

## DISSOLUTION OF URANYL-OXIDE-HYDROXY-HYDRATE MINERALS. II. BECQUERELITE

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### ABSTRACT

The morphology of etch pits on the basal surface of becquerelite,  $\text{Ca}(\text{H}_2\text{O})_8 [(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$ , is predicted using the bond-valence deficiency of anion-terminations on chains of polyhedra parallel to its edges. The predicted morphology is compared with observations in batch-dissolution experiments on single crystals. These experiments were done in HCl solutions of pH 2 and 3.5, in ultrapure water, in 0.1 and 0.5 mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> solutions of pH 10.5, in 1.0 mol L<sup>-1</sup> MCl solutions of pH 2 ( $M = \text{Na}, \text{K}$ ), in 0.5 mol L<sup>-1</sup> MCl<sub>2</sub> solutions of pH 2 ( $M = \text{Ba}, \text{Sr}, \text{Mg}$ ) and in a 0.5 mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solution of pH 2. Dissolution features on the (001) basal surface of the becquerelite crystals were examined with atomic-force microscopy, scanning electron microscopy and optical microscopy. Hillocks on the basal surface occur in the pH range 3.5–10.5. Etch pits form on the basal surface only in solutions of pH 2, indicating that their formation is promoted by high activity of protons in solution. Etch pits formed in an HCl solution of pH 2 do not display the symmetry elements of the bulk structure (space group  $Pn2_1a$ ), possibly a result of nonstoichiometric detachment of the uranyl-bearing and  $\text{Ca}\phi_n$  polyhedra. Symmetry and elongation of etch pits formed in electrolyte solutions of pH 2 vary with the type of cation in solution. Etch pits elongate parallel to [100] form in aqueous solutions of BaCl<sub>2</sub>, KCl, NaCl and MgCl<sub>2</sub>, whereas etch pits elongate parallel to [010] form in aqueous solutions of SrCl<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub>. Etch pits on an untreated basal surface formed during synthesis in a Ca-bearing solution are elongate parallel to [010]. Etch pits formed on becquerelite in Ba-, K-, and Ca-containing solutions are elongate parallel to the rows of Ba, K and Ca atoms in the bulk structures of billietite, compreignacite and becquerelite, and to the elongation of their crystals. The different elongation of etch pits can be explained with an adsorption model involving the cations in solution and specific sites on the basal surface. The stability of the basal surface and its edges in the presence of various cations in solution was determined using the dimensions of the etch pits and the relief of dissolution features. The stability of the basal surface in the electrolyte solutions decreases in the sequence  $\text{MgCl}_2 > \text{KCl} > \text{BaCl}_2 > \text{Pb}(\text{NO}_3)_2 > \text{NaCl} > \text{SrCl}_2$ , and the stability of the edges decreases in the sequence  $\text{MgCl}_2 > \text{KCl} > \text{BaCl}_2 > \text{SrCl}_2 > \text{NaCl} > \text{Pb}(\text{NO}_3)_2$ . Both rankings indicate that solutions with cations of ionic radius similar to that of Ca<sup>2+</sup> have the greatest influence on the dissolution processes of single crystals of becquerelite.

**Keywords:** becquerelite, dissolution, etch pit, surface, mineral, uranyl oxide of Ca, bond valence.

### SOMMAIRE

Nous prédisons la morphologie des figures de corrosion sur la face de base des cristaux de becquerelite,  $\text{Ca}(\text{H}_2\text{O})_8 [(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$ , selon le déficit des valences de liaison des terminaisons anioniques des chaînes de polyèdres parallèles aux arêtes. La morphologie prédite est comparée aux observations faites lors des expériences de dissolution globale de monocristaux. Ces expériences ont été effectuées dans des solutions de HCl à un pH de 2 et de 3.5, dans l'eau ultrapure, dans des solutions de Na<sub>2</sub>CO<sub>3</sub> à une concentration de 0.1 et 0.5 mol L<sup>-1</sup> et à un pH de 10.5, dans des solutions de MCl à une concentration de 1.0 mol L<sup>-1</sup> et un pH de 2 ( $M = \text{Na}, \text{K}$ ), dans des solutions de 0.5 mol L<sup>-1</sup> MCl<sub>2</sub> à un pH de 2 ( $M = \text{Ba}, \text{Sr}, \text{Mg}$ ), et dans une solution de Pb(NO<sub>3</sub>)<sub>2</sub> à une concentration de 0.5 mol L<sup>-1</sup> à un pH de 2. Les figures de dissolution sur la face (001) des cristaux de becquerelite ont été examinées en utilisant la microscopie à force atomique, la microscopie électronique à balayage et la microscopie optique. Les monticules de croissance sur la surface basale apparaissent à un pH dans l'intervalle 3.5–10.5. Les figures de corrosion apparaissent seulement dans les solutions ayant un pH de 2, indication que leur formation est favorisée par une forte activité de protons en solution. Les figures de corrosion formées dans une solution de HCl à un pH de 2 ne répondent pas aux exigences des éléments de symétrie de la structure globale (groupe d'espace  $Pn2_1a$ ), peut-être en raison du détachement non stœchiométrique des polyèdres uranylés et à  $\text{Ca}\phi_n$ . La symétrie et l'allongement des figures de corrosion formées dans des solutions d'électrolytes

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de pH 2 varient selon le cation en solution. Les figures de corrosion allongées parallèles à [100] se forment dans des solutions aqueuses de  $\text{BaCl}_2$ ,  $\text{KCl}$ ,  $\text{NaCl}$  et  $\text{MgCl}_2$ , tandis que les figures de corrosion allongées parallèles à [010] se forment dans des solutions aqueuses de  $\text{SrCl}_2$  et  $\text{Pb}(\text{NO}_3)_2$ . Les figures de corrosion développées sur des surfaces non traitées lors d'une synthèse dans une solution porteuse de Ca sont allongées parallèles à [010]. Les figures de corrosion formées en présence de solutions contenant Ba, K, et Ca sont allongées parallèles aux rangées d'atomes de Ba, K et Ca dans les structures globales de billietite, compreignacite et becquerelite, et à l'allongement de leurs cristaux. Nous expliquons les différences dans l'allongement des figures de corrosion par un modèle d'absorption impliquant les cations en solution et les sites spécifiques sur la surface à la base. La stabilité de cette surface de base et de ses arêtes en présence de divers cations en solution a été déterminée en utilisant les dimensions et le relief des figures de corrosion. La stabilité de la face de base diminue selon la séquence  $\text{MgCl}_2 > \text{KCl} > \text{BaCl}_2 > \text{Pb}(\text{NO}_3)_2 > \text{NaCl} > \text{SrCl}_2$  en solution, et la stabilité des arêtes diminue selon la séquence  $\text{MgCl}_2 > \text{KCl} > \text{BaCl}_2 > \text{SrCl}_2 > \text{NaCl} > \text{Pb}(\text{NO}_3)_2$  en solution. Les deux séquences indiquent que les solutions contenant des cations de rayon ionique semblable à celui de  $\text{Ca}^{2+}$  exercent la plus grande influence sur les processus de dissolution de monocristaux de becquerelite.

(Traduit par la Rédaction)

**Mots-clés:** becquerelite, dissolution, figures de corrosion, surface, minéral, oxyde uranylé de Ca, valence de liaison.

## INTRODUCTION

Uranyl-oxide hydroxy-hydrates that form as products of the oxidation of U mine and mill tailings are important for understanding water-rock interactions in uranium deposits. They are prominent alteration-induced phases in laboratory experiments involving  $\text{UO}_2$  and spent nuclear fuel in a moist, oxidizing environment similar to the proposed repository at Yucca Mountain (Wronkiewicz *et al.* 1996, Finn *et al.* 1996, Finch *et al.* 1999). Many of the radionuclides released from spent nuclear fuel during alteration in a geological repository may be either incorporated into uranyl oxide hydrates (Burns *et al.* 1997, 2004, Burns & Li 2002, Chen *et al.* 1999, 2000) or adsorbed on their surface (Schindler *et al.* 2006). Owing to the complexity of their structures, our understanding of the water – mineral surface interactions for uranyl-oxide-hydroxy-hydrates lags behind that for other mineral groups.

In this paper, we examine dissolution processes on the (001) surface of the common uranyl-oxide-hydroxy-hydrate mineral becquerelite,  $\text{Ca}(\text{H}_2\text{O})_8[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$ , focusing on the effects of pH and different electrolyte solutions. Furthermore, we discuss the relation between the structure and morphology of crystals of the becquerelite-group minerals, and use these relations to predict the morphology of etch pits that form on the basal surface of becquerelite. These predictions are subsequently compared with the observations in the dissolution experiments.

## PREVIOUS DISSOLUTION EXPERIMENTS ON URANYL-OXIDE-HYDROXY-HYDRATE MINERALS

In a recent study on the dissolution of the basal (100) surface of curite,  $\text{Pb}^{2+}_3(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]_2$ , Schindler *et al.* (2006) showed that with increasing degree of protonation of edges, etch pits grow faster laterally than perpendicular to the basal surface. They further observed that the general symmetry of etch pits formed in  $\text{H}_2\text{O}$  and  $\text{HCl}$  solutions does not reflect the

symmetry of the bulk structure, whereas dissolution experiments in aqueous  $\text{SrCl}_2$  solution resulted (even at low pH) in highly symmetrical etch-pits. Dissolution experiments in an aqueous  $\text{Na}_2\text{CO}_3$  solution of pH 10.5 resulted in the formation of hillocks, which do not form in neutral ( $\text{H}_2\text{O}$ ) and acidic ( $\text{HCl}$ ) solutions.

Numerous bulk-dissolution experiments on uranyl minerals and synthetic phases have been carried out (*e.g.*, Vochten *et al.* 1991, 1995, Sandino & Bruno 1992, Sandino & Grambow 1994, Torrero *et al.* 1994, Casas *et al.* 1997). Bulk-dissolution experiments on becquerelite and schoepite show that the lowest solubilities of these minerals occur in the pH range 7–8 (Torrero *et al.* 1994, Casas *et al.* 1997). The experimentally determined solubility-constant for becquerelite is  $\log K_s = 29 \pm 1$  (Casas *et al.* 1997). The saturation indices with respect to becquerelite in our experiments have been calculated on the basis of this solubility constant and the recently determined value of the enthalpy of formation ( $H_f^\circ$ ) of becquerelite (Kubatko *et al.* 2006).

## BEQUERELITE, BILLIETITE AND COMPREIGNACITE: STRUCTURAL UNIT, INTERSTITIAL CATIONS AND CRYSTAL MORPHOLOGY

The structures of becquerelite,  $\text{Ca}(\text{H}_2\text{O})_8[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$  (Burns & Li 2002, Pagoaga *et al.* 1987), billietite,  $\text{Ba}(\text{H}_2\text{O})_7[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$  (Finch *et al.* 2006), and compreignacite,  $\text{K}_2(\text{H}_2\text{O})_3[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]$  (Burns 1998a), contain the structural unit  $[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]^{2-}$  in which  $\text{U}^{6+}$  occurs only in [7]-coordination (Fig. 1a). Becquerelite, compreignacite, and billietite adopt orthorhombic symmetry, but the space-group symmetry and unit-cell dimensions vary with the type of interstitial cation and the number of interstitial ( $\text{H}_2\text{O}$ ) groups. We will use the dimensions  $a = 13.8527 / 2 = 6.926$ ,  $b = 12.393$  and  $c = 14.930$  Å from the structure data of becquerelite (Burns & Li 2002, space group  $Pn2_1a$ ) to describe the morphology and the orientation of the chains of polyhedra in the structural units of becquerelite, billietite and compreignacite.

