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Amorphous silica ordering on the level of colloidal and atomic dimensions

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Amorphous silica precipitation and mineralogical maturation play a key role in virtually all surface and subsurface environments of the Earth system. However, fundamental knowledge of natural amorphous silica crystallization at the atomic and colloidal scale is limited. To understand the processes that drive the amorphous silica system from a disordered to an ordered state, we investigated vein-filling and replacement silica collected at four opal fields (Andamooka, Coober Pedy, Mintabie, Yowah) from chemically weathered sedimentary rocks of the Great Artesian Basin (central Australia). Using a combination of electron microscopy, nanotomography, electron probe microanalysis, and X-ray microdiffraction, we characterized precisely the structural state and chemical composition of the inorganically precipitated amorphous silica. We found that twinned, silica-replaced calcite crystals (<2 mm) are composed of close-packed, ordered arrays of uniform silica spheres 270-400 nm in diameter. Silica sphere arrays in periodically changing orientations perfectly replicate polysynthetic twin lamellae and cleavage planes of calcite. Electron microscopy and nanotomography show that lamellae are preserved through cubic closed-packed (fcc) sphere arrangements. We conclude in a novel model that the ordered sphere lattice forms by continuous nanoparticle nucleation close to the carbonate dissolution front, particle aggregation, and subsequent layer-by-layer deposition of fcc (111) lattice planes. This face-specific replacement process proceeds via a nanoparticle-based, nonclassical crystallization route.

At the atomic scale, X-ray microdiffraction ($\sim$50 μm spot size), heating experiments, and calculated diffractograms show that during early-stage diagenesis metastable opal-A transforms into more crystalline opaline material via nanoscale in situ nucleation and growth of low-tridymite/cristobalite domains in an amorphous matrix. This process is decoupled from opal chemical and micromorphological properties. We identified a positive and almost linear correlation between peak shapes and positions in X-ray diffraction patterns toward more crystalline opal phases. Our results show that the mineralogical early-stage transformation of opal-A is a gradual process traceable by systematic peak shifts and symmetry variations. Using X-ray diffraction pattern asymmetry offers a simple approach to quantify the early-stage diagenesis of opal-A with a widely available analytical method.