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From solutes to solids: towards a supramolecular view on mineralization processes

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The formation of a solid-state material from solution is a ubiquitous process of fundamental importance not only for synthesis in solid-state chemistry but for a wide range of disciplines such as geosciences and biology. However, established classical crystallization theories fall short in explaining the outcome of crystallization and mineralization processes in complex environments, such as in biomineralizing organisms or geochemical and industrial settings. The misfit between classical textbook knowledge and the plurality of conflicting experimental evidence facilitated the advent of an array of new crystallization concepts. These so-called nonclassical crystallization processes are fuelled by the attachment of multiatomic assemblies rather than by attachment of single ions drive crystal formation. Some of these models, such as oriented attachment, were unequivocally backed by experimental evidence and thus accepted by the science community. Other models have encountered distinct resistance from peers. At the centre of this intense dispute, we find the calcium carbonate system, which is of crucial importance for a range of disciplines. For this system, in particular, the existence of prenucleation clusters in the form of dynamically ordered liquid-like polyoxoanions (DOLLOP) has been suggested, and it has been claimed that nonclassical nucleation processes take place. However several groups have challenged this claim, claiming an entirely classical crystallization behaviour

Based on our results, we will draw a different picture of calcium carbonate formation. We show that the issues with this very systems root in its solute chemistry and the fact that this renders a calcium carbonate solution into a multicomponent system. We show liquid-liquid phase separation of near-neutral calcium carbonate solutions along with the first ultrastructural model of amorphous calcium carbonate (ACC). This findings give insight into the formation mechanisms of calcium carbonate under kinetically controlled conditions. Our findings further demonstrate that the formation of a liquid-condensed mineral precursor phase is not solely a “quirk of the peculiar calcium carbonate system” but a general phenomenon: it is an early stage precursor in the formation pathway of calcium carbonate under geo- and biochemical relevant conditions. Moreover, we show that this unexpected demixing behaviour is widespread, many inorganic components go through spinodal decomposition, when the reaction conditions are kinetically controlled and the solution chemistry disadvantage burst nucleation. Our data suggest that it is not the misconception and oversimplification of classical theories but our oversimplification of the solution chemistry which causes the current dispute on classical vs nonclassical nucleation of inorganic compounds. Currently, we see no need for invoking “non-classical” notions of nucleation

since our exceptional observations can entirely be explained by established physicochemical concepts apart from CNT. Our results raise the awareness that a supramolecular solution and coordination chemistry provides the key to a thorough understanding of the genesis of inorganic solids under kinetically controlled conditions.