Figures 2a, b and c show the arrangements of the interstitial cations Ca, Ba and K in becquerelite, billietite and compreignacite, respectively. The interstitial Ca atoms in becquerelite are arranged in rows parallel to [010], whereas the interstitial Ba and K atoms in billietite and compreignacite are arranged in rows parallel to [100]. In the latter case, the K cations occur disordered over two sites (Fig. 2c, Burns 1998a).

Becquerelite, billietite and compreignacite crystals strongly resemble each other in color and form. However, becquerelite crystals are most commonly elongate parallel to [010], whereas billietite and compreignacite crystals can be elongate parallel to [100] (Figs. 2a, b, c; Perloff 1998; <http://www.trinityminerals.com/sm2001/uranium.shtml>). The basal surface is commonly bounded by the [100], [110] and [010] edges in becquerelite, the [110] and [100] edges in billietite,

and the [100], [010], [110] and [310] edges in compreignacite (Schindler *et al.* 2004b, Protas 1964).

#### PREDICTION OF THE MORPHOLOGY OF ETCH PITS

Schindler *et al.* (2004a) developed a new approach to calculate the relative stability of edges on basal surfaces of uranyl-sheet minerals; it has been used to predict the morphology of basal surfaces of uranyl-sheet minerals (Schindler *et al.* 2004b) and to explain growth features of schoepite,  $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}](\text{H}_2\text{O})_{12}$  (Schindler & Putnis 2004), becquerelite,  $\text{Ca}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_8$ , and wyartite,  $\text{Ca}[\text{U}^{5+}(\text{UO}_2)_2(\text{CO}_3)_4(\text{OH})](\text{H}_2\text{O})_7$  (Schindler *et al.* 2004c). Furthermore, Schindler *et al.* (2006) applied this approach to determine the stability of edges of etch pits on the basal (100) surface of curite,  $\text{Pb}^{2+}_3(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]_2$ .

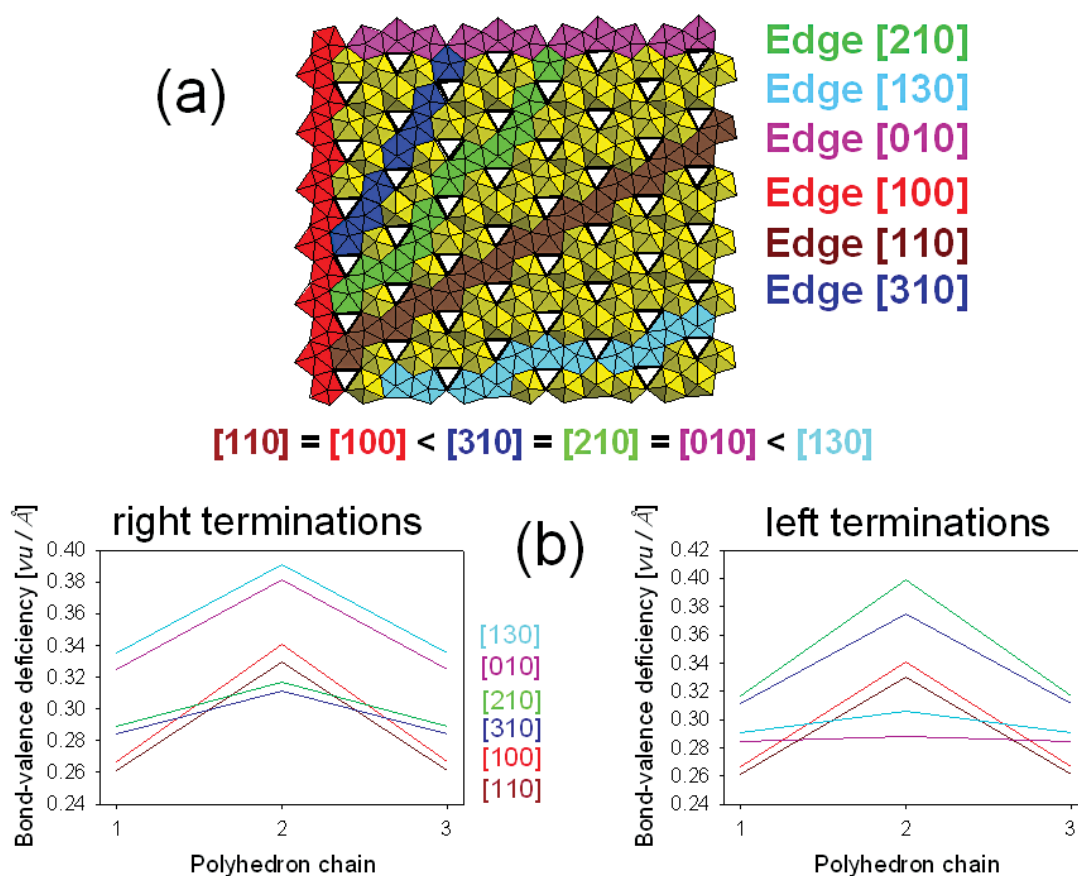


FIG. 1. (a) Polyhedron representation of the uranyl-oxide-hydroxy-hydrate sheet in becquerelite; polyhedron chains parallel to [100], [010], [110], [210], [310] and [130] are highlighted in red, pink, brown, green, dark blue and light blue, respectively, and the positions of the (OH) groups are shown as vertices of black triangles. (b) Calculated bond-valence deficiencies of the left and right forms of chain terminations on chains parallel to the edges [100], [010], [310], [110], [130] and [210] [shown in the same colors as in (a)].

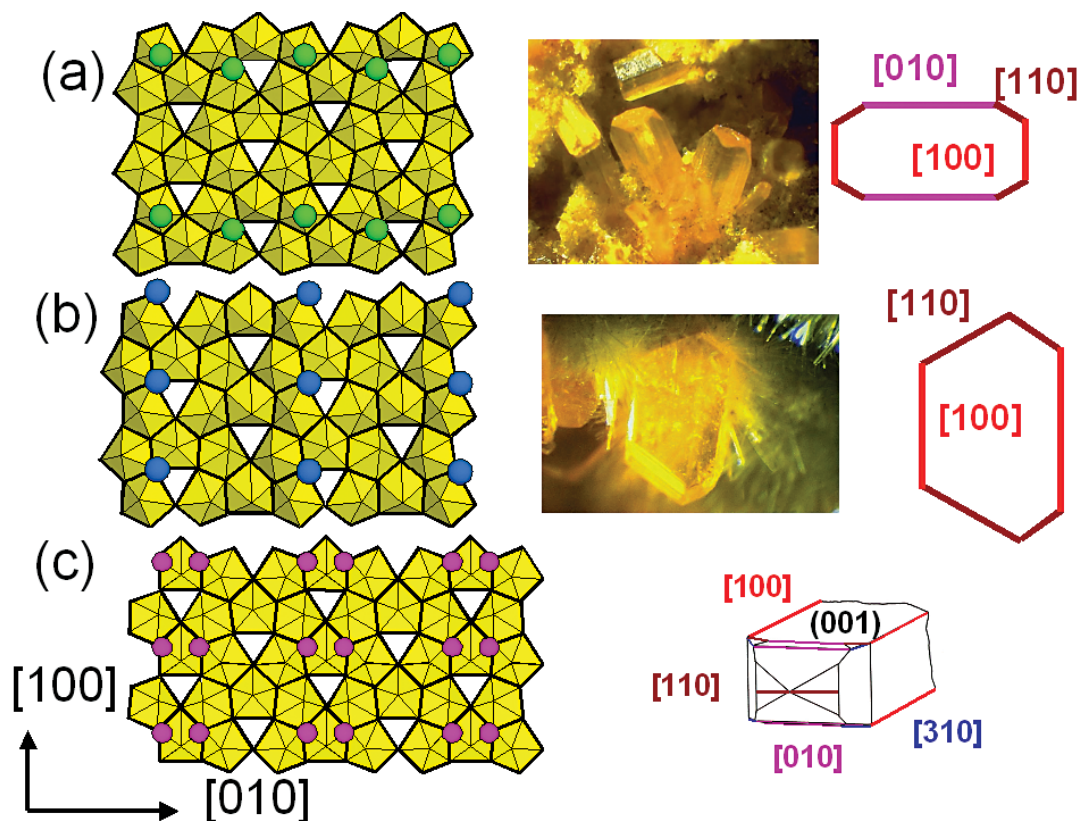


FIG. 2. Polyhedron illustrations of layers in (a) becquerelite, (b) billietite, and (c) compreignacite, showing the positions of interstitial Ca (green circles), Ba (blue circles) and K (pink circles). Right: examples of the corresponding (001) surface morphologies on becquerelite, billietite and compreignacite crystals (Perloff 1998, <http://www.trinityminerals.com/sm2001/uranium.shtml>, Protas 1964; for details, see text).

#### *Polyhedron chains in the $[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]^{2-}$ structural unit*

Schindler *et al.* (2004a) showed that the extent of interaction of anions with an aqueous solution at an edge correlates with the bond-valence deficiency (calculated for no interaction with the ambient solution) along a terminating chain of polyhedra parallel to a specific edge.

Chains with the lowest bond-valence deficiency are chains in which the anions have the lowest interaction with the aqueous solution (*i.e.*, chains with the lowest number of activated sites after interaction with the aqueous solution). The corresponding edge has a high stability and will most likely occur on the final morphology of a crystal or an etch pit. Figure 1b shows the variation in bond-valence deficiency per unit length [ $\text{vu} / \text{\AA}$ ] of anions along different chains parallel to edges defining the basal surface of becquerelite. The bond-valence deficiencies were calculated using the

average bond-valence of 0.51  $\text{vu}$  for  $^{17}\text{U}-\text{O}$  bonds in becquerelite (based on the structural parameter of Burns & Li 2002).

Considering the bond-valence deficiency of the left and right terminations of the chains of polyhedra, the extent of interaction of an edge with the aqueous solution increases in the following sequence  $[110] = [100] < [310] = [210] = [010] < [130]$  (for details see Schindler *et al.* 2004a).

#### *Sheet displacement and the arrangement of interstitial complexes*

Schindler *et al.* (2004a) showed that displacement between the layers in uranyl-sheet minerals increases the extent of interaction between an edge and any aqueous species in an ambient solution. The displacement between the layers is the horizontal shift between two adjacent layers. If these layers are terminated by the same type of chain of polyhedra, the displacement

results in an additional kink-site along the corresponding edge.

In the structures of becquerelite, billietite and compreignacite, displacements between the layers are minimal and may not significantly affect the extent of interaction of the different edges with species in solution. Schindler *et al.* (2004a) also showed that the arrangement of interstitial complexes in rows parallel to specific edges favors growth of the crystals in that direction. This is the case for becquerelite, billietite and compreignacite, where elongation of the crystals is parallel to the rows of interstitial cations in the bulk structure (Figs. 2a, b, c).

Considering only the bond-valence deficiency and not the arrangement of the interstitial species, Schindler *et al.* (2004b) predicted that the [110] and [100] edges are the most stable edges, followed by [010], [210] and

[310], in minerals with the becquerelite structure. This prediction is in agreement with observations on natural crystals, where the [110] and [100] edges invariably bound the basal surfaces (Figs. 2a, b, c).

