

Uranium isotope composition in ferromanganese crusts: Implications for the paleoredox proxy

GOTO, Kosuke T.^{1*} ; ANBAR, Ariel D.² ; GORDON, Gwyneth W.² ; ROMANIELLO, Stephen J.² ; SHIMODA, Gen¹ ; TAKAYA, Yutaro³ ; TOKUMARU, Ayaka³ ; NOZAKI, Tatsuo⁴ ; SUZUKI, Katsuhiko⁴ ; MACHIDA, Shiki⁵ ; HANYU, Takeshi⁴ ; USUI, Akira⁶

¹GSJ, AIST, ²Arizona state University, ³The University of Tokyo, ⁴JAMSTEC, ⁵Waseda University, ⁶Kochi University

Variations of the $^{238}\text{U}/^{235}\text{U}$ ratio ($d^{238}\text{U}$) in sedimentary rocks have been proposed as a possible proxy for decoding the paleo-oceanic redox conditions, although the marine U isotope system is not fully understood (Stirling et al., 2007 GCA; Weyer et al., 2008 EPSL).

Here we investigate the spatial variation of $d^{238}\text{U}$ in modern ferromanganese crusts by analyzing U isotopes in the surface layer (0-3 mm depth) of 19 samples collected from 6 seamounts in the Pacific Ocean. The $d^{238}\text{U}$ values in the surface layers show little variation and range from -0.59 to -0.69 permil. The uniformity of $d^{238}\text{U}$ values is consistent with the long residence time of U in modern seawater (Dunk et al., 2002 Chem. Geol.), although the $d^{238}\text{U}$ values are lighter than that of present-day seawater by ~ 0.24 permil (Stirling et al., 2007 GCA; Weyer et al., 2008 EPSL). The light $d^{238}\text{U}$ is consistent with the isotope offset found during the adsorption experiment of U to birnessite (Brennecke et al., 2011 ES&T). Our results suggest that removal of lighter U from seawater to ferromanganese crusts is responsible for the second largest uranium isotopic fractionation in the modern marine system and could provide a source of heavy U to seawater.

Depth profiles of U isotopes ($d^{234}\text{U}$ and $d^{238}\text{U}$) in two ferromanganese crusts were investigated to reconstruct the evolution of oceanic redox state during the Cenozoic. The depth profiles of $d^{238}\text{U}$ show very limited ranges, and have similar values with those of the surface layer samples. The absence of any resolvable variations in the $d^{238}\text{U}$ depth profiles suggests that the relative proportions of oxic and reducing uranium sinks have not varied significantly over the past 40 Myr. However, the $d^{234}\text{U}$ depth profiles in the same samples suggest the possible U redistribution after deposition. Therefore, the $d^{238}\text{U}$ values may have been overprinted by secondary mobilization with pore-water or seawater. These results suggest that careful evaluation of secondary disturbance is required before applying chemical and isotope depth profiles of ferromanganese crusts to understand paleocean environmental changes.

To assess the potential effect of U removal by Mn oxides on seawater $d^{238}\text{U}$, we calculated the seawater $d^{238}\text{U}$ under different fractions of U removal by Mn oxides using a simple isotope balance model. This calculation suggests that seawater $d^{238}\text{U}$ could have varied significantly throughout the Earth's history along with the changes of the Mn oxides accumulation rate.

Keywords: Uranium, $^{238}\text{U}/^{235}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, paleoredox, ferromanganese crust, isotope geochemistry