The interaction of *n*-octanohydroxamate with chrysocolla and oxide copper surfaces

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ABSTRACT

Vibrational spectroscopy and XPS have been used to investigate the interaction of *n*-octanohydroxamate with the surfaces of chrysocolla and other oxide copper minerals, as well as with the native oxide on copper metal. XPS investigations of low collector coverage at pH 9.5 confirmed that copper hydroxamate was formed at the mineral/collector interface. Multilayers were formed at all surfaces investigated, probably with minor (∼15%) co-adsorption of hydroxamic acid. The coverage at conditioned chrysocolla surfaces tended to be less uniform than coverage at the 'well-defined' oxide minerals. There was also some evidence for the formation of an Al hydroxamate species at the chrysocolla surface.

1. Introduction

The oxide copper minerals are an important copper resource. These are found in the weathered regions of most copper sulfide ore bodies. The overlaying oxide ore is usually stockpiled after it is removed from the sulfide lode and left unprocessed as the sulfide ore is simpler to recover by conventional flotation procedures and thus, more attractive to the mine operator. Oxide ore can be concentrated using flotation or, if it has a low acid demand, it may be economic to acid heap leach the stockpile. For ore with high acid requirements, either controlled potential sulfidization (CPS), followed by flotation, or direct flotation using hydroxamate reagents (Lee et al., 2009) are more attractive options.

It is generally recognised that hydroxamates are good collectors for the 'well-defined' oxide copper minerals, such as malachite (Lee et al., 1998). Most well-defined oxide minerals exhibit flotation maxima at pHs within ±0.5 of the pKa of the hydroxamate (Fuerstenau, 2007). We have previously proposed a mechanism for the interaction of *n*-octanohydroxamate collector with the surface of oxide Cu minerals based on photoelectron spectra for hydroxamate adsorbed on the native oxide layer of air-exposed Cu metal and on sulfide minerals (Parker et al., 2012a,b). Both the multilayer and the initially adsorbed hydroxamate were present as an enolate (thus, strictly speaking, making it hydroximate) and, in the absence of multilayer Cu(hydroxamate), the N in each chemisorbed hydroxamate interacts with a Cu in the oxide surface; *i.e.*, initially, the chemisorbed hydroxamate is oriented parallel to the surface rather than 'upright' so that both hydroxamate O atoms can interact with one Cu and the hydroxamate N can interact with another

Cu. For the oxide Cu substrates investigated, the onset of multilayer formation appeared to occur in patches before a uniform chemisorbed monolayer had been completed.

Chrysocolla is a significant oxide copper resource. The chemical composition of chrysocolla is generally accepted as $Cu_{2-x}Al_x(OH)_4$-$H_{2-x}Si_2O_5 \cdot nH_2O$, with $x < 1$. The mineral usually appears amorphous in X-ray diffraction measurements, and this has been attributed to crystallites that are too small to give rise to a diffraction pattern. The description of the mineral structure has varied from a Cu silicate phase dispersed in an amorphous silica hydrogel, to predominantly cupric hydroxide, amorphous silica and water (Farges et al., 2007). The latter description was based mostly on Cu K-edge X-ray absorption fine structure (XAFS) spectra from powdered samples finely ground in water. McKeown (1994) had interpreted his XAFS data to indicate the presence of CuO_4 units, similar to those in tenorite (CuO) or dioptase ($CuSiO_3 \cdot H_2O$), with the likely arrangement of these units in strips. Neither XAFS investigation was consistent with the presence of Cu_2O.

Although chrysocolla is a poorly defined mineral, hydroxamate has been shown to be an effective collector for it, at least at the laboratory scale, with optimum recovery at pH ∼6.5 (Peterson et al., 1965; Danilova et al., 1975; Fuerstenau and Pradip, 1984; Raghavan and Fuerstenau, 1993). Raghavan and Fuerstenau (1997) reported that difficulties associated with the flotation of chrysocolla in practice were due to its microporous structure. Fuerstenau and Pradip (1984) reviewed the literature available on the use of hydroxamates in flotation and put forward a mechanism involving adsorption on oxide surfaces. In their Hallimond tube flotation studies they found maximum flotation occurred at pH ∼6, which they attributed to hydrolysis of lattice cations in the mineral (Fuerstenau and Pradip, 1984). Contact angle studies subsequently undertaken showed maximum contact angle at pH ∼9 (Fuerstenau

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et al., 2000). Herrera-Urbina et al. (2010) investigated chrysocolla flotation and noted that chrysocolla solubility increased sharply below pH 6 but remained relatively constant above this value. They proposed that optimal recovery of chrysocolla by flotation with n-octanohydroxamate required minimising the dissolution of copper, such as through dry grinding of the ore, followed by short conditioning with reagents prior to flotation at pH ~6.5 (Herrera-Urbina et al., 2010). Recovery at pH ~9.5 was almost as high as at pH 6.5, even after longer conditioning times, as loss of Cu from the mineral was not significant (Herrera-Urbina et al., 2010).

In light of those findings, we have compared the collector coverage on chrysocolla with that on some 'well-defined' oxide Cu minerals after conditioning at pH > 9 to identify whether there are significant differences. We also report on whether hydroxamic acid is significantly co-adsorbed at pH ~9.5. An extended characterisation of chrysocolla prior to, as well as following, its conditioning in hydroxamate collector is also included to shed further light on the nature of this poorly-defined mineral.

