Fe Isotope Biosignatures in the Terrestrial Archean to Phanerozoic Rock Record

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Over two dozen labs across the world are pursuing Fe isotope studies, spurred by the initial NAI-sponsored research in the last five years. This effort has produced several thousand Fe isotope analyses of natural and experimental materials, documenting the origin of the ~ 5 per mil range in $^{56}Fe/^{54}Fe$ ratios that has been measured in terrestrial samples. Although some of the largest Fe isotope fractionations occur during oxidation, either abiotically or during bacterial oxidation, the high-$^{56}Fe/^{54}Fe$ products of this are quite rare in the rock record. In contrast, a low-$^{56}Fe/^{54}Fe$ signal that is produced by dissimilatory Fe(III) reduction (DIR) is common in the rock record from 3.3 billion years ago to modern environments. Detailed experiments by our group have identified the exact Fe pathways involved in producing this low-$^{56}Fe/^{54}Fe$ component, including production of biogenic magnetite and Fe carbonate. The low-$^{56}Fe/^{54}Fe$ aqueous Fe(II) reservoirs that are produced by DIR cannot be produced by abiologic means such as sulfide formation, which, in fact, produce isotopic compositions in the opposite direction. Although oxidation and precipitation of high-$^{56}Fe/^{54}Fe$ ferric Fe produces residual low-$^{56}Fe/^{54}Fe$ $Fe(II)_{aq}$, this occurs only if near complete precipitation occurs, which is unlikely in an Archean $Fe(II)_{aq}$-rich ocean. Sorption of Fe(II) to ferric oxides has been proposed as a means for producing low-$^{56}Fe/^{54}Fe$ $Fe(II)_{aq}$, although new experiments by our group show this to be inadequate for producing the observed isotopic compositions. The evidence appears clear, therefore, that Fe isotopes may be used as a biosignature for ancient microbial life.