Cation substitution in uranyl phosphates of the autunite group: equilibrium relations and crystallization between metatorbernite and metauranocircite

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Abstract: Uranyl phosphate minerals play an important role in the uranium immobilization within weathering and supergene enrichment profiles. This work consists on the morphological, structural and chemical characterization of natural and synthetic minerals of Cu and Ba – metatorbernite and metauranocircite, respectively. SEM imaging has revealed an extended range of morphologies, from tabular to rosette-like crystals, with the presence of epitaXial growths. These studies have also revealed natural heterogeneities affected by cationic substitution along preferred crystallographic directions. The experimental results suggest that the precipitation of metatorbernite is easier than metauranocircite. Simulations of the chemical system show that precipitation depends on supersaturation evolution, which in turn in a function of aqueous complex formation between phosphate and free uranyl ions. An electron probe microanalysis suggests that the failure to precipitate metauranocircite may be due to later ionic depletion of the solution media.

Keywords: uranyl phosphates, uranium, metatorbernite, metauranocircite, supergene environment.

1. Introduction

Uranyl phosphate minerals are major constituents in weathered U deposits and can display a multi-stage evolving history in the environment they crystalize. Their importance is two-fold: as main U-bearing phases in weathering profiles with potential economic value (as in Nisa and Tararabu, where natural uranyl phosphates of Cu and Ba were identified; Pinto et al., 2012; Prazeres, 2011) and as fixing phases of U limiting its long-term, million-year scale, dispersion in the oxidized surface environment. It is thus important to understand the thermodynamic stability of these phases and how they respond to chemical changes of the surrounding environment. Building on previous knowledge on substitution mechanisms and crystallization relations between metatorbernite and metauranocircite (Pinto et al., 2012; Sanchez-Pastor et al., 2013) this work further investigates this relation in order to understand what drives the often late substitution of the Cu-phase by the Ba-phase, and how they compete for crystallization in the same chemical media. Hence, it’s of major importance to consider the general chemical formula of the autunite group (A(UO$_2$)$_2$(XO$_4$)$_3$·10-12H$_2$O with A = Cu, Ca, Ba, or Mg and X = P or As) in order to understand the cationic substitutions mentioned above.

2. Methods

The crystals studied were crystalized in laboratory in a silica-gel medium as described by Sánchez-Pastor et al. (2013). Also, natural metatorbernite crystals from Musonoi Mine, Kolwezi, Katanga (Shaba) Province, Democratic Republic of Congo were immersed in silica gel and left to react with a BaCl$_2$ solution. Crystals were separated and cleaned for imaging and analysis with an Environmental-SEM (HITACHI 3700N) working at 20 kV, a current ranging from 68 to 89 µA, and low vacuum conditions (40 Pa) and equipped with a BRUKER Xflash 5010SDD EDS for qualitative chemical analyses. X-Ray microdiffraction of the crystals used a BRUKER Discovery X-ray diffractometer with a Linxeye linear detector, a 0.3 mm collimator, and a Göbel mirror. Radiation was generated from a Cu-Kα lamp at 40 kV tension and 40 mA current. Scan ranged from 3-75° 2θ, with 0.05° steps, and 2 s readings per step. Crystal
mounts were prepared for electron probe microanalysis (EPMA) and the crystals were analyzed for U, P, Cu, Ba, and Si (because of the gel medium). Astimex standards were used for Si (Diopside), Ba (Benitoite), U (UO$_2$), P (Apatite), and Cu (Cuprite). Analytical conditions used were a beam diameter of 20 μm (reduced to 10μm for the smaller crystals), 9 nA current (10 nA for the smaller crystals), and 15 kV voltage.

The porous silica-gel crystallizing environment was modelled with PHREEQC (Parkhurst and Appelo, 1999) for transport and multicomponent counter-diffusion of cationic and anionic species in the gel, without precipitation. The database used was the phreeqc.dat with data on the solubility of metatorbernite and metauranocircite from Cretaz et al. (2013) and Vochten et al. (1992), respectively. The U speciation was taken from the llnl.dat. U diffusion coefficient was taken from Awakura et al. (1987).

3. Results and Discussion

3.1 Crystal morphologies

Only 3 experiments were described by Sánchez-Pastor et al. (2013) which had a successful outcome, while the rest had crystallization times > 2 years or did not crystallize anything. It was these ones that we used in this study, and their major difference to the set of experiments of Sánchez-Pastor et al. (2013) was that the gel in the horizontal column was reactive (containing a fixed constant concentration of 50 ppm of U) instead of being diffused along with the remaining cations (Cu and/or Ba). Both experiment groups with either Cu or Ba in solution revealed the presence of metatorbernite or metauranocircite, respectively, showing different morphologies and crystal aggregates. However, experiments with Cu and Ba in solution showed only metatorbernite crystals with no direct indication of the presence of a Ba-phase (Fig. 1). This was only detected in some crystals as mixed phases of Cu and Ba with limited Ba incorporation, as observed in SEM and EPMA (see below).

The crystals from Cu-dominated experiments show aggregates with tabular and micaceous habit, with sizes from 5 to 10 μm, also exhibiting macroscopic green colored dendritic morphologies. Crystals from Ba-dominated experiments show rosette-like morphologies, with sizes from 50 μm to more than 500 μm, essentially yellow to brownish-white colored, in macroscopic acicular, capilar or dendritic aggregates. In the Cu and Ba experiments, the crystals show similar morphologies to the previously described for both metatorbernite and metauranocircite ranging from tabular to spheroidal, with sizes from 50 to 100 μm. They form macroscopic aggregates showing dendritic to tabular habits, along crystallization zones, where the abundance and density of small crystals is significant.

