Constraints on the carbon cycle changes during the PETM

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The ocean will absorb increasing amounts of CO_2 resulting in a decrease in the *p*H of surface waters by up to 0.5-0.6 *p*H over the next 250 years [1] which will push ocean geochemistry outside of the envelope of at least the last few tens of millions of years [2]. The Palaeocene-Eocene thermal maximum (PETM) has been suggested as a palaeo-analogue for future climate change and ocean acidification [3], with carbon release comparable to that in predictions of future releases over the coming centuries.

To use ecological and geochemical changes during the PETM to better predict effects of our future climate, constraints on ocean pH and other carbonate system proxies are prerequisite. We used *in situ* high-spatial resolution secondary ionization mass spectrometry (SIMS) to characterize the B/Ca proxy for carbonate saturation [4] and the Li/Ca proxy for DIC in the benthic foraminifer Oridorsalis umbonatus at Maud Rise (Site 690B) across the PETM. Mg/Ca indicates a two step temperature increase from 12.7°C to 18.5°C, in agreement with previous work. B/Ca before the onset of the $\delta^{13}C$ excursion equates to an Ω value of 1.1, dropping to undersaturation during the event. The B/Ca ratio does not recover to pre-event values, even after the temperature and $\delta^{13}C$ returned to background values. Li/Ca ratios show a minor reduction which does not indicate a major change in DIC, contrary to expectations about this massive carbon release event. Further analyses are nesecessary to increase our understanding of Li/Ca as a proxy for the carbonate system.

[1] Caldeira & Wickett (2003) *Nature* **425**, 365. [2] Ridgwell (2005) *Marine Geology* **217**, 339-357. [3] Zachos *et al.* (2005) *Science* **308**, 1611-1615. [4] Yu & Elderfield (2007) *EPSL* **258**, 73-86.

Fractionation of Zr/Hf and Nb/Ta in aqueous systems – The role of marine Fe-Mn oxides

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The geochemical twins Zr-Hf and Nb-Ta behave very similar during magmatic processes controlled by ionic charge and radii, even though limited fractionation is reported in the presence of water, e.g., in subduction zones. In aqueous systems, however, chemical speciation and particle reactivity control the element mobility, potentially causing fractionation of these elemental ratios. Available concentration data for Zr and Hf in deep seawater show strongly superchondritic ratios of ~120-180 (wt/wt), increasing with depth, thus suggesting that Hf is more particle-reactive than Zr (e.g., Godfrey *et al.* [1]). Ferromanganese oxides are known to control the distribution pattern of several elements in the water column, e.g. Ce, and may play a predominant role in the fractionation of high-field strength elements. To better understand the fractionation mechanisms of Zr/Hf and Nb/Ta in seawater we investigated the composition of Fe-Mn oxides formed in different marine environments. Hydrogenetic crusts and hydrogenetic/diagenetic nodules are characterized by highly variable, superchondritic Zr/Hf and Nb/Ta ratios (up to 106 and 133, respectively), with the strongest enrichment of these elements in the hydrogenetic crusts. Depth profiles of individual crusts show increasing Zr, Hf, Nb, Ta concentrations with increasing Fe/Mn ratio. This preferential adsorption onto the Fe phase is controlled by the chemical speciation of HFSE in the water and the surface charge of the oxide particles. Decreasing Zr/Hf and Nb/Ta ratios with increasing element concentration within single profiles indicate that Hf and Ta are preferentially adsorbed relative to Zr and Nb, respectively. This relationship may explain superchonditic Zr/Hf ratios measured in seawater. In marked contrast, Mn crusts formed in hydrothermal environments from diffuse hydrothermal fluids exhibit a different pattern with chondrite-like Zr/Hf and Nb/Ta ratios, indicating a different source (high-temperature hydrothermal fluid) and/or a different fractionation behavior compared to hydrogenetic crusts.

[1] Godfrey, L.V., White, W.M. & Salters, V.J.M. (1996) *Geochim. Cosmochim. Acta* **60,** 3995-4006