



Calcium isotope evidence for pulses of increased continental weathering during the early Toarcian (Early Jurassic)

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The Toarcian interval is punctuated by a number of episodes of environmental changes and mass extinctions that are considered as some of the most severe of the Mesozoic era. Significantly, the corresponding strata record marked negative carbon isotope excursions that point to pulses of massive injection of isotopically light carbon to the superficial reservoirs. Potential causes of these perturbations include gas hydrate dissociation, wildfires, and massive inputs of thermogenic and volcanogenic carbon related to the onset of volcanic activity of the Karoo-Ferrar province. All these scenarios imply large increases in chemical weathering rate as key drivers of the accompanying biotic and environmental perturbations (e.g., productivity-driven anoxia and coastal eutrophication). Nevertheless, detailed examination of most likely cause(s) of these events has been hampered by the uncertainty surrounding the timing and intensity of coeval changes in continental weathering. In this study, we reconstruct changes in continental weathering during the Toarcian using new calcium isotope ratios $\delta^{44/42}\text{Ca}$ of brachiopods and bulk rock sediments from the Peniche section in Portugal. The data reveal two marked ($>0.4\text{permil}$) negative Ca-isotope excursions near the Pliensbachian-Toarcian transition (Pl-To) and at the base of the *levisoni* ammonite Zone recording the Early Toarcian Oceanic Anoxic Event (T-OAE). The comparison of the brachiopod and bulk rock Ca isotope data indicates that these excursions reflect changes in the global Ca-isotope composition of seawater rather than changes in the dominant mineralogy of calcifying organisms. Mass balance calculations suggest that the Ca-isotope excursions recorded across the Pl-To transition and T-OAE interval can be explained by the Ca inputs from rivers corresponding respectively to 90% and 34% of the initial mass of oceanic Ca. Based on these values, the injection of tens of thousands of gigatons of carbon with a C-isotope composition comprised between -5‰ and -20‰ appears as the most likely cause of the C-isotope excursions characterizing these two events. These results point to the massive injection of volcanogenic carbon by the Karoo-Ferrar volcanism as the main cause of the Toarcian environmental and biotic changes.