Stable Ca and Sr isotopes indicate biocalcification crisis during OAE1a

JIUYUAN WANG*, ANDREW D. JACOBSON, BRADLEY B. SAGEMAN, MATTHEW T. HURTGEN

Department of Earth and Planetary Sciences, Northwestern University, Evanston, IL, USA, 60208 (*correspondence: jwang@earth.northwestern.edu)

Large Igneous Province eruptions are expected to trigger biocalcification crises via numerous local-to-global scale mechanisms. The Aptian nannoconid crisis, which correlates with emplacement of the Ontong Java Plateau (OJP) and Ocean Anoxic Event 1a (OAE1a, ~120 Ma), may represent one such example [1]. The Ca isotope ($\delta^{44/40}$Ca) system offers potential to detect biocalcification fluctuations in the rock record because Ca isotope fractionation is sensitive to precipitation rate. However, other primary and secondary processes, such as input-output flux perturbations and early diagenesis, can produce similar signals. The stable Sr isotope ($\delta^{88/86}$Sr) system can help resolve the origin of $\delta^{44/40}$Ca variability because Sr isotope fractionation is also rate-dependent [2], but the proxy appears less prone to diagenetic overprinting [3]. We report high-precision TIMS $\delta^{44/40}$Ca, $\delta^{88/86}$Sr, and $^{87}Sr/^{86}Sr$ records for Hole 866A of ODP Leg 143 drilled in Resolution Guyot, mid-Pacific. The samples span from the Barremian (~127 Ma) to the Albian (~100 Ma). $^{87}Sr/^{86}Sr$ ratios gradually decrease from ~0.70750 to ~0.70727, in agreement with the global record. $\delta^{44/40}$Ca and $\delta^{88/86}$Sr values range from -0.74‰ to -1.07‰ and 0.25‰ to 0.37‰, respectively. The $\delta^{44/40}$Ca and $\delta^{88/86}$Sr secular trends differ from the $^{87}Sr/^{86}Sr$ record, but mimic each other. $\delta^{44/40}$Ca and [Sr], as well as $\delta^{44/40}$Ca and $\delta^{88/86}$Sr, strongly correlate and yield slopes expected for kinetic control [3, 4]. These results indicate that variable mass-dependent fractionation rather than end-member mixing regulated the isotopic relationship between carbonates and seawater. Positive $\delta^{44/40}$Ca and $\delta^{88/86}$Sr shifts within the OAE1a interval are consistent with reduced biocalcification rates. The data support a causal connection between eruption of the OJP and the Aptian nannoconid crisis. Noting that [CO_3^{2-}] provides a first-order control on precipitation rates, we hypothesize that volcanic CO_2 emissions affected the carbonate geochemistry of seawater.

[1] Erba et al. (2010). Science **329**, 428-432. [2] Böhm et al. (2012). Geochim. Cosmochim. Acta **93**, 300-314. [3] Voigt et al. (2015). Geochim. Cosmochim. Acta **148**, 360–377. [4] Tang et al. (2008). Geochim. Cosmochim. Acta **72**, 3733–3745.