6.5.25

Low redox-level of Neoarchean surface-seawater: Evidence from Fe isotopes and rare earth elements

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Neoarchean stromatolitic carbonates from the Hamersley Group, Western Australia, contain some of the lightest iron measured in the geosphere to date. The shallow-marine Carawine Dolomite, formed at ca. 2.6 Ga, contains high iron concentrations of 0.48 % to 1.5 %. This iron is isotopically very light ($\delta^{56}Fe_{IRMM14}$as low as –2.1 ‰). Iron-rich dolomites from the deeper water Wittenoom and Marra Mamba Formations cover a range of isotopic compositions from –1.8 ‰ to –0.4 ‰. All of the carbonates are significantly lighter than oxide-facies banded iron-formation (Marra Mamba Formation and Dales Gorge Member) from the same sequence. These contain iron with $\delta^{56}Fe_{IRMM14}$ values between –0.1 ‰ and +0.9 ‰. Banded iron-formation (BIF) samples from the 3.9 Ga Isua Formation, West-Greenland, fall within the same range as those from the younger Hamersley Group, indicating the absence of secular changes in the iron-isotopic composition of the deep water iron source to the BIFs. High concentrations of isotopically light iron are in marked contrast to what is seen in Phanerozoic marine sedimentary carbonates that contain low concentrations of almost unfractionated iron.

All carbonate samples studied are characterized by REY patterns that are very similar to that of modern seawater, except for the lack of any negative Ce anomaly. The occurrence of Ce anomalies in chemical sediments is evidence for Ce oxidation in an oxygenated Earth’s surface system.

The high content of isotopically light iron in Neoarchean sedimentary carbonates, in particular in the stromatolitic shallow-water Carawine dolomites, indicates high dissolved concentrations of isotopically light ferrous iron in Neoarchean surface-seawater. This requires a low oxygen content in the Neoarchean atmosphere, which agrees well with the lack of Ce anomalies in REE patterns of the Hamersley dolomites. Our study suggests that iron isotopes in carbonates might potentially provide a proxy for the secular evolution of seawater oxygenation.

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Microbial sulfate reduction and methanogenesis in the Archean Ocean

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Sulfur isotope fractionation at low sulfate concentrations

The Archean sulfur isotope record shows isotope fractionations of <10‰ between sulfate and sedimentary sulfide. It is thought that the low isotope fractionations are produced by microbial sulfate reduction in an Archean ocean low in sulfate. In continuous culture experiments with the hyperthermophilic sulfate reducer *Archaeoglobus fulgidus*, and with natural populations of both freshwater and marine sulfate reducers, we measured the isotope fractionation at millimolar and submillimolar sulfate concentrations. Low isotope fractionations were generally produced at sulfate concentrations of less than 200µM. At these low concentrations both sulfate reduction and isotope fractionation is inhibited by the supply of sulfate in to the cell

Carbon mineralization in the Archean

We explored in a diagenetic model the relative importance of sulfate reduction and methanogenesis for organic carbon mineralization as a function of sulfate concentration. An Archean ocean with sulfate concentration of 200µM suppresses sulfate reduction rate by about 75% compared to the modern day where sulfate concentrations are about 28 mM. Instead, from 30 to 70% of the total carbon mineralization is coupled to methanogenesis. Therefore, low sulfate concentrations in the Archean may have contributed to an increase flux of methane from the ocean to the atmosphere.