

The structures of becquerelite and Sr-exchanged becquerelite

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ABSTRACT

The crystal structures of becquerelite, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_8$, and Sr-exchanged becquerelite obtained by ion exchange, $\text{Sr}_{1.27}[(\text{UO}_2)_3\text{O}_{3.54}(\text{OH})_{1.46}](\text{H}_2\text{O})_3$, have been refined using diffraction data collected with $\text{MoK}\alpha$ X-rays and a CCD-based detector. The structure of becquerelite, orthorhombic, space group $Pn2_1a$, $a = 13.8527(5)$, $b = 12.3929(4)$, $c = 14.9297(5)$ Å, $V = 2563.2(1)$ Å³, has been refined on the basis of F^2 for 4875 unique reflections to $R1 = 3.39\%$, calculated using 4581 unique observed reflections ($|F| \geq 4\sigma_F$), and a goodness-of-fit (S) of 1.04. Sr-exchanged becquerelite was obtained by placing single crystals of synthetic becquerelite in 2.5 M SrCl_2 solution for 60 h at 160 °C. The structure of Sr-exchanged becquerelite is trigonal, space group $P3$, $a = 7.020(4)$, $c = 6.992(6)$ Å, $V = 298.4(3)$ Å³, and has been refined on the basis of F^2 for 683 unique reflections to $R1 = 4.26\%$, calculated using the 564 unique observed reflections ($|F| \geq 4\sigma_F$), and an S of 1.01. The results for becquerelite confirm the cation polyhedra and structural connectivity reported previously, but collection of data for a high-quality crystal using a CCD-based detector has substantially improved the precision of the atom positions. The structure contains α - U_3O_8 -type sheets of uranyl pentagonal bipyramids, with a single symmetrically distinct Ca cation and eight symmetrically distinct H_2O groups located in the interlayer. The structure of Sr-exchanged becquerelite also contains α - U_3O_8 -type sheets of uranyl pentagonal bipyramids, although the amount of H in the sheets is lower than for becquerelite. The interlayer contains two symmetrically distinct Sr cations and a single H_2O group. Ion exchange of Sr into the interlayer of becquerelite without destruction of the crystals has potential important implications for the mobility of ^{90}Sr in contaminated areas, and for the geologic disposal of nuclear waste.

INTRODUCTION

Uranyl oxide hydrates are common constituents of the oxidized portions of U deposits, and are typically the first U^{6+} phases to form at the onset of alteration of uraninite (Fronde 1958). They are important for understanding water-rock interactions in U deposits, form as products of the oxidation of U mine and mill tailings, and are prominent alteration phases in laboratory experiments involving 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 incorporated into uranyl oxide hydrates (Burns et al. 1997a; Chen et al. 1999, 2000).

The known structures of uranyl oxide hydrate minerals are each based upon sheets of edge- and corner-sharing uranyl polyhedra, with low-valence cations and H_2O groups located in interlayer positions (Burns 1999a). Analogous to clays, in some cases the interlayer cations are exchangeable. Burns (1999b) demonstrated ion exchange of Cs for K and Na in the interlayers of single crystals of boltwoodite, as shown by crys-

tal structure analyses before and after cation exchange. The single crystals of boltwoodite remained intact with optically smooth faces and sharp edges following exchange, ruling out a solution-reprecipitation mechanism. The capacity of uranyl phases to exchange interlayer cations, particularly radionuclides such as ^{90}Sr , ^{135}Cs , and ^{137}Cs , may have important implications for the geological disposal of nuclear waste.

Becquerelite, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_8$, is a common uranyl oxide hydrate in natural systems. The crystal structure of becquerelite was determined by Piret-Meunier and Piret (1982) using single-crystal X-ray data and was refined to an agreement index (R) of 7.0% on the basis of 1983 unique observed reflections. Pagoaga et al. (1987) also published the structure of becquerelite, and reported an R of 8.3% for 2853 unique observed reflections. In the latter case, problems with the refinement were attributed to disorder in the crystals, as reflected by moderate to intense streaking in the diffraction patterns, a feature that presumably contributed to reported uncertainties in the U-O bond lengths that ranged from 0.04 to 0.09 Å.

Here we present a modern refinement of the structure of a natural crystal of becquerelite, and report the ion exchange of Sr for Ca in the interlayer of single crystals of synthetic becquerelite, as demonstrated by a single-crystal structure determination for Sr-exchanged becquerelite.

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EXPERIMENTAL METHODS

Synthesis of becquerelite

Crystals of becquerelite were grown from an aqueous solution containing 0.313 g uranyl acetate, 0.05 g calcium carbonate, and 4 mL ultrapure water, with a U:Ca molar ratio of 3:2. The solution was placed in a 23 mL Teflon-lined Parr vessel and heated at 160 °C for 50 hours. The crystals were recovered by filtration, washed with de-ionized water, and dried in air. The resulting crystals are platy with maximum diameters up to 0.3 mm.

Ion exchange experiments

Prior to ion exchange experiments, the structure of synthetic becquerelite was shown to be identical to natural becquerelite by structure determination ($R1 = 5.3\%$). Several crystals of synthetic becquerelite with maximum dimensions of ~ 0.2 mm were selected for ion-exchange experiments. The purpose of these experiments was to determine if the Ca in the interlayer of becquerelite could be replaced by Sr without destroying the structure. The crystals were placed in a 23 mL Teflon-lined Parr vessel, together with 6 mL of 2.5 M SrCl_2 solution, and were heated to 160 °C for 60 hours. Following treatment, the solution was removed using a hypodermic needle and the crystals were recovered. Optical examination showed that the crystals were intact with planar faces and sharp edges, with no outward signs of alteration, although the crystals had become translucent.

Diffraction data collection for natural becquerelite and Sr-exchanged becquerelite

Data were collected for each phase using a Bruker SMART CCD diffractometer with a crystal-to-detector distance of 5.0 cm and $\text{MoK}\alpha$ X-radiation. More than a hemisphere of data were collected over the angular range $3^\circ \leq 2\theta \leq 56.7^\circ$ for each crystal. The three dimensional data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT.

