

## Carbonate isotopic constraints on seawater chemistry during Pliensbachian – Toarcian

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Sharp, negative excursions in C and O isotopic records (3‰ in  $\delta^{13}\text{C}$  and 1.3‰ in  $\delta^{18}\text{O}$ ) and a positive shift by 0.7 ‰ in  $\delta^{44/40}\text{Ca}$  were reported in brachiopods at the Pliensbachian – Toarcian (Pl-T) boundary from the Peniche section in Portugal [1-2]. These changes have been attributed to increased global weathering associated with Karoo-Ferrar volcanic activity. We present ‘clumped’ and Ca isotopic data of well-preserved marine carbonates from the Peniche Pl-T boundary section, to constrain the variations in seawater temperatures through the boundary, and to test the above hypothesis.

Clumped isotope ( $\Delta_{47}$ ) temperatures of Pl-T belemnites vary from 33.1 to 57.4°C, similar to the range of 33.5 – 54.4°C found in Toarcian brachiopods from 22 – 26m above the Pl-T boundary. This range of temperatures corresponds to burial-diagenetic environments and indicates variable preservation quality among these visually and chemically screened samples. The small variability in  $\delta^{18}\text{O}$  (~0.85‰) of them and a modelled burial temperature of <108 °C [3] indicate a closed-system, rock-buffered diagenetic alteration of the  $\Delta_{47}$  signal through recrystallization and possibly solid state isotopic reordering.

$\delta^{18}\text{O}$  of the interstitial water, calculated using the  $\Delta_{47}$  temperature and the  $\delta^{18}\text{O}$  of carbonates, show a strong positive correlation with  $\Delta_{47}$  temperatures – consistent with the modification of porewater in rock-buffered environment. Assuming seawater  $\delta^{18}\text{O}$  of -1 ~ 0.5 ‰ in early Jurassic [4], the positive correlation can be extrapolated to intersect the temperature axis at this range to estimate seawater temperatures. Belemnites show a 3.6°C warming across Pl-T boundary, and brachiopods reflect a further 3-4°C increase in seawater temperature around 25m above the boundary.

Compared with published brachiopod records [1-2], our belemnites show less than half of the variations in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , and reflect a 0.4 ‰ decrease in  $\delta^{44/40}\text{Ca}$  (rather than a 0.7‰ increase in [2]) through the Pl-T boundary. Our isotopic data indicate a slight warming at Pl-T boundary that was not necessarily triggered by the Karoo-Ferrar volcanism.

[1] Suan et al., EPSL, 2010, 290(3), 448-458. [2] Brazier et al., 2015. EPSL, 411, 164-176. [3] Ryb et al., 2017, 6th International Clumped-Isotopes Workshop in Paris. [4] Cummins et al., GCA, 140, 241-258.