#### *Possible role of interstitial cations during crystal growth and dissolution*

As described above, crystals of the becquerelite-group minerals are elongate parallel to the arrangement of interstitial complexes. Schindler *et al.* (2004b) gave a possible explanation for this phenomenon (Fig. 3a). The uranyl sheet is constructed entirely of clusters of three pentagonal bipyramids, and growth parallel to [100] and [010] corresponds to attachment of a cluster at the [010] and [100] edges, respectively. If the cluster attaches to the [010] edge, it will share five ligands with

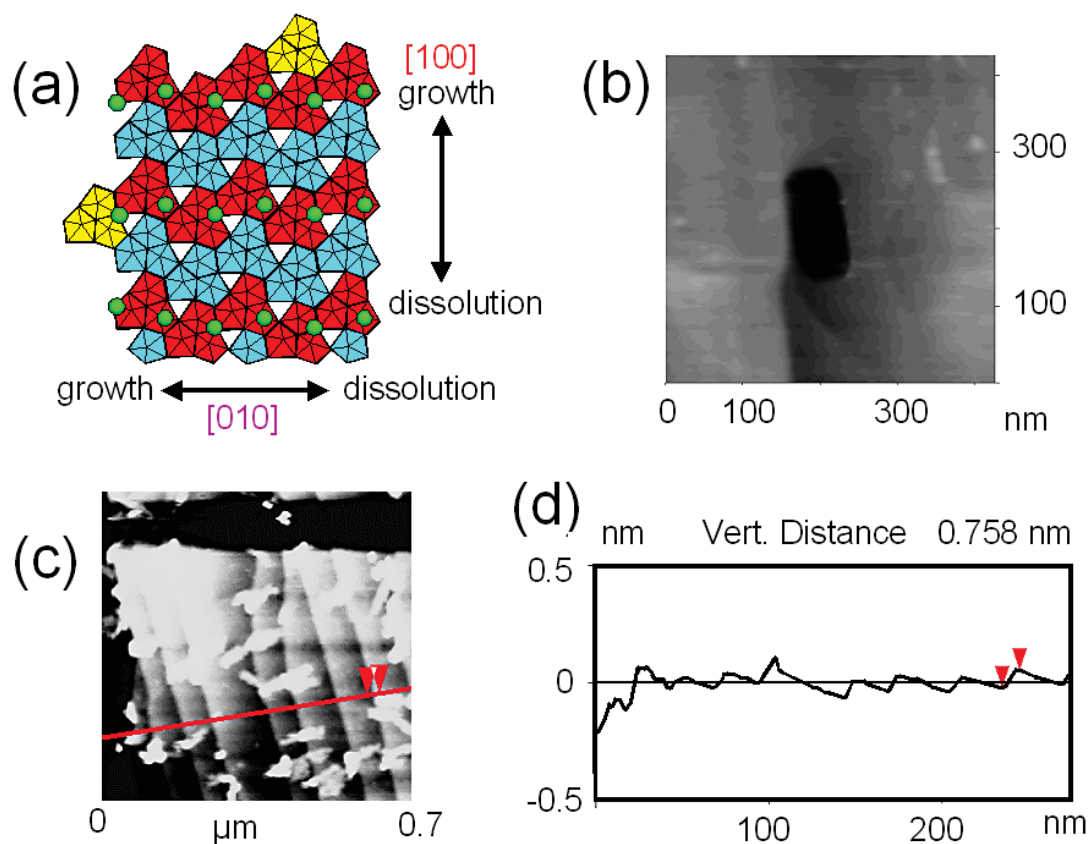


FIG. 3. (a) Growth model of a uranyl layer in becquerelite (Schindler *et al.* 2004b). The layer of polymerized uranyl-polyhedra can be constructed from clusters of three pentagonal bipyramids (shown in red and blue). These clusters are structurally identical to the principal aqueous species  $[(\text{UO}_2)_3(\text{OH})_5(\text{H}_2\text{O})_5]^+$  in a weakly acidic solution. The position of the interstitial complex is indicated by the Ca atoms in the interlayer (green circles). Clusters attached to [100] and [010] edges are indicated in yellow (see text for details). (b) AFM image of an etch pit on an untreated basal (001) surface of becquerelite. (c) AFM image and (d) a cross-section of an untreated basal surface of becquerelite (for details, see text).

the corresponding kink-site. If there is no layer above or below this layer, ligands (mainly O-atoms of the uranyl ion) of the attached cluster do not receive bonds from the interstitial complex. If the cluster attaches to the [100] edge, there are only four common ligands of the cluster and the kink site, but the ligands of the cluster will accept bonds from the interstitial complex. During dissolution, clusters or single polyhedra will detach. Following the argument given above, detachment of a polyhedron or a group of polyhedra at the [100] edge involves breaking of bonds between the interstitial complex and the corresponding ligands of the uranyl polyhedra. If, during dissolution, cations from the aqueous solution are adsorbed on the surface or incorporated between the upper surface-layers, their arrangement should influence the orientation of etch pits in the same way as it does during crystal growth. Thus, the morphology of etch pits formed in different electrolyte solutions should also depend on the (unknown) arrangement of aqueous species on the surface.

## EXPERIMENTAL

### *Synthesis of becquerelite*

Becquerelite crystals were synthesized according to the procedure of Burns & Li (2002): 0.31 g uranyl acetate, 0.05 g calcium carbonate, and 4 mL ultrapure water were placed in a 23 mL Teflon-lined Parr vessel and heated at 160°C for 50 h. The resultant platy crystals were found to have maximum diameters of 0.5 mm. Crystals were washed rapidly in ultra-pure water and dried in air.

### *Dissolution experiments*

For each dissolution experiment, we selected four to five platy crystals; the size of the basal surface varied between  $0.04 \times 0.06$  and  $0.2 \times 0.3$  mm. These crystals were placed in small polyethylene cups that contained

1 mL of a solution of different pH and composition. In Table 1, we list the types and concentrations of electrolyte solutions used, their pH and their ionic strengths and their saturation index with respect to becquerelite; note that the electrolyte solutions of pH 2.0 have equal normality with respect to the cation in solution, and that the standard deviation of the measured pH in the solutions of high ionic strength is *ca.*  $\pm 0.2$ .

All dissolution experiments were performed at room temperature. The experiment in ultrapure water ran for 24 hours, the experiments in the aqueous HCl solution of pH 3.5 and in the aqueous  $\text{Na}_2\text{CO}_3$  solution of pH 10.5 for one hour, and the experiments in solutions of pH 2 for 30 minutes. After the experiment, the crystals were washed in pure water, quickly dried in air and mounted for atomic-force microscopy, scanning electron microscopy, and optical-reflection microscopy. We did not do any *in situ* dissolution experiments because we focused on the stability of edges and basal surfaces rather than on the kinetics of etch-pit formation, step retreat and formation of hillocks. For our purposes, suitable information can be collected from batch-dissolution experiments and subsequent examination of the becquerelite surface. The ionic strengths of the electrolyte solutions and their saturation indices with respect to becquerelite were calculated using Visual MINTEQ 2.22 (Gustafsson 2003) and PHREEQC (Parkhurst 2003).

### *Atomic-force microscopy and scanning electron microscopy*

After the dissolution experiments, the (001) surface of the becquerelite crystals was examined with a Digital Instruments Nanoscope III atomic-force microscope (AFM) with an extended module for phase imaging. The surface was scanned with a standard silicon nitride ( $\text{Si}_3\text{N}_4$ ) contact-mode tip in air. In order to verify that contact mode and scanning direction did not affect shape and orientation of the etch pits, we scanned the areas at least twice in orthogonal directions.

The studies using a scanning electron microscope were done with a 120 Stereoscan Cambridge instrument, and the samples were analyzed with an EDAX Genesis system 4000 spectrometer.

TABLE 1. DISSOLUTION EXPERIMENTS ON BECQUERELITE: CONCENTRATION OF ELECTROLYTE SOLUTION, pH, IONIC STRENGTH AND THE SATURATION INDEX WITH RESPECT TO BECQUERELITE

| Electrolyte solution                                                          | pH value (measured) | Ionic strength (calculated) | Saturation index <sup>1</sup> |
|-------------------------------------------------------------------------------|---------------------|-----------------------------|-------------------------------|
| 0.5 mol L <sup>-1</sup> BaCl <sub>2</sub> · nH <sub>2</sub> O                 | 2.0                 | 1.23                        | -117                          |
| 0.5 mol L <sup>-1</sup> SrCl <sub>2</sub> · nH <sub>2</sub> O                 | 2.0                 | 1.15                        | -117                          |
| 0.5 mol L <sup>-1</sup> MgCl <sub>2</sub> · nH <sub>2</sub> O                 | 2.0                 | 0.98                        | -117                          |
| 0.5 mol L <sup>-1</sup> Pb(NO <sub>3</sub> ) <sub>2</sub> · nH <sub>2</sub> O | 2.0                 | 0.51                        | -117                          |
| 1.0 mol L <sup>-1</sup> NaCl                                                  | 2.0                 | 0.84                        | -117                          |
| 1.0 mol L <sup>-1</sup> KCl                                                   | 2.0                 | 0.84                        | -117                          |
| HCl                                                                           | 2.0                 | 0.001                       | -114                          |
| HCl                                                                           | 3.5                 | 0.0002                      | -92                           |
| Ultrapure H <sub>2</sub> O                                                    | 7.0                 | 0                           | -49                           |
| 0.1 mol L <sup>-1</sup> Na <sub>2</sub> CO <sub>3</sub>                       | 10.5                | 0.2                         | -103                          |
| 0.5 mol L <sup>-1</sup> Na <sub>2</sub> CO <sub>3</sub>                       | 10.5                | 0.2                         | -110                          |

<sup>1</sup> Saturation index = log (ion activity-product) - log K.

## DISSOLUTION FEATURES OBSERVED ON BECQUERELITE

Figure 3c shows an AFM image of steps on an untreated (001) surface of becquerelite. The minimum height of these steps corresponds to the distance between two uranyl sheets: half the unit cell in [001] with  $14.930 / 2 = 7.46$  Å (Fig. 3d). The occurrence of steps or terraces with heights of one uranyl sheet is not necessarily a common feature on the basal surface of uranyl-oxide-hydroxy-hydrate minerals. For example, Schindler *et al.* (2006) did not observe any steps or

terraces with heights in the lower nanometer range ( $<5$  nm) on the basal surface of curite. Figure 3b shows an etch pit on the untreated (001) surface, which presumably formed during synthesis of becquerelite. Its morphology is identical to the morphology of the basal surface, which is elongate parallel to [010] and bounded by the [010], [100] and [110] edges (Fig. 2a).

*Crystals treated with an aqueous HCl solution of pH 2*

Figure 4 shows SEM, reflected-light and AFM images of characteristic surface-features on the basal surface and edges of becquerelite crystals treated with an aqueous HCl solution of pH 2. Closer inspection of the images obtained by SEM and reflected light microscopy indicates that dissolution on the edges occurs primarily at the [010] edge (framed with red squares in Fig. 4). The corresponding dissolution-induced features

are elongate parallel to [100] (Fig. 4c). Two different types of dissolution features occur on the basal surface: (1) linear grooves that Honess (1927) referred to as “channels”, and (2) etch pits (Figs. 4e, f). The dissolution channels extend parallel to [010] (Fig. 4b), are bounded by steep walls, and have minimum widths of  $\sim 0.50$   $\mu\text{m}$  (Fig. 4e). The dissolution channels consist of elongate etch-pits parallel to [100] that have merged at a later stage of dissolution. Etch pits outside the dissolution channels are generally bounded by rounded non-uniform edges and are also elongate parallel to [100] (Fig. 4f).