2. Experimental methods

2.1. Reagents and mineral specimens

Electrolyte and reagent solutions were made with Analytical Reagent (AR)-grade chemicals and doubly de-ionised (DDI) water. Potassium hydrogen n-octanohydroxamate was supplied by Axis House, recrystallised from methanol and dried in air before use. The n-octanohydroxamic acid was precipitated by neutralising a concentrated, alkaline (KOH) solution of potassium hydrogen n-octanohydroxamate with sulfuric acid, filtered, washed with DDI water and dried in air. The sample was then recrystallised from methanol and dried in air before investigation. Copper salts were synthesised as described previously (Hope et al., 2011).

Natural malachite and azurite samples were obtained from mine sites in the Democratic Republic of Congo, Canada and Morocco. Chrysocolla, sourced from Clifton AZ, was purchased as a hand-picked lump from Tucson Mineral and Gem World, Tucson AZ. The pseudomalachite was sourced from the West Bogan Mine, Tottenham, NSW.

2.2. Vibrational spectroscopy

Raman studies were conducted on a Renishaw InVia spectrometer. 632.8 nm excitation from a HeNe laser was used and the scattered light was detected with a Peltier-cooled CCD detector with spectral resolution ~2 cm^{-1}. The laser and scattered light were usually focused through a ×50 Leica N Plan lens (NA = 0.75). Raman spectra were calibrated using the 520 cm^{-1} silicon band. Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed either with the Renishaw WiRE 3.2 software or with GRAMS32AI software (Galactic Industries, Salem, NH, USA). Fourier transform infrared (FT-IR) spectra were collected on a Thermo Nicolet Nexus FT-IR spectrometer equipped with EverGlo IR source optics which provides a stabilised signal and 0.5 cm^{-1} resolution. The spectrometer had a DTGS detector with KBr window and Ge on KBr beamsplitter. Spectra were acquired in the range of 4000–500 cm^{-1}.

2.3. X-ray photoelectron spectroscopy

Most X-ray photoelectron spectra were collected from a surface of single piece specimens of area approximately 5 mm × 5 mm rather than mineral particles of floatable size. Each surface was abraded until relatively smooth to the unaided eye before conditioning in a saturated aqueous KH(n-octanohydroxamate)$_2$ solu-

tion, rinsing with water, and subsequent characterisation by XPS at either ~150 K or ambient temperature. Crushed mineral particles can provide information that is more representative of the bulk, and in the few cases such specimens were characterised, the fine particles were pressed into a freshly exposed surface of indium. Specimens of n-octanohydroxamic acid were prepared in a similar way.

XPS data were obtained on an ESCALAB 250Xi spectrometer using monochromatised Al Kα X-rays focused to a spot size of 0.5 mm and an electron analyser pass energy of 20 eV for narrow range scans. Included in the binding energies employed for calibration, were 83.96 eV for Au $4f_{7/2}$ of metallic gold and 932.6 eV for Cu $2p_{3/2}$ of Cu metal. The pressure in the analysis chamber was better than 5×10^{-9} mbar during spectral acquisition. Apart from low collector coverage on Cu, because of the poor electrical conductivity of the minerals or materials investigated, photoelectron spectra had to be obtained while the specimen was under the influence of a low energy electron beam (4 V, 175 μA) from an in-lens charge-neutralisation flood gun. The observed binding energies, which were lower than the correct values because of over-compensation of charging to achieve minimum linewidth, were referenced to 285.0 eV for the hydrocarbon C 1s photoelectrons. The possibility of beam damage by the low energy electrons was monitored, and in order to minimise any damage, spectra were obtained as quickly as possible at the expense of signal-to-noise. The data were collected and processed under Thermo Scientific $Avantage$ 4.58 and 4.54 software.

3. Results and discussion

Characterisation of hydroxamate interaction with oxide copper surfaces is an important aspect of the study of the flotation of copper oxide ores. Spectroscopic techniques are able to observe the interaction of collectors with a mineral surface, both in situ and ex situ, identifying compound formation, chemisorption, bonding and layering. The sensitivity of the techniques varies from the multilayer compound formation required for normal Raman spectroscopy through to the ability to characterise sub-monolayers using XPS.

3.1. Chrysocolla characterisation

The characterisation of malachite, azurite and pseudomalachite specimens has been reported (Hope et al., 2010; Parker et al., 2012a). We have previously reported XPS data for the interaction of hydroxamate with chrysocolla (Parker et al., 2012a), however, the mineral specimen investigated contained significant concentrations of Ca and Mg, and consequently it was not possible to obtain definitive information on the composition and distribution of the adsorbed multilayer. More recently, an essentially pure sample of chrysocolla from Clifton (Arizona) was obtained, thereby obviating interferences. We report here our characterisation of the Clifton chrysocolla. Chrysocolla specimens have not been extensively characterised by vibrational spectroscopy and XPS. In particular, there has been confusion concerning the structure and properties of chrysocolla. In the RRUFF database (2011), developed by Downs (2006), the two entries for chrysocolla both exhibit silicate vibrations in the region below 700 cm^{-1} and an O—H stretch at 3613 cm^{-1}. The RRUFF samples did not exhibit significant X-ray diffraction peaks, a result consistent with a non-crystalline sample. Raman and FT-IR spectra of the Clifton chrysocolla are presented in Fig. 1.

The Raman spectrum obtained is consistent with those reported in the RRUFF database, with the exception of the absence of the 2850 cm^{-1} hydrocarbon (contamination) bands evident in the