Interfacial Fe(II)-Fe(III) electron transfer and atom exchange in smectites: effect of smectite properties

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Heterogeneous reactions between aqueous Fe(II) and Fe(III) oxides have extensively been studied, leading to a new conceptual framework which includes electron transfer between aqueous Fe(II) and structural Fe(III), bulk electron conduction, and Fe(II)-Fe(III) atom exchange [1]. A recent study showed that interfacial electron transfer between aqueous Fe(II) and structural Fe(III) also occurred in one clay mineral [2]. Whether this observation can be generalized for all clay minerals and whether similar processes as observed for the heterogeneous redox reaction in Fe(III) oxides are also crucial for clay mineral redox reactions is unclear.

Studies on chemical reduction of structural Fe in smectites showed that the type of reductant as well as smectite structural properties determined the extent of Fe reduction and the resulting structural Fe(II) entities. Thus, we investigated well-characterized smectites differing in structural Fe content, location of structural Fe (octahedral vs. tetrahedral), and location of excess charge (octahedral vs. tetrahedral) for their reaction with aqueous Fe(II), a reductant abundant in natural anaerobic environments.

Stable isotope specific Mössbauer spectroscopy was used to determine the extent of reduction of structural Fe in smectites after exposure to aqueous ^{56}Fe(II), which is invisible in Mössbauer spectra. Experiments with aqueous Fe(II) enriched in ^{57}Fe were carried out to determine the exchange of stable Fe isotopes between aqueous Fe(II) and structural Fe(III) in smectites. Different pools of Fe(II) and Fe(III) were investigated by sequential extraction procedures and solid reaction products were characterized with X-ray diffraction and electron-based microscopic methods.

[1] Gorski & Scherer (2011) *Aquatic Redox Chemistry*, **1071**, 315-343, [2] Schaefer, Gorski & Scherer (2011) *Environ. Sci. Technol.* **45**, 540-545.

Paired ^{87}Sr/^{86}Sr - $\delta^{88/86}$Sr values in Paleozoic conodonts

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The isotopic composition of Sr (^{87}Sr/^{86}Sr) is widely used as a tracer in paleooceanographic, paleoclimatologic, paleotectonic, and stratigraphic investigations. Until recently, the stable Sr-isotopic ratio (^{88}Sr/^{86}Sr) was assumed to be constant and was used for internal normalization to correct for instrumental mass fractionation, thus masking any natural mass-dependent Sr-isotopic fractionation. Newly developed MC-ICPMS and Double Spike (DS) TIMS methods, however, document measurable Sr isotope fractionation in natural systems.

We present the first DS TIMS $\delta^{88/86}$Sr (‰) data ($\delta^{88/86}$Sr = (^{88}Sr/^{86}Sr$_{sample}$/^{88}Sr/^{86}Sr$_{NBS\text{-}987}$-1)×1000) for fossil biogenic marine phosphates (conodonts). The ^{84}Sr-^{87}Sr DS preparation and data reduction followed recommendations in [1]. Our DS was calibrated against NIST SRM-987 assuming ^{88}Sr/^{86}Sr = 8.375209 to give $\delta^{88/86}$Sr = 0.002 ± 0.024 ‰ (2SD). External reproducibility was evaluated using USGS Sr isotope standard EN-1 (a carbonate shell of a giant clam Tridacna collected live from the floor of the Enewetak lagoon, Marshall Islands), which yielded $\delta^{88/86}$Sr = +0.262 ± 0.032 ‰ (2SD) and NRC Canada sea-water trace element reference material NASS-6, which yielded $\delta^{88/86}$Sr = +0.371 ± 0.026 ‰ (2SD).

Paired ^{87}Sr/^{86}Sr - $\delta^{88/86}$Sr values were measured in 30 Paleozoic conodont samples from different stratigraphic horizons (Middle Ordovician to Middle Mississippian). The samples were screened for diagenetic alteration so that only conodonts with Color Alteration Index CAI$\leq$ 3.0 were analyzed. The $\delta^{88/86}$Sr values in these samples vary from slightly positive to significantly negative (up to –1.05 ‰). This range is significantly broader than the variability observed in Paleozoic marine brachiopods [2] but is similar to the range in human tooth enamel and bone [3]. The reasons for this variability in conodonts are not well understood, but likely reflect changes in seawater composition and/or biogenic fractionation of Sr isotopes. The range in $\delta^{88/86}$Sr also causes ^{87}Sr/^{86}Sr values based on DS measurements to deviate appreciably from ^{87}Sr/^{86}Sr values determined using conventional mass-fractionation corrections.

Our results indicate that the study of conodont $\delta^{88/86}$Sr values has the potential for better constraining the marine Sr cycle and its relation to secular changes in marine chemical and biologic systems.

[1] Rudge et al. (2009) *Chemical Geology* **265**, 420-431.
[2] Vollstaedt et al. (2011) *Geophysical Research Abstracts* **13**, EGU2011-7257
[3] Knudson et al. (2010) *J. Archaeol. Sci.* **9**, 2352-2364.