Carbonate clumped-isotope constraints on recrystallization rates in deep-sea sediments from ooze to chalk to limestone

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Deep-sea carbonate sediments are important archives of the thermal and geochemical history of the oceans. Dissolution-reprecipitation (recrystallization) reactions alter carbonates in these systems during burial such that their chemical and isotopic compositions can reflect their original formational conditions and those of recrystallization in the sedimentary column.

Various models have been developed (e.g., [1]) to constrain the effects of recrystallization during burial. A general result of these models is that recrystallization rates are highest at the shallowest depths and decrease exponentially with sample age (and depth) to lower or near-zero background rates. At depths where modeled recrystallization rates are at a minimum (~0.5-1 km), some deep-sea carbonate sediments undergo a significant chemical and physical change as chalk sediments convert to limestone. Pore-fluid Mg isotopic measurements [2] suggest that recrystallization rates at the chalk-limestone transition in deep-sea sediments could increase to values similar to the higher rates observed at shallower depths.

We present here newly measured clumped-isotope (δ_{47}-based) temperatures and ^{18}O values from 57 replicated bulk carbonate sedimentary samples over a range of 2-1375 mbsf in ODP Site 807 from the equatorial Pacific. This depth range includes a chalk-limestone transition, which begins in this core at ~850 mbsf [3]. Across and below the chalk-limestone boundary, we observe a decrease in ^{18}O of ~2.3‰ and an increase in δ_{47}-based temperature of ~15°C with increasing depth. Preliminary modelling based on recrystallization rates from [4] indicates that <4°C of this temperature change can be explained by an exponentially decaying recrystallization rate with depth. Instead, either early Cenozoic equatorial sea-surface temperatures were ~10°C warmer than modern, significant recrystallization has occurred during the chalk-limestone transition, or some combination of these two has occurred. We will explore the data with a model of recrystallization that includes both typical depth-dependent recrystallization rates and incorporates increased recrystallization across the chalk-limestone transition. Finally, we will discuss the implications of the model for interpretations of limestone ^{18}O and δ_{47} records.

[1] Richter and DePaolo, 1987, *EPSL* 83(1-4), 27-38.
[2] Higgins and Schrag, 2012, *EPSL* 357, 386-396.
[3] Borre and Fabricius, 1998, *Sedimentology* 45(4), 755-769.
[4] Fantle and DePaolo, 2007, *GCA* 71(10), 2524-2546.