*The basal surface treated with solutions of higher pH*

Figures 5a, b, c show typical hillocks on the basal (001) surface of becquerelite after treatment in (a) aqueous HCl solution of pH 3.5, (b)  $\text{H}_2\text{O}$ , and (c) aqueous  $\text{Na}_2\text{CO}_3$  solution of pH 10.5. The hillocks are

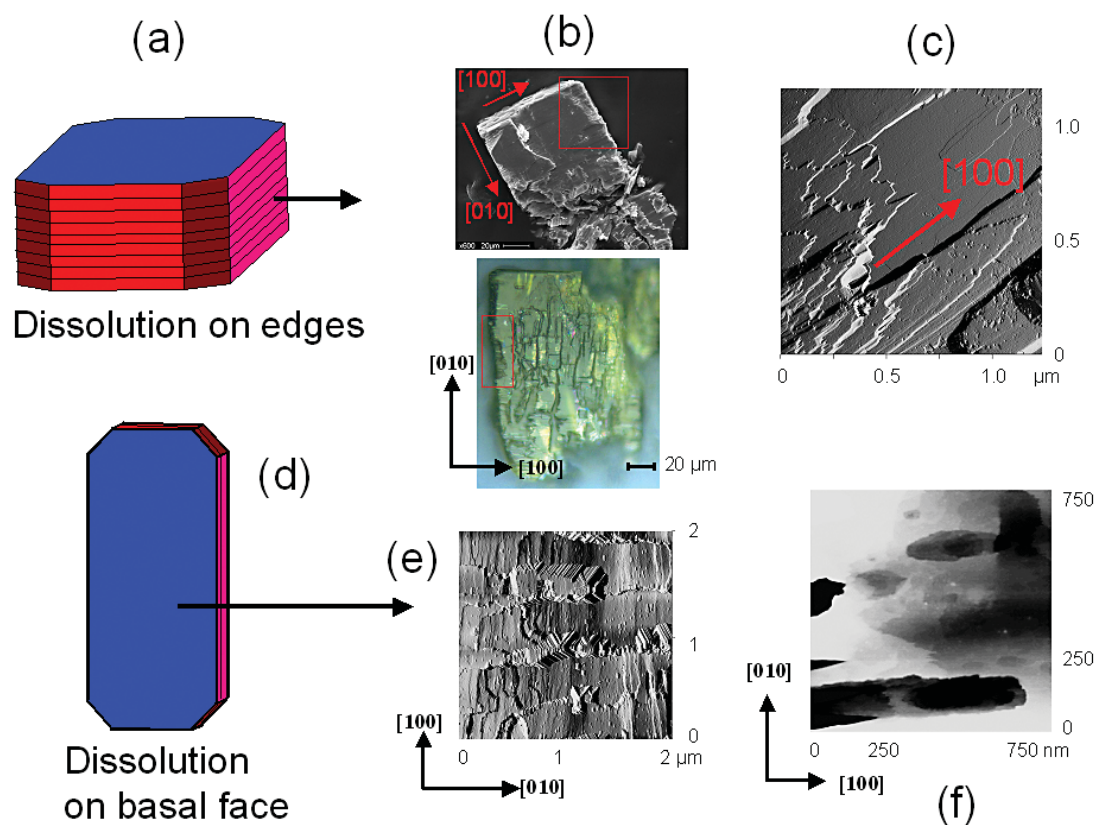


FIG. 4. (a)–(f) Evidence of dissolution features on the basal surface of becquerelite crystals treated with aqueous HCl solution of pH 2. (b) Images of single crystals obtained by SEM and reflected-light microscopy; characteristic dissolution-induced features along the edge are framed in a red box. (c) AFM image in deflection mode of the dissolution features on the edge indicated in (b). (e) AFM image in deflection mode of dissolution channels on the basal surface; note that parts of the channel walls contain artifacts due to tip–surface interaction. (f) AFM image of etch pits on the basal surface.

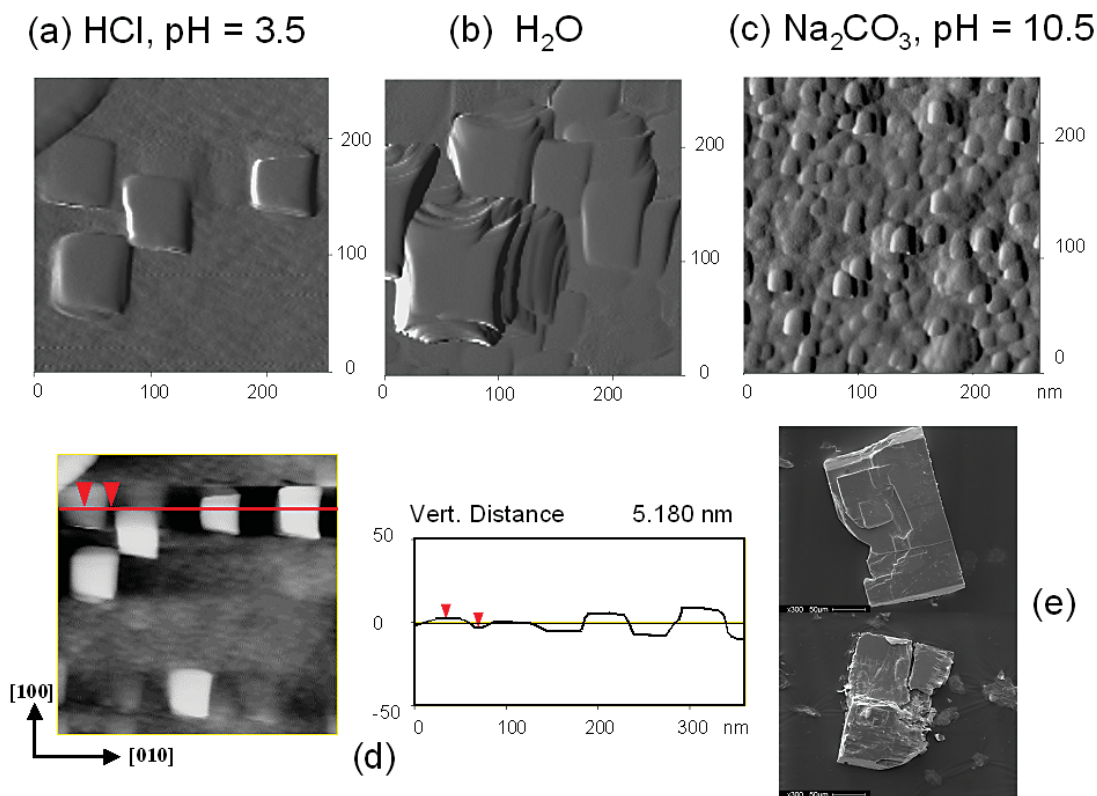


FIG. 5. Hillocks on the basal surface of bequerelite crystals treated with (a) aqueous HCl solution of pH 3.5, (b) ultrapure water, and (c) 0.1 mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> of pH 10.5 (all images are in deflection mode). (d) Cross-sections of hillocks formed in aqueous HCl solution of pH 3.5 (AFM image in height mode). (e) Typical appearance of a single crystal treated with an aqueous Na<sub>2</sub>CO<sub>3</sub> solution (top) and an HCl solution of pH 3.5 (bottom).

slightly elongate parallel to [100], they are defined by [100] and [010] edges, and they are more rounded on the bequerelite (001) surface treated with aqueous Na<sub>2</sub>CO<sub>3</sub> solution. Inspection of a cross section of the hillocks formed in aqueous HCl solution of pH 3.5 shows that their lateral dimensions are  $\sim 50 \times 75$  nm, and their height is 5–15 nm (Fig. 5d). The height of the smallest hillocks is around 5.2 nm (Fig. 5d), which corresponds to a thickness of approximately seven sheets of uranyl polyhedra. Figure 5e shows typical SEM images of crystals treated with an aqueous Na<sub>2</sub>CO<sub>3</sub> solution (top) and an aqueous HCl solution of pH 3.5 (bottom). It is apparent that the basal surface and edges of the crystal treated with Na<sub>2</sub>CO<sub>3</sub> solution do not show macroscopic dissolution-channels or etch-pits, in contrast to the basal surface and edges of the crystal treated with the HCl solution. This observation clearly indicates that the density of hillocks (Figs. 5a, c) does not correlate with the degree of development of dissolution channels at the edges of the basal surface.

*The basal surface treated with an aqueous 0.50 mol L<sup>-1</sup> BaCl<sub>2</sub> solution of pH 2*

Figure 6a shows typical etch-pits on the basal (001) surface of bequerelite after treatment with 0.50 mol L<sup>-1</sup> aqueous BaCl<sub>2</sub> solution of pH 2. The etch pits are elongate parallel to [100] and are bounded by the edges [100], [210] (and, to a lesser extent, [110]). The outline of the etch pits observed in Figure 6a invariably displays mirror symmetry perpendicular to [010] and, in some cases, mirror symmetry perpendicular to [100]. In the latter case, two perpendicular mirror-symmetries produce a two-fold axis perpendicular to the basal plane. Hence the maximum plane-group symmetry of the outline of the pits is  $2mm$ , which contrasts with the symmetry of the bulk structure of bequerelite (plane-group symmetry  $m2m$ ). The high symmetry of the etch pits is also in contrast to the less symmetrical etch-pits formed in aqueous HCl solution of pH 2. The pits have steep sides, and some of them have a flat bottom, and retain their hexagonal shape at all depths.

Figure 7 shows SEM images of crystals treated with different electrolyte solutions of pH 2, where the corresponding cation of the solution is indicated below the image. Treatment with an aqueous  $0.50 \text{ mol L}^{-1} \text{ BaCl}_2$  solution of pH 2 results in very shallow dissolution-induced features: channels parallel to  $[010]$  are shallow and broad, and steps, terraces and plateaus are flat and bounded by rounded edges. Along the edges of the basal surface, there are deep dissolution-induced channels parallel to the elongation of the crystal ( $[010]$ ).

*The basal surface of becquerelite treated with an aqueous  $1.00 \text{ mol L}^{-1} \text{ KCl}$  solution of pH 2*

Figure 6b shows etch pits observed after dissolution with an aqueous  $1.00 \text{ mol L}^{-1} \text{ KCl}$  solution of pH 2. The etch pits are elongate parallel to  $[100]$  and are bounded by the edges  $[100]$ ,  $[310]$  and  $[210]$ . The morphology of the etch pits does not change with depth, and the outline

of some of the etch pits display plane-group symmetry  $2mm$ . The etch pits formed in aqueous KCl solution of pH 2 are slightly more elongate parallel to  $[100]$  than the etch pits formed in aqueous  $\text{BaCl}_2$  solution of pH 2. The basal surface of the corresponding crystal contains deep dissolution-induced channels parallel to  $[010]$ , steps, terraces and plateaus are not flattened, and their edges are well defined (Fig. 7). Furthermore, the edges of the basal surface apparently do not contain dissolution features.

