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Thermodynamics of the basic copper sulfates antlerite, posnjakite, and brochantite

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ABSTRACT

Weathering of primary copper sulfides leads to the formation of copper sulfate minerals, among them antlerite, $Cu_3(SO_4)(OH)_4$, brochantite, $Cu_4(SO_4)(OH)_6$, and posnjakite, $Cu_4SO_4(OH)_6{\cdot}H_2O$. In this work, we performed a series of experiments to determine the stability of these phases. First, batches of 0.001 M $CuSO_4$ solution were titrated with 0.1 M NaOH at temperatures between 20 and 85 °C to various end-point pH values. The phases obtained were brochantite, posnjakite, or tenorite (CuO), or mixtures thereof. From these samples, the well-crystallized brochantite and posnjakite samples, plus an antlerite sample synthesized in a separate way, were investigated by calorimetric techniques. The enthalpies of formation determined by acid-solution calorimetry in 5 *N* HCl for antlerite, brochantite, and posnjakite are -1733.6 ± 5.3, -2194.4 ± 7.0, and -2468.2 ± 7.0 kJ mol^{-1}, respectively. The standard entropies retrieved from heat capacity data (measured by relaxation calorimetry) are 274.3 ± 2.7, 343.1 ± 3.4, 390.9 ± 3.9 J mol^{-1} K^{-1}, respectively. The calculated Gibbs free energies of the three phases are -1453.6 ± 5.4, -1824.9 ± 7.1, and -2043.4 ± 7.1 kJ mol^{-1}, respectively. We have reviewed all available thermodynamic data for the three basic copper sulfates, compared them to our results, and found a rough agreement. Of the phases considered here, posnjakite has no stability field but is always moderately metastable with respect to brochantite by +4.7 kJ mol^{-1} (assuming water activity of unity). Brochantite is predicted to precipitate under mildly acidic and oxidizing conditions at low Cu(II) and S(VI) aqueous activities. Antlerite forms if the activity of Cu(II) is higher or if temperature is elevated. Tenorite will crystallize under neutral or basic conditions. Our data can describe the titration experiments and the phase relationships between the copper sulfates well.

1. Introduction

The oxidizing and water-rich environment on the Earth's surface is responsible for the transformation of primary ore minerals to the secondary ones (Reich et al., 2009). A common example is the alteration of the primary Cu–Fe sulfides such as chalcopyrite or bornite. The secondary minerals are usually carbonates or sulfates, less commonly phosphates or arsenates. The secondary copper sulfates include antlerite [$Cu_3SO_4(OH)_4$], brochantite [$Cu_4SO_4(OH)_6$], posnjakite [$Cu_4SO_4(OH)_6{\cdot}H_2O$], langite and its dimorph wroewolfeite [$Cu_4SO_4(OH)_6{\cdot}2H_2O$], redgillite and its dimorph montetrisaite [$Cu_6SO_4(OH)_{10}{\cdot}H_2O$]. These copper sulfate minerals were reported individually or together at many sites where alteration of Cu ores took place (Fatyanov et al., 2000; Bowell and Parshley, 2005; Hammerstrom et al., 2005; Laux et al., 2005; Lattanzi et al., 2008; McDonald and Chao, 2007; Orlandi and Bonaccorsi, 2009; Pluth et al., 2005; Mills et al., 2010). Many copper arsenates, carbonates, and phosphates are also known but will not be treated in detail here because they are not the subject of this paper.

Brochantite and posnjakite are commonly identified as products of corrosion of man-made objects, such as copper metal and copper alloys (Marani et al., 1995). They crystallize during the pitting corrosion of copper tubes (Lytle and Nadagouda, 2010) or as corrosion products of Cu-alloys, so-called patina which occurs as a light-green coating on brass statues, e.g., on the Statue of Liberty (Livingston, 1991). The chemical composition of the copper patina (i.e., the sulfates brochantite, antlerite versus the chloride atacamite [$Cu_2Cl(OH)_3$]) can be correlated to the air quality and air pollution (Nord et al., 2001).

Studies on copper sulfates started with analytical work and synthesis experiments in the early decades of the 20th century (Margulis et al., 1965). The early experimental studies of Young and Stearn (1916) have shown that the titration of sodium hydroxide

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into a copper sulfate solution does not simply result in a precipitation of copper hydroxide but basic copper sulfate hydroxides form instead. Later, Posnjak and Tunell (1929) investigated the system CuO–SO_3–H_2O in a temperature range of 50–200 °C and developed a synthesis protocol for brochantite. Many synthesis procedures were published since then, for example for antlerite (Mrose, 1961; Effenberger, 1985; Pollard et al., 1992; Lin'ko et al., 2001a,b; Vilminot et al., 2002; Yoder et al., 2007; Koga et al., 2008), brochantite (Tanaka and Koga, 1988; Tanaka et al., 1991; Fitzgerald et al., 1998; Vilminot et al., 2002; Yoder et al., 2007), and posnjakite (Tanaka and Koga, 1988; Tanaka et al., 1991; Pollard et al., 1992; Fitzgerald et al., 1998; Yoder et al., 2007). A synthesis method for langite was mentioned in the dissertation of Silman (1958) but the product was later shown to be posnjakite (Marani et al., 1995). A recipe for wroewolfeite synthesis was developed by Dabinett et al. (2008). In contrast to all minerals mentioned previously, there are no procedures for the preparation of langite, redgillite, and montetrisaite.

