GEOL 235 Homework 6 – Redox Geochemistry Fall 2011

Iron cycling is a critical redox process in Lake Champlain waters and porewaters, and the first Fe3+ solid to form is the mineral ferrihydrite, sometimes simplified as Fe(OH)3.

1. The following half reaction describes the oxidation of Fe2+ and precipitation of the Fe3+ as Fe(OH)3:

Fe2+ + 3 H2O 🡪 Fe(OH)3(ppd) + e- + 3 H+ log K = -17.9

Determine the pe and Eh for this reaction at pH 7 and an Fe2+ activity of 1 x 10-4.

2. The stability field of Fe(OH)3 is key to understanding the precipitation and dissolution of the mineral in lake sediments and waters. As Eh and pH are relatively easy to monitor, we need to develop expressions for the limits of Fe(OH)3 stability as a function of pH and Eh. For the reaction above in question 1, put the equation into the form of a line (y=mx+b) where Eh is y and pH is x. Do the same for the Reactions between Fe2+ and Fe3+ and Fe3+ and Fe(OH)3:

Fe2+ 🡪 Fe3+ + e- log K = -13.01

Fe(OH)3(ppd) + 3 H+ 🡪Fe3+ + 3 H2O log K = 4.89

These lines define the Eh-pH diagram:

3. Now using the Nernst equation applied to the Fe2+/Fe3+ couple, determine the Eh conditions for a Lake Champlain porewater containing 35 g/l Fe3+ and 100 g/l Fe2+, where E0= +0.77V (where the activity coefficient for Fe3+=0.85 and for Fe2+=0.73). Compare this to the Eh condition if that same amount of Fe2+ is in equilibrium with Fe(OH)3 at pH 6, where E0= -0.975 for the reaction as written in question 1.