



Interface-coupled dissolution-precipitation processes allow a photonic crystal to replace an ionic crystal along lattice planes

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Nanocolloidal amorphous silica ($\text{SiO}_2 \times n\text{H}_2\text{O}$) is a major component of environmental aqueous solutions and surface coatings on rocks or mineral grains. Detailed knowledge of amorphous silica formation is indispensable for a better understanding of silicate rock alteration and diagenetic processes. We analyzed a wide range of samples from the Australian precious opal fields in South Australia and Queensland using petrographic microscopy, XRPD, SEM, and EPMA to characterize opaline silica, the mineral assemblage, and the host rock. Over the past 90 Ma the Lower Cretaceous lithologies of central Australia have undergone a weathering regime ranging from sub-tropical to arid, in which pH fluctuated from alkaline to acidic. The prolonged chemical alteration of sedimentary rocks derived from andesitic volcanoclastics and organic matter liberated large volumes of silica into solution, eventually leading to precipitation of nanocolloidal amorphous silica and formation of opal-A. A regular arrangement of close-packed uniform (monodisperse) spheres permits diffraction of white light and gives rise to the famous play-of-color.

The opals in this study consist of silica spheres with an average diameter of 100-320 nm and often show a prominent core-shell structure. Two groups are separated by their relative standard deviation (RSD): monodisperse spheres ($\text{RSD} < 6\%$) and polydisperse spheres ($\text{RSD} > 10\%$). Monodisperse and polydisperse spheres are separated by their Na/K ratio, restricting the appearance of monodisperse spheres to values < 1.2 and polydisperse spheres to values > 3.0 . We suggest that the Na/K ratio represents significant differences in the overall solution characteristics. The associated minerals (e.g., alunite, gypsum, kaolinite, K feldspar) indicate large variations of fluid composition and pH. Probably, uniform spheres grew at acidic pH, with repulsive forces large enough to arrange them in an ordered array prior to the evaporation of interstitial fluids.

The investigation of fossil shells replaced by opal-A reveals clues for the understanding of structural and chemical reorganization mechanisms behind silica pseudomorphism. Fundamental knowledge about the highly selective replacement process is absent so far, impeding an adequate interpretation of the observations. The replacement of calcitic shells by amorphous silica spheres (~ 300 nm in size) is a unique example for the transformation of an ionic to a photonic crystal accompanied by a large size contrast of ions and spheres, respectively, but preserving lattice planes. The observed replication of polysynthetic twinning and cleavage planes of calcite by opal-A spheres indicates that silicification occurs via dissolution of shell material and immediate precipitation of amorphous silica. This follows the interface-coupled dissolution-precipitation mechanism model (Putnis and Putnis, 2007), but requires some modification to allow for open space necessary to form spheres in the 100s-nm size range with a core-shell structure. While sphere growth by a gravitational ordering process is implausible, we assume that the ordered array of monodisperse spheres forms via layer-by-layer deposition.

References: Putnis A. and Putnis C.V. (2007), *J. Solid State Chem.*, 180, 1783-1786