*The basal surface of becquerelite treated with an aqueous  $0.50 \text{ mol L}^{-1} \text{ MgCl}_2$  solution of pH 2*

Etch pits formed on becquerelite in an aqueous  $\text{MgCl}_2$  solution of pH 2 are elongate parallel to  $[100]$ , and are bounded only by  $[100]$  and  $[010]$  edges (Fig. 8a). If one of the  $[010]$  edges is in some cases rounded, the mirror symmetry perpendicular to  $[100]$  disappears,

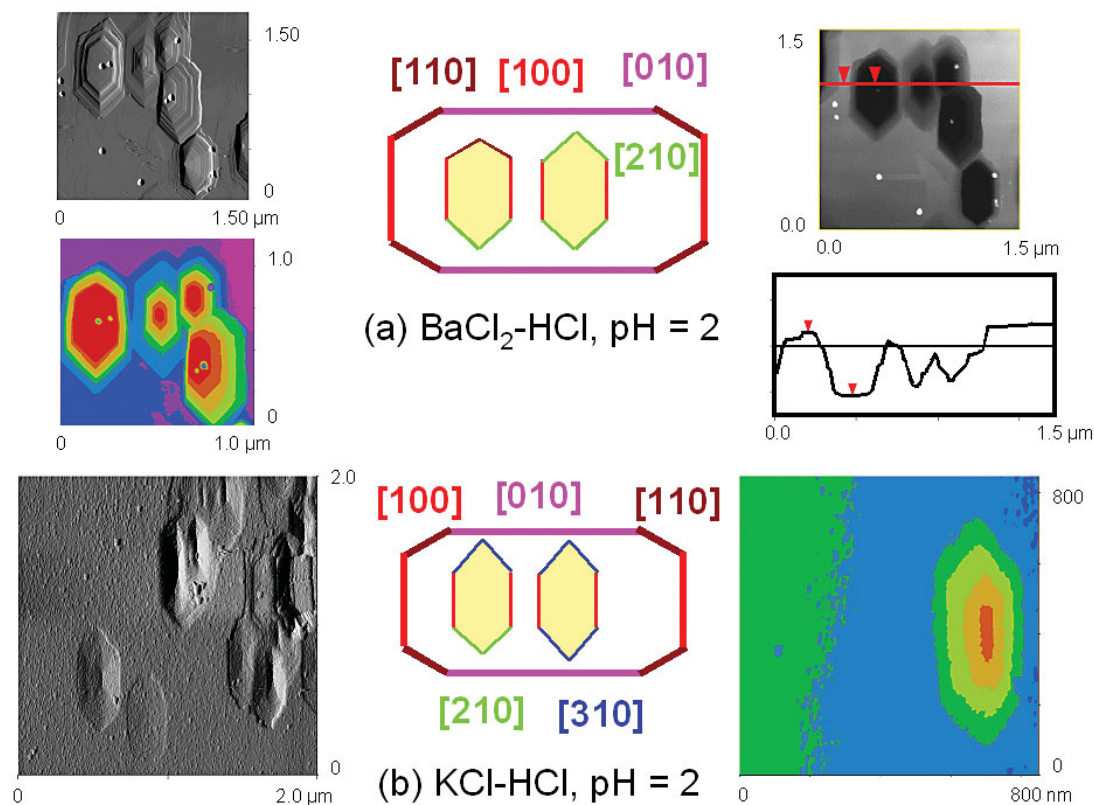


FIG. 6. (a) AFM images of etch pits formed in aqueous  $\text{BaCl}_2$  solution of pH 2.0 and their orientation on the basal surface of becquerelite. Left top: AFM image in deflection mode; left bottom: AFM image in height mode, in which various colors indicate the morphology of the pit at different depth; right: cross sections of the etch pits with AFM image in height mode. (b) AFM images of etch pits formed in aqueous KCl solution of pH 2.0 and their orientation on the basal surface of becquerelite; the AFM image on the left is in deflection mode, and the image on the right is in height mode.

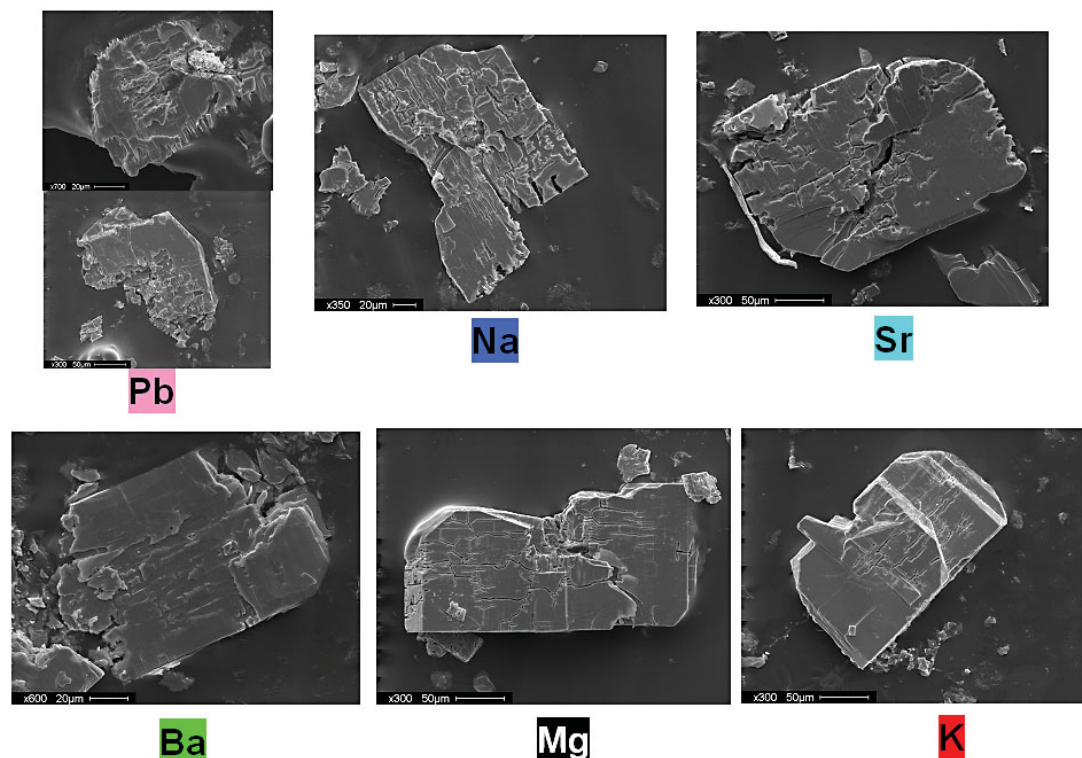


FIG. 7. SEM images of becquerelite crystals treated with electrolyte solutions of pH 2; the major cation in the electrolyte solution is indicated in a colored box below the image.

and the symmetry of the outline of the pits reduces to  $m$  (perpendicular to  $[010]$ ). Different colors at various depths indicate that the form of each edge (rounded or straight) does not significantly change as a function of depth (Fig. 8a). Etch pits commonly link together, forming dissolution channels parallel to  $[010]$  (Fig. 7). Similar to the crystals treated with an aqueous KCl solution of pH 2, steps, terraces and plateaus are not flattened, and the edges of the basal surface do not show any dissolution features.

*The basal surface treated with an aqueous  
1.00 mol L<sup>-1</sup> NaCl solution of pH 2*

After treatment with an aqueous 1.00 mol L<sup>-1</sup> NaCl solution of pH 2, the basal surface of becquerelite seems very rough. Dissolution channels are very deep, particularly along the edges of the crystal, and extend parallel to  $[100]$  and  $[010]$  (Fig. 7). Individual etch-pits are rare (Fig. 8b). If they occur outside the dissolution channels, they are elongate parallel to  $[100]$ , are very deep, and have large lateral dimensions. The terminations of the etch pits on the  $[010]$  edge are irregular

and, as a result, the outline of the etch pits displays plane-group symmetry 1.

*The basal surface treated with an aqueous  
0.50 mol L<sup>-1</sup> SrCl<sub>2</sub> solution of pH 2*

Figure 9a shows large etch-pits on the basal surface of becquerelite after treatment with an aqueous 0.50 mol L<sup>-1</sup> SrCl<sub>2</sub> solution of pH 2. The etch pits are slightly elongate parallel to  $[010]$  and are bounded by the edges  $[010]$ ,  $[210]$ ,  $[310]$  and, to a lesser extent,  $[110]$ . The latter edge occurs only in the upper part of the etch pits, which emphasizes that it becomes more stable during lateral growth of the pit (Fig. 9a). The outline of the etch pits displays in the lower part a mirror plane perpendicular to  $[100]$ , which disappears if the  $[110]$  edge occurs in the upper part of the pit. These etch pits have the largest lateral dimensions and the greatest depth of all etch pits observed on the basal (001) surface of becquerelite. The basal surface has shallow dissolution-induced channels and rounded edges along flattened steps, terraces and plateaus (Fig. 7).

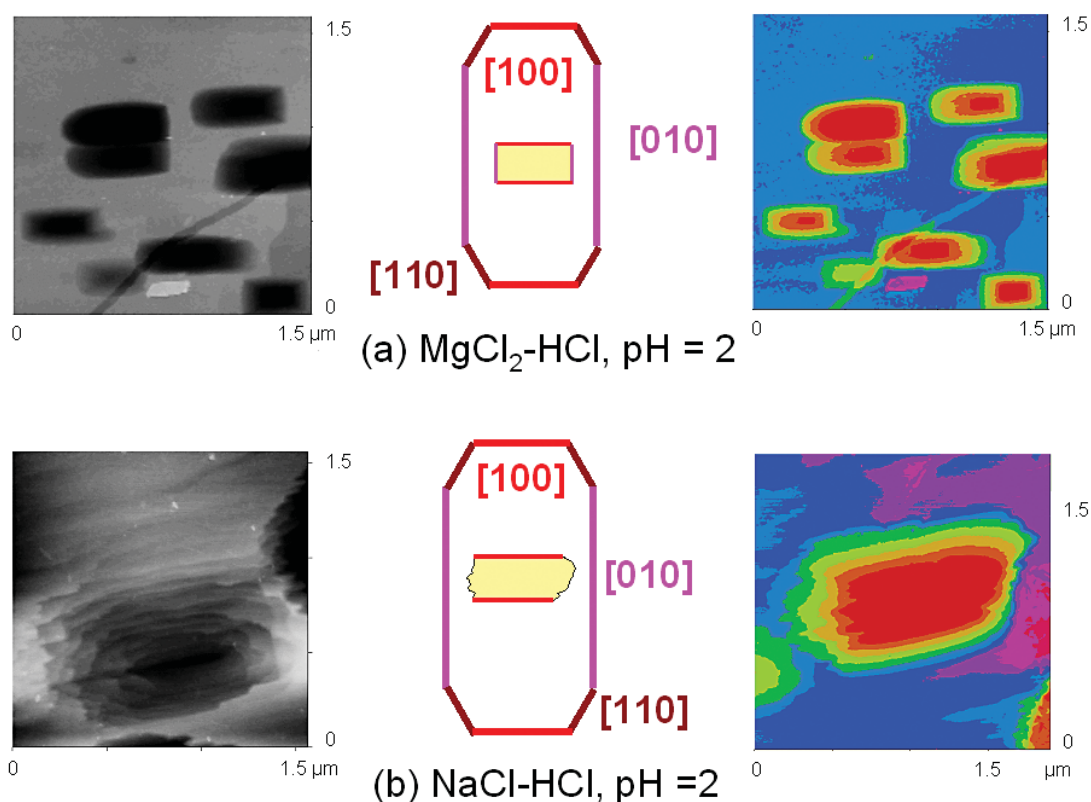


FIG. 8. (a) AFM images of etch pits formed in aqueous  $\text{MgCl}_2$  solution of pH 2.0 and their orientation on the basal surface of bequerelite. Left: image in height mode; right: image in height mode, in which various colors indicate the morphology of the pit at different depths. (b) AFM images of etch pits formed in aqueous NaCl solution of pH 2.0 and their orientation on the basal surface of bequerelite; types of images on the left and right are the same as in (a).