The crystal of natural becquerelite selected for study was from a specimen collected in Shinkolobwe, Democratic Republic of Congo, and was provided by Mr. Forrest Cureton. The crystal, which displayed uniform optical properties, is acicular with well-developed faces and dimensions $0.27 \times 0.08 \times 0.028$ mm. Frame widths of 0.2° in ω were used for the collection of data, with 20 s spent counting per frame. Unit-cell dimensions (Table 1) were refined on the basis of 8192 reflections using least-squares techniques. A correction for absorption was done by Gaussian quadrature integration using the measured dimensions of the crystal faces. The resulting minimum and maximum transmission factors were 0.025 and 0.375. A total of 13 800 intensities were collected, and merging of equivalent reflections gave 4875 unique reflections ($R_{\text{int}} = 6.1\%$), with 4581 classed as observed ($|F_o| \geq 4\sigma_F$). Peaks in the diffraction pattern were sharp with no streaking observed, in contrast to the data collected by Pagoaga et al. (1987). The large increase in the number of unique observed reflections, as compared to the data collected for becquerelite by Pagoaga et al. (1987) and Piret-Meunier and Piret (1982), may be attributed to the much

TABLE 1. Crystallographic data and details of the structure refinements of becquerelite and Sr-exchanged becquerelite

	Becquerelite	Sr-exchanged becquerelite
<i>a</i> (Å)	13.8527(5)	7.020(4)
<i>b</i> (Å)	12.3929(4)	
<i>c</i> (Å)	14.9297(5)	6.992(6)
<i>V</i> (Å ³)	2563.1(1)	298.4(3)
Space group	<i>Pn</i> 2 ₁ <i>a</i>	<i>P</i> 3
<i>Z</i>	4	1
Formula	$\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_3] \cdot 8\text{H}_2\text{O}$	$\text{Sr}_{1.27}[(\text{UO}_2)_3\text{O}_{3.54}(\text{OH})_{1.48}](\text{H}_2\text{O})_8$
<i>F</i> (000)	3336	443
μ (mm ⁻¹)	38.09	49.51
<i>D</i> _{calc} (g/cm ³)	5.106	5.877
Crystal size (mm)	$0.27 \times 0.08 \times 0.028$	$0.15 \times 0.05 \times 0.01$
Total ref.	13,800	1623
Unique ref.	4875	683
<i>R</i> _{int} (%)	6.10	6.25
Unique $ F_o \geq 4\sigma_F$	4581	564
<i>R</i> ₁ (%)	3.39	4.26
<i>R</i> _w (%)	8.80	7.20
<i>S</i> (GOF)	1.04	1.01
Flack parameter	0.05(2)	0.10(8)
Max., min., $\Delta\rho$ e.Å ⁻³	2.66 and -1.66	2.16 and -2.05

enhanced sensitivity of the CCD-based detector for weak reflections, as compared to a scintillation detector mounted on a serial diffractometer (Burns 1998a).

The crystal of Sr-exchanged becquerelite selected for study has the dimensions $0.15 \times 0.05 \times 0.01$ mm. Preliminary examination of the diffraction pattern showed that the peak widths were $\sim 2^\circ$ in ω , indicating that the crystal quality was diminished relative to the untreated crystals. Owing to the fairly large peak widths, frame widths of 0.6° in ω were used for the collection of data, with 60 s spent counting per frame. Unit-cell dimensions (Table 1) were refined on the basis of 625 reflections using least-squares techniques. A semi-empirical correction was done for absorption with the crystal modeled as a plate; reflections with a plate-glancing angle less than 3.0° were discarded, and the R_{int} of 429 intense reflections was lowered from 11.4 to 3.2%. A total of 1623 intensities were collected, and merging of equivalent reflections gave 683 unique reflections ($R_{\text{int}} = 6.2\%$), with 564 classed as observed ($|F_o| \geq 4\sigma_F$).

Electron microprobe analysis of Sr-exchanged becquerelite

A crystal of Sr-exchanged becquerelite was mounted in epoxy, polished and coated with carbon. Electron microprobe analyses were done using a Cameca SX-50 in wavelength-dispersive spectroscopy (WDS) mode. Data were reduced using the method of Pouchou and Pichoir (1984).

The analyses were done with an accelerating voltage of 15 kV and a probe current of 25 nA. A defocused beam 10 μm in diameter was used to minimize beam damage. Counting times on peaks and backgrounds were 30 s for $\text{Sr}(L\alpha)$ and $\text{Cl}(K\alpha)$, and 10 s for $\text{U}(M\alpha)$. A 100 s energy-dispersive scan indicated no elements with *Z* greater than eight, other than those reported herein. Analytical standards used were: Sr-anorthite ($\text{Sr}L\alpha$), Cl-apatite ($\text{Cl}K\alpha$), and synthetic UO_2 from Oak Ridge National Laboratory ($\text{U}M\alpha$). The results of the chemical analysis are given in Table 2.

We also obtained chemical analyses for the same crystal of Sr-exchanged becquerelite as was used for the collection of X-ray data. However, we were unable to polish the crystal as well

TABLE 2. Chemical analysis (wt%) for Sr-exchanged becquerelite

Pt	UO ₃	SrO	Cl	Total
1	77.17	13.30	1.07	91.54
2	77.40	12.64	1.15	91.19
3	79.84	14.17	1.32	95.33
4	80.29	13.91	1.22	95.42
5	81.43	14.23	1.21	96.87
Average	79.23	13.65	1.19	94.07

as would have been desirable; the analyses are probably inferior to those given in Table 2. The analyses of three points gave (wt%) UO₃ = 73.1–78.6, SrO = 14.8–16.7, CaO = 0.03–0.06, Cl = 0.75–0.90.

Structure refinement of becquerelite

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography* (Ibers and Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the refinement of the crystal structure. Systematic absences and reflection statistics indicated space group *Pn*2₁*a*, as reported earlier for becquerelite by Pagoaga et al. (1987) and Piret-Meunier and Piret (1982). The structure was refined on the basis of *F*² for all 4875 unique reflections. The final model included all atomic positional parameters, anisotropic displacement parameters for the cations, isotropic displacement parameters for the anions, and a weighting scheme of the structure factors. The final *R*1 was 3.39%, calculated for the 4581 unique observed ($|F_o| \geq 4\sigma_F$) reflections. A model that included anisotropic displacement of the anions was tried, but did not lead to an improvement in the refinement, and resulted in a few physically unrealistic atom shapes. The final atomic positional parameters and anisotropic displacement parameters are given in Tables 3 and 4, and selected interatomic distances and angles are given in Table 5. Calculated and observed structure factors are provided in Table 6¹.

