

Thermodynamic properties of antlerite, brochantite, and posnjakite

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Weathering of primary copper minerals (e.g., chalcopyrite, bornite) leads to the formation of secondary copper sulfates, phosphates, and arsenates. In this work, we focused on Cu sulfate-hydroxide minerals antlerite ($\text{Cu}_3\text{SO}_4(\text{OH})_4$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) and posnjakite ($\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$). We synthesized these phases in the laboratory and measured their thermodynamic properties.

The synthesis procedure was a titration of a 0.1 M sodium hydroxide solution into a 0.001 M solution of copper sulfate. The temperature of the CuSO_4 solution ranged from 25 to 80 °C and the end-point pH was set between 6 and 11. By variations of temperature and the end-point pH, the precipitates contained brochantite, posnjakite, and tenorite (CuO). We were able to determine systematic variations of the nature of the precipitated product with temperature and pH. Antlerite was synthesized as described in [1]. All these samples were characterized by X-ray diffraction (XRD). Subsequently, the best samples were analyzed by scanning electron microscopy (SEM) for phase purity and prepared for calorimetric measurements.

The calorimetric measurements were carried out by an acid-solution calorimeter at $T = 298 \text{ K}$ in 5 N HCl as the solvent, using CuO , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and KCl as the reference compounds. For all measurements, appropriate thermochemical cycles were constructed. The formation enthalpies ($\Delta_f H^\circ$) of antlerite, brochantite and posnjakite are $-1734.9 \pm 4.0 \text{ kJ/mol}$, $-2157.8 \pm 7.0 \text{ kJ/mol}$, and $-2457.1 \pm 7.0 \text{ kJ/mol}$, respectively.

The results presented here will be soon augmented by heat capacity measurements and standard entropy calculations. Once the data are complete, we will calculate phase diagrams and compare them to the synthesis results described above. Our ultimate goal is a comprehensive model of Cu- and sulfate-rich fluids present in oxidation zones of ore deposits and tailings of Cu ores.

[1] Lin'ko et al. (2001) *Russ J Inorg Chem* **46**, 298-301.

The initial stage of mica weathering

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19c. Kinetics of interfacial geochemical processes

We investigated the early stage of muscovite alteration combining chemical analysis of the interacting solution with *in situ* Atomic Force Microscopy determinations of the reacting mineral surface. Experiments were carried out using a liquid cell of an Atomic Force Microscopy determining simultaneously the evolution of the reacting fluids and the nanometers size details of the mineral surface. The state of the muscovite monocrystal's pristine (001) surface after cleavage was observed to be perfectly flat, with no apparent evidence of defect points or dislocations. The surface's molecular periodicity resolution showed the hexagonal-like formations typical of the nanoscale occurrence of Si-centered tetrahedral arrangements along muscovite sheets. However, when a solution was introduced in the liquid cell by way of a peristaltic pump, pits appeared rapidly displaying a stair-shape pattern consistent with the mineral structure of a T-O-T periodicity. This early stage evolution is responsible for the stoichiometric Al/Si ratio in solutions. Our nanometer scale determinations allowed us to estimate the anisotropic loss of matter generated by the step movement. We found the directional lateral velocity $\mathbf{V}_{(hk0)}$ to be 3 fold higher than the basal velocity $\mathbf{V}_{(000)}$, demonstrating the higher reactivity of the lateral compared to basal surfaces during the dissolution process. The directional velocity of dissolution at the lateral face decreased by more than one order of magnitude for a 5-fold increase in pH, while velocity at the basal face did not change significantly as a function of pH. We observed also the formation of new phases of nanometer size that coating the dissolving mineral surface inhibits the step movement with consequence loss in congruency. Coatings that initially form at the lateral higher reactive faces control the overall dissolution process. Coat formation and growth depends on both aqueous solution composition and dissolving mineral structure.