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# A new nanocrystalline $CaCO_3$ polymorph, a key player for the formation of metastable aragonite

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Aragonite is a wide-spread crystalline form of $CaCO_3$ on the Earth surface. Although calcite is the thermodynamically stable $CaCO_3$ form at ambient conditions, aragonite precipitates in the ocean and in some continental settings. It is a common biomineral in shells of various organisms. Despite decades of research it is still unclear why metastable aragonite is so abundant. Here, we show an unexpected discovery from a mountain cave (Obstanser Eishöhle, Austria), which sheds light on this long-standing question. Using the state-of-the-art 3D electron diffraction tomography, we identified a new nanocrystalline $CaCO_3$, which precipitates prior to aragonite in Mg-rich environments, i.e. at conditions, where aragonite abundantly forms. The new phase, which we term monoclinic aragonite (mAra), is crystallographically related to ordinary, orthorhombic aragonite. The new results suggest that mAra is the precursor of metastable aragonite and forms by incorporating Mg atoms and hydroxyl groups into its crystal structure. The features diagnostic of mAra are not restricted to this alpine cave but have previously been reported from biogenic aragonite in stromatolites, from molluscs, and from cyanobacteria, as well as from synthetic materials. Therefore, we propose that mAra is a widespread crystalline $CaCO_3$ that plays a key role in metastable aragonite formation.