*The basal surface treated with an aqueous  $0.50 \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$  solution of pH 2*

Figure 9b shows etch pits on the basal surface of bequerelite after treatment with an aqueous  $0.50 \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$  solution of pH 2. The etch pits are elongate parallel to  $[010]$ , are bounded by rounded edges parallel to  $[010]$  and  $[100]$ , and their outline displays mirror symmetry perpendicular to  $[100]$ . The edges and basal surfaces of the corresponding crystals have very rough surfaces, which indicates strong dissolution on edges and the basal surface.

#### DISCUSSION

Dissolution of sheet minerals such as micas and clays normally begins at the edges of the crystal; the effect on the basal surface is small and increases significantly only in the final stages of dissolution (*e.g.*, Zysset & Schindler 1996, Rufe & Hochella 1999, Bosbach *et*

*al.* 2000). However, Huertas *et al.* (1999) and Aldushin *et al.* (2004) showed that the basal surfaces of kaolinite and “apophyllite” are involved significantly in the overall process of dissolution. For bequerelite, SEM images show that involvement of edges and the basal surface in the overall process of dissolution varies with pH and the type of cation in solution (Figs. 4b, 5e, 7). Dissolution at edges is observed in bequerelite crystals treated with aqueous  $\text{Pb}(\text{NO}_3)_2$ , NaCl,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$  and HCl solutions of pH 2, whereas dissolution occurs dominantly on the basal surfaces of crystals treated with KCl and  $\text{MgCl}_2$  solutions of pH 2.

*Change in dissolution features on the basal surface with pH*

Casas *et al.* (1997) examined the solubility of bequerelite in the pH range 5–9 and showed that the minimum solubility occurs at pH 7.5–8.0. Our experiments show that hillocks are the dominant feature on

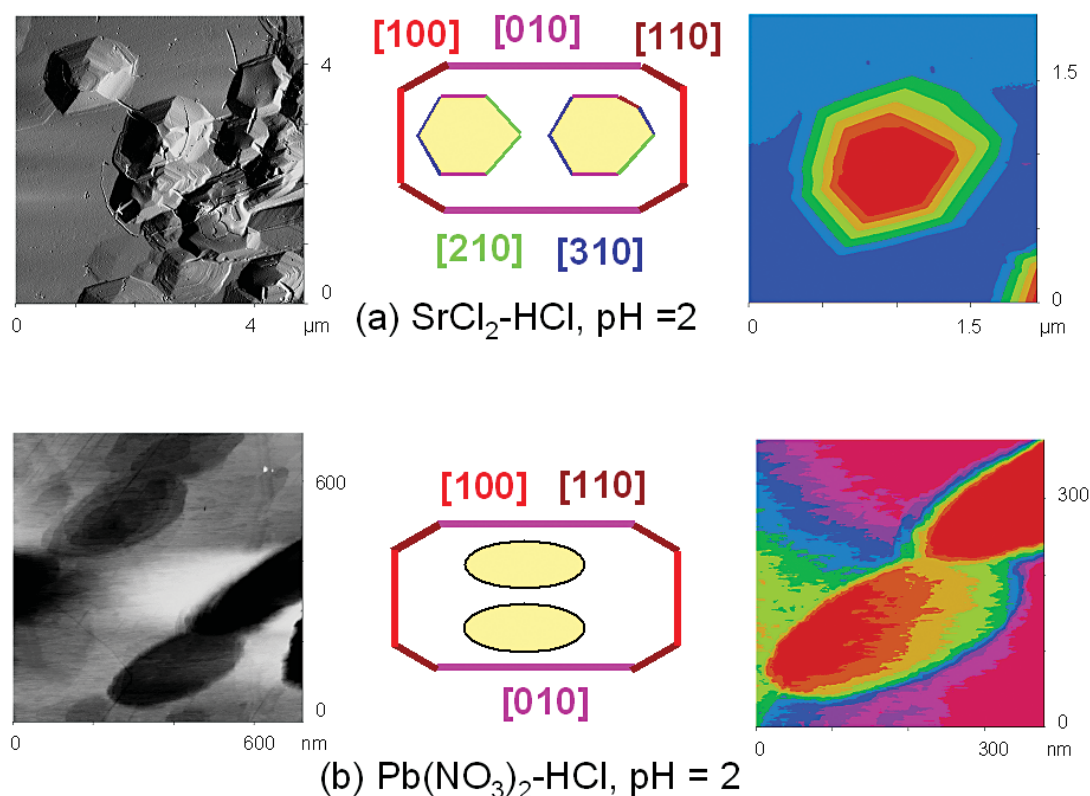


FIG. 9. (a) AFM images of etch pits formed in aqueous  $\text{SrCl}_2$  solution of pH 2.0 and their orientation on the basal surface of becquerelite. Left: image in deflection mode; right: image in height mode, in which various colors indicate the morphology of the pit at different depth. (b) AFM images of etch pits formed in an aqueous  $\text{Pb}(\text{NO}_3)_2$  solution of pH 2.0 and their orientation on the basal surface of becquerelite; images are both in height mode and in the left image, various colors indicate the morphology of the pit at different depth.

the basal surface of becquerelite crystals over a large pH range [including the pH range examined by Casas *et al.* (1997) and the interval of minimum solubility at pH 7.5–8.0 (Figs. 5a, b, c)]. Etch pits form only on the basal surface of becquerelite in strongly acidic solutions of pH 2. The formation of etch pits normally depends on the undersaturation of the solution with respect to the mineral (Carbera & Levine 1956, Lasaga 1983). However, the saturation index with respect to becquerelite is similar in a basic  $0.5 \text{ mol L}^{-1}$  solution of pH 10.5 and an aqueous HCl solution of pH 2 (Table 1). Hence, the activity of hydronium ions in solution has a stronger effect on the formation of etch pits at pH 2 and 10.5 than does the saturation index.

This observation is in agreement with recent AFM examinations of dissolution features of curite,  $\text{Pb}^{2+}_3(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]_2$  (Schindler *et al.* 2006). Here, etch pits formed in strongly acidic to neutral solutions, and the density of the etch pits increased with decreasing pH. Hillocks on the basal surface of curite have been

observed under basic conditions (aqueous  $0.1 \text{ mol L}^{-1}$   $\text{Na}_2\text{CO}_3$  solution of pH 10.5) where the undersaturation with respect to curite was most likely higher than in a near-neutral solution of pure water. Schindler *et al.* (2006) argued that formation of etch pits on the basal surface of curite is promoted primarily by the activity of protons in solution, and only secondarily by the undersaturation of the solution with respect to curite.

The occurrence of hillocks and etch pits on the basal surfaces of becquerelite and curite can be summarized as follows:

- (1) The formation of hillocks is independent of the type of anion and cation in solution (*i.e.*,  $[\text{H}_3\text{O}^+, \text{Na}^+, \text{Cl}^-, (\text{CO}_3)^{2-}]$ );
- (2) The formation of etch pits (rather than hillocks) is favored by increased protonation of edges and the basal surface.

The latter point is in contrast to the formation of hillocks and etch pits during dissolution on the basal surface of sheet-silicate minerals. Aldushin *et al.* (2004)

showed that the formation of hillocks *versus* etch pits is promoted by increasing activity of protons in solution; they ascribed the formation of hillocks to a swelling process of the interlayer. Kalinowski & Schweda (1996) attributed the swelling to incorporation of a hydroxyl interlayer, whereas Aldushin *et al.* (2004) suggested that swelling occurs through protonation of the terminal O-atoms of the silicate sheet.

*Etch pits formed in solutions with and without alkaline and alkaline-earth cations*

AFM images of etch pits show that their morphology is strongly controlled by the type of cation in solution. Etch pits formed in an aqueous HCl solution of pH 2 differ significantly in morphology from etch pits formed in the presence of alkaline, alkaline-earth and  $\text{Pb}^{2+}$  cations, indicating that the cations in solution affect dissolution on the basal surface of becquerelite.

The etch pits formed in an aqueous HCl solution of pH 2 have rounded edges, and their morphology does not display a mirror symmetry, as do etch pits formed in the presence of alkaline and alkaline-earth cations (Figs. 4f, 6a, 6b, 8a, 9a). Schindler *et al.* (2006) observed similar differences in the morphology of etch pits on the basal surface of curite, where etch pits formed in aqueous HCl and  $\text{H}_2\text{O}$  solutions display lower symmetry than etch pits formed in an aqueous  $\text{SrCl}_2$  solution. As discussed by Schindler *et al.* (2006), the lower-symmetry etch-pits in the aqueous HCl and  $\text{H}_2\text{O}$  solutions may be due to nonstoichiometric detachment of uranyl and ( $M\phi_n$ ) polyhedra ( $M$ : interstitial cation) at the edges that define the etch pits. The situation changes if cations from the solution are adsorbed on the surface. The rates of dissolution perpendicular to the edges are now controlled by the arrangement of cations on the surface, rather than by the rate of detachment of the different types of polyhedra.

*Orientation of etch pits*

The influence of the arrangement of adsorbed or incorporated cations on dissolution can be evaluated *via* inspection of the shape of etch pits. Etch pits elongate parallel to [100] form in aqueous  $\text{BaCl}_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{MgCl}_2$  solutions, whereas etch pits elongate parallel to [010] form in aqueous  $\text{SrCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$  solutions. Etch pits on the surface of untreated surfaces of becquerelite (which form in a solution containing Ca) also are elongate parallel to [010]. Table 2 lists ionic radii of these cations for characteristic coordination-numbers observed in uranyl-hydroxy-hydrate minerals (Shannon 1976, Schindler & Hawthorne 2004). Here, all monovalent (Na, K) cations and divalent cations most different from  $^{18}\text{Ca}$  in ionic radius (Ba, Mg) result in etch pits parallel to [100], whereas cations with the smallest difference in ionic radii to  $^{18}\text{Ca}$  produce etch pits parallel to [010] (Sr,  $\text{Pb}^{2+}$ ). Furthermore, the elonga-

tion of etch pits formed in aqueous  $\text{BaCl}_2$ -,  $\text{KCl}$ - and Ca-bearing solutions are identical to (1) the elongation of bilietite, compreignacite and becquerelite (Figs. 2, 10), and (2) the rows of Ba, K and Ca atoms in the bulk structures of bilietite, compreignacite and becquerelite, respectively (Fig. 10). In order to explain this phenomenon, we need to develop a mechanistic model for dissolution that involves the presence of the cation in solution, and that considers the degree of protonation of the anion terminations on edges and the basal surface. [Note added at the proof stage: Recent X-ray photoelectron spectroscopy and *in situ* atomic force microscope measurements by the first author show that the hillocks formed on the surface of becquerelite are the product of precipitation of a U-enriched phase].

