

Climate during the last glacial cycle in the Pyrenees inferred from ^{10}Be dating and paleoglacier modeling

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Extracting quantitative, temporally referenced, paleoclimatic information from glacial geomorphic features is often limited by 1) the poorly dated glacial records commonly available and 2) a lack of constraints on the relative roles of precipitation and temperature in producing a given glacier extent. ^{10}Be surface exposure dating of glacial features addresses the first problem in the Noguera Ribagorçana valley (South-Central Pyrenees) [1] and allows us to correlate the glacial record with other paleoclimate proxies around the Pyrenees. To address the second problem, we explored use of the Plummer & Phillips 2D numerical model [2] as a means of constraining paleoclimatic conditions by the inverse approach. Model results matching Last Glacial Maximum (LGM) and Greenland Stadial 1 (GS-1) moraines, combined with information from other proxies appear to provide further constraints on likely paleoclimatic conditions (fig. 1).

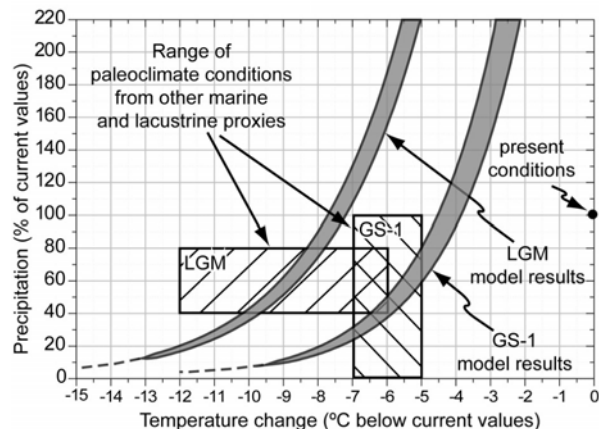


Figure 1: Paleoclimatic conditions of the Pyrenees during the last glacial cycle deduced from inverse modeling (grey areas).

[1] Pallàs *et al.* (2006) *Quaternary Science Reviews* **25**, 2937-2963. [2] Plummer & Phillips (2003) *Quaternary Science Reviews* **22**, 1389-1406.

The realtime kinetics and mechanisms of the amorphous to crystalline CaCO_3 transformation

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Amorphous CaCO_3 (ACC) is an unstable precursor to crystalline CaCO_3 phases –vaterite (V), calcite (Cc) and aragonite (A) [1]. ACC precipitates instantaneously in highly supersaturated CaCO_3 aqueous solutions and then rapidly transforms (e.g., < 3 min at 25°C [1]) to V, Cc or A. The fast kinetics of the reaction represents a significant challenge when quantifying the nucleation, growth and transformation of ACC. We have used *in situ*, time resolved synchrotron-based X-ray diffraction combined with high-resolution imaging to characterise the homogeneous nucleation and growth of ACC and its transformation to V and Cc under a variety of environmentally relevant conditions. Experiments were conducted at 1 to 25°C by fast and controlled mixing of equimolar $\text{Ca}^{2+}:\text{Mg}^{2+}$ (1:0 to 1:9) and CO_3^{2-} aqueous solutions. The reactions were characterised using Energy Dispersive X-Ray Diffraction (ED-XRD) and Small and Wide Angle Scattering (SAXS/WAXS) with patterns collected every 15 sec.

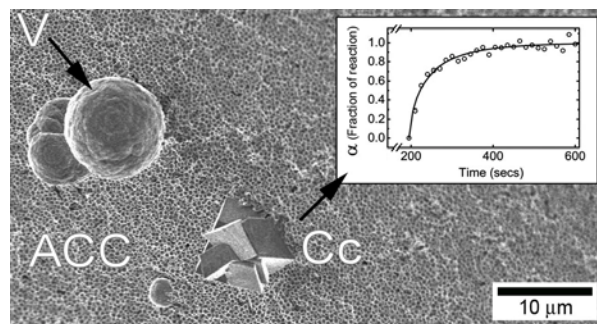


Figure 1: Photomicrograph of V and Cc crystals in ACC matrix (~ 50 nm ϕ spheres in the background). Inset: Degree of reaction (α) determined from EDXRD for the crystallisation of Cc from ACC at ~ 15°C.

The results show that although the ACC to Cc transformation is fast (< 400 sec at ~ 15 °C, inset above), a highly quantitative evaluation of kinetic rates, mechanisms and activation energies at sub-minute time scales is achievable.

[1] Ogino *et al.* (1987) *Geochim. Cosmochim. Acta* **51**, 2757-2767.