Carbonates, riverine chemistry and incongruent weathering of hafnium

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The variability of dissolved hafnium (Hf) and neodymium (Nd) isotopic compositions and concentrations in four Swiss rivers are reported and compared to the concomitant changes in riverine chemistry. The rivers were sampled ten times between March 2004 and July 2005. The dissolved Hf and Nd isotopic compositions are compared to those in the suspended load to determine incongruent weathering effects for both elements.

The average dissolved Hf isotopic compositions of the four analyzed rivers (εHf = -1.7, +5.4, -1 and +2.3) are markedly more radiogenic than the isotopic compositions in the river suspended matter (εHf = -9.3, -6, -5.4 and -4.2), documenting strong incongruent weathering effects on Hf. Furthermore, the seasonal variability in the dissolved Hf isotopic composition of the individual rivers is large and spans a range from 2.7 to 9.2 εHf. In contrast, the isotopic composition of the dissolved Nd is virtually identical to that of the suspended load and varies by only 1 εNd throughout the seasons.

The abundance of Hf in the weathered lithologies does not seem to exert the primary control on the riverine dissolved Hf concentrations. Hafnium concentrations are approximately one order of magnitude higher in rivers dominated by carbonate weathering than in those draining gneissic catchments. The Hf/Ca ratios in the dissolved load of the Hf–rich rivers, are about two orders of magnitude lower than in carbonates. It seems likely that Hf concentrations are controlled by the availability of appropriate ligands to keep Hf in solution, although there are no firm constraints on the speciation of Hf in these rivers.

The data suggest that the offset between terrestrial rocks and seawater in εHf vs. εNd includes recycling of radiogenic Hf stored in carbonates. The large isotopic contrast in Hf between the presumably nearly zircon free riverine suspended particles and the dissolved load indicates that other factors apart from the incomplete weathering of zircon contribute to the isotopic compositon of dissolved Hf, consistent with preferential weathering of minerals containing radiogenic Hf, as previously proposed by others.

Evolution of MORB at fast-spreading ridges

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The composition of magmas erupted at fast spreading ridges, such as the East Pacific Rise, integrate a variety of processes that modify the compositions of melts sourced within the underlying asthenosphere. It is generally accepted that the majority of MORB erupt from one or more shallow melt lenses located below, but proximal to, layer 2 of the oceanic crust. These reservoirs act as catchments for melts that percolate through several kilometers of crystal mush that form the nascent layer 3 crust. Within these reservoirs melts are homogenized and cooled allowing them to traverse specific liquid lines of descent (LLD). Consequently, the compositions of erupted magmas, which normally include N_MORB, ferrobasalts and Fe-Ti basalts, principally reflect the processes of shallow level mixing and crystal and *in situ* fractionation. In some specific tectonic settings, such as segment terminations and overlapping spreading centers, andesites and dacites are erupted in significant volumes. Commonly, their major and trace element compositions are decoupled and cannot be modeled as extensions of the LLD from N-MORB to FeTi basalt. Specifically, their concentrations of Cl and the most incompatible trace elements are too high and appear to require the input of an external chemical component. Modeling of magmatic fractionation coupled with partial melting of surrounding country rock (probably the base of layer 2b) and assimilation of anatectic melt provide a close, although not perfect, fit to the major and trace element chemistry. Rare gabbroic xenoliths enclosed in neovolcanic lavas provide further details about the complex melt-mineral reactions, mixing of melts, and precipitation of crystals that take place as melts percolate upward through the crystal mushes of the developing crust. Thus, lavas and xenoliths provide complementary information with which to decipher the evolution of MORB.