of component bands used for the fitting process. The
Gaussian-Lorentzian 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**

**X-ray diffraction**

The PXRD results are reported in Figure 1. Only two XRD patterns were obtained as there
was insufficient sample remaining of the third sample to obtain a XRD pattern. It is clear
from the XRD patterns that the chrysocolla mineral samples are non-diffracting and no other
phases are present in the minerals, thus showing the chrysocolla samples are pure. An XRD
pattern is given in the RRUFF data base (see http://rruff.info/chrysocolla/display=default/R050053). No peaks were observed in this XRD pattern.

**Raman spectroscopy**

The Raman spectra of three samples of chrysocolla in the 100 to 4000 cm$^{-1}$ region are
displayed in Figure 2. These spectra show bands around 3400 cm$^{-1}$ and in the 100 to 1100
cm$^{-1}$ region. There are large parts of the spectra where no bands are observed. Similarly, the
infrared spectra of chrysocolla over the 500 to 4000 cm$^{-1}$ range are shown in Figure 3. The
results of the Raman and infrared spectral analysis are given in Table 1. This table gives the
peak positions of the Raman and infrared bands together with their half width.

The Raman spectra show considerable variation in the 800 to 1200 cm$^{-1}$ spectral range. This
variation reflects the composition of the mineral from the different origins and also variations
in the nature of the amorphous colloidal gel. A common peak in the three spectra appears to
be around 1042 cm$^{-1}$. This band is attributed to a SiO$_3$ stretching vibration of silicate. Dowty
[24-26] showed the relationship between crystal structure of silicate minerals and their
vibrational spectra. Importantly, this work showed that from the position of the SiO peaks,
the structure of the silicate mineral could be predicted. Dowty calculated the band positions
for the different ideal silicate units. He showed that the -SiO$_3$ units had a unique band
position of 1025 cm$^{-1}$ [26] (see Figures 2 and 4 of this reference). Crystalline and amorphous

The mineral chrysocolla is said to be orthorhombic (with a query). Two other copper silicate minerals with an orthorhombic crystal system are planchéite and shattuckite. The mineral planchéite is a hydrated copper silicate mineral with formula Cu$_8$Si$_8$O$_{22}$(OH)$_4$·H$_2$O [27]. The two minerals shattuckite Cu$_5$(SiO$_3$)$_4$(OH)$_2$ [28] and planchéite were first thought to be the same mineral [29]. However it was proven that the minerals were different [29, 30]. Shattuckite is closely allied to planchéite Cu$_8$Si$_8$O$_{22}$(OH)$_4$·H$_2$O in structure and appearance [13, 31, 32]. The fact that planchéite follows a pyroxene type structure means that the siloxane units for polymeric chains and thus the degeneracy of the vibrational modes above will be lifted. The result of this, is that the spectra will show much greater complexity. Two types of oxygens may be distinguished, namely terminal and bridging oxygens. Additional bands should be observed related to the Si-O-Si bending vibrations. The Raman spectrum of planchéite displays a very intense band at 1081 cm$^{-1}$ with a shoulder band at 1048 cm$^{-1}$. Dowty’s calculations predicted the band at 1081 cm$^{-1}$ is attributable to a Si$_2$O$_5$ silicate unit. The 1048 cm$^{-1}$ band of planchéite is in a similar position to the 1042 cm$^{-1}$ of chrysocolla.

Shattuckite [33, 34] is a copper silicate hydroxide mineral with formula Cu$_5$(SiO$_3$)$_4$(OH)$_2$ [28]. It crystallizes in the orthorhombic - dipyramidal crystal system and usually occurs as well formed prismatic crystals [27, 31, 35]. According to Evans and Mrose [27] the structure of shattuckite, Cu$_5$(SiO$_3$)$_4$(OH)$_2$, was refined in the orthorhombic space group Pcab. The structure consists of brucite-like (CuO$_2$) layers with pyroxene-type (SiO$_3$)$_n$ chains joined to their surfaces. It is likely that chrysocolla shows a similar type of structure, at least in the short order range. The Raman spectrum of shattuckite shows a complex spectrum with overlapping bands. A prominent Raman band is observed at 1043 cm$^{-1}$ for shattuckite from New Cornelia Mine, Ajo, Pima County, Arizona.