Structure determination and refinement of Sr-exchanged becquerelite

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography* (Ibers and Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the solution and refinement of the crystal structure. There were no systematic absences of reflections, indicating that the space group lacks translational symmetry operators. We attempted structure solutions in each of the possible hexagonal and trigonal space groups. We achieved partial structures in many, but only space group *P*3 permitted the full structure to be resolved. The structure was refined on the basis of *F*² for all 683 unique reflections. The final model included all atomic

TABLE 3. Atomic positional parameters and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for becquerelite

	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*]
U1	1.0	0.9104(1)	0.4404(1)	0.7417(1)	95(1)
U2	1.0	0.8717(1)	0.7513(1)	0.7525(1)	96(1)
U3	1.0	0.9058(1)	0.0597(1)	0.7493(1)	87(1)
U4	1.0	0.6267(1)	0.2479(1)	0.7221(1)	87(1)
U5	1.0	0.6574(1)	0.5614(1)	0.7087(1)	103(1)
U6	1.0	0.6515(1)	0.9333(1)	0.7112(1)	92(2)
Ca	1.0	0.9572(2)	0.4221(3)	0.4656(2)	175(6)
O1	1.0	0.9463(8)	0.457(1)	0.6264(8)	175(25)
O2	1.0	0.869(1)	0.418(1)	0.8523(9)	286(30)
O3	1.0	0.9265(7)	0.7668(9)	0.6445(7)	219(24)
O4	1.0	0.8221(6)	0.743(1)	0.8627(6)	177(19)
O5	1.0	0.9411(8)	0.029(1)	0.6345(7)	137(24)
O6	1.0	0.8708(8)	0.094(1)	0.8611(8)	194(27)
O7	1.0	0.6037(6)	0.250(1)	0.6035(6)	195(19)
O8	1.0	0.6569(6)	0.249(2)	0.8388(6)	209(19)
O9	1.0	0.6631(8)	0.550(1)	0.5895(7)	169(25)
O10	1.0	0.6477(9)	0.580(1)	0.8266(9)	290(30)
O11	1.0	0.6679(7)	0.951(1)	0.5929(7)	161(25)
O12	1.0	0.6263(8)	0.904(1)	0.8280(7)	155(24)
O13	1.0	0.8179(8)	0.585(1)	0.7190(8)	185(23)
O14	1.0	0.0654(8)	0.415(1)	0.7758(7)	138(24)
O15	1.0	0.8080(7)	0.916(1)	0.7429(7)	127(22)
O16	1.0	0.5629(8)	0.084(1)	0.7232(8)	179(25)
OH1	1.0	0.9904(8)	0.620(1)	0.8024(8)	137(24)
OH2	1.0	0.9496(6)	0.244(1)	0.7199(5)	157(18)
OH3	1.0	0.7561(8)	0.379(1)	0.6924(7)	109(23)
OH4	1.0	0.6959(6)	0.748(1)	0.6839(6)	162(17)
OH5	1.0	0.9858(7)	0.8822(9)	0.8077(7)	84(22)
OH6	1.0	0.7554(7)	0.126(1)	0.6939(8)	110(22)
H ₂ O1	1.0	0.8897(9)	0.605(1)	0.4870(8)	230(28)
H ₂ O2	1.0	0.1230(9)	0.412(1)	0.5223(9)	314(33)
H ₂ O3	1.0	0.9469(7)	0.245(1)	0.5220(6)	261(21)
H ₂ O4	1.0	0.777(1)	0.388(1)	0.4980(8)	256(30)
H ₂ O5	1.0	0.6983(8)	0.758(2)	0.4978(8)	391(31)
H ₂ O6	1.0	0.977(1)	0.886(2)	0.983(1)	633(53)
H ₂ O7	1.0	0.545(1)	0.091(1)	0.477(1)	385(33)
H ₂ O8	1.0	0.7829(9)	0.125(1)	0.5050(8)	265(30)

* $U_{eq} = U_{eq} \times 10^4$.

TABLE 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for becquerelite

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
U1	72(3)	87(4)	127(3)	8(3)	−9(2)	11(3)
U2	79(2)	68(2)	141(2)	−5(3)	2(1)	13(3)
U3	56(3)	79(4)	126(3)	−14(2)	1(2)	−3(2)
U4	74(2)	63(2)	124(2)	−10(3)	−2(1)	8(3)
U5	73(3)	81(4)	154(3)	9(3)	−16(2)	−12(2)
U6	66(3)	101(4)	108(3)	−1(3)	−1(2)	14(3)
Ca	197(14)	204(17)	123(12)	55(12)	−49(11)	−62(12)

positional parameters, anisotropic displacement parameters for the cations, isotropic displacement parameters for the anions, a weighting scheme of the structure factors, and allowance for twinning with the operator $[0\bar{1}0, \bar{1}00, 001]$. Inclusion of the twin operation lowered *R*1 by 1.0%. The occupancies of the interlayer cation positions were refined using the atomic scattering factor for Sr, and gave Sr1 = 61(2) and Sr2 = 66(2)% occupied. The final *R*1 was 4.26%, calculated using the 456 unique observed ($|F_o| \geq 4\sigma_F$) reflections. A model that included anisotropic displacement of the anions was tried, but did not lead to an improvement of the refinement, and resulted in physically unrealistic shapes for several anions. The structure exhibits strong pseudosymmetry corresponding to space group *P*6. Refinement of the structure in *P*6 was done, but resulted in unrealistic displacement parameters for some anions, and two anions of the uranyl polyhedron could not be located in this

¹For a copy of Tables 6 and 10, Document AM-02-005 contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue for price information). Deposit items may also be available on the American Mineralogist web site (see inside back cover of a current issue for a web address).

