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Iron isotope fractionation in river colloidal matter

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It has been argued that Fe isotope variations in continental input to the oceans is unlikely, considering the Fe isotope homogeneity of terrestrial igneous rocks. However, data presented in this study from a boreal river system show that colloidal river suspended matter may have a range of iron isotope ratios, clearly different from the bedrock ratio. The results show the existence of two types of Fe-rich colloids with distinctly different $\delta^{56}\text{Fe}$ values. A simple model is presented, suggesting that two different hydrogeochemical processes can explain the temporal variations observed for the $\delta^{56}\text{Fe}$ value in the suspended fraction in the river. The variations are caused by mixing of Fe derived from two different sources in the drainage basin. One source is Fe-oxyhydroxides, formed by the precipitation of dissolved Fe in inflowing anoxic groundwater (positive $\delta^{56}\text{Fe}$ value), and the other from flooding of Fe-C colloidal material (negative $\delta^{56}\text{Fe}$ value) from the upper soil horizon during storm events. Most of river transported particulate and colloidal Fe are deposited in the estuarine environment. However, there are indications that Fe might reach the open ocean via the small sized C-Fe-enriched colloidal material observed in boreal river systems. The size of the C-Fe-colloids is smaller than approximately 10 nm whereas colloidal Fe-oxyhydroxides are generally larger than 10 nm. A hydrodynamic diameter of 1.2 nm has been calculated for the C-Fe carrier colloid in boreal systems. River discharge, and Fe pathways to the open ocean via these two types of colloidal material must be carefully evaluated before river input can be ruled out as a significant source for Fe-isotope variation in the ocean.

The findings in this study have implications not only for the source of Fe isotopes to the ocean, but also shed light upon the physicochemical speciation of dissolved Fe in natural waters. Fe(III) compete significantly with trace metals for binding by natural organic matter. As a result of these competition effects, humic matter may be less important for trace metal binding in the field than they are in laboratory systems. Hence, the extent of association of Fe(III) with humic material versus Fe-oxyhydroxides might regulate the speciation of trace metals in natural systems. The results of this work indicate that Fe isotopes might be used to distinguish between these two phases.

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Fe isotopic composition of rivers

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Iron isotope measurements of bulk river water samples suggest that isotopically-light Fe is carried in the dissolved phase of river waters. Streams that carry large suspended loads, such as the Yukon River, have Fe isotopic compositions which are similar to or slightly heavier than igneous rocks. However dilute streams (Fe < 70 ppb), such as the Eel and Klamath Rivers, are isotopically lighter than the Yukon and igneous rocks by as much as -1‰. Preliminary analyses of filtered (< 0.2 μm) stream waters support the assertion that the dissolved load of streams can be isotopically light by as much as -1 to -1.5‰. A limited analysis of soil profiles suggests that small amounts of isotopically-light Fe may be mobilized within, and perhaps leached from, soil profiles during weathering.

The idea that dissolved Fe is isotopically distinct from particulate Fe in rivers is supported by other researchers' analyses of filtered stream waters [1] and experimental studies that show a large (~3‰) difference between isotopically light Fe(II) and heavy Fe(III) in solution [2]. This distinction is critical to understanding the effect of Fe inputs on the ocean's isotopic composition and, ultimately, differences in the isotopic composition of marine paleo-indicators, such as Fe-Mn crusts, over time. The modern ocean has a small Fe reservoir with a small residence time, and is susceptible to changes in isotopic composition. Our analysis of the modern Fe cycle indicates that while the *total* Fe flux to the global ocean is dominated by rivers (as opposed to atmospheric or hydrothermal sources), estimated *dissolved* Fe fluxes are more evenly distributed. Therefore characterizing and understanding the processes affecting the isotopic composition of riverine Fe is integral to unraveling both the modern and ancient Fe cycles.

References

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