Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.30180

Thallium oxidative fractionation on hexagonal birnessite: insights from mineralogical and isotope analyses on long adsorption time series

YI WANG[1], RACHEL PHILLIPS[2], COLLEEN M HANSEL[3] AND SUNE NIELSEN[4]

[1]Tulane University
[2]University of South Carolina
[3]Woods Hole Oceanographic Institution
[4]Centre de Recherches Pétrographiques et Géochimiques, CNRS, Université de Lorraine

The thallium (Tl) isotope system has become a promising tracer for global ocean oxygen by tracking manganese (Mn) oxide burial, because Tl has a significant isotopic fractionation upon oxidative adsorption on certain Mn oxides. Laboratory adsorption experiments have suggested that Tl oxidation only occurs on hexagonal birnessite (e.g., δMnO2), but these experiments have never reproduced the theoretical isotope fractionation between reduced and oxidized Tl (Schauble, 2007) . To investigate Tl isotopic fractionation during adsorption under environmentally relevant conditions and to improve our mechanistic understanding of Tl oxidative adsorption on a microscopic level, we conducted adsorption time series experiments on two synthesized hexagonal birnessites (δMnO2 and acid birnessite) that have different specific surface areas. All experiments were performed in an artificial seawater matrix, and the initial aqueous Tl concentrations varied between 5 and 2000 ng/g with the time span from 5 min up to ~8 months. Our results reveal that all sites on hexagonal birnessites have strong affinity for Tl, and kinetic adsorption dominates during the earlier stages (less than 24 hrs) for low to intermediate concentrations (5 to 100 ng/g). However, Tl isotope and X-ray absorption near edge structure (XANES) measurements suggest that Tl oxidation only occurs on select sites on δMnO2 and is kinetically much slower than the initial kinetic adsorption. Although no δMnO2 experiment reached isotopic equilibrium, the regression between Tl isotope fractionation factors and Tl oxidation states from XANES shows that the Tl oxidative fractionation factor is ~30 ε-units, consistent with the theoretical calculation for equilibration fractionation between reduced and oxidized Tl (Schauble, 2007) . Additionally, we observed gradual Tl desorption and δMnO2 mineralogy changes as Tl oxidation progressed (e.g., gradual reduction of Mn(IV) within δMnO2 and growth of the Mn carbonate rhodochrosite). Our results ultimately contribute to a more complete picture of Tl oxidation and associated isotopic fractionation on a microscopic level.