Mercury as a proxy for volcanic activity during extreme environmental turnover: Neoproterozoic Snowball Earth and the Cretaceous-Paleogene boundary

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Mercury (Hg) tends to concentrate in sediments deposited right after major glacial events as a result from leaching of volcanogenic Hg from land surface and accumulation along argillaceous sediments. The usually low geological background concentrations of Hg makes this trace element suitable for identifying accumulation pulses in sediments that can be tentatively related to weathering processes and thus to climatic changes.

Volcanism is assumed to be one cause responsible for CO_2 build up in the atmosphere during Neoproterozoic snowball events, eventually leading to subsequent enhanced greenhouse effect, ice melting and cap carbonate deposition. Intense volcanism may have witnessed the Cretaceous-Paleogene transition (KTB) and was, perhaps, responsible for dramatic climatic changes responsible for the decrease in biodiversity and mass extinction.

We have used Hg a proxy for volcanic activity and atmospheric Hg and CO_2 buildup during snowball events in the Neoproterozoic, and concentrated our efforts on cap carbonates in northeastern Brazil. Localities where carbonates with $\delta^{13}C$ values of ca. −5‰ are in sharp – but not erosional – contact with basal diamictites (reflecting earliest stages of deglaciation) were selected and analyzed. Proper cap carbonates analyzed in this study, resting right on top of glacial diamictites, show only modest enrichment or even near-background Hg levels. In most sections Hg concentrations increase up section into the transgressive carbonate successions. Concentrations in marls and marly limestones 5 to 50 m on top of cap carbonates of the Jacoca, Olhos D´Água, Acauã and Frecheirinha formations are typically much higher (up to ~ 300 $ng.g^{-1}$) than estimated Hg background values. We suggest that relatively low Hg concentrations in the cap carbonates *sensu stricto* do not support a protracted and/or full isolation of the atmosphere from the continents and hydrosphere by thick ice. Alternatively, organic matter and bioproductivity would be the overriding factor leading to low Hg concentrations in cap carbonates, which only increase afterwards concomitantly with biotic recovery.

Across the KTB in the Yacoraite Formation, northwestern Argentina, Hg contents up to 250 $ng.g^{-1}$ have been found. In three drill cores across the KTB in the Paraiba Basin, northeastern Brazil, Hg contents increase from the late Maastrichtian to early Danian. Hg spikes predating the KTB are, perhaps, the record of volcanic activity before (but very close to) this transition. At Stevns Klint, Denmark, Hg contents reach almost 250 $ng.g^{-1}$ within a 5 cm thick-clay layer (Fish Clay) that comprises the KTB transition, and exhibits a marked

$^{87}Sr/^{86}Sr$ positive excursion and $^{206}Pb/^{204}Pb$ (t = 65 Ma) and $^{187}Os/^{188}Os$ (t = 65Ma) negative excursions that have been previously reported.

A co-variation between Hg and Al_2O_3 contents has been observed in all of the studied sections of Neoproterozoic cap carbonates and across the KTB transitions, suggesting that Hg is probably adsorbed onto clays.

The combined Hg and C-isotope chemostratigraphies may become a powerful tool for the eventual assessment of the role of volcanic activity during extreme climatic and biotic events, such as those during the Cryogenian/Ediacaran and the Cretaceous-Tertiary boundary. This study points to Hg as a promising tracer for volcanic activity.

PALAVRAS CHAVE: CARBON ISOTOPES, MERCURY