

## Efficient bromine-induced mercury oxidation observed under temperate conditions at the Dead Sea

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We measured massive conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> in the presence of halogens at the Dead Sea producing among the highest observed levels of Hg<sup>2+</sup> in the Earth's atmosphere, levels as high as 136 ppqv. High Hg<sup>2+</sup> concentrations were accompanied by strong depletions of Hg<sup>0</sup>, down to 22 ppqv, or below 10% of the global tropospheric background concentration. Most observed Hg<sup>2+</sup> occurred in gaseous form ( $\geq 96\%$ ) with only minor contributions of Hg<sup>2+</sup> bound to particulates. Inverse correlations of Hg<sup>0</sup> to Hg<sup>2+</sup> showed that only two-thirds (summer) and three-quarter (winter) of depleted Hg<sup>0</sup> was recovered as Hg<sup>2+</sup>, an indication of substantial and immediate deposition of converted Hg<sup>2+</sup>.

Hg<sup>2+</sup> production and Hg<sup>0</sup> depletion temporally coincided with high BrO levels and depletion of O<sub>3</sub> with no apparent time lags between species. Our observations show faster Hg<sup>2+</sup> oxidation than current lifetimes suggest, and indicate that bromine-induced mercury oxidation is very efficient under warm conditions. Enhanced Hg<sup>2+</sup> started at BrO levels below 6 pptv, and Hg<sup>2+</sup> levels increased substantially at BrO levels above 6 pptv up to 50–60 pptv, above which Hg<sup>2+</sup> levels stabilized. These data provide direct evidence of frequent Hg<sup>2+</sup> formation by bromine species in the temperate zone under both moderate and high temperatures. Fast oxidation rates and low thresholds of bromine species needed to initiate oxidation suggest that this mechanism is important across temperate and tropical oceans when low levels of gaseous BrO are present.

## Ca-isotope fractionation during interaction with clay minerals

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Ca-isotope ratios of marine organic and inorganic mineral precipitates have been used as a proxy for multiple purposes in marine geochemistry, e.g. monitoring the oceanic Ca-budget or recording changes in paleo-temperature. However, only little is known about diagenetic processes involving Ca, which have the potential to alter the proxy archives.

Findings in porewaters from the Cascadia margin suggest a relationship between Ca-isotopy and ammonium concentration, which might be due to fractionation of Ca-isotopes during desorption from marine clay minerals [1]. In order to determine if Ca-isotope fractionation happens during adsorption and desorption of Ca onto clay minerals laboratory experiments on well characterized montmorillonite were carried out.

Adsorption of Ca onto montmorillonite at 21 °C and total desorption of Ca at different temperatures showed no evidence for Ca-isotope fractionation. However, during partial desorption Ca-isotope fractionation was observed. The degree of Ca-isotope fractionation during partial desorption depends on the amount of released Ca as well as on temperature.

Processes observed in the lab experiments will contribute to a better understanding of natural occurring processes. Therefore, we analyzed porewaters from 3 different sites of IODP Exp. 303 from the North Atlantic with different dominating lithologies (siliciclastic vs. calcareous) and different Ca-concentration trends with depth. The results show that a strong correlation between ammonium and  $\delta^{44/40}\text{Ca}$  can be observed at siliciclastic clay-bearing sites while this correlation is missing at carbonate-dominated sites. This indicates that ammonium which is produced during organic matter remineralization, displaces isotopically light Ca from clay minerals. Our new findings suggest that the release of light Ca into the porewater is a general diagenetic process in siliclastic, organic-bearing sediments.

[1] Teichert *et al.* (2009) *EPSL* **279**, 373–382.