Perturbation to the marine Ca isotope cycle across Oceanic Anoxic Event 2

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Several isotope proxies (e.g., C, Mo, Nd, Os, Sr) have been used to examine the effect of OAEs on global climate and elemental cycling. Here, we evaluate the behaviour of Ca isotopes ($\delta^{44/40}$Ca) across the late Cretaceous OAE2 (Cenomanian-Turonian) in the Western Interior of North America (NA), where significant perturbations in $\delta^{44/40}$Ca track the concommitant changes in C and Os isotope records.

We present a high-precision ($2\sigma_{SD} = \pm 0.04$‰), high-resolution (±20 kyr) record of $\delta^{44/40}$Ca values from the GSSP Pueblo core. A relatively large, positive excursion in $\delta^{44/40}$Ca values occurs at the onset of OAE2. The maximum extent of variation (~0.30‰) is ~8 times larger than the external reproducibility of the measurements. Several processes could explain this pattern, including mineralogical variations, changes in the fractionation factor, and perturbations to the input and output fluxes of marine Ca. We note that initial Os isotope ratios trend toward unradiogenic values during the same time interval. This trend clearly reflects the input of a mantle-like Os isotope composition, most likely derived from the emplacement of basalts of the Caribbean Large Igneous Province. Because basalts have relatively high $\delta^{44/40}$Ca values (Huang *et al*.., 2010) compared to other marine Ca inputs, such as river runoff and submarine groundwater discharge, we infer that the Pueblo $\delta^{44/40}$Ca record also reveals a large volcanic signature. Previous Ca isotope records for OAE2 from the UK did not record the putative basalt weathering signature (Blattler *et al*.., 2011), and were interpreted to reflect increased terrestrial weathering. The difference in Ca records from NA and the UK may reflect a combination of factors, including proximity to the LIP and an improved MC-TIMS method (Lehn *et al*.., 2013) employed in the present study.

Huang *et al*.., 2010, Earth Planetary Science Letters, 292
Blattler *et al*.., 2011, Earth Planetary Science Letters, 309
Lehn *et al*.., 2013, International Journal of Mass Spectrometry (in review)

Impacts of porous structure, organic matter and mineralogy on atrazine fate in two contrasting tropical soils

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The fate of reactive solutes in soils is the result of complex coupled processes including convective dispersive transport, sorption to organo-mineral surfaces and biochemical transformations. These processes, occuring at different space and time scales, are difficult to identify and rank by classical laboratory experiments.

Multidisciplinary studies were performed to evaluate soil characteristics impacting atrazine fate in two contrasting soil types, namely an Andosol and a Vertisol from Mexico. The 3D-macro pore networks and pore morphological parameters were calculated after imaging intact soil cores through X-ray tomography at 50 μm resolution. Reactive organo-mineral phases such as allophanes, clays, oxydes and organic matter were characterized and quantified. The different processes involved in atrazine fate were studied independently and statically in closed reactors. Displacement experiments in intact cores allowed to mimic natural dynamic environmental and application conditions. A stable oxygen isotope used as water tracer permitted obtaining the convective dispersive parameters.

Water transfer in physical non equilibrium transfer was observed in the surface Vertisol and subsurface Andosol horizons and was correlated to pore shape, connectivity and size. Sorption capacity and degradation rate were compared in static and dynamic experiments. The roles of organic matter composition, clay types and pH variations were assessed. This study shows how the soil physico-chemical and microbial propreties at the pore and pedon scales affect reactive solute fate at the macroscale. It also demonstrates the difficulty to decouple the different processes involved.

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