The variability of the copper minerals in nature and in the laboratory leads to the questions about their stability and precipitation sequences. Apart from observations in nature or syntheses in the laboratory, these questions can be addressed by thermodynamic modeling with codes such as PHREEQCI (Parkhurst, 1995), WATEQA (Allison et al., 1991), or others. These programs calculate chemical speciation in aqueous solutions and evaluate the saturation state of these solutions with respect to selected solids. The limitations of thermodynamic modeling applied in natural waters arise from the completeness and accuracy of the input data (chemical composition of natural waters) as well as from the availability and reliability of the appropriate thermodynamic data for solids and aqueous species (Rabadjieva et al., 2009). There are some estimates of thermodynamic data for the copper sulfate minerals (e.g., Yoder et al., 2010). These estimates, however, may not describe the phase relationships properly and the distinction between valid and flawed approximations is difficult. Some thermodynamic data have been reported, e.g., for antlerite (Yeriomin et al., 2006), brochantite (Barton and Bethke, 1960), posnjakite (Dabinett et al., 2008, Yeriomin et al., 2006), langite (Alwan and Williams, 1979), and wroewolfeite (Dabinett et al., 2008).

The objective of this study was to synthesize antlerite, brochantite, and posnjakite as pure phases in order to measure their thermodynamic properties by a combination of calorimetric techniques. We determined the enthalpy of formation and standard entropy of these phases separately and combined them into Gibbs free energy of formation and solubility products. These measurements were augmented by extensive syntheses from aqueous solutions, where temperature, aqueous ion concentrations, and pH was varied. We review the thorny history behind some of the thermodynamic values reported in the literature and show that a number of them is questionable.

2. Materials and methods

2.1. Titration experiments

For the titration experiments, a 0.001 M copper sulfate solution (Merck, for analysis) was titrated with a drop-wise addition of 0.1 M sodium hydroxide (Merck, 98%) with continuous stirring. Many samples were prepared and the products are discussed in a detail below. The titrations were carried out at temperatures between 20 and 85 °C with end-point pH values between 5 and 11. Throughout the titrations, pH was monitored by a hand-held unit of Mettler/Toledo – SevenGo SG2. Calibration of the pH-meter was done at 25 °C by buffer solutions with pH values of 4.01 and 6.86 (Hanna Instruments).

2.2. Samples for calorimetry

The *posnjakite* and *brochantite* samples for calorimetric experiments were chosen from the suite of samples prepared in the titration experiments. For this purpose, we selected the samples with the highest crystallinity. For brochantite, the end-point pH was 6.23 and the synthesis temperature was 55 °C. After reaching the end-point pH, the solution was held for 20 min under continuous stirring in the glass beaker at 55 °C. During these 20 min, the pH value of the solution decreased to 6.08. Our syntheses showed that the pH value of $\sim$6.2 must not be exceeded when pure brochantite is the desired product. The pale green precipitate was filtered and washed with distilled water and dried overnight. Posnjakite was produced in a similar way as brochantite but the synthesis was carried out at 25 °C. The end-point of the pH-value was same (6.2) as brochantite.

The synthesis procedure of *antlerite* was published by Lin'ko et al. (2001b) and followed here. A 1 M $CuSO_4$ (Merck, for analysis) and 4 M urea (Merck, for synthesis) solution was heated under continuous stirring to 90 °C. After 10 min, the first visible solid appeared and the suspension was held for 1 h at 90 °C, then filtered hot through paper filter. The thick greenish-blue product was allowed to cool for 5 min and was then washed three times with small portions of ethanol.

2.3. Characterization of the samples

X-ray diffraction (XRD) patterns were collected with a Bruker D8 ADVANCE with DAVINCI design, with Cu Kα radiation, Ni filter, and a Lynxeye 1D detector. A step size of 0.02°2Θ and a time per step of 0.25 s were used. The samples were identified by matching the lines of International Center for Diffraction Data (ICDD) PDF-2 Release RDB 2010. The lattice parameters were refined with the program Topas 4.2 (commercial software of Bruker AXS). Microphotographs of the calorimetric samples were acquired with a Carl Zeiss ULTRA plus FEG-SEM with an in-lens secondary electron (SE) detector at an accelerating voltage of 20 kV. The Fourier-transform infrared (FTIR) spectra were recorded in the region of 400–4000 cm^{-1} by a Nicolet Avatar 370 DTGS (ThermoElectron). A small amount of sample (1–2 mg) was mixed with KBr (100 mg), thoroughly mixed, and pressed into pellets for the FTIR measurements.

2.4. Calorimetric techniques

The enthalpies of solution were measured in a commercial IMC-4400 isothermal microcalorimeter (Calorimetry Sciences Corporation). Solvent was 25 g of 5 *N* HCl (standardized solution, Alfa Aesar) and poured in the sample PEEK (polyetheretherketone) cup. The liquid bath of the calorimeter (44 L) maintains the temperature of the cups and the thermopiles of the calorimeter precisely at 298.150 K. Calibration of the calorimeter was performed by dissolving KCl (Merck, suprapur) in deionized water. The measured heat effect was compared to the expected dissolution enthalpy of KCl from Parker (1965). The average mass of the KCl pellets was 16.554 (±0.998) mg. The average masses of samples pellets were for antlerite 19.965 (±0.611) mg, brochantite 18.179 (±0.419) mg, and posnjakite 19.824 (±0.140) mg). The masses of other phases used in the calorimetric experiments were calculated relative to the masses of copper sulfates such that the final molality of all species in the acid was the same in each part of the cycle. The masses for the cycle with antlerite were 8.885 (±0.159) mg of CuO and 14.035 (±0.095) mg of $CuSO_4{\cdot}5H_2O$. The average sample masses of the compounds for the cycle of brochantite and posnjakite were 9.441 (±0.255) mg of CuO and for 10.019 (±0.017) mg of $CuSO_4{\cdot}5H_2O$.