Hemimorphite solubility and stability of low-T zinc minerals

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Hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$) is an alteration mineral that can precipitate during the weathering of zinc-bearing mineralisation and formation of non-sulfide zinc ore deposits, e.g., the Skorpion deposit in Namibia. Its stability is unknown, though, limiting our understanding of how hemimorphite affects the mobility of zinc. We have measured the solubility of hemimorphite and hemimorphite + quartz at 50°C and 80°C in either acetate or TRIS pH-buffer solutions (pH ~4.7 to 7.7), where apparent steady-state was reached after approximately 40 days at 50°C and 20 days at 80°C. At 50°C, dissolved Zn decreased from 1.2 x 10^{-2} *m* at pH 4.7 to less than 10^{-5} *m* at pH 7.3 and dissolved Si decreased from 6.4 x 10^{-3} *m* at pH 4.7 to 2 x 10^{-3} *m* at pH > 6. At pH 4.7, the Si concentration was higher than amorphous silica solubility, even in quartz-bearing experiments, whereas at higher pH it was close to quartz solubility. This indicates that hemimorphite dissolved faster than any silica precipitation. At 80°C, Zn decreased from 1.1 x 10^{-1} *m* at pH 4.9 to 9 x 10^{-4} *m* at pH 6.9. Si decreased from 6.6 x 10^{-3} *m* at pH 4.9 to 8.8 x 10^{-4} *m* at pH 6.9. The Si values are all less than amorphous silica solubility and closer to quartz solubility than in the 50°C experiments. Preliminary interpretation of the experimental results give log K for hemimorphite + $8H^+ = 4Zn^{2+} + 2SiO_2(aq) + 6\ H_2O(l)$ as ~22 at 50°C and ~20 at 80°C; this indicates that hemimorphite is stable with respect to willemite, the anhydrous zinc silicate, at this temperature. The gap decreases with increasing temperature and willemite is stable above approximately 90-100°C. Calculated activity-activity diagrams at 25°C, using extrapolated log K values, indicate that hemimorphite is stable at slightly acidic to alkaline pH values at quartz saturation and dissolved zinc concentration of 10^{-5} *m*. Hemimorphite is also predicted to be stable with respect to many other zinc alteration minerals, except under specific conditions. For example, smithsonite (zinc carbonate) is predicted to be unstable until log f $CO_2(g)$ > -2, and the Zn phosphate, hopeite, is predicted to be stable under neutral to acidic conditions at phosphate concentrations greater than 10^{-4} *m* and Zn at 10^{-4} *m*. Sauconite, a zinc smectite (e.g., observed at Skorpion, Namibia), is predicted to be more stable than hemimorphite at alkaline pH, under conditions of kaolinite saturation and dissolved Na concentration of ~ 0.1 *m*. From these experiments and calculations, we can predict the conditions under which hemimorphite and other zinc alteration minerals will occur, and better understand zinc mobility in the regolith.