Another common band in the Raman spectra of the three chrysocolla samples is around 931 cm$^{-1}$. This band is also assigned to the SiO$_3$ symmetric stretching vibration of SiO$_3$ silicate units. Amorphous silica does not show Raman bands at these positions. These bands do not correspond to that of amorphous silica which displays Raman bands at 493 and 607 cm$^{-1}$. Variability in the band positions for amorphous silica has been proven [36]. Other bands are observed at around 1303 and 1350 cm$^{-1}$. 
The infrared spectra of all three chrysocolla samples are similar but variation in the peak position is observed between the three spectra. The spectra are dominated by and intense peak at 1016 cm\(^{-1}\) for sample a, with a resolved shoulder at 933 cm\(^{-1}\); 1009 cm\(^{-1}\) for sample b with a resolved shoulder at 942 cm\(^{-1}\); and 1028 cm\(^{-1}\) for sample c with shoulder bands at 1008 and 1087 cm\(^{-1}\). Dowty [26] calculated the position of the infrared bands in the spectra of single type ideal silicate units. Infrared bands at wavenumbers slightly greater than 1000 cm\(^{-1}\) were assigned to \(-\text{SiO}_3\) units. Van Oosterwyck-Gastuche and Grégoire [15] suggested a chain structure for chrysocolla. This proposal fits well with the concept of \(\text{SiO}_3\) units. It is suggested that the bands at 747, 807 cm\(^{-1}\) (a); 750, 776, 799 and 833 cm\(^{-1}\) (b); 699, 733, 784 cm\(^{-1}\) (c) are due to the chain Si-O-Si stretching vibrations. The infrared bands at around 663 cm\(^{-1}\) are the bending vibrations of these units. Dowty calculated the infrared spectra for individual silicate units and showed the intense infrared band was at 400 cm\(^{-1}\).

The infrared spectra of chrysocolla have been published by Chukhrov et al. The infrared spectra of spertiniite have been reported [37]. The infrared spectrum of spertiniite displays bands at 420 (s), 694 (w), 939 (w), 1440 (m), 1556 (m), 3323 (s) and 3572 (s) cm\(^{-1}\). No infrared band for chrysocolla was found at 694 cm\(^{-1}\). There are infrared bands for chrysocolla at 663 cm\(^{-1}\) (a), 672 cm\(^{-1}\) (b) 673 cm\(^{-1}\) (c). These bands do not correspond to the 694 cm\(^{-1}\) band of spertiniite. An intense Raman band at 674 cm\(^{-1}\) with a shoulder at around 651 cm\(^{-1}\) is assigned to the \(-\text{SiO}_3\) \(\nu_4\) bending modes. An intense sharp Raman band is observed at 699 cm\(^{-1}\) for planchète. A very intense sharp Raman band is found for shattuckite at 677 cm\(^{-1}\). Dowty [26] predicted a Raman band for \(-\text{SiO}_3\) units at around 650 cm\(^{-1}\). Dowty calculated the position of this band for not only \(\text{SiO}_3\) units but also for \(\text{Si}_4\text{O}_{11}\) and \(\text{Si}_2\text{O}_5\) units. The band is in the same position for these units. This is explainable when the assignment of this band is to the \(\nu_4\) bending modes.
The series of Raman bands for sample (a) at 388, 409, 433 and 489 cm\(^{-1}\); for sample (b) 406, 431, 486 and 516 cm\(^{-1}\); for sample (c) 401, 427, 481 and 501 cm\(^{-1}\) are assigned to the \(-\text{SiO}_3\,\nu_2\) bending modes. The Raman spectra of planchéite and shattuckite show bands at 403 and 505 cm\(^{-1}\) and at 439 cm\(^{-1}\) respectively. The Raman spectrum of spertiniite displays an intense band at 488 cm\(^{-1}\). A Raman band is found at 489 cm\(^{-1}\) (sample 1), 486 cm\(^{-1}\) (sample b) and 481 cm\(^{-1}\) (sample c) (very weak). These bands do correspond to the Raman band of spertiniite. The intensity of these bands is weak to very weak. If chrysocolla consists of a gel of spertiniite, amorphous silica and water, it would be expected that a very intense band at 488 cm\(^{-1}\) would be observed. Further, the Raman spectrum of spertiniite shows a strong Raman band at 378 cm\(^{-1}\). No band is observed in this position for any of the chrysocolla spectra. Raman bands are observed at 334 cm\(^{-1}\) (a), 338 cm\(^{-1}\) (b) and 336 cm\(^{-1}\) (c). The lack of correspondence between the Raman spectrum of spertiniite and those of chrysocolla mitigates against the proposal that chrysocolla is a colloidal gel based upon spertiniite. The spectral profiles are broad and a number of bands may be curve resolved. The Raman spectrum of spertiniite shows an intense band at 287 cm\(^{-1}\). No band in this position is found in the spectra of chrysocolla. Thus, vibrational spectroscopy suggests that chrysocolla is not a gel of spertiniite and amorphous silica. There is no correspondence in the spectra of spertiniite and chrysocolla.

