Tungsten isotopic ratios in ferromanganese crust and seawater

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We report W isotope compositions for surface scrapings of 13 globally distributed hydrogenetic ferromanganese (Fe-Mn) crusts and a time-series for an Atlanitic Ocean Fe-Mn crust. Hydrogenetic Fe-Mn crusts precipitate directly from seawater and have been used as paleoceanographic recorders of temporal changes in seawater composition [1]. Tungsten has a ~61ka residence time in seawater, mainly as WO_4^{2-} [2]. Water depth profiles show conservative behaviour. During adsorption on Fe-Mn crusts, W species form inner-sphere complexes in the hexavalent state [3]. Double-spike MC-ICP-MS results are expressed relative to NIST 3136 as $\delta^{186/184}W$ (‰). Surface scrapings display $\delta^{186/184}W$ from +0.08 to +0.22‰ (±0.03‰, 2sd). A trend toward heavier $\delta^{186/184}W$ exists with increasing water depth (~1500 to ~5200m) and W concentration. One hydrothermal Mn-oxide crust sample is anomalously heavy and Mn nodules are both heavy and light relative to Fe-Mn crusts. The time-series (Alvin 539, Atlantic) shows an inverse correlation between $\delta^{186/184}W$ and $^{187}Os/^{188}Os$ isotopes, increasing in $\delta^{186/184}W$ from the crust surface to the base +0.08 to +0.32‰ (±0.03‰, 2sd). This might reflect a variable mantle-like hydrothermal component. A preliminary analysis of surface seawater gives $\delta^{186/184}W$=+0.17 (±0.03‰, 2sd). This resembles the isotope composition of shallow-water crusts indicating little or no isotopic fractionation during formation.

[1] Hein, Koschinsky, Halbach, Manheim, Bau & Kang (1997), *Geol. Soc. Spec. Publ.* **119**, 123–138, edited by Nicholson *et al.*, doi:10.1144/GSL.SP.1997.119.01.09. [2] Sohrin, Isshiki, Kuwamoto & Nakayama (1987), *Mar. Chem.* **22**, 95-103. [3] Kashiwabara, Takahashi, Marcus, Uruga, Tanida, Terada & Usui (2013), *Geochim. Cosmochim. Ac.* **106**, 364-378.