The role of green rust in the genesis of iron formations and implications for trace metal and nutrient cycles

I. HALEVY1, M. ALESKER1, E. SCHUSTER1, R. POPOVITZ-BIRO2, Y. FELDMAN2

1Dept. of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel (itay.halevy@weizmann.ac.il)
2Dept. of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel

Iron formations provide strong evidence for the mobility of iron in Earth’s oceans prior to ~2.3 billion years ago (Ga), which in turn implies that both dissolved oxygen and marine sulfide levels were low. However, despite decades of research, driven by economic interest and the potential of iron formations to constrain marine paleoenvironments, several aspects of their genesis remain incompletely understood. Notably, though recent hypotheses focus on amorphous Fe(III) hydroxides, the precursor to the observed mineral assemblages in iron formations has not been conclusively identified. One heretofore neglected precursor is the Fe(II)-Fe(III) hydroxy-salt green rust (GR). Combining thermodynamic calculations, laboratory experiments and dynamic models of the early Fe cycle, we find that GR likely had a quantitatively important role in iron formation genesis.

In laboratory experiments, carbonate GR readily precipitates from Precambrian-analog seawater solutions of variable composition and transforms upon aging into mineral assemblages observed in iron formations. These assemblages include predominantly Fe(II) or mixed-valence minerals, which form in the absence of organic matter, and may explain the existence of such minerals in some very organic-poor iron formations. Incorporating these experimental insights into a model of the early Fe cycle, we expect that GR was a quantitatively important shuttle of Fe from the photic zone to the sediments through much of the Precambrian. Spatio-temporal heterogeneity in aqueous silica, inorganic carbon and oxidant concentrations, and in light-driven rates of Fe(II) oxidation would result in heterogeneity in the proportion of GR in the flux of Fe to the sediments.

Well known from environmental remediation studies, GR is highly reactive towards various metals (e.g., U, Cr, Zn, Ni, As), silica and phosphate. Therefore, a Precambrian GR Fe shuttle would affect the cycles of these metals and nutrients, with implications for the construction of proxy records of Earth’s surface oxidation state and for early primary production. Thus, our findings require a revision of the current understanding of the Precambrian Fe cycle, and of interpretations of the Fe isotope and trace element records.