*Degree of protonation and specific surface-sites on edges and on the basal surface*

The change in morphology of etch pits with the type of cation in aqueous solution suggests that the corresponding cations are adsorbed on the (001) surface of becquerelite and that their presence modifies rates of dissolution perpendicular to the edges. Negatively charged anion-terminations on edges can be protonated and can accept bonds from cations in solution. Protonation or adsorption of cations on the surface depends on pH, the equilibrium constants of the acid-base reactions involved in protonation of surface sites, the total number of surface sites, and the activity of the cations in solution. In the electrolyte solutions of pH 2, there will be a competition between the protonation of the anion terminations on the edges and the adsorption of the cations on the corresponding surface-sites (Fig. 1a). However, there will be no competition between protonation and adsorption of the anion termination on the basal surface of becquerelite. Here, the equatorial and apical O atoms of the uranyl polyhedra of the  $[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]^{2-}$  structural unit accept  $\sim 2.0$  and  $1.7$  *vu* from  $\text{U}=\text{O}$ ,  $\text{U}-\text{O}$  and  $\text{O}-\text{H}$  bonds, respectively. Hence, these O atoms and (OH) groups cannot be further protonated, as each  $\text{O}-\text{H}$  bond has an average bond-valence of  $0.80$  *vu*, and the aggregate incident bond-valence at the O atoms would be  $2.0 + 0.8 = 2.8$  and  $1.7 + 0.8 = 2.5$  *vu*, in conflict with the valence-sum rule (Brown 1981, Hawthorne

TABLE 2. IONIC RADII AND CHARACTERISTIC COORDINATION-NUMBERS OF CATIONS IN URANYL OXIDE MINERALS

| Cations                                        | Ionic radius ( $\text{\AA}$ )* | $r_{\text{CaO}^{2+}} - r_{\text{cation}}$ ( $\text{\AA}$ ) |
|------------------------------------------------|--------------------------------|------------------------------------------------------------|
| $^{18}\text{Ca}^{2+}$                          | 1.12                           | 0.00                                                       |
| $^{10}\text{Na}^+$                             | 1.02                           | 0.10                                                       |
| $^{16}\text{Sr}^{2+}$ , $^{100}\text{Sr}^{2+}$ | 1.26, 1.36                     | 0.14, 0.24                                                 |
| $^{16}\text{Pb}^{2+}$ , $^{100}\text{Pb}^{2+}$ | 1.29, 1.40                     | 0.17, 0.28                                                 |
| $^{17}\text{K}^+$ , $^{160}\text{K}^+$         | 1.46, 1.51                     | 0.34, 0.39                                                 |
| $^{16}\text{Mg}^{2+}$                          | 0.72                           | 0.40                                                       |
| $^{160}\text{Ba}^{2+}$                         | 1.52                           | 0.40                                                       |

\* Shannon (1976).

1994, 1997) [note that the apical O-atoms can never be protonated, and the equatorial O-atoms and (OH) groups can be only protonated if the corresponding U–O–U linkages will be broken].

The apical O-atoms of the uranyl bonds can accept bonds from  $(\text{H}_3\text{O})^+$  and from cations in solution. The competition between  $(\text{H}_3\text{O})^+$  and the cation in solution depends on their activities in solution, their coordination geometry and their Lewis acidities. In all electrolyte solutions of pH 2, the activity of the cations in the initial solution was 5 (for  $\text{Pb}^{2+}$ ) to 50 (for  $\text{Na}^+$ ) times higher than the activity of  $(\text{H}_3\text{O})^+$ . These ratios in activity indicate that the cations of the electrolyte solution bond more commonly to the apical O-atoms of the uranyl bonds than hydronium ions. Depending on its coordina-

tion geometry and size, the cation can bond to several apical O-atoms on the surface. For example, interstitial Ba and Ca cations in the bulk structures of billietite and becquerelite bond to three apical O-atoms of the same sheet of uranyl polyhedra (Finch *et al.* 2006, Burns & Li 2002; Figs. 10c, h). In Sr-exchanged becquerelite,  $\text{Sr}_{1.27}[(\text{UO}_2)_3\text{O}_{3.54}(\text{OH})_{1.46}(\text{H}_2\text{O})_3]$ , Sr also bonds to three apical O-atoms (Burns & Li 2002), whereas in compreignacite, K bonds only to two apical O-atoms of the same sheet of uranyl polyhedra (Burns 1998a). In masuyite,  $^{110}\text{Pb}^{2+}(\text{H}_2\text{O})_3[(\text{UO}_2)_3\text{O}_3(\text{OH})_2]$ ,  $\text{Pb}^{2+}$  bonds to three O-atoms of the same sheet (Burns & Hanchar 1999), whereas in richetite,  $^{16}\text{M}_x^{[8.4]}\text{Pb}^{2+}_{8.57}(\text{H}_2\text{O})_{31}[(\text{UO}_2)_{18}\text{O}_{18}(\text{OH})_{12}(\text{H}_2\text{O})_{10}]$  ( $M$ : Mg, Fe), Mg bonds to only one apical O-atom of the same sheet of uranyl

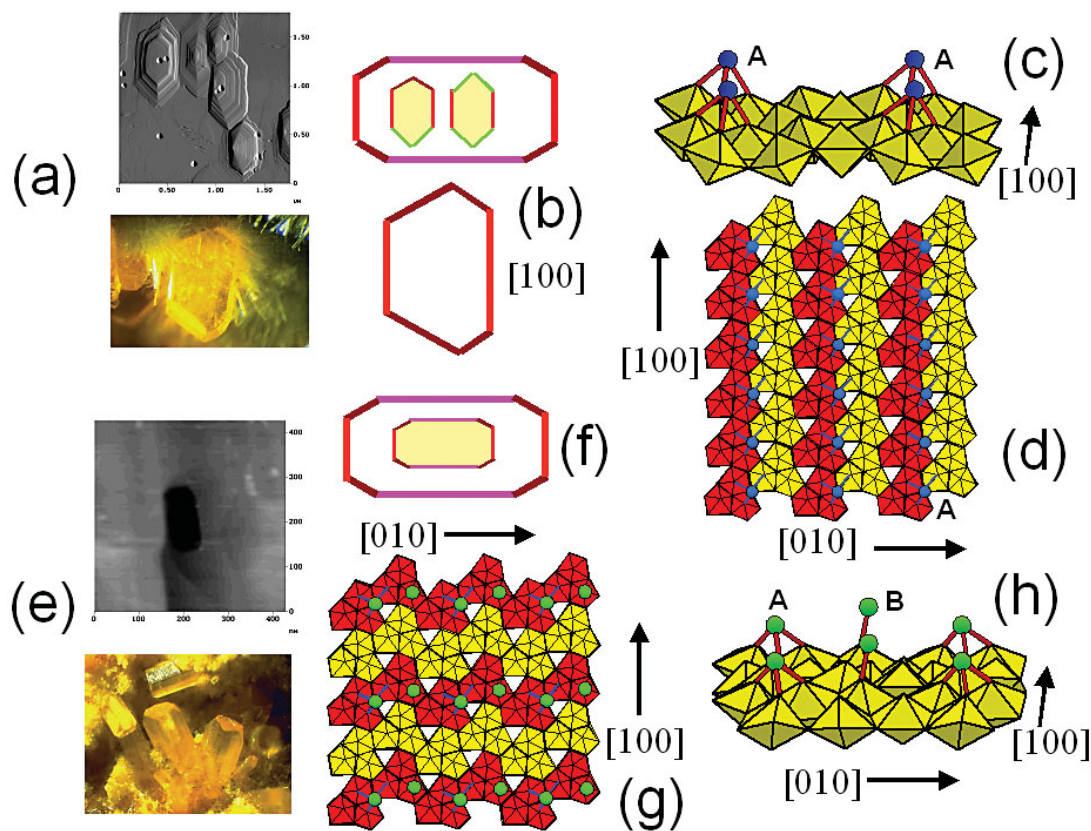


FIG. 10. (a) Image of a billietite crystal (bottom) and AFM image of etch pits formed on the basal surface of becquerelite in the presence of  $\text{Ba}^{2+}$  (top). (b) Elongation and morphology of billietite crystals (bottom) and etch pits. (c)  $\text{Ba}^{2+}$  at position A on the surface of the uranyl sheet in the bulk structure of billietite;  $\text{Ba}^{2+}$  atoms are shown as blue circles, and the bonds between  $\text{Ba}^{2+}$  and O atoms of the uranyl groups are shown as red lines. (d) Rows of  $\text{Ba}^{2+}$  atoms parallel to  $[100]$  in the bulk structure of billietite. (e) Becquerelite crystals (bottom) and AFM image of an etch pit formed on the basal surface of becquerelite in the presence of  $\text{Ca}^{2+}$  (top). (f) Elongation and morphology of becquerelite crystals and an etch pit. (g) Rows of  $\text{Ca}^{2+}$  atoms parallel to  $[010]$  in the bulk structure of becquerelite. (h)  $\text{Ca}^{2+}$  atoms at positions A and B on the surface of the uranyl sheet in the bulk structure of becquerelite;  $\text{Ca}^{2+}$  atoms are shown as green circles, and the bonds between  $\text{Ca}^{2+}$  and O atoms of the uranyl groups are shown as red lines.

polyhedra (Burns 1998b). Note that the structural units in Sr-exchanged becquerelite, masuyite and richetite have identical anion-topologies but different compositions than the structural unit in becquerelite (Burns 1999).

In the structural unit of becquerelite, the cations occur at specific sites in the interlayer that are related to the distance between the apical O-atoms. In the structures of becquerelite and billietite, one can distinguish two distinct cation-sites at the surface, which we designate here as *A* and *B*. At site *A*, the cation bonds to three apical O-atoms of the same sheet of uranyl polyhedra, whereas at site *B*, the cation bonds to only one O-atom of the same sheet. In billietite, Ba occurs only at the *A* site, which results in rows of Ba parallel to [100] (Fig. 10d). In becquerelite, the smaller Ca occurs at both the *A* and *B* sites, which results in rows of Ca parallel to [010] (Fig. 10g).

#### *Dissolution mechanism involving the cation attached to the basal surface*

Figures 10d, g show the sheets of uranyl polyhedra in billietite and becquerelite with the cation positions of Ba and Ca, respectively. The sheets are again constructed entirely of clusters of three pentagonal bipyramids, which are the major aqueous species in weakly acidic uranyl-bearing solution (Moll *et al.* 2000). Schindler *et al.* (2004a) proposed a dissolution model for a uranyl sheet that involves detachment of these clusters. In the first step, the equatorial O atoms or (OH) groups of a cluster become (more) protonated, which results in an incident bond-valence sum at an O atom that violates the valence-sum rule. In order to reduce the incident bond-valence sum, the average bond-valence of the U–O bonds must decrease, which weakens the corresponding U–O–U linkages and ultimately forces detachment of the cluster. Schindler *et al.* (2004a) designated such terminations, at which the O atoms are either protonated or accept strong bonds from cations, as *activated sites*.

