

The speciation of marine particulate iron adjacent to active and passive continental margins

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We use synchrotron chemical-species mapping techniques to compare the speciation of marine particulate iron collected in two open ocean environments adjacent to active and passive continental margins. Chemical-species mapping combines the spatial information provided by microfocused X-ray fluorescence (XRF) mapping with chemical information gleaned from single particle X-ray absorption near-edge structure (XANES) spectroscopy to allow a rapid and statistically meaningful assessment of the speciation of a large number of heterogeneous micron-scale iron-rich particles. It is especially good for detecting spectroscopically distinct rare species that could not be detectable by other methods.

We find that the average oxidation state of marine particulate iron determined by chemical-species mapping is comparable to that determined by standard bulk X-ray Absorption Near Edge Structure spectroscopy. Fe (II)-containing minerals such as biotite, hornblende, and magnetite contribute up to 45% of total suspended marine particulate iron in the Northwest Pacific, with the balance comprised of Fe (III) compounds. Depth profiles of the mineralogy and oxidation state of marine particulate iron trace the source of iron to the volcanic Kuril-Kamchatka continental margin about 600km away. In contrast, particulate iron in the eastern tropical North Atlantic, which receives the highest dust deposition on Earth, is dominated by weathered and oxidized Fe compounds, with Fe (III) comprising 90% of total iron. The balance is composed primarily of Fe (II)-compounds, but we detected individual pyrite particles in some samples within an oxygen minimum zone in the upper thermocline. Several lines of evidence point to the adjacent Mauritanian continental shelf as the source of pyrite to the water column. We find that the speciation of suspended marine particulate iron reflects the mineralogy of iron from the adjacent continental margins.

Cd behaviour in arctic estuarine systems using Cd isotopes and concentrations analysis

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In the oceans, Cd exhibits a behaviour that is similar to the nutrient phosphate: the concentrations are low at the surface due to uptake by organisms, and higher in deep water where regeneration of biological debris occurs [1]. This behaviour is reflected in Cd isotope data, as surface waters commonly display large isotopic fractionations and heavy Cd isotope compositions [2].

Rivers are a significant source of marine Cd, but the behaviour of the element in estuaries is only poorly understood. Therefore, we have determined the Cd isotopic compositions and concentrations of 19 water samples collected along the Arctic Siberian Shelf during the ISSS-08 cruise.

The results for the majority of the samples are in accord with conservative mixing between river water and seawater. Six samples, however, deviate from the mixing trend. One displays a very light Cd isotope composition, which is in accord with release of anthropogenic Cd from particles. This interpretation is based on the light Cd isotope compositions reported for anthropogenic Cd in previous studies [3]. The remaining five samples also exhibit “excess” Cd and the isotope data indicate that this reflects release of natural Cd from particulates at intermediate salinities.

These observations emphasize the importance of trace metal stable isotope analyses for investigations of marine biogeochemical cycles. For Cd, the isotopic data (i) corroborate the reactive behaviour of Cd in estuaries, where Cd is released from particles and (ii) indicate that they may be a useful tool for tracing anthropogenic Cd in the environment.

[1] Boyle *et al.* (1976) *Nature* **263**, 42–44. [2] Ripperger *et al.* (2007) *EPSL* **261**, 670–684. [3] Cloquet *et al.* (2006) *ES&T* **40**, 2525–2530.