The Raman spectra in the OH stretching region consist of a sharp band at 3624 cm\(^{-1}\) for sample (a); 3619 cm\(^{-1}\) for sample (b) and 3615 cm\(^{-1}\) for sample (c) with a broad tail which extends out to 2600 cm\(^{-1}\). The sharp band is assigned to the symmetric stretching vibration of the OH units. The OH units are bonded to the Cu and/or Al in the chrysocolla structure. The broad profile between 3000 and 3600 is attributed to water stretching vibrations. Additional bands are observed at 2925 cm\(^{-1}\) for sample (a); 2926 cm\(^{-1}\) for sample (b); 2744 and 2913 cm\(^{-1}\) for sample (c). It is thought that these bands are due to surface organic impurities. The Raman spectrum of spertiniite shows an intense band at 3556 cm\(^{-1}\) and a less intense band at 3307 cm\(^{-1}\). The intense band at around 3620 cm\(^{-1}\) does not correspond to the intense peak of spertiniite at 3556 cm\(^{-1}\). The Raman spectra of chrysocolla do show a resolved shoulder band at 3583 cm\(^{-1}\) (a), 3597 cm\(^{-1}\) (b) and 3568 cm\(^{-1}\) (c). However the intensities of these bands are low. It is concluded that the Raman spectrum of chrysocolla does not correspond to that of spertiniite. However, Raman spectra do show the presence of OH units and thus, confirms the OH units in the formula (Cu, Al)\(_2\)H\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\)·nH\(_2\)O.
Compared with the Raman spectra, the infrared bands which are attributable to water are intense. The band observed in the Raman spectrum at around 3620 cm\(^{-1}\) is barely visible. The Raman band observed at around 2925 cm\(^{-1}\) is not present in the infrared spectra. Perhaps the intense infrared bands of water swamp the other bands. The bands may be under the umbrella of the water bands. Infrared bands are observed at 3591 cm\(^{-1}\) (a); 3583 cm\(^{-1}\) (b); may be due to the OH stretching bands of the OH units bonded to the Cu and/or Al. In the infrared spectrum of spertiniite, two intense bands are observed at 3323 and 3572 cm\(^{-1}\). The first band is broad with a long tail. The latter band is quite sharp and easily distinguished from the 3323 cm\(^{-1}\) band. In the infrared spectrum of chrysocolla, broad bands are resolved at 3840 and 3425 cm\(^{-1}\) (a), 3237 and 3415 cm\(^{-1}\) (b) and 3310 and 3386 cm\(^{-1}\). It is difficult to state that these bands correspond to the infrared band of spertiniite at 3323 cm\(^{-1}\). An infrared band may be resolved at 3591 cm\(^{-1}\) (a), 3583 cm\(^{-1}\) (b) 3588 cm\(^{-1}\) (c). These infrared bands appear to correspond to the infrared band of spertiniite at 3572 cm\(^{-1}\). The spectra in the 1400 to 1800 cm\(^{-1}\) region are of low intensity. This is not unexpected as water is a very poor Raman scatterer. Raman bands are observed at 1593 cm\(^{-1}\) (a), 1601 cm\(^{-1}\) (b), 1602 cm\(^{-1}\) (c) and are assigned to water bending vibrations. The position of the bands provides evidence that water is weakly hydrogen bonded in the chrysocolla structure and gives credence that chrysocolla is a gel-like material. Additional bands are found at 1470 cm\(^{-1}\) (a), 1463 cm\(^{-1}\) (b) and 1472 cm\(^{-1}\) (c) and are attributed to hydroxyl deformation modes. Infrared bands are observed at 1626 and 1646 cm\(^{-1}\) for sample (a), 1626 and 1659 cm\(^{-1}\) for sample (b) and 1632 and 1658 cm\(^{-1}\) for sample (c). These bands are assigned to water bending vibrations. In addition infrared bands are observed at 1412 cm\(^{-1}\) for sample (a), 1403 and 1462 cm\(^{-1}\) for sample (b) and 1376 cm\(^{-1}\) for sample (c). These bands may be attributed to the hydroxyl deformation modes. The variation in band position reflects the variation in gel structure of the chrysocolla gels. The infrared spectrum of spertiniite shows bands of medium strength at 1440 and 1586 cm\(^{-1}\). In the infrared spectrum of chrysocolla, a resolved component band at 1569 cm\(^{-1}\) (a), 1584 cm\(^{-1}\) (b) and 1582 cm\(^{-1}\). These bands seem to correspond to the infrared band of spertiniite at 1586 cm\(^{-1}\). However this band is swamped by the water bending modes in chrysocolla. Infrared bands for chrysocolla are observed at 1414 cm\(^{-1}\) (a), 1462 cm\(^{-1}\) (b) and 1376 cm\(^{-1}\) (c). The position of these bands does not appear to correspond to that of spertiniite.
CONCLUSIONS