TABLE 5. Selected bond distances (Å) for becquerelite

U1-O2	1.77(1)	U2-O4	1.786(9)
U1-O1	1.80(1)	U2-O3	1.79(1)
U1-O14 <i>a</i>	2.23(1)	U2-O15	2.23(1)
U1-O13	2.23(1)	U2-O13	2.24(1)
U1-OH3	2.39(1)	U2-OH5	2.41(1)
U1-OH2	2.51(2)	U2-OH1	2.43(1)
U1-OH1	2.64(1)	U2-OH4	2.642(8)
<U1- ϕ_{eq} >	2.40	<U2- ϕ_{eq} >	2.39
U3-O6	1.79(1)	U4-O8	1.792(9)
U3-O5	1.82(1)	U4-O7	1.799(9)
U3-O15 <i>b</i>	2.23(1)	U4-O16	2.21(1)
U3-O16 <i>c</i>	2.23(1)	U4-O14 <i>c</i>	2.24(1)
U3-OH6	2.39(1)	U4-OH6	2.37(1)
U3-OH2	2.41(2)	U4-OH3	2.46(1)
U3-OH5 <i>b</i>	2.61(1)	U4-OH2 <i>d</i>	2.602(8)
<U3- ϕ_{eq} >	2.37	<U4- ϕ_{eq} >	2.38
U5-O10	1.78(1)	U6-O11	1.79(1)
U5-O9	1.79(1)	U6-O12	1.82(1)
U5-O14 <i>c</i>	2.23(1)	U6-O15	2.23(1)
U5-O13	2.25(1)	U6-O16 <i>e</i>	2.25(1)
U5-OH4	2.40(2)	U6-OH5 <i>d</i>	2.40(1)
U5-OH1 <i>d</i>	2.43(1)	U6-OH4	2.41(2)
U5-OH3	2.66(1)	U6-OH6 <i>e</i>	2.80(1)
<U5- ϕ_{eq} >	2.39	<U6- ϕ_{eq} >	2.42
Ca-H ₂ O3	2.36(2)	Ca-H ₂ O2 <i>a</i>	2.45(1)
Ca-O12 <i>f</i>	2.37(1)	Ca-H ₂ O1	2.47(1)
Ca-O1	2.44(1)	Ca-H ₂ O4	2.58(1)
Ca-O5 <i>g</i>	2.45(1)	Ca-O3 <i>h</i>	3.00(1)
<Ca1- ϕ_{eq} >	2.51		

Notes: $a = x + 1, y, z, b = x, y - 1, z, c = x + 1/2, y, -z + 3/2, d = x - 1/2, y, -z + 3/2, e = x, y + 1, z, f = -x + 3/2, y - 1/2, z - 1/2, g = -x + 2, y + 1/2, -z + 1, h = -x + 2, y - 1/2, -z + 1$

TABLE 7. Atomic positional parameters and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for Sr-exchanged becquerelite

	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
U1	1.0	0.9564(4)	0.6605(7)	0.365(2)	238(5)
Sr1	0.61(2)	2/3	1/3	-0.137(4)	389(79)
Sr2	0.66(2)	0	0	0.866(3)	395(87)
O1	1.0	0.981(6)	0.693(6)	0.117(6)	761(119)
O2	1.0	0.949(7)	0.689(6)	0.630(5)	474(84)
OH3	1.0	0.319(5)	0.914(4)	0.320(4)	330(59)
O4	1.0	2/3	1/3	0.314(6)	196(96)
O5	1.0	0	0	0.314(6)	61(77)
H ₂ O6	1.0	0.334(7)	0.921(5)	0.892(7)	381(75)

* $U_{eq} = U_{eq}^* \times 10^4$.

TABLE 8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for Sr-exchanged becquerelite

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	176(16)	121(11)	275(5)	0(5)	0(14)	-32(16)
Sr1	200(68)	200(68)	767(186)	0	0	100(34)
Sr2	435(104)	435(104)	315(143)	0	0	217(52)

TABLE 9. Selected bond distances (Å) for Sr-exchanged becquerelite

U1-O1	1.75(4)	Sr1-H ₂ O6 <i>e,f,g</i>	2.67(4) x3
U1-O2	1.86(3)	Sr1-O2 <i>h,i,j</i>	2.81(5) x3
U1-O4	2.206(8)	Sr1-O1 <i>k,l</i>	2.97(4) x3
U1-O5 <i>a</i>	2.274(8)	Sr1-O4	3.16(6)
U1-OH3 <i>b</i>	2.29(3)	<Sr1- ϕ >	2.85
U1-OH3 <i>c</i>	2.40(3)		
U1-OH3 <i>d</i>	2.63(2)	Sr2-O2 <i>p,d,l</i>	2.61(4) x3
<U1- ϕ_{eq} >	2.36	Sr2-H ₂ O6 <i>m,n,o</i>	2.67(4) x3
		Sr2-O1 <i>q,r,s</i>	2.73(5) x3
		Sr2-O5 <i>t</i>	3.13(6)
		<Sr2- ϕ >	2.72

Notes: $a = x + 1, y + 1, z, b = x + 1, y, z, c = -y + 2, x - y + 1, z, d = -x + y, -x + 1, z, e = -y + 2, x - y + 1, z - 1, f = x, y - 1, z - 1, g = -x + y, -x + 1, z - 1, h = -x + y + 1, -x + 1, z - 1, i = x, y, z - 1, j = -y + 1, x - y, z - 1, k = -x + y + 1, -x + 1, z, l = -y + 1, x - y, z, m = -x + y - 1, -x, z, n = -y + 1, x - y + 1, z, o = x, y - 1, z, p = x - 1, y - 1, z, q = -y + 1, x - y, z + 1, r = -x + y, -x + 1, z + 1, s = x - 1, y - 1, z + 1, t = x, y, z + 1$.

space group. The final atomic positional parameters and anisotropic displacement parameters are given in Tables 7 and 8, and selected interatomic distances and angles are given in Table 9. Calculated and observed structure factors are provided in Table 10¹.

