

Tetrahedral Fe promotes atom exchange between aqueous Fe(II) and structural Fe(III) in clay

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Clay minerals are a significant player in the redox cycling of iron (Fe) in near-surface environments. Isotope fractionation between aqueous Fe(II) and structural (mainly octahedral) Fe(III) of clay occurs via coupled electron transfer and atom exchange (ETAE) involving edge-bound Fe atoms [1]. However, the role of tetrahedral Fe during structural Fe(III) reduction is still uncertain. To probe this role, we mixed dissolved Fe(II) with two clay minerals under fully anoxic conditions: 1) N Au-2, which contains ~7% tetrahedral Fe(III), and 2) S Yn-1, which contains no Fe. In addition, Fe(III) in N Au-2 was reduced by *Shewanella oneidensis* MR-1 with excess lactate as the electron donor. The results show that Fe(II) predominantly adsorbed onto the basal planes of the clay particles. The kinetic effect of adsorption on Fe isotope fractionation was negligible: throughout the 7-day experiment basal-sorbed Fe(II) on S Yn-1 differed <0.1‰ from the initial aqueous Fe(II). However, basal-sorbed Fe(II) on N Au-2 was 0.84 ‰ isotopically lighter than the initial Fe(II), and 7.2% of structural Fe(III) was reduced to Fe(II), indicating direct electron transfer (ET) from basal-sorbed Fe(II) to structural Fe(III). During microbial reduction of N Au-2 atom exchange (AE) occurred between basal-sorbed Fe(II) and structural Fe(III): even as AE between edge-bound Fe(II) and structural Fe(III) ceased, isotope fractionation between basal sorbed Fe(II) and structural Fe increased from -2.09‰ to -3.66‰. We therefore conclude that (1) tetrahedral Fe promotes ETAE between basal-sorbed Fe(II) and structural Fe(III) of N Au-2, and (2) reactive Fe in clay minerals is not limited to edge-bound Fe. Thus, in acidic environments, for instance hydrothermal vents or acid mine drainage, clay minerals containing tetrahedral Fe could readily react with aqueous Fe(II), resulting in relatively large Fe isotope fractionations.

[1] Shi *et al.* (2016) *Environ. Sci. Technol.* **50**, 8661-8669.