American Mineralogist, Volume 107, pages 1369–1377, 2022

Inclusions in calcite phantom crystals suggest role of clay minerals in dolomite formation

Stefan Farsang[1,*], Péter Pekker[2], Giulio I. Lampronti[1], Zsombor Molnár[2], Rastislav Milovský[3], Mihály Pósfai[2], Daniel Ozdín[4], Timothy D. Raub[5], and Simon A.T. Redfern[6,†]

[1]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
[2]Research Institute of Biomolecular and Chemical Engineering, University of Pannonia, 8200 Veszprém, Egyetem u. 10, Hungary
[3]Earth Science Institute, Slovak Academy of Sciences, Ďumbierska 1, 974 11 Banská Bystrica, Slovak Republic
[4]Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
[5]School of Earth & Environmental Sciences, University of St Andrews, Irvine Building, St Andrews, KY16 9AL, U.K.
[6]Asian School of the Environment, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

Abstract

Micro- and nano-inclusions embedded in calcite phantom crystals from Gemerská Ves, Slovak Republic, have been characterized by a combination of Raman spectroscopy, scanning and transmission electron microscopy, X-ray powder diffraction, and C and O isotope analysis. Whereas the outer, colorless part of the phantom crystal is relatively homogeneous and cavity and inclusion-free, the inner terracotta-colored part contains abundant cavities, dolomite, hematite, goethite, titanite, phyllosilicates (mainly kaolinite and illite), and apatite inclusions and nanostructures that have formed on the walls of cavities. The nanostructures comprise hematite and goethite particles sandwiched between either two phyllosilicate crystals or a phyllosilicate and a carbonate (calcite or dolomite) crystal. Our observations suggest that all inclusions in the terracotta calcite originate from the terra rossa (a common soil type in karstic areas) and limestone outcropping adjacent to the calcite crystals. While the micrometer-sized phyllosilicate and hematite particles were likely transported from the terra rossa and attached to the surface of growing calcite, the presence of phyllosilicates that are only a few atomic layers thick and of euhedral hematite, goethite, and dolomite crystals suggests that these particles precipitated along with the phantom calcite in situ, from an aqueous solution carrying terra rossa-derived and limestone-derived solutes. The compositional differences between the terra rossa (e.g., smectite as the only major Mg-rich phase) and terracotta calcite inclusions (e.g., dolomite as the only major Mg-rich phase and the presence of only Mg-free clays) hint that a smectite-illite conversion provides the Mg necessary for the precipitation of dolomite and possibly the Fe associated with the iron oxyhydroxide nanostructures. Phyllosilicate nucleation on calcite and dolomite nucleation on phyllosilicates, as inferred from nanoscale mineralogical associations, suggest that carbonates and phyllosilicates may mutually enhance nucleation and growth. This enhancement may result in the formation of large-scale clay-carbonate successions in aqueous settings, including the enigmatic, pink-colored cap dolostones succeeding late Neoproterozoic "Snowball Earth" deposits. The distribution of inclusions in the terracotta calcite and the preferred nucleation of hematite and goethite on phyllosilicate, rather than on carbonate surfaces, indicates that phyllosilicates have a potential to not only disrupt crystal growth and trigger the formation of cavities in the structure of the calcite host, but also to provide surfaces for the precipitation of different phases in the cavities and to uniformly distribute otherwise incompatible materials in a calcite host crystal. This calls for further exploration of the potential application of phyllosilicates in composite structure development.

Keywords: Calcite, cap carbonate, clay, dolomite, hematite, goethite, illite, kaolinite, nanoparticle, nucleation, phantom crystal, phyllosilicate, Raman spectroscopy, SEM, Snowball Earth, TEM, XRD