

Fe²⁺ catalyzed iron atom exchange and re-crystallization in soils from the Luquillo Critical Zone Observatory

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Aqueous ferrous iron (Fe²⁺) is known to transfer electrons and exchange structural positions with solid-phase ferric (Fe^{III}) atoms in many Fe minerals. However, this process has not been demonstrated in soils or sediments. In a 28-day sterile experiment, we reacted ⁵⁷Fe-enriched aqueous Fe²⁺ (^{57/54}Fe=5.884±0.003) with a tropical soil (natural abundance ^{57/54}Fe=0.363±0.004) under anoxic conditions and tracked ^{57/54}Fe in the aqueous phase and in sequential 0.5 M and 7 M HCl extractions targeting surface-adsorbed and bulk-soil Fe, respectively. In 28 days, the aqueous and bulk pools both moved ~7% toward the isotopic equilibrium (^{57/54}Fe=1.33). The aqueous and surface Fe initially exchanged atoms fast (~100 mmol kg⁻¹ d⁻¹) decreasing to a near constant rate of 1 mmol kg⁻¹ d⁻¹ that was close to the 0.74 mmol kg⁻¹ d⁻¹ exchange-rate between the surface and bulk pools. Removing the effect of initial Fe²⁺(aq) adsorption using a process-based numerical model, we calculate final sorption-corrected ^{57/54}Fe ratios of 5.56±0.05 and 0.43±0.03 in the aqueous and bulk pools, respectively. Based on Mössbauer spectroscopy, we show that the ⁵⁷Fe label re-crystallizes as short-range-ordered Fe^{III}-oxyhydroxides. Our work suggests Fe atom exchange occurs in natural environments at rates fast enough to impact ecological processes, but slow enough that changes in redox conditions will likely occur before complete Fe mineral turnover.