

## On the mechanisms of nucleation pathways in aqueous solutions

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In recent years, detailed studies of the early stages of mineral formation have challenged the notions of classical nucleation theory (CNT). This has led to the development of new concepts, including the so-called pre-nucleation cluster (PNC) pathway [1]. While it is classically assumed that ion-by-ion growth of un- and metastable species is central to nucleation events, phase separation via PNCs is based on the aggregation of larger nanoscopic entities. This process initially yields amorphous nanoparticles, and represents a pathway, which has been studied in the most abundant biomineral, calcium carbonate, in particular.

In this contribution, we will present the newest developments in this field, which allow delineating a unifying mechanism of phase separation via “non-classical” nucleation. This includes the quantification of the driving force for PNC formation, and the localization of relevant metastable areas in the phase diagrams, but also the demonstration that the effects of common mineralization modifiers such as antiscalants can be understood within this framework in a straightforward manner, as opposed to CNT [2].

Seizing the opportunity to comment on recent prominent claims that classical models would provide accurate and sufficient speciations of aqueous systems, we demonstrate that a better understanding of the mechanism of phase separation via PNCs can enable us to eventually predict, control and tailor mineralization processes in technological applications. On the other hand, the crucial role of the solvent, water, during phase separation via PNCs, which is typically neglected within the notions of CNT, suggests that the concepts of “non-classical” nucleation may be relevant for a better understanding of a wide range of important geochemical processes.

[1] Gebauer, Kellermeier, Gale, Bergström, & Cölfen (2014) *Chem. Soc. Rev.* **43**, 2348–2371. [2] Sebastiani, Wolf, Born, Luong, Cölfen, Gebauer & Havenith (2016) *Angew. Chem. Int. Ed.* **56**, 490–495.