

Effect of organic C on stable Fe isotopic fractionation between aqueous Fe(II) and ferrihydrite

CHANDA P.^{1*}, ZHOU Z.², LATTA D. E.², SCHERER M. M.²,
BEARD B. L.¹, JOHNSON C. M.¹

¹University of Wisconsin-Madison, WI 53706, USA;

*correspondence: pchanda2@wisc.edu,

beardb@geology.wisc.edu, clarkj@geology.wisc.edu

²University of Iowa, IA 52242, USA; zhe-zhou@uiowa.edu,

drew-latta@uiowa.edu, schererm@engineering.uiowa.edu

Ferrihydrite is ubiquitous in nature although it is easily transformed to more stable iron oxides upon interaction with aqueous Fe(II) (Fe(II)_{aq}) at circumneutral pH. Mineralogical transformation makes it challenging to directly measure the equilibrium Fe isotope fractionation between ferrihydrite and Fe(II)_{aq}. Recent studies have found that a coprecipitate of organic C with ferrihydrite at C:Fe molar ratios ≥ 1.0 can stabilize ferrihydrite in the presence of Fe(II)_{aq} [1]. This observation provides a method to investigate the equilibrium Fe(II)_{aq}-ferrihydrite Fe isotope fractionation in depositional environments with abundant organic matter and Fe(II)_{aq}.

Experiments were performed using Suwannee river natural organic matter (SRNOM) coprecipitated with ferrihydrite (C:Fe =1.2) to determine the equilibrium Fe(II)_{aq}-ferrihydrite fractionation factor via the three-isotope method. A solution (pH ~7) with 2 mM ⁵⁷Fe-enriched dissolved Fe(II) was reacted with SRNOM-Ferrihydrite (C:Fe =1.2) over 28 days at 25°C. There was significant Fe isotope exchange between Fe(II)_{aq} and SRNOM-Ferrihydrite during the experiment with the aqueous and solid phase having ⁵⁷Fe/⁵⁶Fe ratios that approached (~87%) the system mass balance. No secondary iron hydroxides were detected by XRD and Mössbauer spectroscopy. The ⁵⁶Fe/⁵⁴Fe fractionation factor is estimated to be $-2.37 \pm 0.07\text{‰}$ between Fe(II)_{aq} and SRNOM-Ferrihydrite. This fractionation factor differs from the equilibrium fractionation factor between Fe(II)_{aq} and pure ferrihydrite (-3.20‰) predicted by [2], but is similar to the measured Fe(II)_{aq}-Si-ferrihydrite (Fe:Si =1.0) fractionation factor of $-2.58 \pm 0.14\text{‰}$ [2]. The presence of organic C in ferrihydrite distorts the Fe octahedral structure [1, 3] and may cause the difference in fractionation factors between Fe(II)_{aq} and ferrihydrite precipitated with and without organic C. As ferrihydrite often occurs with organic matter in soils and sediments these results are important in the interpretation of Fe isotope fractionation during mineral-fluid interactions.

[1] Chen et al. (2015) *ES&T* **49**, 10927–10936. [2] Wu et al. (2011) *ES&T* **45**, 1847–1852. [3] Eusterhues et al. (2008) *ES&T* **42**, 7891–7897.