

Crystallization kinetics of apatite nanocrystals from amorphous calcium phosphate in water by *in situ* synchrotron powder diffraction

H. BIRKEDAL^{1*}, H. LEEMREIZE¹ AND C. J. S. IBSEN¹

¹INANO & Department of Chemistry, Aarhus University, Aarhus 8000, Denmark
(*correspondence: hbirkedal@chem.au.dk)

Crystallization of minerals from amorphous precursor phases is emerging as a major pathway for crystallization in several systems but remains poorly understood. Here we use *in situ* X-ray diffraction to study the crystallization kinetics of nanocrystalline apatite from amorphous calcium phosphate in water. We find a striking dependence of crystallization behavior on whether K⁺ or Na⁺ is used as counter ion.

In situ X-ray diffraction experiments were performed with ~10 s time resolution [1, 2, 3]. The data were analyzed by Rietveld refinement procedures determining the nanocrystal size, the amount of crystalline material present, the lattice constants, and the background [1, 2]. The amorphous precursor phase was clearly observed in the first time points [2] and was gradually replaced by the nanocrystal diffraction pattern of the forming apatite phase.

The crystals were found to be formed as almost spherical crystallites that soon after formation started growing preferentially in the *c*-axis direction of the hexagonal apatite crystals giving needle-shaped nanocrystals. This rapid anisotropic growth was followed by an Ostwald ripening stage, with slower crystallite size growth rates. During this stage, growth was preferentially perpendicular to the *c*-axis slightly lowering the shape anisotropy.

Using K⁺ instead of Na⁺ as counter ion resulted in drastic changes in growth kinetics. Sodium allows the incorporation of dissolved carbonate into the forming apatite while potassium does not. This difference led to more rapid crystallization for sodium as a counter ion and resulted in crystallites with different sizes and size anisotropies.

The present work provides detailed insights into how anisotropic crystal morphologies develop and shows that seemingly innocent changes in environment, such as choice of counter ions may have profound impacts on crystallization behavior.

[1] Ibsen & Birkedal (2010) *Nanoscale* **2**, 2478-2486. [2] Ibsen & Birkedal (2012) *J. Appl. Cryst.* **45**, 976-981. [3] Jensen *et al.* (2010) *Chem. Mater.* **22**, 6044-6055.

Origin of porphyries related to Cu-Mo mineralization, California-Vetas district, Colombia

THOMAS BISSIG^{*1}, LUIS C. MANTILLA²
AND CRAIG J.R. HART¹

¹Mineral Deposit Research Unit, University of BC, Vancouver, Canada.

(*correspondence: tbissig@eos.ubc.ca)

²Universidad Industrial de Santander, Bucaramanga, Colombia.

Porphyry Mo- Cu mineralization in the California-Vetas district, Eastern Cordillera, Colombia is coeval with 10.9 - 8.4 Ma granodiorite porphyry stocks and overprinted by epithermal Au-Ag mineralization. Mineralization is hosted by Grenvillian-aged paragneisses (Bucaramanga Gneiss) and Late Triassic to Early Jurassic peraluminous granites with > 70% SiO₂ and metaluminous diorites with SiO₂ 54.9 - 60.4 wt%. Late Miocene rocks are weakly peraluminous granodiorite porphyries with SiO₂ 61- 67%, sharing some characteristics with adakite-like rocks widely associated with porphyry mineralization elsewhere in the Andes. Although Miocene rocks do not have low Y (<15 ppm) or depleted HREE, they have high Ba (930-1500 ppm), high Ba/La (28 to 50), high Sr (850 to 1100 ppm), high Sr/Y (50-78) only minor Eu anomalies and depleted MREE compared to the Mesozoic granites (400-700 ppm Ba; Ba/La 14-25; 80-150 ppm Sr; Sr/Y 2.5-14), and diorites (900 -1200 ppm Ba; Ba/La 20-32; 610-750 ppm Sr; Sr/Y 22-25). Their initial ⁸⁷Sr/⁸⁶Sr ratios of 0.7052-0.7066 are significantly less radiogenic than those of the Mesozoic diorites (0.70712-0.7072), granites (0.7094-0.710) and the paragneiss (0.7144-0.7332, @ 199 Ma). Miocene granodiorite porphyries represent water-rich subduction related melts. Their initial ⁸⁷Sr/⁸⁶Sr is less radiogenic than Neogene Caribbean sediments, precluding a sedimentary source for the high Sr and Ba. Instead, a fluid source from serpentinized lithospheric mantle, fluxing the overlying subducted oceanic crust and mantle wedge is suggested. The geochemical signal may have been enhanced by the overlapping subducting Nazca and proto-Caribbean slabs at depth.