ELSEVIER

Journal of Nuclear Materials 265 (1999) 218–223

journal of nuclear materials

Letter to the Editors

Cs boltwoodite obtained by ion exchange from single crystals: Implications for radionuclide release in a nuclear repository

Peter C. Burns *

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA

Received 30 June 1998; accepted 28 September 1998

Abstract

Spent nuclear fuel is unstable under the oxidizing conditions present in the proposed repository at Yucca Mountain, and the dominant products of alteration are expected to be uranyl oxide hydrates and uranyl silicates. Incorporation of radionuclides into the structures of the uranyl phases may impact upon the mobility of radionuclides under repository conditions. Boltwoodite, $(K,Na)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, will form under repository conditions when groundwater contacts the spent fuel waste form. Cs-exchanged boltwoodite, $Cs[(UO_2)(SiO_3OH)]$, has been obtained from single crystals of natural boltwoodite by ion exchange with 2 M CsCl solutions at 90°C (14 days) and 185°C (24 h). Exchange of Cs^+ for K^+ and Na^+ in the interlayer of the structures was demonstrated by single-crystal structure determinations for exchanged crystals. This is the first demonstration of ion exchange in a single crystal of a uranyl phase, as well as the first evidence that Cs can be incorporated into the structure of a uranyl phase that is expected to form due to alteration of spent fuel under repository conditions. Boltwoodite that crystallizes under repository conditions is likely to incorporate Cs into its structure, thereby inhibiting Cs mobility. Earlier-formed Na- and K-rich boltwoodite may also exchange Cs with fluids that contact the crystals. The strongly bonded sheets of uranyl and silicate polyhedra in the structure of boltwoodite are only relatively weakly bonded to the interlayer constituents, permitted exchange of the interlayer cations without the loss of structural integrity. The structures of many uranyl phases are based upon similar sheets of polyhedra of higher bond-valence, suggesting that ion exchange may be possible in many other uranyl phases. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Commercial spent nuclear fuel is the largest potential source of radionuclides in the proposed high-level nuclear waste repository at Yucca Mountain, Nevada [1]. Experiments have repeatedly demonstrated that spent nuclear fuel is unstable under the moist-oxidizing conditions expected in the proposed repository. Many of the radionuclides in the fuel could be released to the environment during alteration, and alteration rates are likely to be appreciable [2–7]. Laboratory-scale experiments indicate that the dominant alteration products under repository conditions are uranyl minerals, and the paragenetic sequence observed in the laboratory is similar to that seen in nature [7–10].

Uranyl phases that are likely to form in a geological repository for high-level nuclear waste are listed in Table 1. The impact of uranyl phase formation on radionuclide mobility is poorly understood and often overlooked, despite experimental evidence that uranyl-based alteration phases can limit the release of radionuclides such as ^{90}Sr, ^{137}Cs and ^{237}Np [6]. Many radionuclides of concern can be incorporated into the structures of uranyl minerals [11,12], with a potentially profound impact on radionuclide release. Two of the many environmentally hazardous radionuclides in spent nuclear fuel are ^{137}Cs (half life $= 30.2$ y) and ^{135}Cs (half life $= 3 \times 10^6$ y). The mobility of Cs in natural waters can be reduced by exchanging Cs into the structures of zeolite [13,14], or by adsorption of Cs onto clays [15]. It has been proposed that Cs may also be incorporated

---

* Corresponding author. Tel.: +1-219 631 7380; fax: +1-219 631 9236; e-mail: peter.burns.50@nd.edu.

0022-3115/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(98)00646-1

Table 1
Uranyl phases predicted to form in a geological repository during alteration of spent nuclear fuel [5–7]

Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	Dehydrated schoepite	$UO_3 \cdot 0.8–1H_2O$
Becquerelite	$Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$	Na-compreignacite	$Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$
Na-boltwoodite	$(Na,K)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$	Sklodowskite	$Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$
Uranophane	$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	Soddyite	$(UO_2)_2(SiO_4)(H_2O)_2$
Boltwoodite	$(K,Na)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$	Compreignacite	$K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$

into the structures of uranyl minerals such as boltwoodite and compreignacite [16,17], both of which are likely to form under repository conditions [7]; however, this has not been demonstrated until now.

Boltwoodite [16,18], $(K,Na)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, contains α-uranophane-type sheets of composition $[(UO_2)(SiO_3OH)]^{1-}$ (Fig. 1). Topologically identical sheets occur in α-uranophane, sklodowskite, cuprosklodowskite, and kasolite [19], although the interlayers differ. A K^+–Na^+ solid-solution series exists for natural boltwoodite, with K^+ and Na^+ occupying different interlayer sites [16]. On the basis of crystal-chemical arguments, Burns [16] predicted that the structure of boltwoodite may accommodate Cs in the interlayer, thus boltwoodite may impact upon the mobility of Cs when spent nuclear fuel is corroded under repository conditions. Here I report ion exchange of Cs^+ for K^+ and Na^+ in single crystals of natural boltwoodite, with confirmation by single-crystal structure refinement.