RESULTS

Structure of becquerelite

The refined structure of becquerelite confirms the cation polyhedra and structural connectivities proposed by Pagoaga et al. (1987) and Piret-Meunier and Piret (1982), but refinement with modern data collected for a high-quality crystal using a CCD-based area detector has substantially improved the precision of the structure. The structure of becquerelite was described by Pagoaga et al. (1987) and Piret-Meunier and Piret (1982), and was included in the structural hierarchy of uranyl phases presented by Burns et al. (1996) and Burns (1999a). In brief, the structure contains six symmetrically distinct U sites, each of which is occupied by a U⁶⁺ cation (Table 11) that is part of a nearly linear (UO₂)²⁺ uranyl ion (designated Ur), with U-O_{Ur} bond lengths ranging from 1.77 to 1.82 Å, in good agreement with the average uranyl ion bond-length for ¹⁷¹U⁶⁺ of 1.79(4) Å obtained from numerous well-refined structures (Burns et al. 1997b). For comparison, the U-O_{Ur} bond lengths from the earlier refinements ranged from 1.71 to 1.91 Å (Pagoaga et al. 1987) and 1.76 to 1.93 Å (Piret-Meunier and Piret 1982). Each uranyl ion is coordinated by five additional anions arranged at the equatorial corners of pentagonal bipyramids that are capped by O_{Ur} atoms, with <U- ϕ_{eq} > (ϕ : un-

specified ligand, eq: equatorial) ranging from 2.37 to 2.42 Å, in agreement with the average of 2.37(9) for ¹⁷¹U⁶⁺- ϕ_{eq} bonds from numerous well-refined structures (Burns et al. 1997b). The structure also contains a single symmetrically distinct Ca cation that is coordinated by four O_{Ur} atoms and four H₂O groups, with a <Ca- ϕ > bond length of 2.51 Å.

The uranyl pentagonal bipyramids in becquerelite share equatorial edges and vertices, forming infinite sheets parallel to (001) (Fig. 1a). The sheet is based upon the α -U₃O₈ (protasite) anion topology (Burns et al. 1996); other minerals with topologically identical sheets of uranyl polyhedra are compregnacite (Burns 1998b), billietite (Pagoaga et al. 1987), masuyite (Burns and Hanchar 1999), agrinierite (Cahill and Burns 2000), richetite (Burns 1998c), and protasite (Pagoaga et al. 1997). The interlayer of the structure contains the Ca cation as well as eight symmetrically distinct H₂O groups, four of which are bonded to Ca, whereas the remaining four are held in the structure by hydrogen bonding only (Fig. 1b). The Ca cation serves to connect adjacent sheets of uranyl polyhedra by bonding to four O_{Ur} atoms, three of which are in the same sheet. Projection of the interlayer constituents onto the sheet of uranyl polyhedra (Fig. 2) shows that the Ca ϕ_8 polyhedra and hydrogen-bonded H₂O groups occur in strips that alternate and that are parallel to [010].

Hydrogen bonding in the structure of becquerelite

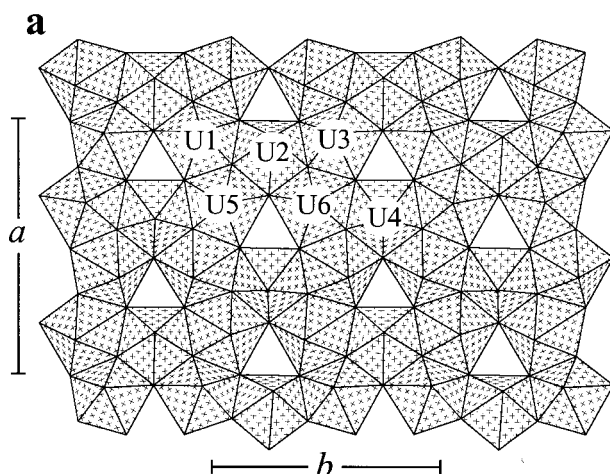
As is usual for uranyl minerals, it was impossible to determine the positions of the H atoms using the X-ray data. Some aspects of the hydrogen bonding can be established on the basis of crystal-chemical arguments.

The structure contains six symmetrically distinct OH groups, all of which are contained within the sheet of uranyl polyhedra. Each OH group is bonded to three U^{6+} cations; owing to repulsion between the U^{6+} and H^+ cations, it is unlikely that

TABLE 11. Bond valence* (v.u.) analysis for becquerelite

	U1	U2	U3	U4	U5	U6	Ca	Σ
O1	1.6						0.28	
O2	1.72							1.72
O3		1.64					0.06	1.70
O4		1.66						1.66
O5			1.55				0.27	1.82
O6			1.65					1.65
O7				1.62				1.62
O8				1.64				1.64
O9					1.66			1.66
O10					1.68			1.68
O11						1.64		1.64
O12						1.57	0.34	1.91
O13	0.69	0.68			0.67			2.04
O14	0.70			0.68	0.70			2.08
O15		0.69	0.69			0.70		2.08
O16			0.69	0.72		0.67		2.08
OH1	0.31	0.47			0.47			1.25
OH2	0.40		0.49	0.34				1.23
OH3	0.51			0.45	0.30			1.26
OH4		0.31			0.50	0.49		1.30
OH5		0.49	0.33			0.50		1.32
OH6			0.51	0.52		0.23		1.26
H ₂ O1							0.25	0.25
H ₂ O2							0.27	0.27
H ₂ O3							0.35	0.35
H ₂ O4							0.19	0.19
H ₂ O5							0	0
H ₂ O6							0	0
H ₂ O7							0	0
H ₂ O8							0	0
Σ	5.94	5.94	5.91	5.97	5.98	5.80	2.01	

* Bond-valence parameters for U^{6+} from Burns et al. (1997b) and for Ca from Brese and O'Keeffe (1991).



hydrogen bonds occur within the sheet of uranyl polyhedra. The hydrogen bonds donated by the OH groups are likely accepted by H_2O groups in the interlayer, and in each case there is only one H_2O group that is close enough to serve as the acceptor of the hydrogen bond. The probable $OH \rightarrow H_2O$ hydrogen bonds are listed in Table 12.

Of the eight symmetrically distinct H_2O groups in the interlayer, four are bonded to Ca (H_2O groups 1–4), whereas the others are held in the structure by hydrogen bonds only. The H_2O groups bonded to Ca may accept one hydrogen bond as well as donating two hydrogen bonds. Where the H_2O group is held in the structure by hydrogen bonding only, the most common situation is for the O atom of the H_2O group to accept two hydrogen bonds, as well as donating two hydrogen bonds (Hawthorne 1992).

