U isotopes disentangle atmosphere-ocean oxygenation dynamics

TAIS W. DAHL[1], JAMES N. CONNELLY[1], BENJAMIN C. GILL[2], DONALD E. CANFIELD[3] AND MARTIN BIZZARRO[1]

[1]Natural History Museum of Denmark, University of Copenhagen, DK1350 Copenhagen, Denmark.
[2]Dept. of Geosciences at Virginia Tech, Blacksburg, VA 24061, USA.
[2]Nordic Center for Earth Evolution, Insitute of Biology, Univ. of Southern Denmark, DK5230 Odense, Denmark.

Anoxic marine zones were common in early Paleozoic oceans (542-400 Ma) [1-4], and they profoundly influenced atmospheric pO_2 via feedbacks associated with marine phosphorous recycling, global primary productivity and marine organic carbon burial [5-6]. Uranium (U) isotopes in carbonate rocks track the extent of ocean anoxia, and carbon (C) and sulphur (S) isotopes track the burial of organic carbon and pyrite sulphur and thus the sources of oxygen to the atmosphere. When used in combination, these proxies allow one to study the dynamics between ocean anoxia and oxygen liberation to the atmosphere over million-year time scales.

Here, we report high-precision uranium isotopic data in marine carbonates deposited during the Late Cambrian 'SPICE' event. Results document a well-defined -1.7 negative $\varepsilon^{238}U$ excursion that occurs at the onset of positive carbon and sulphur isotope excursions, consistent with expanded marine sinks of reduced C, S and U as expected during the expansion of marine anoxia. However, the $\varepsilon^{238}U$ excursion peaks before the $\delta^{13}C$ and $\delta^{34}S$ excursions, marking a period of continued O_2 release from the marine C and S cycles after the oceanic anoxic event. Simple biogeochemical ocean modeling reveals that the different behaviors of the various isotope systems occurred because organic carbon and pyrite were buried with negligible U at high deposition rates in shallower oxygenated settings.

This second stage of the SPICE event suggests high weathering rates and P delivery from the continents to overcome the limited P-recycling from smaller anoxic marine zones. Intriguingly, this marine nutrient boost, perhaps induced by a tectonic-driven sea level drop, comes before the diversification of phytoplankton and the development of more extended trophic chains marking the beginnings of the Great Ordovician Biodiversification Episode.

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Micro-X-ray-diffraction investigations of an altered cement-clay interface

R. DÄHN[1*], P. SCHAUB[1], D. POPOV[2], P. PATTISON[3], A. JENNI[4], U. MÄDER[4] AND E. WIELAND[1]

[1]Paul Scherrer Institut, 5232 Villigen, Switzerland (*correspondence: rainer.daehn@.psi.ch)
[2]Carnegie Institution of Washington, Argonne 60439, USA
[3]EPFL, 1015 Lausanne, Switzerland
[4]University of Bern, 3012 Bern, Switzerland

Cement-based materials and argillaceous rocks play an important role in multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in deep geological repositories. An approximately 180 million year old marine clay-rich sediment (Opalinus Clay) was identified and selected as the first-priority host-rock for the disposal of high-level radioactive waste in Switzerland. Both materials, i.e. Opalinus Clay and cement used for construction of the repository, are heterogeneous mineral assemblages with discrete nano- to micro-scale particles. Hardened cement paste (HCP) consists of mainly calcium (aluminium) silicate hydrates, portlandite, calcium aluminates, and some minor phases such as calcite and hydrotalcite, in hyper-alkaline environment (pH > 11), while Opalinus Clay (OPA) is a mineral assemblage consisting mainly of illite, illite-smectite mixed layers, kaolinite, quartz and calcite in near neutral conditions. Micro-scale information on the chemical reactions and the secondary phases formed in the disturbed zone at the HCP/OPA interface with its large chemical gradients is almost completely lacking.

In this study synchrotron-based micro-X-ray-diffraction (microXRD) was employed to characterise the complex heterogeneous phase assemblages at the HCP/OPA interface. MicroXRD with a beam size focussed down to a few micrometres makes it possible to perform a variety of novel diffraction experiments on fine-structured materials with a high spatial resolution. For example, micro-diffraction experiments allow probing of heterogeneously composed materials, which show chemical and structural alteration zones on a micrometre scale. The investigated samples were obtained from a long-term Cement/OPA-Interaction experiment ("CI-project") in the Mont Terri Rock Laboratory (St-Ursanne, Switzerland). The alteration zone was found to extend over a few hundred micrometres into the concrete material. First microXRD data of the HPC/OPA interface will be presented here.

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