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Experimental determination of Fe isotope fractionations in the iron-sulfide system at low temperature

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Initial published work suggested that Fe isotope fractionations recorded in sediments were a product of biological activity [1]. Experiments and measurements of natural samples now indicate that Fe isotope fractionation can be the product of both biological and inorganic processes [2]. Sedimentary iron sulfides provide unique information about the evolution of Early Life which developed under anoxic conditions. It is in these sedimentary Fe-S species and, in particular, Precambrian pyrites, that the highest Fe isotope fractionations (up to a range of $\sim$5‰ for $\delta^{56/54}$Fe) [3] have been measured. We examined experimentally where Fe isotope fractionations occur during the formation of iron sulfides in order to explain the measured ratios and assess whether large natural variations can be achieved abiotically.

The Fe-S system constitutes a diverse group of stable and metastable phases, the ultimate Fe sequestrating phase being pyrite. The first experimental investigations focussed on the formation of mackinawite, a metastable FeS phase that is involved in pyrite formation. Studies showed that the fast precipitation of mackinawite from a Fe(II) solution involves a kinetic fractionation of 0.85 ± 0.30 %¸) [4].

In this contribution, we investigate the influence of temperature on the kinetics of the isotopic exchange, and on the equilibrium fractionation factor. $^{56/54}$Fe and $^{57/54}$Fe ratios were measured on an IsoProbe Micromass MC-ICP-MS, and all experiments were performed under N_2 atmosphere. We show that the kinetics of isotopic exchange between FeS and aqueous Fe(II) are temperature dependent (experiments were carried out at 25˚C and 2˚C). At these temperatures, the equilibrium fractionation factor can be experimentally extrapolated. Isotopic equilibrium between FeS and Fe(II) was not reached after four months. During this period, the percentage of isotopic exchange increases to a maximum of 70% at which it remains constant. The rate of isotopic exchange slows down with time asymptotically to zero. We interpret the decrease of the rate of isotopic exchange by Ostwald-ripening crystal growth. As mackinawite dissolves to form pyrite, the results we present on Fe isotopic fractionations associated with mackinawite have thus direct implications on the final Fe isotopic signature of pyrite. Where Fe is initially sequestrated in mackinawite, the subsequent Fe isotopic signature of pyrite will be a trade off between the kinetic fractionation, the equilibrium distribution, pyrite formation rate and the extent of reactive Fe utilisation.

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