Cd isotopic composition of ferromanganese crusts as a proxy of ocean productivity

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The Cd geochemistry of seawater has attracted scientific interest due to its nutrient-like behavior. The precice Cd isotope dataset for seawater showed Cd-depleted surface water with heavier isotope and uniform isotopic composition of deep water, resulting from preferential uptake of light isotopes by photoplankton [1]. Ferromanganese deposits record the Cd isotope composition of ambient seawater with no detectable isotopic fractionation [2, 3] and could be useful to reconstract past ocean productivity. In this study, we present the modern water-depth profile (953–6000 m) and the secular variation over the past ~20 Myr of Cd isotopic composition ($\varepsilon^{114/110}Cd_{NIST\text{-}3108}$) using ferromanganese crusts collected from the northwestern Pacific. The determined external uncertainty obtained from analyses of three reference satandards is $\pm 1.3\varepsilon^{114/110}Cd$ (2SD). The water-depth profile of $\varepsilon^{114/110}Cd$ values showd clear offset between shallow and deep waters. The surface sections of the ferromanganese crusts from 953–1838 m depth showed $\varepsilon^{114/110}Cd$ values of +1.2 to +2.6, while at the depths greater than 2000 m, the $\varepsilon^{114/110}Cd$ values ranged from -1.8 to +0.1, with one exception of +3.7 at 3770 m depth. This trend is generally consistent with variation in water column and the values are similar or slightly lighter relative to the $\varepsilon^{114/110}Cd$ value (+2.3±1.0) of deep water at >900 m [1]. The time-series data reconstracted from ferromanganese crust (1440 m water depth) showed high $\varepsilon^{114/110}Cd$ values before ~9 Ma (+0.8 to +4.5), significant peak between 4.6 and 7.3 Ma (+3.4 to +8.1), and constant values close to zero from 3.0 to 0.2 Ma (–0.03 to +0.5). The paleoceanographic evidence indicated a global increase in primary productivity during the late Miocene-early Pliocene, termed the 'biogenic bloom' [e.g. 4]. It is suggested that the long-term $\varepsilon^{114/110}Cd$ variations in ferromanganese crust reflect changes of productivity in the past ocean.

[1] Ripperger *et al* (2007), [2] Schmitt *et al* (2009), [3] Horner *et al* (2010), [4] Diester-Haass *et al* (2002)