

Method development and validation for B isolation from Roman glass

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The provenancing of the raw materials used in Roman glass production is of great interest in archaeological sciences as the corresponding information can give more insight into the trade routes in ancient times and the glass manufacturing process. Glass is made from sand as silica source and natron as a flux. The major source of this flux is thought to be the evaporites from the Wadi Natrun region in Egypt. This assumption is mainly based on the writing of Pliny the Elder, a Roman author, and some geochemical evidence [1]. However, Pliny also mentions other sources [2]. But until now, no unambiguous evidence exists for the exploitation of other natron sources for glass production in the Roman empire. The isotopic composition of B, determined by means of multi-collector ICP-MS (MC-ICP-MS), might provide this valuable information as B is introduced into the glass with the flux and different flux sources (i.e. lakes) can have different B isotopic signatures. Therefore, a method for isolation of B from archaeological glass was developed and validated. After sample dissolution, B is isolated via a two-step separation process, based on the use of a strong cation and an anion exchange resin. Only Sb (which is used as decolorizer or opacifier) was not completely separated from B, but its presence did not exert a significant influence on the $\delta^{11}\text{B}$ determination. The sample preparation method and some first sample results will be presented.

[1] Shortland *et al.* (2006), *Journal of Archaeological Science* 33, 521-530. [2] Dotsika, E. (2009) *Journal of Geochemical Exploration* 103, 133-143

Classical vs. non-classical pathways of crystallization

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Recent investigations on diverse mineral systems suggest formation begins with pre-nucleation clusters and proceeds by particle-mediated growth processes involving amorphous or disordered precursors, with the primary nanoparticles often found to be co-aligned in the final crystal. Little is known, however, about the energetics of pre-nucleation clusters, the role of mineral interfaces in altering formation pathways, or the mechanism by which co-alignment of primary particles occurs. Here we analyze the impact of pre-nucleation clusters on predictions of classical nucleation theory (CNT) and report results of novel *in situ* TEM, AFM and optical investigations of both the early stages of CaCO_3 and Ca-phosphate nucleation and post-nucleation oriented aggregation of ferrihydrite nanoparticles.

Our analyses show the classical barrier to homogeneous calcite nucleation is prohibitive even at concentrations approaching the ACC solubility limit [1]. Introducing a population of metastable clusters can dramatically reduce the barrier, but clusters stable with respect to the free ions will increase it. To explore the impact of surfaces on barriers, we examined calcite nucleation on alkane thiol SAMs and found it to be described well by CNT through a reduction in the barrier due to decreased interfacial free energy, which we found scales linearly with SAM-crystal binding free energies, as expected classically. In contrast, AFM data in the Ca-phosphate system [2] shows the amorphous precursor phase forms at supersaturations too low to be sensible within CNT.

To follow initial growth after nucleation, we investigated the interactions between ferrihydrite nanoparticles using high-resolution fluid cell TEM [3]. The particles undergo continuous rotation and interaction until they find a perfect lattice match. A sudden "jump to contact" then occurs over $< 1\text{nm}$, followed by lateral ion-by-ion addition at the contact point. We show that direction-specific interactions drive oriented attachment and likely result from electrostatic forces.

[1] Hu *et al.* (2012), *Faraday Disc.* **159**, 509-523.

[2] Habraken *et al.* (2013) *Nature Comm.* **4**, 1507.

[3] Li *et al.* (2005), *Science* **306**, 1014-1018.