3.2 Chemical features of the crystals

The images showing EDS qualitative chemical maps revealed some particular aspects worth emphasizing:

1. Epitaxial crystal growth is a mechanism of precipitation of a Ba-rich phase over metatorbernite (Fig. 2), which is shown by a higher signal of Ba over the topographic highs as opposed to a lower signal elsewhere.

2. Natural metatorbernite crystals showed chemical heterogeneities where a square domain core of metautunite (Ca) is surrounded by metatorbernite (Fig. 3), indicating that the cationic substitution in uranyl-phosphates of the metautunite group affects a wider range of cations and mineral species than previously expected, as it has also been recently confirmed in natural environments (Prazeres et al., submitted).

3. Cation substitutions of both Ca$^{2+}$ and Cu$^{2+}$ for Ba$^{2+}$ in natural samples (Fig. 4). This substitution occurs pervasively along structural discontinuities, essentially through cleavage plans and other crystallographic directions with a clear progression inward the crystal.

Fig. 1. SEM images for the different crystal morphologies: (a) metauranocircite; (b) metatorbernite; (c) to (f) metatorbernite crystals in the Cu and Ba system.

Fig. 1. Imagens de microscópio electrónico de varrimento evidenciando as diferentes morfologias: (a) metauranocircite; (b) metatorbernite; (c) a (f) cristais de metatorbernite em sistemas de Cu e Ba.
EPMA on the synthetic crystals confirm the previous observations on SEM, admitting the existence of mixed crystals (Fig. 5) with a variable proportion of Cu:Ba from 0.13:0.97 to 0.37:0.85. Furthermore, the analyses didn’t reflect an exact 1:1 stoichiometry of U:P, but rather richer in uranium (UO₂²⁺) relative to phosphorous (PO₄³⁻). This can be either the result of cation substitution in the interlayers (Ba²⁺ for Cu²⁺) or the presence of hypothetical vacancies. Nevertheless, Pinto et al. (2012) already observed such stoichiometries in natural metatorbernite-metauranocircite crystals.

3.3 Modelling the chemical system

Geochemical modelling simulations show the distribution, along the tubes, of species concentration and the saturation index (SI) of metatorbernite and metauranocircite. The location of the highest SI should coincide with the highest rates of crystal precipitation and growth in the tubes. While short time simulations (up to 100 h) showed results that were not coherent with experimental observations, extended simulation, up to 1000 h, showed areas of higher growth rates coincident with what is experimentally observed (real experiments lasted more than 2 years, actually).

These longer experimental times (1000 h) gradually stabilize the chemical system into a steady-state in which the system does not evolve but clearly shows the domains where supersaturation conditions are maintained. The rest is the result of the kinetics of crystallization and crystal growth, in which to obtain sizeable crystal dimensions to work with at least 2 years were necessary to grow the uranyl-phosphate crystals. Experiment R2 (with Cu and Ba as diffusing cations) shows that the nucleation front migrates towards the left as phosphate diffuses from the right and complexes with uranium in the silica gel (Fig. 6a). Modelling results also show the key role of uranyl in solution (UO₂²⁺ with Cu and Ba as diffusing cations), because in this experiment (Fig. 6b) as in some others, crystals were either scant or failed to precipitate altogether. In the initial stage, and because we used reactive gel with U, phosphate diffusion establishes a low concentration profile and limited complexation with U allowing supersaturation conditions in the middle part of the tube allowing the precipitation of metauranocircite and/or metatorbernite. However, as the system evolves in time, the diffusion of phosphate raises its concentration along the tube which in turn complexes the U in the gel, reducing their activity in solution and depressing the SI so much that further nucleation of crystals in the gel is prevented.

Therefore, only in a very limited time window and chemical conditions does uranyl-phosphate minerals precipitate, unless U concentration in the gel is higher as in the other experiments.

4. Conclusions

The most relevant observation in this work is the preferential precipitation of metatorbernite relative to metauranocircite in conditions apparently favourable for both minerals to nucleate and grow. This is somewhat counterintuitive since the processes of Cu (and Ca) substitution by Ba are common in nature (Pinto et al., 2012; Prazeres et al., submitted) and in experiments. This difference may be primarily due to kinetic factors, but is at present unresolved.
The metatorbernite crystals obtained in a Ba and Cu solution environment also have bigger dimensions than those in monocationic systems.

The reacted natural samples with BaCl₂ solutions showed that secondary cationic substitution of Ca and Cu by Ba is thermodynamically favourable. However, epitaxial growth may be the process by which Ba-rich phases preferentially grow which also explains the variety of forms displayed by metatorbernite crystals precipitated in mixed chemical environments (Sanchez-Pastor et al., 2013). Chemical modelling showed that mineral precipitation depends on how supersaturation evolves as a function of the free chemical species, especially with the complexation between uranyl and phosphate. The absence and low abundance of metauranocircite in the experiments may be related to the solubility difference relative to metatorbernite, but we must bear in mind that accurate and sufficiently reliable solubility data for these minerals is lacking. EPMA results show only evidence for the joint metauranocircite and metatorbernite crystallization in the form of mixes crystals, mostly copper-rich phases with a limited incorporation of barium. This result implies that Ba should build-up its concentration in the gel with time, but still conditions are not favourable for the Ba-phase to precipitate. Therefore, another explanation is that later nucleation may be hindered by the depletion of ions (uranyl and phosphate) in solution, as shown by the numeric models.

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References


