The oceanic cycles of the transition metals and their isotopes

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The transition metals show variable behaviour in the oceans, from the conservative but redox-dependent behaviour of Mo, through control by scavenging for Cu, to clearly biologically cycled elements like Ni and Zn. Thus, the abundances of these elements in ocean sediments have been used to understand temporal variability in a variety of key parameters for ocean biogeochemistry. Their isotopic systems are also often now available for study, but much remains to be done to understand the important processes fractionating the isotope systems. Here we assess their oceanic mass balance from an elemental and isotopic perspective.

A common feature of all the elements considered here (Mo, Zn, Cu, Ni) is the fact that the dissolved riverine input to the oceans is isotopically heavier than the continental crust, requiring isotopic fractionation during weathering and riverine transport. Moreover, the oceanic dissolved pool is, in all cases, heavier still. For example, the dissolved phase in rivers has δ^{60}Ni ~0.8‰, versus silicate rocks at around +0.1 to +0.2 ‰. The dissolved pool in the oceans has $\delta^{60}\text{Ni} = +1.44\pm0.15$‰. Such isotopic data, for Ni and other metals, impose significant constraints on the marine budgets of these elements. There must, for example, be at least one isotopically light sink that renders seawater heavy.

Our approach to elemental mass balance has been to couple the size of the better-known Mo sinks with their metal/Mo ratios. For Cu and Zn the total known outputs are of the same order as, but slightly smaller than, the dissolved riverine input. However, the same approach with Ni highlights a major problem: the output of Ni to Fe-Mn oxides (isotopically close to seawater [1]) is close to an order of magnitude greater than the dissolved riverine input, a finding that is also made for Mn. This imbalance requires a large input for these two elements that is not significant for Mo. One possibility, given the high Ni/Mo and Mn/Mo ratios of riverine suspended load, is that both these elements are mobilised by reduction of oxide coatings in anoxic sediments in estuaries. But either these coatings are isotopically heavy or such a proposal would make simultaneous balancing of the oceanic elemental and isotopic mass budgets impossible.

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Isotopic Fingerprint of Ice-Rafted Debris from the Antarctic Margin: A Spatial Record of Initial Ice Growth

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The onset of widespread Antarctic glaciation across the Eocene-Oligocene transition (~34 Ma) marks one of the most fundamental climate shifts in recent Earth history representing a major step from the greenhouse world of the Cretaceous and early Cenozoic to the icehouse world of today. State-of-the-art climate models suggest that ice expansion initiated at high elevation nucleation points in response to declining atmospheric carbon dioxide concentrations. While marine oxygen isotope records indicate a very rapid ice growth across the Eocene-Oligocene transition, models differ as to which parts of the continent were actually ice covered during the first extensive pulse of glaciation. Such knowledge however may be crucial for understanding important carbon cycle feedbacks in the Southern Ocean.

Here we investigate the geochemical fingerprint of early Oligocene ice-rafted debris (IRD) layers at two locations off East Antarctica: ODP Site 738 (Kerguelen Plateau) and IODP Site U1356 (Adélie Coast). ^{40}Ar/^{39}Ar ages of ice-rafted hornblende grains (>150 μm) reveal the tectono-metamorphic age of the grains, and hence provide a way to constrain spatial distribution of the initial ice surges. The first peak of IRD on the Kerguelen Plateau is well characterised and shows a clear Pan-African provenance, with ^{40}Ar/^{39}Ar hornblende ages of ~520 Ma, pointing to an origin from the nearby Prydz Bay sector. In contrast, one of the first prominent Oligocene IRD layers offshore the Adélie Coast reveals ^{40}Ar/^{39}Ar hornblende ages of ~1500 Ma. Such ages indicate provenance from the local Mertz Shear Zone. We will discuss details of our new data set in the context of model results on initial ice expansion and potential Southern Ocean feedbacks.

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