Stable iron isotope fractionation between aquoeus Fe(II) and smectite

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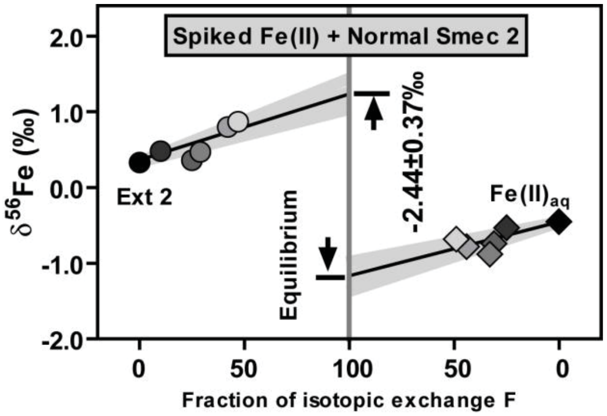
Redox transformations of Fe-bearing phyllosilicate minerals play an important role in Fe cycle in the subsurface environments. This experimental study determined the stable Fe isotopic exchange and fractionation factor between a ^{57}Fe-enriched aqueous Fe(II) and an isotopically “normal” smectite SWa-1 (iron oxide impurities stripped off by purification) using a three-isotope method. Leaching of solid with 0.5 M HCl for 0.5 hr, following separation with aqueous Fe(II) at different time points, yielded mostly Fe(II) in extract 1 and subsequent leaching with 0.5 M HCl for 24 hrs yielded mostly Fe(III) in extract 2.

Isotopic exchange between different components was monitored by changes in their $\delta^{57/56}$Fe values. Isotopic exchange was limited between aqueous Fe(II) and bulk smectite. When excluding bulk smectite from the system, however, about 90% of exchange was achieved between aqueous Fe(II) and extract 1 (a weakly sorbed component) in the beginning of the experiments and leveled off with time, suggesting a steady-state condition was reached early on in the experiments between aqueous Fe and extract 1. Fraction of isotopic exchange (F) reached ~50% between aqueous Fe(II) and extract 2. The equilibrium fractionation factor betweem aquoues Fe(II) and extract 2 has been determined to be ~ –2.4‰ (below figure represents one of the duplicate experiments). Extract 2 could be an iron oxide phase as observed during eletron transfer between aqueous Fe(II) and smectite [1] and the mineralogy nature of extract 2 will be further identified using Mössbauer spectra. Nevertheless, the equilibrium Fe isotope fractionation between aqueous Fe(II) and smectite, driven by redox changes, has important implications for understanding redox processes in subsurface environments that is enriched in ferrous iron and clay minerals.



[1] Schaefer et al. (2011) *Environ. Sci. Technol*. **45**, 540-545

Multiple sulfur isotopic composition of carbonate associated sulfate in Carboniferous brachiopods: oceanic sulfur cycling and its implications

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We present multiple sulfur isotopic records of carbonate associated sulfate from Carboniferous rocks in the Ukraine, Belgium and Moscow Basin [1, 2]. The most significant feature of this data is that the values of δ^{34}S change from higher values (18.4±3.5‰) in the early Carboniferous to lower values (12.6±1.8‰) in the late Carboniferous. In contrast, Δ^{33}S remains similar throughout the early and late Carboniferous (-0.003±0.028‰ and -0.006±0.027‰, respectively). These sulfur isotope records also show evidence for shorter timescale variations that are superimposed on the first order observations in δ^{34}S and Δ^{33}S.

The decline in δ^{34}S is concurrent with a 3‰ increase in δ^{13}C observed in Carboniferous brachiopod shells of the Russian platform [3]. This negative correlation between δ^{34}S and δ^{13}C is similar to the long term linkage between the carbon and sulfur cycles throughout the Phanerozoic. The favored interpretation of carbonate δ^{13}C is that higher δ^{13}C reflects an increasing fraction of organic matter burial. In line with this, we hypothesize that the perturbation of the terrestrial organic carbon cycle plays a more prominent role in the global carbon cycle, based on the observation of significant coal deposits in the late Carboniferous. In this context, the shift in δ^{34}S may reflect the decreasing burial of marine organic matter and reduced burial of pyrite and/or a change in the quality of organic matter that can be used for sulfate reduction because of an increasing fraction of terrestrial organic carbon in the marine sediments, and/or enhanced delivery of sulfate with low δ^{34}S to the late Carboniferous oceans coupled to increasing sulfate levels.

The relatively constant Δ^{33}S record, in conjunction with falling δ^{34}S, may be attributed to a decrease in the sulfur isotope fractionation between sulfate and pyrite with a constant fraction of pyrite burial, and no change in the parameter λ that relates $^{34}S/^{32}S$ to $^{33}S/^{32}S$. Alternatively, it could implicate a change in λ but with constant $^{34}S/^{32}S$ fractionation associated with pyrite burial to compensate for an increasing influx of sulfur to oceans. The changes in λ would imply that sulfide re-oxidation played a smaller role in the sulfur cycle. Ongoing work will further explore the implications of the high-order variation in these sulfur isotopic records.

[1] Kampschulte et al., (2001) *Chem Geol* **175**, 145-173.
[2] Kampschulte and Strauss, (2004) *Chem Geol* **204**, 255-286.
[3] Mii et al., (2001) *Chem Geol* **175**, 133-147.