The bond-valence sums (Table 11) at the anion positions help to identify possible hydrogen bond acceptors. Four O at

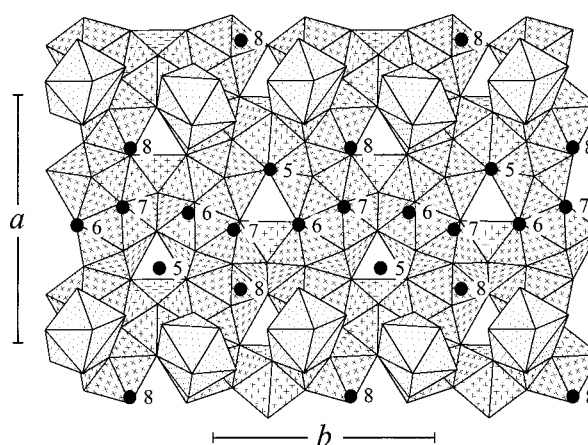


FIGURE 2. The structure of becquerelite projected along [001]. Legend as in Figure 1 except that H_2O groups are shown as black circles. The H_2O groups are labeled consistent with Table 3.

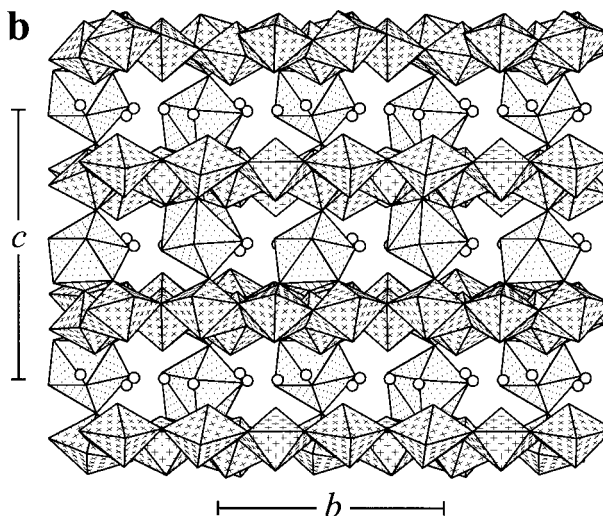


FIGURE 1. Polyhedral representations of the structure of becquerelite. (a) Sheet of uranyl polyhedra parallel to (001). (b) Structure projected along [100] showing sheets of uranyl polyhedra and the interlayer constituents. Uranyl polyhedra are shown shaded with crosses, CaO_8 polyhedra are stippled, and H_2O groups are indicated with open circles.

TABLE 12. Atomic separations corresponding to possible hydrogen bonds in becquerelite

OH groups		
OH1→H ₂ O7 <i>a</i>	2.68(2)	OH4→H ₂ O5 2.78(1)
OH2→H ₂ O3	2.96(1)	OH5→H ₂ O6 2.63(2)
OH3→H ₂ O4	2.92(2)	OH6→H ₂ O8 2.85(2)
H ₂ O groups		
H ₂ O1→O3	3.13(2)	H ₂ O6→O7 <i>a</i> 2.70(2)
H ₂ O1→O8 <i>b</i>	2.91(2)	H ₂ O6→O11 <i>k</i> 2.99(2)
H ₂ O2→O10 <i>e</i>	3.10(2)	H ₂ O6→H ₂ O7 <i>j</i> 2.77(2)
H ₂ O2→H ₂ O5 <i>f</i>	3.13(2)	H ₂ O7→O2 <i>i</i> 3.08(2)
H ₂ O3→H ₂ O1 <i>h</i>	2.85(2)	H ₂ O7→O4 <i>i</i> 3.14(2)
H ₂ O3→H ₂ O8	2.73(2)	H ₂ O7→O7 2.84(2)
H ₂ O4→O4 <i>i</i>	3.03(2)	H ₂ O7→O9 <i>f</i> 3.09(2)
H ₂ O4→O9	2.89(2)	H ₂ O7→O11 <i>m</i> 2.98(2)
H ₂ O5→O2 <i>b</i>	3.09(2)	H ₂ O7→H ₂ O6 <i>l</i> 2.77(2)
H ₂ O5→O6 <i>b</i>	3.03(2)	H ₂ O8→O4 <i>i</i> 2.96(2)
H ₂ O5→O8 <i>b</i>	3.11(1)	H ₂ O8→H ₂ O2 <i>f</i> 2.97(2)
H ₂ O5→O9	2.96(2)	
H ₂ O5→O11	2.81(2)	

Notes: $a = -x + 3/2, y + 1/2, z + 1/2$; $b = -x + 3/2, y + 1/2, z - 1/2$; $c = 2 - x, y + 1/2, 1 - z$; $d = x - 1, y, z$; $e = x - 1/2, y, 3/2 - z$; $f = 1 - x, y - 1/2, 1 - z$; $g = 1 - x, y + 1/2, 1 - z$; $h = 2 - x, y - 1/2, 1 - z$; $i = 3/2 - x, y - 1/2, z - 1/2$; $j = x + 1/2, y + 1, 3/2 - z$; $k = x + 1/2, y, 3/2 - z$; $l = x - 1/2, y - 1, 3/2 - z$; $m = x, y - 1, z$.

oms occur at the equatorial positions of the uranyl polyhedra within the sheets, but each has a bond-valence sum in the range 2–2.1 valence unit (v.u.), indicating it is unlikely that these atoms accept hydrogen bonds. There are 12 symmetrically distinct O_{Ur} atoms in the structure. Calculation of the bond valence sums incident upon each of these atoms, excluding possible contributions from H atoms, gives results in the range 1.6 to 1.9 v.u., indicating that any of these atoms may accept hydrogen bonds.

