

Diagenesis affects carbonate $\delta^{53}\text{Cr}$: Evidence from the K-Pg boundary section at Stevns Klint (Denmark)

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The chromium isotopic composition ($\delta^{53}\text{Cr}$) of marine sediments is a valuable tool to detect changes of the redox state of paleoenvironments [1, 2]. Recently, the $\delta^{53}\text{Cr}$ of marine carbonates has shown to be a very sensitive tracer of atmospheric O_2 , weathering and hydrothermal input [3]. We applied this new tracer to the K-Pg boundary sequence at Stevns Klint (Denmark), comprising non-cemented chalk and bryozoan limestones of the uppermost Maastrichtian to lower Danian. The $\delta^{53}\text{Cr}$ data was complemented with other geochemical tracers in order to explore environmental changes before and after the K-Pg extinction event.

We observe a conspicuous 3-step $\delta^{53}\text{Cr}$ evolution from strongly positive values at the base of the section ($\sim +0.7\%$) to intermediate values just below the boundary layer ($\sim +0.3$) and finally to mostly negative $\delta^{53}\text{Cr}$ values (~ -0.07) after the K-Pg event, reflecting mantle inventory [4]. Several lines of evidence suggest that this distinct trend may not reflect a primary oceanographic signal but is the result of post-depositional alteration. A prominent diagenetic component is implied by the Sr concentration and Sr/Ca data, which match the decreasing Cr trends. Increasing Mn and Fe concentrations as well as Mg/Ca ratios further support this interpretation. In addition, the Cr shifts can be linked to lithological changes, controlled by sea-level fluctuations. Differences in primary sediment composition may thus have led to differential diagenetic alteration of the Cr signal.

We hypothesize that the isotopically most positive $\delta^{53}\text{Cr}$ values, preserved in the pure chalks of the lowermost part of the section, reflect a typical marine signal. By contrast, the moderately positive to negative $\delta^{53}\text{Cr}$ values of the more coarse grained limestones in the upper part of the section, reflect removal of heavy $\delta^{53}\text{Cr}$ in an open-system diagenetic regime.

[1] Frei *et al.* (2009) *Nature* **461**, 250–253. [2] Frei *et al.* (2012) *Gondwana Res.* **23**, 797–811. [3] Frei *et al.* (2011) *Earth Planet. Sci. Lett.* **312**, 114–125 [4] Schoenberg *et al.* (2008) *Chem. Geol.* **249**, 294–306.

Arsenic sequestration by fresh and aged Fe oxidation products

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The oxidation of dissolved Fe(II) by O_2 leads to the formation of amorphous to poorly crystalline Fe(III)-precipitates. Because of their high sorption capacity, Fe oxidation products critically affect the fate and impact of trace elements like As in soils and sediments as well as in Fe-based engineered systems for soil, sediment and water remediation or treatment

Related to studies on As and trace metal dynamics in soils and sediments and As removal from drinking water, we perform laboratory experiments to determine how major dissolved species in near-neutral aqueous solution affect the formation, structure and aging of Fe oxidation products. In continuation of earlier work [1,2], we currently explore the effect of molar P/Fe ratio and dissolved Si and Ca on (i) the structure of fresh Fe(III)-precipitates formed by oxidation of 0.5 mM Fe(II) at pH 7.0 and their counterparts after 30 days of aging at 40°C and (ii) the uptake and solubility of co-transformed arsenate (As(V); 500 $\mu\text{g/L}$). Both phosphate and silicate interfere with Fe(III) polymerization. The strong interaction of phosphate with Fe(III) reduces As(V) uptake in fresh precipitates above a P/Fe ratio of ~ 0.55 in the absence and ~ 0.75 in the presence of Ca. The presence of Si (at molar Si/Fe ratio of 2) does not interfere with initial As(V) uptake but effectively reduces As(V) re-solubilisation during aging by inhibiting precipitate crystallisation.

The mechanistic insight gained from well-constrained laboratory experiments helps to rationalize observations from natural and technical systems, for example related to As and Fe co-sequestration at natural redox interfaces or to Fe-based drinking water treatment for As removal. The results are also relevant with respect to the sequestration of other trace elements by fresh and aged Fe oxidation products, a topic that we will address in future experiments.

[1] Voegelin *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 164–186. [2] Kaegi *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 5798–5816.