Towards an understanding of the non-classical nucleation of $CaCO_3$

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Introduction

Nucleation of calcium carbonate from aqueous solution can proceed via an alternative pathway that involves stable pre-nucleation clusters [1] and results in the initial precipitation of amorphous calcium carbonate (ACC) nanoparticles, which may subsequently transform into crystalline species. This pathway is referred to as "non-classical nucleation", because it challenges the major concepts and assumptions made by classical nucleation theories [2]. Additive-free ACC formed in this manner exhibits distinct short-range structural features, which (depending on pH) can relate to the long-range order of different crystalline $CaCO_3$ polymorphs [3]. The presence of such proto-structures in ACC is well-known from biogenic, though additive-containing specimens [4], and may be the clue to a novel understanding of polymorph selection and control.

The atomistic background underlying non-classical nucleation of calcium carbonate should thus offer an explanation for at least three major experimental observations; (i) the thermodynamic stability of pre-nucleation clusters, (ii) the existence of a distinct barrier for nucleation separating solution (pre-nucleation) and solution/solid (post-nucleation) states, and (iii) the possibility of different structures in precipitated ACC.

Results and Conclusions

The non-classical pre-nucleation behavior of calcium carbonate can be rationalized by means of results obtained from computer simulation in combination with re-evaluations of experimental data [5], which show that stable pre-nucleation clusters are highly dynamic, liquid- and chain-like structures of $CaCO_3$ ion pairs. Various experimental observations [6–9] are put into context with this theoretical speciation, eventually allowing for speculations about what happens at the point of nucleation.

It appears that solid calcium carbonate can only be nucleated from homogeneous solutions if pre-nucleation clusters aggregate and coalesce to build larger entities above ca. 20 nm in size [8]. In turn, these considerations suggest that the classical pathway via ion-by-ion growth of un- and metastable nuclei may indeed be blocked under the conditions that have been investigated so far. Finally, implications of these findings for additive-controlled crystallization of calcium carbonate are outlined.

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Eruption and crystallization ages for Breccia Museo plutonic ejecta

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The Campi Flegrei volcanic district (Naples region, Italy) is a 12 km wide, restless caldera system that has erupted at least six voluminous ignimbrites throughout the late Pleistocene, including the >300 km^3 Campanian Ignimbrite (CI), originated by the largest known volcanic event of the Mediterranean region. One of these deposits, the Breccia Museo (BM), a petrologically heterogeneous and stratigraphically complex volcanic deposit extending over 200 km^2 in close proximity to Campi Flegrei [1], has long remained contentious regarding its age and stratigraphic relation to the CI. Here, we present crystallization and eruption ages for BM plutonic ejecta clasts that were determined via uranium decay series and (U-Th)/He dating of zircon, respectively. Plutonic clasts were examined by scanning electron microscopy, and zircon crystals were extracted for geochronologic analysis. Despite mineralogical and textural heterogeneity of these syenitic clasts, their U-Th zircon crystallization ages are indistinguishable with an average age of 49.2±3.0 ka (2σ errors; mean square of weighted deviates MSWD = 1.2; n = 34). Disequilibrium-corrected (U-Th)/He zircon ages for three plutonic clasts average 42.2±2.6 ka; MSWD = 0.7; n = 10). One exception is a single clast where zircon crystals yielded older (U-Th)/He ages of 50.6±3.9 ka (MSWD = 1.6, n = 6) that overlap with the U-Th zircon crystallization ages. The limited range in U-Th zircon ages indicates rapid crystallization within the plutonic margins of the pre-CI magma system. For most clasts, the limited range of (U-Th)/He ages suggests complete resetting during the eruption, or lack of pre-eruptive ^{4}He accumulation due to high ambient temperatures. Only in one instance we suspect that the explosive eruption that ejected the BM plutonic clasts may not have heated zircon sufficiently to completely degas pre-eruptive ^{4}He. There, the close overlap between crystallization and (U-Th)/He ages would imply very rapid cooling within the shallow intrusive complex. Our (U-Th)/He zircon eruption age overlaps with published $^{40}Ar/^{39}Ar$ sanidine ages for BM which, however, display considerable variation (i.e., plateau ages ranging between 34.2 and 41.0 ka; [1]). It is marginally older than the commonly cited $^{40}Ar/^{39}Ar$ CI eruption age (39.5±0.1 ka; [2]), but significantly pre-dates published ^{14}C ages for BM (17.9 ka [3]) and CI (between 42 and 27 ka reported in [4]). These results underscore the potential of combined U-Th and (U-Th)/He zircon geochronology for high-accuracy chronostratigraphy, and reconstruction of the thermal history of the magmatic feeder systems of supereruptions.

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