Consider first the H₂O groups that are bonded to Ca. There is no ambiguity concerning the hydrogen bonding associated with these ligands; each probably accepts a single hydrogen bond as well as donating two hydrogen bonds. The H₂O1O atom accepts a hydrogen bond from H₂O3, with a donor-acceptor distance of 2.85(2) Å. It donates hydrogen bonds that are accepted by O3 and O8, both of which are O_{Ur} atoms, with donor-acceptor distances of 3.13(2) and 2.91(2) Å, respectively, and a O3–H₂O1–O8 angle of 102.4(6)°. The H₂O2 group donates hydrogen bonds that are accepted by O10 and H₂O5, with donor-acceptor distances of 3.10(2) and 3.13(2) Å, respectively, and a O10–H₂O2–H₂O5 angle of 113.1(5)°. The O atom of the H₂O2 group accepts a hydrogen bond that is donated by the H₂O8 group, with a donor-acceptor distance of 2.97(2) Å. The H₂O3 O atom accepts a hydrogen bond donated by OH2, which is located 2.96(1) Å away. The hydrogen bonds donated by the H₂O3 group are accepted by the H₂O1 and H₂O8 groups, with donor-acceptor distances of 2.85(2) and 2.73(2) Å, respectively, and a H₂O1–H₂O3–H₂O8 angle of 109.0(7)°. Note that the H₂O3···H₂O1 bond bridges between symmetrically related CaΦ₈ polyhedra, rather than being located along a polyhedral edge. The O atom of the H₂O4 group accepts a hydrogen bond from the OH3 group in the adjacent sheet of uranyl polyhedra, and donates hydrogen bonds to O4 and O9, both of which are O_{Ur} atoms, with donor-acceptor distances of 3.03(2) and 2.89(2) Å, respectively, and a O4–H₂O4–O9 angle of 118.7(5)°.

The hydrogen bonding about the H₂O8 group is unambiguous. The O atom probably accepts hydrogen bonds from OH6

and H₂O3, with a OH6–H₂O8–H₂O3 angle of 90.9(5)°, and donor-acceptor distances of 2.85(2) and 2.73(2) Å, respectively. The H₂O group donates hydrogen bonds that are accepted by O4 (an O_{Ur} atom) and H₂O2, with donor-acceptor distances of 2.96(2) and 2.97(2) Å, respectively, and a O4–H₂O8–H₂O2 angle of 123.8(6)°. The resulting coordination about H₂O8 is approximately tetrahedral.

Ambiguity exists in the interpretation of the hydrogen bonding involving the H₂O5, H₂O6, and H₂O7 groups, as there are more than two potential acceptors of the hydrogen bonds in each case. H₂O5 probably accepts hydrogen bonds from OH4 and H₂O2, with donor-acceptor distances of 2.78(1) and 3.13(2) Å, respectively, and a OH4–H₂O5–H₂O2 angle of 97.6(5)°. The hydrogen bonds donated by the H₂O5 group may be accepted by any of the O2, O6, O8, O9, or O11 O_{Ur} atoms, with potential donor-acceptor distances in the range 2.81(2) to 3.11(1) Å. The O atom of the H₂O6 group accepts a hydrogen bond donated by the OH5 group. It donates hydrogen bonds that may be accepted by the O7 or O11 O_{Ur} atoms, or the H₂O7 group. The potential donor-acceptor distances range from 2.70(2) to 2.99(2) Å. The H₂O7 group accepts a hydrogen bond that is donated by OH1. All of O2, O4, O7, O9, O11, and H₂O6 are potential acceptors of the hydrogen bonds donated by H₂O7, with possible donor-acceptor distances in the range 2.77(2) to 3.14(2) Å. Each of these potential acceptors would result in a reasonable coordination environment about the H₂O7 group.

Structure of Sr-exchanged becquerelite

The chemical analysis for a Sr-exchanged crystal of becquerelite (Table 2) indicate that the crystal contains ~13 wt% SrO, thus most of the Ca in the interlayer of becquerelite has been replaced by Sr. The transformation also resulted in a change in unit cell and space group.

The structure of Sr-exchanged becquerelite contains a single symmetrically distinct U⁶⁺ cation that is in a uranyl pentagonal bipyramidal coordination polyhedron, similar to the U⁶⁺ cations in becquerelite. Uncertainties in the U–Φ bond lengths are higher for the exchanged crystal than for untreated becquerelite, presumably owing to crystal degradation associated with the ion exchange process. However, the average bond lengths for the uranyl pentagonal bipyramid, <U–O_{Ur}> = 1.80 Å and <U–Φ_{eq}> = 2.36 Å, are in line with those observed in well-refined structures (Burns et al. 1997b).

The structure of Sr-exchanged becquerelite contains sheets of edge-sharing uranyl pentagonal bipyramids (Fig. 3a) that are topologically identical to those in becquerelite. However, analysis of the bond-valence sums incident upon the anions located at the equatorial vertices of the uranyl pentagonal bipyramids in both structures indicates that the hydration states of the sheets are not identical. Consider the sheet anion topology, derived using the procedure of Burns et al. (1996), for each structure (Fig. 4). The anion topologies are identical in the distribution of nodes, but the bond-valence sums incident upon the vertices that constitute the triangles in the topologies are significantly different. In the case of the becquerelite sheet, these bond-valence sums range from 1.23 to 1.32 v.u., consistent with each site being occupied only by OH groups. In the sheet from Sr-exchanged becquerelite, the bond-valence sums

at the vertices of the triangles, which are all equivalent in space group $P3$, are 1.43 v.u. This is high enough to conclude that the site is occupied by both O and OH. Note that the substitution $O \rightarrow OH$ at the equatorial positions of uranyl polyhedra in sheets has recently been demonstrated in the structure of the Pb uranyl oxide hydrate fourmarierite (Li and Burns 2000).

Relative to the sheet of uranyl polyhedra in becquerelite, the sheet in Sr-exchanged becquerelite has less H. This sug-

gests that a higher M:U (M = divalent cation) ratio is required in the structure of Sr-exchanged becquerelite to account for charge balance. The Ca:U ratio in becquerelite is 1:6, whereas the Sr:U ratio in Sr-exchanged becquerelite is 2.54:6. The structure of the crystal of Sr-exchanged becquerelite has two Sr sites, with Sr1 = 61(2) and Sr2 = 66(2)% occupied. Each of these sites is coordinated by ten ligands, and bond-valence sums incident upon the Sr1 and Sr2 sites are 1.65 and 2.07 v.u., respectively (Table 13). The $Sr\phi_{10}$ polyhedra share faces, resulting in sheets parallel to (001) (Fig. 3b).

