

## Dissimilatory iron reduction and the redox cycling of green rust

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### Introduction

Green rusts (mixed Fe<sup>II</sup>/Fe<sup>III</sup> layered double hydroxides) have been identified in Fe<sup>III</sup>/Fe<sup>II</sup> transition zones in a variety of natural and engineered subsurface environments including groundwater, soils, and sediments, and among corrosion products in zero valent iron permeable reactive barriers. Many of these environments are characterized by periodic or seasonal cycling of redox conditions (e.g., redoximorphic soils in areas with seasonal flooding) that create the opportunity for cycling of Fe between oxidized and reduced forms. In recent years evidence has been building that suggests that the green rust mineral fougurite plays a central role in Fe redox cycling in these environments.

### Experimental Methodology

Carbonate green rust was produced in anoxic defined mineral medium containing 75 mM formate and 80 mM Fe<sup>III</sup>, in the form of phosphate doped (0.7 mass % P) lepidocrocite, inoculated with *Shewanella putrefaciens* CN32. The green rust was then oxidized by introducing sterile air into the headspace. After 24 h the suspensions were sparged with sterile Ar and re-inoculated with *S. putrefaciens* CN32. Samples were collected for measurement of Fe<sup>II</sup> and characterization of the secondary mineralization products by powder X-ray diffraction, scanning electron microscopy, and <sup>57</sup>Fe Mössbauer spectroscopy.

### Discussion of Results

Results of the analysis of the product of green rust oxidation were consistent with ferric green rust. In our experiment, the oxidation of green rust by O<sub>2</sub> to ferric green rust occurred over a period of 24 h without the formation of other Fe<sup>III</sup> oxide phases. However, the initial green rust was formed in the presence of phosphate and sorption of phosphate or silicate by green rust has been shown to promote oxidation of green rust to ferric green rust by suppressing the dissolution of green rust, a prerequisite for the formation of other ferric phases such as lepidocrocite or goethite. After re-inoculation, total Fe<sup>II</sup> concentrations rebounded to pre-oxidation concentrations and green rust was observed as the dominant secondary mineralization product. Since phosphate and silicate are typically available in soils and sediments, similar conditions may be encountered in-situ. Thus, our results indicate the potential for cycling of green rust between reduced and oxidized forms under redox dynamics similar to those encountered in environments that alternate between iron-reducing and oxic conditions and are consistent with the identification of green rust in soils/sediments with seasonal redox cycling.

## Using laboratory-derived mineral dissolution rates to test biogeochemical weathering in the field

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Chemical weathering controls the long-term carbon cycle over million year timescales. Accurate modeling of atmospheric CO<sub>2</sub> requires an understanding of the feedbacks between weathering and CO<sub>2</sub> in natural waters and the atmosphere. However, field-based chemical weathering rates are notoriously hard to measure. Conversely, laboratory-derived mineral dissolution rates are generally two to five orders of magnitude faster than those measured in the field (see [1] and cited references). Additionally, biology plays a critical role in weathering that is very difficult to simulate in the lab or measure in natural environments.

We measured serpentinite dissolution in both laboratory dissolution experiments and in field weathering experiments and modeled our results using the reactive transport code CrunchFlow to try to quantitatively interpret field weathering of serpentinite at two recently glaciated sites in Maine and California. Serpentinites exert a strong control on the ecosystems that form on them due to the bulk chemistry of serpentinite rocks, high in Mg and trace elements, and low in nutrients such as Ca, K, P, and N, which causes an extreme and stressful environment for biota. Laboratory dissolution studies showed that lizardite dissolves six times faster in the presence of oxalate, a biological exudate, than in inorganic acids at pH 5. Field samples of a deep profile of the Pine Hill Serpentinite on Little Deer Isle, Maine, show that Ca and other major elements are depleted from the bedrock at depths of up to 1 m, most likely due to the weathering of Ca-rich pyroxenes. Conversely, some trace metals including Cu and Zn show enrichment in the upper meter of the profile. Ongoing reactive transport modeling will allow us to quantitatively interpret the processes contributing to these observed profiles.

[1] Maher et al. (2006) *Geochimica et Cosmochimica Acta* 70, 337-363.