

Geochemical evidence for volcanic activity prior to and enhanced terrestrial weathering during the Paleocene Eocene thermal maximum

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The current study presents geochemical measurements from a gray shale sequence from the Central Basin in Spitsbergen, Svalbard Archipelago (Core BH 9/05) that samples the Paleocene Eocene thermal maximum (PETM) at extremely high resolution. The data, including Re and Os concentrations, ¹⁸⁷Os/¹⁸⁸Os, and major element geochemistry over ~60 meters of shale representing ~220 ka, suggest that a significant volcanic episode occurred just prior to or coincident with the onset of the PETM. The precise correlation between the timing of the PETM and the volcanic episode is possible due to previously published, high resolution δ¹³C organic carbon data measured in the same core. The presence of a significant volcanic component is indicated primarily by a large drop in ¹⁸⁷Os/¹⁸⁸Os (Δ¹⁸⁷Os/¹⁸⁸Os ~ -0.23) and confirmed by elemental mixing calculations. The geochemistry of the inferred ash component, which persists in the sedimentary record for ~8 ka, is distinct and consistent with the geochemistry of contemporaneous ashes in Denmark. Based on the substantial size of the ¹⁸⁷Os/¹⁸⁸Os decrease, the volcanic event must have involved widespread ash deposition in the local catchment and subsequent, rapid weathering of the ash that shifted the ¹⁸⁷Os/¹⁸⁸Os of the basin water column to <0.5. Temporally, the volcanic event coincides with (or predates by a few ka) the onset of the PETM, suggesting northwest European shelf volcanism as the trigger for the PETM.

As the planet warmed, dissolved and detrital indicators of weathering indicate a relatively short-lived <10 ka pulse of more weathered material to the basin. The pulse shifted authigenic ¹⁸⁷Os/¹⁸⁸Os to more radiogenic values and deposited clastic materials with higher Chemical Index of Alteration and lower Na/Ti, suggesting more intense chemical weathering prior to the peak carbon isotope excursion. The pulse is consistent with open ocean observations of changing ¹⁸⁷Os/¹⁸⁸Os. In addition, anoxia appears to have initiated close to the onset of the PETM, persisting for ~50 ka and ending abruptly during the recovery stage.

The inheritance of source Hf isotopic diversity in S-type granites

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S-type granites typically record substantial Hf isotopic diversity within their magmatic zircon population. The 538 Ma old Peninsula pluton (South Africa) typifies this behavior exhibiting a zircon ε_{Hf(538)} range of 8ε units. In the smallest rock samples investigated (<0.5 dm³) and within individual thin sections, an ε_{Hf(538)} range is recorded that is almost as large as that recorded within the whole sample set. At all scales, the ε_{Hf} variability in the magmatic zircon fraction matches well that portrayed by the time evolved inherited zircon population, suggesting that the ε_{Hf} heterogeneity of magmatic zircon is inherited from the source [1]. However, the Hf dispersion exhibited by the inherited zircons is greater (12 ε_{Hf} units) than that shown by magmatic zircons indicating a minor degree of Hf isotope homogenization in the time interval between dissolution of detrital zircon and the growth of the magmatic fraction. Moreover, the ε_{Hf(t)} frequency of occurrence in the two populations is not identical, with a greater proportion of magmatic zircons having higher ¹⁷⁶Hf/¹⁷⁷Hf. This is interpreted to result from the relatively minor contribution of ¹⁷⁶Hf from Lu-bearing phases that did not re-equilibrate with zircon during metamorphism and partial melting. These phases have higher Lu/Hf ratios than zircon and thus their break down provides a more juvenile signature to the melt, mimicking the effect of mixing with a mantle-derived magma.

The occurrence of magmatic zircons with diverse ε_{Hf} at the sub-cm scale reflects the existence of micro domains within the melt whose Hf isotopic composition is controlled by the in-situ availability and composition of detrital zircons as well as by the ratio between detrital zircons and other Hf-bearing phases dissolved into the melt. Hf isotopic equilibration between micro domains was poor, due to the very low Hf diffusivity and short residence time of the melt in the source. Moreover, Hf homogenization is not achieved during far-field melt transport suggesting that the magma emplaces prior to any significant dissolution of inherited zircon.

[1] Villaros *et al* (2012) *Contrib Mineral Petr* **163**, 243-257.