The electron microprobe analyses indicate the crystals of Sr-exchanged becquerelite contain ~1 wt% Cl. However, the structure determination failed to reveal a site consistent with occupancy by only Cl. The Cl may not be ordered in the structure, but instead it may be distributed over several sites, possibly including some of the sites that contain primarily H_2O .

The structure of Sr-exchanged becquerelite contains one symmetrically unique U site located on a general position in space group $P3$. The Sr1 and Sr2 sites, which are 61(2) and 66(2)% occupied, respectively, are located on Wyckoff positions b and a , respectively. The structure contains six O positions; the bond-valence analysis indicates four of these (O1, O2, O4, O5) contain O^{2-} , one (H_2O6) contains H_2O , and one (OH3) contains both O^{2-} and OH^- . The O4 and O5 sites are on Wyckoff positions b and a , respectively, whereas the remaining O sites are on general positions. The formula of the crystal studied is therefore $Sr_{1.27}[(UO_2)_3O_{3.54}(OH)_{1.46}](H_2O)_3$.

DISCUSSION

Our experiments have demonstrated interlayer ion exchange in becquerelite single crystals, and Burns (1999b) demonstrated ion exchange of Cs for the K and Na in the interlayer of single crystals of boltwoodite. In both of these experiments, however, crystals were placed in concentrated solutions containing the cation intended for the ion exchange. These experiments demonstrate that ion exchange is possible in the interlayers of becquerelite and boltwoodite without destruction of the corresponding crystal structures. However, it is not yet clear if cation exchange will occur to an appreciable extent where crystals are in contact with geologically realistic solutions containing ~100–1000 ppm cations, or under conditions that may occur in a geological repository for nuclear waste. Additional experiments are planned to address this issue.

Becquerelite has been found in the alteration products of

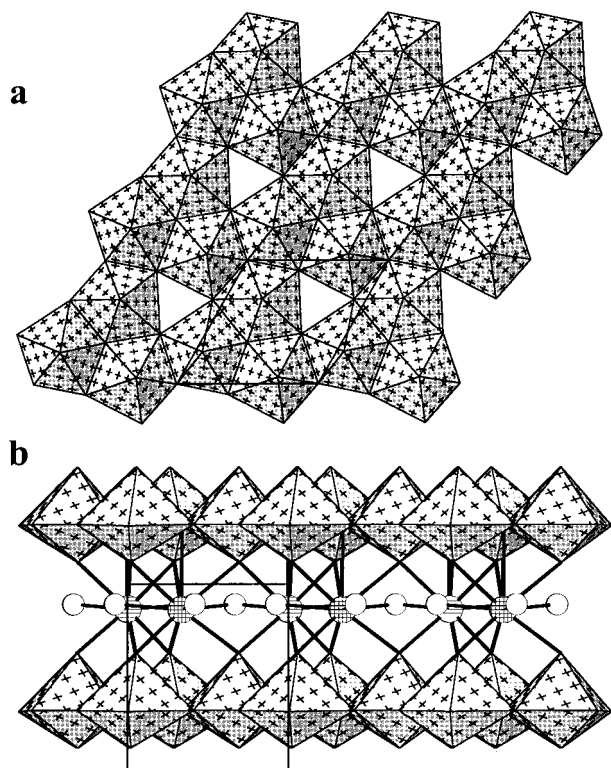


FIGURE 3. Polyhedral representations of the structure of Sr-exchanged becquerelite. (a) Sheet of uranyl polyhedra projected along [001]. (b) Structure projected along [100]. The unit cell is outlined by a solid line. The Sr1 and Sr2 atoms are shown shaded with cross hatching and parallel lines, respectively. The uranyl polyhedra are shaded with crosses, and O atoms of the H_2O6 group in the interlayer are shown as open circles.

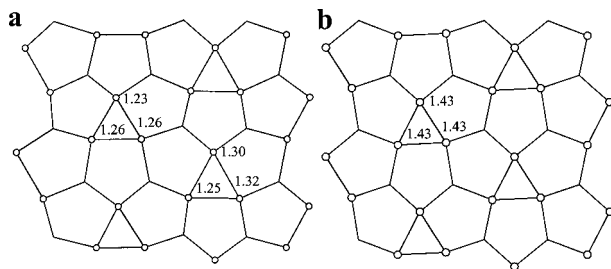


FIGURE 4. Sheet anion topologies for (a) becquerelite and (b) Sr-exchanged becquerelite. The locations of OH groups are shown by open circles. The bond-valence sums (v.u.) incident upon the OH sites from bonds to U^{6+} are given.

TABLE 13. Bond valence* (v.u.) analysis of Sr-exchanged becquerelite

	U1	Sr1	Sr2	$\Sigma \dagger$
O1	1.79	0.10 ^{<3‡}	0.19 ^{<3‡}	1.97
O2	1.43	0.16 ^{<3‡}	0.26 ^{<3‡}	1.70
OH3	0.62, 0.49, 0.32		1.43	
O4	0.73 ^{<3→}	0.06		2.23
O5	0.64 ^{<3→}		0.06	1.96
H_2O6		0.23 ^{<3‡}	0.22 ^{<3‡}	0.29
Σ	6.02	1.65	2.07	

* Bond-valence parameters for U^{6+} from Burns et al. (1997b) and for Sr from Brese and O'Keeffe (1991).

† Bond-valence attributed to anions have been scaled by the occupancy of Sr1 and Sr2 sites.

spent nuclear fuel from hydrologically unsaturated tests intended to simulate conditions that are possible in the proposed geological repository at Yucca Mountain (Finn et al. 1996). Monitoring of radionuclide release rates from the spent fuel in these tests has indicated that ^{90}Sr is largely retained with the products of alteration, which are mostly uranyl phases (Finn et al. 1996). Although ^{90}Sr has a half life that is sufficiently short as to render it relatively unimportant for long term geological repository performance, it is important to understand the factors controlling the release rates of radionuclides under test conditions. It is possible that Sr is incorporated into the structures of the uranyl phases, that it is sorbed onto alteration phases or experimental apparatus, or that a Sr phase is precipitating. Our experiments demonstrating ion exchange of Sr into single crystals of becquerelite support the hypothesis that ^{90}Sr will be at least in part retained in the becquerelite-like phases that form due to the alteration of spent fuel.

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