Tungsten isotope constraints on the Cenozoic sulfur cycle

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The global sulfur cycle is intimately linked to the cycling of other biogeochemically important elements such as C, O, P and Fe. Here we present a novel stable W-isotope record for three ferromanganese crusts, which shows a close match with previously recognised changes in seawater $\delta^{32/34}S$ (e.g. *1*). Both isotope systems show rapid and stepwise changes mainly during the early Cenozoic which contrasts with the dramatic late Cenozoic changes in ocean chemistry reflected by other isotope systems such as Sr (*2*) and Li (*3*).

The low concentration of tungsten in oceanic crust and seawater suggests limited hydrothermal input and output of tungsten in the ocean. However, interpreting the $\delta^{186/184}W$ of ferromanganese crusts as an archive of total tungsten inputs, cannot be reconciled with the known riverine and hydrothermal inputs. Diagenetic benthic flux, which has been identified to occur along shelves and deltas environments (*4, 5*), is proposed as the mechanism by which isotopic balance of tungsten in the ocean is achieved. The present-day tungsten isotope budget of the ocean suggests that the relatively high $\delta^{186/184}W$ value of the late Cretaceous to early Cenozoic that we recognise indicates an expansion of sulfidic pore-waters in response to an increase in seawater sulfate concentration to a threshold value. This in turn induced formation of highly soluble thiotungstate and the release of light tungsten isotopes attached to terrigenous Fe-Mn hydroxides. The spreading sulfidic porewater also maximizes the formation of pyrite, helping to maintain stable and high $\delta^{32/34}S$ in late Cenozoic seawater.

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