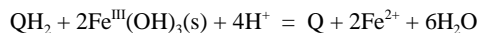


## Movements and redox status of iron: Influence of naturally-occurring organic compounds

M. UCHIMIYA AND A. T. STONE

Department of Geography and Environmental Engineering,  
Johns Hopkins University, Baltimore, Maryland, USA  
(uchimiya@jhu.edu)

It has long been recognized that weathering of Fe<sup>III</sup> (hydr)oxides by organic compounds influences the movement, redox status, and bioavailability of iron within hydrosphere. Redox interactions between quinones and iron are of biogeochemical significance, due to the abundance of quinones in aqueous environments and their reversible and facile redox chemistry. For example, the role of quinones as redox catalysts in microbial iron respiration has received considerable interest in past years [1]. Quinones may be encountered in aqueous environments as allelochemicals, siderophores, and other plants/microorganisms exudates, synthetic organic chemicals, and as constituents of natural organic matter. As shown in the following reaction, hydroquinones and catechols (QH<sub>2</sub>) can reduce Fe<sup>III</sup>, while corresponding quinones (Q) can oxidize Fe<sup>II</sup>. ΔG for the reaction determines whether the forward or reverse direction is thermodynamically favorable.



For a quinone to catalyze microbial iron respiration, the forward reaction must proceed at an appreciable rate. Quinone structure, iron speciation, and pH are the primary factors that determine the reaction direction under a given environmental setting. For a thorough understanding of the role played by iron-quinone interactions in biogeochemical phenomena, reaction rates and pathways must be understood in both forward and reverse directions. We have investigated the reduction of a series of quinone structures by Fe<sup>II</sup> under anoxic conditions. Reduction of 50 μM of p-naphthoquinone and a series of substituted p-benzoquinone by 250 μM Fe<sup>II</sup> completed within five hours. Reaction rates increased as a function of pH and reactions became negligibly slow below pH 5. In the presence of 250 mM of naturally-occurring iron-coordinating ligand malonate, reduction of 100 μM quinones by 500 μM Fe<sup>II</sup> completed within an hour and reaction rates increased as a function of pH. These findings suggest that the reduction of single- and double-ring quinone structures by Fe<sup>II</sup> predominates at neutral and alkaline pH ranges, especially when iron-coordination ligands are present. Such conditions may favor some ecological niches that utilize quinone-facilitated Fe<sup>II</sup> oxidation.

### Reference

- [1] Lovley, D. R., Coates, J. D., Blunt-Harris, E. L., Phillips, E. J. P., and Woodward, J. C., (1996), *Nature* **382**, 445-448.

## Litho- and chemostratigraphy of the Vendo-Cambrian mid-oceanic paleo-atoll carbonates in the Gorny Altai mountains, Siberia

Y. UCHIO<sup>1</sup>, Y. ISOZAKI<sup>2</sup>, H. KAWAHATA<sup>3</sup> AND  
S. MARUYAMA<sup>4</sup>

<sup>1</sup> Dept. Earth & Planet. Sci., Tokyo Inst. Tech. Japan  
(yuchio@geo.titech.ac.jp)

<sup>2</sup> Dept. Earth Sci. & Astron., Graduate School of Arts and Sci.  
Univ. of Tokyo. Japan (isozaki@chianti.c.u-tokyo.ac.jp)

<sup>3</sup> Geological Survey of Japan, AIST, Japan  
(h.kawahata@aist.go.jp)

<sup>4</sup> Dept. Earth & Planet. Sci., Tokyo Inst. Tech. Japan  
(smaruyam@geo.titech.ac.jp)

Across the Vendian-Cambrian boundary (VCB ca. 543 Ma), a major global environment change associated with the biological reorganization occurred. Previous studies on the VCB revealed remarkable shifts δ<sup>13</sup>C, <sup>87</sup>Sr/<sup>86</sup>Sr and δ<sup>34</sup>S. In this study, we analyzed the Vendian-Cambrian limestone in the Cambrian accretionary complex in the Gorny Altai mountains, southern Siberia.

The limestone conformably overlies pillowed basaltic greenstones with geochemistry similar to that of modern oceanic plateau basalt. This suggests that the limestone was primarily deposited on the seamount / plateau. Absence in coarse-grained terrigenous clastics and occurrence of stromatolites plus ooids suggest that the limestone formed in a shallow-marine environment. Datable fossils are scarce but the bulk Pb-Pb age, 625 Ma, was measured from a part of this limestone (Nohda et al., 2003).

We report the secular changes in δ<sup>13</sup>C and in <sup>87</sup>Sr/<sup>86</sup>Sr of the limestone, and discuss their geologic implications to the environmental change across the VCB in a mid-oceanic domain.

### Reference

- Nohda et al. (2003). the Joint Meeting of Earth and Planetary Sci. Japan. 2003 Abstract, J058-006.