If adsorbed Ba adopts the same arrangement on the (001) surface of becquerelite as it does in the bulk structure of billietite (site *A*), there will be rows of Ba parallel to [100], and each Ba will link a red and a yellow cluster (Fig. 10d). If Ca adopts the same arrangement on the (001) surface of becquerelite as it occupies in the bulk structure (of becquerelite, sites *A* and *B*), there will be rows of Ca parallel to [010], and each Ca will link to two red clusters (Fig. 10g). During dissolution, these two arrangements of cations will have the following consequences: (1) A cation will prevent attachment of a hydronium ion and subsequent protonation of equatorial O-atoms in its immediate surroundings. Hence, the number of activated sites around a cation will be lower than on parts of the surface where no cation is attached. Consequently, the number of activated sites will be lower parallel to a row of cations, and the edge parallel to a row of cations will be more stable than the edge

perpendicular to a row of cations. (2) If the cation bonds to apical O-atoms of different clusters, detachment of a cluster perpendicular to a row of cations will be more difficult than detachment of a cluster parallel to a row of cations. In the case of rows of Ba parallel to [100] (Fig. 10d), it will be easier to remove a yellow and a red cluster from the [010] edge than to remove two yellow or two red clusters from the [100] edge. In the first case, detachment of the cluster does not require breaking of Ba–O bonds, whereas in the second case, one or two Ba–O bonds must be broken for detachment of each cluster. In the case of rows of Ca parallel to [010] (Fig. 10g), it is easier to remove a yellow cluster than a red cluster, because a yellow cluster can be removed without breaking a Ca–O bond.

This model can be used with the observed orientation of the etch pits to predict the arrangement of adsorbed cations during dissolution in aqueous MgCl<sub>2</sub>, SrCl<sub>2</sub>, NaCl and Pb(NO<sub>3</sub>)<sub>2</sub> solutions. The etch pits formed in aqueous MgCl<sub>2</sub> and NaCl solutions are elongate parallel to [100]. Hence, the number of activated sites is larger at the [010] edge, and Mg and Na are probably arranged in rows parallel to [100]. The etch pits formed in aqueous SrCl<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> solutions are elongate parallel to [010]. Consequently, the number of activated sites is larger at the [100] edge, and the Sr and Pb<sup>2+</sup> are likely to be arranged in rows parallel to [010].

#### *Lateral area versus depth of etch pits on the basal surface of becquerelite*

Schindler *et al.* (2006) showed that the average area and the depth of etch pits may be used to express the stability of edges and the change in relief of a surface. Here, a higher relief of an etch pit is not the result of a higher rate of dissolution perpendicular to the basal surface; rather, it is an expression of the difference between the lowering of the surrounding surface and the growth of the etch pit perpendicular to the sheet. Figure 11 shows the area of an etch pit as a function of average depth. Both the lateral dimensions and the depth of the etch pits increase in the following sequence of aqueous solutions: MgCl<sub>2</sub> < KCl < Pb(NO<sub>3</sub>)<sub>2</sub> < BaCl<sub>2</sub> < NaCl < SrCl<sub>2</sub>. The stability of the edges on the basal surface also decreases in the same sequence because a large lateral area of an etch pit represents a high dissolution-rate perpendicular to the edges. The scattering of data points for some samples indicates that dissolution rates perpendicular to edges and sheet have changed during the dissolution process, either as a function of time or with the surroundings of the etch pit.

#### *Factors controlling the relief of dissolution features on a single crystal*

The dissolution behavior of a single crystal depends on its dimensions, the roughness of its surface, and the ionic strength, type of dissolved cation and pH of the

ambient solution. The pH was constant in all acidic electrolyte solutions used here. Crystal dimensions and surface roughness were similar in each experiment. In the electrolyte solutions of pH 2, the ionic strength was very high, and the initial saturation-index with respect to becquerelite was very low (Table 1). The ionic strength was much lower in the aqueous HCl solution of pH 2 than in the aqueous KCl and MgCl<sub>2</sub> solutions (Table 1), but the surface of the crystals treated with the aqueous HCl solution showed a higher relief than the corresponding crystals treated with the latter solutions (Figs. 4a, 7). Hence, the type of the additional cation in solution seems to have a greater effect on the relief of dissolution features on becquerelite crystals at pH 2 than the ionic strength of the solution.

*General stability of edges and basal surfaces in the presence of different cations in solution*

We are now able to use the above observations on the morphology of etch pits and on the dissolution features on basal surfaces and their edges in order to determine the general stability of an edge and a basal surface in the presence of a specific cation in solution. The depth of etch pits and dissolution channels and the general appearance of the basal surface give information on the stability of the basal surface. On the other hand, the lateral areas of etch pits, the form of their edges (rounded or straight), and the dissolution features on the edges along the basal surface give information on the stability of the edges. The following observations and conclusions can be made for the experiments in electrolyte solutions of pH 2.

(1) Etch pits formed in aqueous MgCl<sub>2</sub> and KCl solutions are shallow and small in lateral extent. The edges of the etch pits are well defined, and the edges on

the basal surface do not show any dissolution features. These observations clearly indicate high stability of both edges and the basal surface in these highly acidic solutions.

(2) Etch pits formed in aqueous SrCl<sub>2</sub> solution have larger lateral areas and are deeper than etch pits formed in aqueous BaCl<sub>2</sub> solution. In both cases, the edges bounding the etch pits are well defined, and the edges bounding the basal surfaces contain similar amounts of dissolution features. The basal surface has rounded edges and less relief. Hence, the stabilities of the edges and basal surface are lower than in aqueous KCl and MgCl<sub>2</sub> solutions, and the different dimensions of the etch pits suggest higher stability of edges and basal surfaces in aqueous BaCl<sub>2</sub> than in aqueous SrCl<sub>2</sub> solutions.

(3) Etch pits formed in aqueous Pb(NO<sub>3</sub>)<sub>2</sub> and NaCl solutions are bounded by rounded or irregular edges. Etch pits formed in aqueous NaCl solution have larger lateral dimensions and are deeper than etch pits formed in aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solution. The edges along the basal surface of crystals treated with aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solution are much more corroded, whereas the basal surface of crystals treated with an aqueous NaCl solution contains deeper dissolution-induced channels. The stability of edges in both solutions is lower than in all other solutions. On the basis of the above criteria, edges are more stable (*i.e.*, less corroded) in NaCl solution than in aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solutions, whereas the basal surface is more stable in Pb(NO<sub>3</sub>)<sub>2</sub> than in aqueous NaCl solution.

On the basis of these observations, the stability of the basal surface of becquerelite in aqueous solutions of simple salts decreases in the sequence MgCl<sub>2</sub> > KCl > BaCl<sub>2</sub> > Pb(NO<sub>3</sub>)<sub>2</sub> > NaCl > SrCl<sub>2</sub>, and the stability of edges decreases in the sequence MgCl<sub>2</sub> > KCl > BaCl<sub>2</sub> > SrCl<sub>2</sub> > NaCl > Pb(NO<sub>3</sub>)<sub>2</sub>. Both rankings indicate that solutions with cations of ionic radius similar to that of <sup>18</sup>Ca<sup>2+</sup> (Table 2) have a larger effect on the dissolution processes of single crystals of becquerelite.

*Degree of dissolution in acidic solutions*

We noted above that crystals treated with aqueous KCl and MgCl<sub>2</sub> solutions of pH 2 display a lower degree of dissolution than crystals treated with an HCl solution of pH 2. This observation indicates that the dissolution rate of a single crystal is independent of the formation of etch pits. Furthermore, the number of activated sites on the basal surfaces of becquerelite crystals treated with K<sup>+</sup>- and Mg<sup>2+</sup>-bearing solutions must be lower than for crystals treated with HCl solution (*i.e.*, without any additional cations in solution). However, it is apparent from the SEM images (Figs. 4b, 7) that the basal surfaces of crystals treated with Na-, Ba-, Sr- and Pb<sup>2+</sup>-bearing aqueous solutions show a similar or higher degree in dissolution than the basal surface treated with an HCl solution of pH 2.0. These different

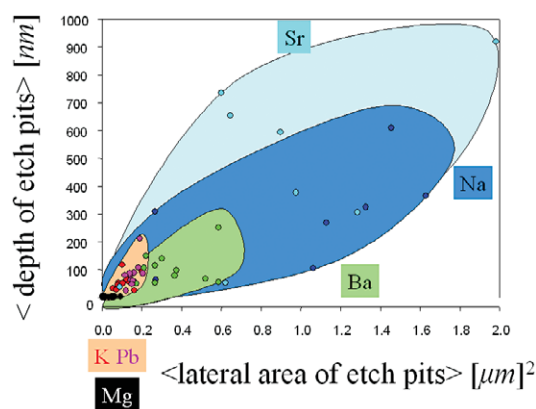


FIG. 11. The average lateral area as a function of the average depth of etch pits formed in electrolyte solution of pH 2; the major cations in solution are shown beside the colored areas.

degrees in dissolution in the presence (or absence) of specific cations in solution may be explained by the role of the cations in solution during the two main mechanisms of a surface-controlled dissolution process: (1) formation of an activated complex, and (2) detachment of the components from the structure (Stumm 1992): (1) If a cation of the solution is adsorbed on the (001) surface (through bonding to the apical O-atoms), it can inhibit protonation of the equatorial O-atoms that link polyhedra or polyhedron clusters on the basal surface; in turn, this will reduce the number of activated sites and hence the degree of dissolution of the basal surface. (2) Once the equatorial O-atoms are protonated and the bonds between polyhedra or polyhedron groups are weakened, the cations of the solution can complex with these polyhedra or polyhedron groups by bonding to their apical O-atoms. This will increase the detachment rate of the polyhedra or polyhedron groups, and thus increase the degree of dissolution of the basal surface.

It is apparent from the observations above that  $K^+$  and  $Mg^{2+}$  are less able to form complexes with polyhedra or polyhedron groups of the structural unit than  $Na^+$ ,  $Pb^{2+}$ ,  $Ba^{2+}$  and  $Sr^{2+}$ . However, their presence on the surface inhibits formation of activated sites, which explains the low degree of dissolution of the corresponding basal face and its edges.

#### CONCLUSIONS

The dissolution experiments on single crystals of becquerelite at different pH and with different cations in solution show the following features on the basal surface and its edges:

(1) Hillocks occur on the basal surface between pH 3.5 and 10.

(2) Etch pits form only in solutions of pH 2, indicating that their formation is favored by an increase in the activity of protons in solution.

(3) Etch pits formed in HCl solution of pH 2 and without any additional cations in solution do not display any symmetry elements of the bulk structure; this may be the result of nonstoichiometric detachment of uranyl and  $(Ca\phi_n)$  polyhedra on the edges of the etch pits.

(4) Etch pits formed in aqueous  $BaCl_2$ ,  $KCl$ ,  $NaCl$  and  $MgCl_2$  solutions are elongate parallel to  $[100]$ , suggesting that adsorbed cations are arranged in rows parallel to  $[100]$  on the basal surface of becquerelite.

(5) Etch pits formed in aqueous  $SrCl_2$  and  $Pb(NO_3)_2$  solution are elongate parallel to  $[010]$ , suggesting that adsorbed cations are arranged in rows parallel to  $[010]$  on the basal surface of becquerelite.

(6) The lateral dimensions of etch pits, the shape of edges along etch pits, and the relief of dissolution features on edges of the basal surface indicate that the stability of edges decreases in electrolyte solutions in the following sequence:  $MgCl_2 > KCl > BaCl_2 > SrCl_2 > NaCl > Pb(NO_3)_2$ .

(7) The lateral dimensions of etch pits and the relief of dissolution features on the basal surface indicate that the stability of the basal face decreases in electrolyte solutions in the following sequence:  $MgCl_2 > KCl > BaCl_2 > Pb(NO_3)_2 > NaCl > SrCl_2$ .

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