

## Non-classical nucleation of minerals and the multiple roles of additives

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Recent reports have demonstrated the existence of stable clusters of calcium carbonate (CaCO<sub>3</sub>) prior to nucleation through various experimental methods and also computer simulations [1, 2, 3, 4]. In contrast to classical notions, it appears cluster aggregation, not the assembly of their constituent ions, plays the significant role in nucleation of amorphous calcium carbonate (ACC), which later transforms into crystalline polymorphs.

This multi-stage process can be influenced by additives in several ways, which is of particular interest for biomineralization, as various additives, *e.g.* proteins, polysaccharides, and inorganic salts, are present throughout the nucleation processes. Though many systems have been investigated [5, 6, 7], the exact roles of additives are yet unknown, especially when it comes to mechanistic insights.

In the current contribution, we summarize the concept of non-classical nucleation of CaCO<sub>3</sub> by means of pre-nucleation clusters and recent advancements, including other mineral systems. Moreover, through potentiometric titration assays in the presence of additives, we exemplify the role of additives from simple salts to complex proteins on the early stages of precipitation, *e.g.* pre-nucleation cluster stability, time of nucleation, solubilities of the subsequently-formed phases, and on further phase transformations to the various crystalline polymorphs. Beyond insight into the fundamentals of biomineralization, understanding of the effect of additives on crystallization is also crucial in the creation of biomimetic materials and the formulation of novel anti-scalant methods of industrial importance.

[1] Gebauer, *et al.* (2008), *Science* **322**, 1819-1822. [2] Gebauer & Cölfen (2011), *Nano Today* **6**, 564-584. [3] Demichelis *et al.* (2011), *Nat. Commun.* **2**, 590. [4] Pouget *et al.* (2009), *Science* **323**, 1455-1458. [5] Gebauer *et al.* (2009) *Adv. Mater.* **21**, 435-439. [6] Gebauer *et al.* (2011) *Phys. Chem. Chem. Phys.* **13**, 16811-16820. [7] Picker *et al.* (2012) *Z. Kristallogr.* **227**, 744-757.

## 3D visualisation of core formation in deforming planetesimals

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Deformation may significantly enhance permeability of small fractions of metallic melt in a solid silicate [1]. This is an important factor in constraining processes of core formation, as a permeable network in solid silicate could have led to segregation of a core and mantle much earlier than previously thought, importantly long before the onset of a molten silicate 'Magma Ocean'. Few experiments examine effects of low strain-rate deformation at realistic conditions of core formation in small planetary bodies. In addition, 3D melt geometry and permeability is usually inferred indirectly from 2D textural analysis of polished sample slices.

We have conducted experiments on a synthetic solid olivine – liquid FeS system at extreme P-T conditions using the rotational Paris-Edinburgh Cell (roPEC), and have analysed 3D melt geometry of quenched samples have using micro- and nano-tomographic imaging techniques. Deformation at strain rates as low as 10<sup>-6</sup> s<sup>-1</sup> aids grain boundary wetting and the formation of melt veins that appear to locally 'drain' certain areas of the sample. Results support theories of complex, multi-stage core formation in which pre-differentiated planetary bodies collided to form the Earth. These proto-cores may have sunk directly to the Earth's centre without re-equilibration with the Earth's mantle, which has major implications for the inferred geochemical composition of the lower mantle [2].

[1] Rushmer, Petford, Humayun, & Campbell (2005) *Earth and Planetary Science Letters* **239**, 185-202. [2] Rudge, Kleine & Bourbon *Nature Geosci* **3**, 439-443 (2010)