

Molybdenum speciation in anoxic aquatic systems: HPLC-ICPMS determination of molybdate and thiomolybdates.

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Dissolved molybdenum in fresh and marine waters is essentially under molybdate form. Though adsorbed on manganese oxides or complexed by natural organic ligands in specific conditions, molybdate is not very reactive. In anoxic condition, molybdenum can be strongly associated with colloidal organic matter [1]. When sulphide is present, transformation of molybdate to thiomolybdates ($\text{MoO}_x\text{S}_{4-x}$) has been proposed to explain Mo precipitation in euxinic water column and sediment Mo enrichment. Such pathway is validated in laboratory [2] but thiomolybdates are not yet detected in natural aquatic samples. Here we present a new method that will allow to fulfil this objective: HPLC-ICP-MS protocol is further discussed and apply to lake Pavin samples (a permanently anoxic, sulphide rich crater lake). Molybdate is separated from tetra-thiomolybdate within 15 minutes (fig 1) with optimal conditions.

References

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Mass independent fractionation of Hg isotopes during evaporation and condensation processes

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We measured mass independent isotope fractionation during experimental evaporation of liquid metal mercury. Recent revision of the theory of first-order mass dependent fractionation by Bigeleisen (1996) introduced nuclear field shift effects as the cause of mass independent fractionation. In equilibrium conditions, Schauble (2007) calculated the proportions of mass dependent and nuclear volume dependent isotope fractionation between several species of mercury relative to metal mercury vapour. We suggest that nuclear volume dependent isotopic fractionation can occur during evaporation and condensation of Hg.

Different sets of experiments were performed: 1) Hg liquid-vapour equilibrium between 0 and 25°C, and 2) evaporation of liquid Hg under vacuum conditions varying i- the fraction of liquid Hg evaporated at 22°C and ii- the temperature of evaporation (20°C to 100°C). Isotopic compositions were measured by generation of mercury vapour (SnCl_2) coupled with an MC-ICP-MS. For the equilibrium experiment, we report $\Delta^{202/198}\text{Hg}_{\text{liq/vap}} = 0.8 \pm 0.3\text{‰}$ (2SD) on the range of temperature. Results from the vacuum experiments fit perfectly to a Rayleigh distillation system and indicate $\alpha^{202/198}\text{Hg}_{\text{liq/vap}} = 6.5 \pm 0.3\text{‰}$ at 22°C, different from the kinetic theoretical value of 10.1‰. Isotopic fractionation between liquid and vapour Hg decreases with temperature to reach close to 0‰ at 100°C. This suggests that both kinetic and equilibrium processes are involved.

The relationship between $\delta^{202/198}\text{Hg}$ and $\delta^{199/198}\text{Hg}$ of vapour Hg in equilibrium with liquid Hg indicates that more than 90% of the total fractionation is explained by nuclear volume processes, while only 15% is required for vacuum experiments at 22°C. This proportion increases exponentially with temperature, as the importance of equilibrium increases over kinetic processes. These results suggest that liquid-vapour equilibrium isotope fractionation is mainly nuclear volume dependent, whereas kinetic fractionation is mass dependent.

Fly ashes from a waste combustor reflecting progressive Hg condensation (300°C-200°C) did not show mass independent isotope fractionation, suggesting a dominance of kinetic fractionation during Hg condensation.

References

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 Schauble E.A., (2007), *GCA*, (in press)