The mineral chrysocolla is a hydrated copper hydroxy silicate of formula (Cu,
Al)₂H₂Si₂O₆(OH)₄·nH₂O. The formula may be simplified to CuSiO₃·2H₂O. Some recent
studies have redefined chrysocolla as the mineral spertiniite [21-23]. However, based upon
vibrational spectroscopy, there is no correspondence between the spectrum of spertiniite and
that of chrysocolla. It is concluded that chrysocolla is not based upon spertiniite but is an
amorphous hydrated copper silicate. Infrared spectroscopy supports this conclusion, since
there is no correspondence between the infrared spectrum of chrysocolla and spertiniite.
Based upon the vibrational spectroscopy of the hydroxyl stretching region, water is involved
in hydrogen bonding in chrysocolla. This work shows that water is involved in the structure
of the mineral.

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology,
Chemistry discipline is gratefully acknowledged. The Australian Research Council (ARC) is
thanked for funding the instrumentation.
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Figure 1 XRD of two of chrysocolla minerals

Figure 2 Raman spectra over the 100 to 4000 cm\(^{-1}\) range of chrysocolla from (a) Congo (b) Arizona (c) Nevada.

Figure 3 Infrared spectrum over the 500 to 4000 cm\(^{-1}\) range of chrysocolla from (a) Congo (b) Arizona (c) Nevada.