Eocene clumped isotope temperature estimates from Seymour Island Antarctica

P. Douglas[1]*, H. Affek[1] and L. Ivany[2]

[1]Geology and Geophysics, Yale University, New Haven, CT 06511, USA (*correspondence: peter.douglas@yale.edu)
[2]Earth Sciences, Syracuse University, Syracuse, NY 13244, USA

Developing accurate records of high-latitude temperatures during the early Paleogene is critical for understanding meridional temperature gradients and polar amplification of climate change in greenhouse climates. To date there are few Eocene temperature records from the Antarctic margin. Oxygen isotope measurements ($\delta^{18}O$) of bivalve shells from the La Meseta Formation of Seymour Island, offshore of the Antarctic Peninsula, provide an estimate of coastal Antarctic sea surface temperatures, but are dependent upon assumptions of seawater $\delta^{18}O$, which is poorly constrained and could be variable in this coastal setting [1]. In order to reconstruct absolute temperature changes, we measured Δ_{47} values in multiple La Meseta bivalves from six stratigraphic horizons from the early to late Eocene. Our measurements indicate a 7°C decrease in Seymour Island sea-surface temperatures between 54 and 36 million years ago, with early Eocene temperatures of approximately 21°C and late Eocene temperatures of approximately 14°C. An inter-laboratory clumped isotopes calibration effort is currently underway and will serve to refine the absolute temperature values, but preliminary results imply changes will be minimal. The decrease in coastal temperatures is consistent with trends seen in benthic foraminifera $\delta^{18}O$ records [2], although the Seymour Island bivalve temperatures are significantly warmer than estimated ice-free deep-sea temperatures. These results confirm large-scale cooling of Antarctic coastal waters through the Eocene.

[1] Ivany et al. (2008) GSA Bull. 120, 659–678. [2] Zachos et al. (2008) Nature 451, 279–283.

Extending BCF theory through nanoscale insights: Kink-limited kinetics of calcite growth and inhibition

P.M. Dove[1]* and J.J. De Yoreo[2]

[1]Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061, USA (*correspondence: dove@vt.edu)
[2]Molecular Foundry, Lawrence Livermore National Laboratory, Berkeley, CA 94720 USA

Studies of crystal growth in biological and inorganic systems widely use the theoretical model of Burton, Cabrera, Frank (BCF) to interpret rates and impurity signatures. A fundamental assumption of BCF theory is that step edges present a large reservoir of kink sites to aqueous solution for attachment and detachment of growth units. That is, step edges are roughened by strong thermal fluctuations to produce an abundance of kinks for attachment of growth units (A). Consequently, steps and solution are equilibrated and described by the thermodynamic Gibbs-Thomson Law. High-resolution *in situ* AFM studies and kinetic Monte Carlo simulations of step-edge structure and dynamics show this physical picture to be invalid for calcite, an important earth material, whose steps exhibit low kink density and weak step edge fluctuations (B). Interactions of impurities with calcite step edges cannot be interpreted with traditional *thermodynamic* models based on minimization of the Gibbs free energy. Instead impurity-step interactions follow a different mechanism determined by the *kinetics* of attachment and detachment. Step advance is unimpeded when the creation of new kinks by attachment of growth units to steps outpace binding of impurities to newly created kinks.
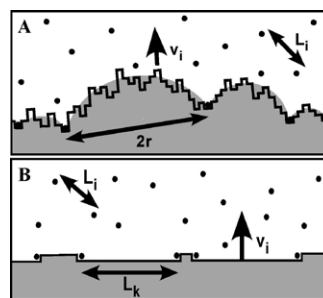
The kink-limited model offers a plausible mechanism-based explanation for reports of 'kinetic disequilibrium' of trace elements measured in some calcites. Because kink densities are tied to solubility, the findings cast doubt on the applicability of the BCF picture to many sparingly soluble crystalline phases and calls for a theory based on weak fluctuations to interpret growth of many common minerals that are stable in the biosphere.