

The role and effect of boron during the crystallization of CaCO₃

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Boron (B) is a crucial element in carbonate biominerals and its isotopic signature is used as a paleo-acidity proxy and to reconstruct atmospheric CO₂ levels through time [1, 2]. Most studies however, focused on compositional or isotopic analyses of natural marine carbonates, but the mechanisms of boron incorporation or the role and effect that [B]_{aq} plays during the nucleation and growth of the various calcium carbonate polymorphs is still unknown. Therefore the aim of this research was to quantitatively assess the crystallization pathways of CaCO₃ polymorph in the presence of [B]_{aq} and to mimic B/Ca ratios in modern seawater.

The experiments were performed at 10-30°C in stirred reactors by mixing equimolar solutions of CaCl₂ and Na₂CO₃ doped with 0-25mM of [B]_{aq}. Reactions were followed for between ten minutes and eight hours, while simultaneously recording changes in pH as a direct proxy for the crystallization reactions. At regular time intervals solid and solution aliquots were collected and characterized by XRD, SEM, FTIR or wet-chemical analysis.

The results show that in the presence of [B]_{aq} the initial amorphous calcium carbonate (ACC) remained stable for up to 5 minutes, while at equivalent conditions with no [B]_{aq} the transformation to vaterite begins after ~1 minute [4]. However, after the full ACC breakdown, the crystallization pathways vary dramatically as a function of temperature and [B]_{aq} concentration compared to the pure system [2]. For example, at 30°C and 10mM [B]_{aq}, the ACC to calcite transformation via vaterite was ~ 25% faster compared to the pure system. Furthermore, when 25mM of [B]_{aq} were added, the initial ACC transformed directly to calcite in less than 10 minutes with no vaterite intermediate. Overall our experiments revealed that the effect of temperature was inverse to that of the B/Ca ratio in solution. The effects were also reflected in the variations in polymorph distribution as a function of time and in the changes in morphologies of the various CaCO₃ polymorphs at the conditions tested.

- [1] Hemming *et al.* (1995) *Geochim Cosmochim Acta* **59**, 371–279. [2] Paris *et al.* (2010) *Geology* **38**, 1035-1038.
[3] Rodriguez-Blanco *et al.* (2011) *Nanoscale* **3**, 265-271.
[4] Bots *et al.* *Min Mag* (this volume)

New characterization of uranium mineralogy in Ukrainian ores

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The economically significant uranium ores of Ukraine form one of the largest uranium ore reserves in Europe. Concentrated in the central Ukrainian shield, these ore bodies (~1, 8 Ga, inferred from U-Pb analyses [1]), are associated with albitites in granites. Carbonates, iron oxides and Ca-Fe garnets are found genetically associated with uranium minerals, while albite and other alkali silicates formed during earlier stage metasomatic processes. Albite has been altered at the margins adjacent to the uranium minerals from low to high albite. We present preliminary work characterizing primary uranium ores in Ukraine, as part of a larger effort to develop a database of nuclear materials for Ukraine.

We have studied uranium minerals from representative samples of the Severinskoje (I), Michurinskoje(II), and Vatutinskoje (III) deposits, as well as from the Adabash fracture zone mineralization (IV), using mineralogy and gamma spectrometry [2]. This study presents new X-ray diffraction (powder and single grains), SEM and TEM characterizations, and microprobe study of the principal U-minerals present:

Uraninite (IV), a₀=0, 542 nm, forming cubic crystals up to 0, 5 mm. Average composition is Na₂O 5, 6%; SiO₂ 0, 8%; CaO 1, 74%; PbO 23%; U₃O₈ 72, 4%. U, Ca, Pb appear to be associated with the host crystal matrix, while Na, Si and trace elements are concentrated in solid inclusions (up to 0, 5 mm). *Coffinite (I, II, III)* forms elongated crystals up to 0, 1 mm. Average composition is Al₂O₃ 0, 9%; SiO₂ 15%; CaO 2, 5%; Fe₂O₃ 1, 4%; U₂O₃ 65%. *Brannerite (II, III)* forms elongated, needle-like crystals up to 0, 1 mm. Average composition is PbO 6, 17%; UO₂ 39, 18%; CaO 3, 15%; SiO₂ 2, 31%; TiO₂ 24, 49%; FeO 2, 08%. This mineral occurs intergrown with an unknown silicate mineral (mixture) with composition ~ (Ca, Pb, U)(Ti, Fe)₂Si₃O₁₁. *Ca-Uraninite (I)* ~CaU₂O₆, is cubic, a₀ = 5, 37 nm. This is possibly a new mineral variety. It forms in thin veins (~20 μm thick) and globules (~1 μm). *Ca-boltwoodite (I)* occurs as thin veins of plate-like crystals up to 20 μm in diameter. The boltwoodite powder XRD pattern suggests a disordered layered structure, possibly representing a new mineral variety. The relative composition is U:Si:(Na+K+Ca_{0,5}) ≈ 1:1:1.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

- [1] Belevtsev *et al.* (1995) *Naukova Dumka*, 396p (in Russian). [2] Valter *et al.* (2007) *Prob. Atom. Sci. Tech.* **5**, 69–75.