Solubility of Sulfate and Chloride Green Rusts during Ageing and Transformation to Magnetite

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Green rusts are metastable, ferrous iron (Fe(II)) bearing phases that commonly form in modern reducing environments. They may also have had a role in the cycling of Fe(II) in ancient oceans (Zegeye et al., 2012). Although estimates for the solubility product (Ksp) values of green rust have been derived from calorimetry, existing estimates are not in good agreement. Furthermore, green rusts have been shown to rapidly transform into magnetite (Li et al., 2017), but the impact of this ageing on mineral solubility remains to be constrained. Here, we use batch solubility experiments to provide new constraints on the Ksp of the sulfate and chloride varieties of green rust, using mineral phases synthesized in both freshwater and simulated seawater conditions. Experiments were conducted across multiple time intervals to measure how Ksp values vary as a function of the degree of green rust ageing. Additional experiments examined the control that temperature exerts on the transformation of green rusts into magnetite and more crystalline phases. Green rust samples collected from batch solubility experiments over time were characterized using drop calorimetry and cryocalorimetry to thermodynamically determine the Ksp values and allow for a direct comparison with those determined from our solubility experiments. Mössbauer spectroscopy, X-ray diffraction, and electron microscopy provided additional insights into the mechanisms and extent of the transformation of green rust phases to magnetite. The findings presented here reveal how green rust reactivity changes in modern environments where it is actively forming. This is important for both predicting the fate of contaminants in naturally reducing and biostimulated aquifers and sediments that contain Fe(II), as well as understanding how Fe may have been cycled in Earth's ancient oceans.