

The Fe isotopic composition of biogenic pyrite formed in euxinic settings

M. MANSOR^{1*}, J. MACALADY¹ AND M. S. FANTLE¹

¹Geosciences Dept., Penn State Univ., University Park, PA 16802, USA (*correspondence: muammar10@gmail.com)

Fe isotopic compositions of sedimentary sulfide minerals may yield valuable insights into redox states on the early Earth. Pyrite deposited during the late Archaean have Fe isotopic compositions ($\delta^{56}\text{Fe}$) as low as -3.5‰ (relative to IRMM-14) [1]. The reason for such low values is unclear, though it has been speculated to be the result of a benthic iron shuttle [2], the formation of isotopically-heavy banded iron formations [1], or a kinetic isotope effect associated with precipitation during pyrite formation [3].

This study investigates the mineralogy, chemistry, and Fe isotopic compositions of sediments and biofilms from below 10 m depth of subsurface euxinic lakes in the Frasassi caves (Italy). As determined by x-ray diffraction, all collected samples contained pyrite. Marcasite, a polymorph of pyrite, was detected only in meter-long microbial “ropes” attached to the submerged limestone walls of the cave.

Fe was sequentially extracted using HCl (reactive Fe), HF (Fe-silicates) and HNO_3 (FeS_2). Reactive Fe makes up less than 7% of total Fe, and this is reflected in the high degree of pyritization (>0.78) in all samples. In sediments, the majority of Fe was in the form of Fe-silicates. In contrast, the majority of Fe in the biofilms was in the form of FeS_2 (pyrite and marcasite). Comparisons of the tau factor ($\tau_{\text{Zr,Fe}}$) and Fe/Al_T ratios indicate that Fe is preferentially enriched in the biofilms in the form of FeS_2 .

Fe isotopic measurements were conducted on a Thermo-Fisher Neptune Plus MC-ICP-MS in Penn State’s Metal Isotope Laboratory (long-term external reproducibility of two in-house standards= 0.06‰ , 2SD). The data reveal limited isotopic variability of silicates ($\delta^{56}\text{Fe} = 0.4$ to 0.5‰) and a small offset with pyrite (-0.2 to 0‰) in the sediments. By contrast, FeS_2 in biofilms have significantly lower $\delta^{56}\text{Fe}$ values (-0.5 to -1.2‰).

Overall, the data suggest that the presence of microbial biofilms can lead to Fe enrichment and the subsequent formation of isotopically light pyrite relative to the ostensible Fe source. The exact mechanism governing this process is as yet unknown, and could be either passive or actively controlled by microorganisms. On the early Earth, abundant microbial biofilms could contribute to the formation of isotopically light FeS_2 minerals, though multiple episodes of cycling are likely necessary to produce the $\delta^{56}\text{Fe}$ values observed in the rock record.

- [1] Rouxel *et al.* (2005) *Science* **307**, 1088-1091. [2] Severmann *et al.* (2008) *Geo Chim Acta* **70**, 2006-2022. [3] Guilbaud *et al.* (2011) *Science* **332**, 1548-1551.