Clumped isotopes in early Cretaceous belemnites: Alteration or vital effects?

JUSTIN H. VAN DE VELDE^{1*}, BENJAMIN H. PASSEY², GREGORY D. PRICE¹ AND STEPHEN T. GRIMES¹

¹Centre for Research in Earth Science, Plymouth University, Plymouth PL4 8AA, UK

*correspondence: justin.vandevelde@plymouth.ac.uk

²Department of Earth and Planetary Science, Johns Hopkins

University, Baltimore MD 21218, USA

Belemnites are an attractive target for Mesozoic paleoclimate reconstructions using clumped isotopes, as they provide large amounts of calcite and have established techniques for assessing preservation. Conflicting evidence in ancient and modern carbonate-producing cephalopods suggest they may exhibit disequilibrium fractionation in their clumped isotope ratios. These apparent vital effects shift $\Delta_{\!\!47}$ to lower values (higher T), and can therefore be difficult to distinguish from partial recrystallization at elevated burial T without independent constraints on the extent of alteration. We analyze Valanginian (140 to 133 Ma) belemnites from southern Spain (28 °N), southeastern France (34 °N), northeastern England (45 °N), and two sites in subarctic Russia (55 and 78 °N). Clumped isotope temperatures are reasonable at the highestlatitude sites, but increasingly exceed plausible marine conditions at lower latitudes by up to 15-20 °C. Using multiple geochemical and petrographic techniques, including elemental chemistry, cathodoluminescence (CL) and electron backscatter diffraction (EBSD), we find that alteration is limited and similar in most samples, regardless of sample site. We suggest that belemnites exhibit a vital effect in Δ_{47} that correlates with latitude, and is likely related to an environmental factor such as growth T. These efforts will be important for any future use of belemnites or other cephalopods in clumped isotope studies.