

Antimony isotopic fractionation during adsorption on ferrihydrite

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Antimony is a potentially toxic trace element, though its physiological function is not known well. In industry, about two-thirds of all Sb production is consumed as Sb₂O₃, added to plastics to act as a flame retardant. The environmental impact by the leaching of Sb into natural water system is concerned. Knowledge of the chemical factors controlling the distribution and mobilization of Sb species in the aqueous systems is therefore important for environmental control and monitoring of Sb as well as for understanding of their geochemical and biological cycling.

Here, we developed a precise isotopic analysis technique of antimony and applied to an adsorption experiment on a mineral surface. Antimony has two stable isotopes of mass number 121 and 123 with relative abundances of 57.362% and 42.638%, and high precision isotopic analysis is possible by a recent introduction of multiple collector ICP-MS. An equilibrium adsorption experiment of pentavalent Sb in aqueous solutions on synthetic ferrihydrite was carried out with a wide range of pH.

Results from XANES and EXAFS analyses indicate Sb⁵⁺ is present as an inner-sphere complex of octahedral Sb species on the surface [1]. Resultant isotope ratios revealed that ¹²³Sb/¹²¹Sb values in the aqueous phases were enriched in heavy isotopes slightly. This Sb isotopic trend was confirmed by the analysis of an interstitial solution from sediments near a stibnite mining area.

[1] Mitsunobu, Harada & Takahashi (2006) *Environ. Sci. Technol.* **40**, 7270-7276.

Towards a global calibration of the *G. ruber* (white) Mg/Ca paleothermometer

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Paired planktonic foraminiferal Mg/Ca and δ¹⁸O analyses are commonly applied to jointly estimate sea surface temperature and δ¹⁸O_{seawater}, a proxy for ocean salinity. Our recent findings from an Atlantic meridional coretop sample transect revealed a significant temperature-independent, influence on *G. ruber* (white) shell Mg/Ca. This effect leads to much higher Mg content than is predicted from traditional SST-Mg/Ca calibration equations and a large, systematic offset between shell derived and observed δ¹⁸O_{seawater} values. The 'excess Mg/Ca' (residual of observed Mg/Ca – expected Mg/Ca at the δ¹⁸O calcification temperature) appears to be highly correlated to salinity and is similar to that found by Ferguson *et al.* (2008). However, culture studies indicate a much lower dependence of shell Mg/Ca on salinity.

A global database (n=122), consisting of coretops of late Holocene age were selected from trigger weight cores in the Pacific, Indian, and Atlantic basins. SEM images of specimens from each basin and from a range of salinities, indicate there are no overgrowths or obvious morphological differences to account for the observed 'excess Mg/Ca'. Flow-through ICP-MS analyses from a global subset of samples yielded similar Mg/Ca ratios as results from batch method analyses, indicating that incomplete cleaning cannot account for the 'excess Mg/Ca' signal either. This implies the 'excess Mg/Ca' signal derives from the primary shell chemistry.

Shells from all coretop samples were cleaned for Mg/Ca using the full oxidative-reductive procedure. Data from these analyses were used to determine new calibration equations for surface ocean temperature and salinity using shell Mg/Ca, δ¹⁸O, bottom water ΔCO₃²⁻, and surface CO₃²⁻ as potential predictors. The relationship of shell Mg/Ca to salinity appears to be non-linear. These results indicate good predictive skill and were validated using published coretop data from all basins.