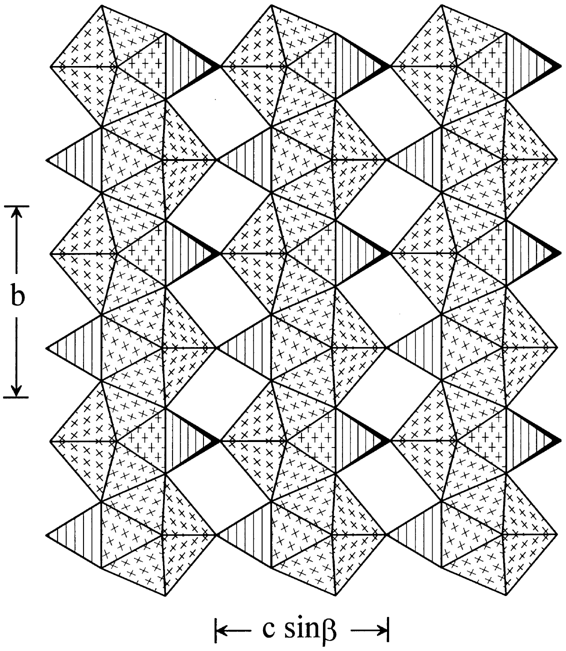

Fig. 1. The sheets of polyhedra contained in the structure of boltwoodite. The projection is along [1 0 0]. The sheets have the composition $[(UO_2)(SiO_3OH)]^{1-}$. Uranyl pentagonal bipyramids are shaded with crosses and silicate tetrahedra are shaded with parallel lines.

2. Experimental

2.1. Ion exchange

The boltwoodite crystals selected for this study are from Namibia, and were removed from a sample that contained several clusters of superb acicular boltwoodite crystals up to ~1 cm in length. An earlier structure determination and chemical analysis of untreated boltwoodite crystals from this sample indicates the formula $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$ and space group $P2_1/m$ [16]. Optical-quality crystals of boltwoodite ~0.1 mm in length were selected for ion-exchange experiments. Preliminary experiments indicated that ion exchange is rapid at ~200°C but requires several days at ~100°C. Several crystals were placed in Teflon-lined Parr bombs, together with 5 ml of 2 M CsCl solution; one bomb was heated at 185°C for 24 h (denoted E185), the other at 90°C for 14 days (denoted E90) in Fisher Scientific mechanical-convection ovens with a temperature uniformity of ±2°C. The pressure buildup in the Parr bomb is minor at 90°C but is substantial at 185°C. Following the treatment, the solutions were removed using hypodermic needles and the crystals were recovered. The treated crystals were intact with no outward signs of alteration; faces were planar and edges were sharp, and all were optically continuous, although translucent.

2.2. X-ray diffraction

A crystal was selected from each experiment for X-ray diffraction studies using a Siemens SMART system consisting of a PLATFORM three-circle goniometer and a 1K CCD-based detector. The recent introduction of CCD-based X-ray area detectors permits the successful determination of structures from small crystals that contain high absorbers of X-rays [20].

Data were collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 20 and 30 s used to acquire frames for crystals E185 and E90, respectively. More than a hemisphere of three-dimensional data was collected over the range $3° \leqslant 2\theta \leqslant 56.6°$ for

Table 2
Miscellaneous information pertaining to data collections

	E185	E90	Bolt [16]		E185	E90
a (nm)	0.74038(8)	0.74756(8)	0.70772(8)	Crystal size (mm)	0.12 × 0.04	0.20 × 0.05
b (nm)	0.70774(7)	0.70867(8)	0.70597(8)		× 0.02	× 0.03
c (nm)	0.66566(7)	0.66657(7)	0.66479(7)	Total ref.	2042	2096
β (°)	104.314(2)	104.155(2)	104.982(2)	Unique ref.	860	869
V (nm^3)	0.3480(1)	0.3424(1)	0.3209(1)	R_{int}	4.18	4.93
				Unique $\lvert F_o\rvert \geqslant 4\sigma_F$	795	802
Space group	$P2_1/m$			Final R	4.84	6.92
Unit-cell contents: 2{Cs[(UO$_2$)(SiO$_3$OH)]}				S	1.11	0.48

$R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, for m observations and n parameters.

each crystal, and data were analyzed to locate diffraction peaks for the refinement of unit-cell parameters by least-squares (Table 2). Data were reduced and corrected for Lorentz, polarization, and background affects using the Siemens program SAINT. An empirical absorption-correction was done using the program SADABS (G. Sheldrick, unpublished computer program). Additional details pertaining to the data are provided in Table 2.

2.3. Structure refinement

Systematic reflection absences were consistent with space group $P2_1/m$ for crystals from both experiments. Initial structure models were based on only the sheets of silicate and uranyl polyhedra in the structure of boltwoodite [16]. The models were refined to agreement indices (R) of 19.6% and 19.0% for E185 and E90, respectively, using the methods of Burns [16]. Difference-Fourier maps were calculated through the interlayers of each structure at $x = 0$ (Fig. 2(a) and (b)). One symmetrically distinct peak with a height of ~30 e/0.001 nm^3 is evident in both difference-Fourier maps; this corresponds to Cs (Fig. 2(a) and (b)). The Cs sites occur as symmetrically equivalent pairs on either side of the mirrors that are perpendicular to y, with adjacent sites separated by ~0.2 nm. Only one site of each pair is occupied locally, and, as was the case for natural boltwoodite [16], the local arrangement of the interlayer is consistent with space group $P2_1$, whereas the long-range symmetry of the structure conforms to $P2_1/m$. Subsequent refinement cycles gave elongated root-mean-square displacements for Cs, indicating a split-site. Each Cs site was replaced by sites designated 'CsA' and 'CsB', and refinement of the positional parameters, Cs site-

Table 3
Atomic parameters for Cs-exchanged boltwoodite

	Occ.	x	y	z	U_{eq} [a]
E185					
U		0.5245(1)	3/4	0.6405(1)	160(3)
Si		0.4357(9)	3/4	0.1510(8)	199(11)
CsA	0.30(2)	−0.0663(9)	0.882(2)	0.256(2)	421(23)
CsB	0.16(2)	−0.047(2)	0.947(3)	0.327(5)	316(53)
O1		0.771(2)	3/4	0.668(3)	304(34)
O2		0.276(2)	3/4	0.601(2)	269(31)
O3		0.558(2)	3/4	0.985(2)	260(31)
O4		0.525(2)	0.076(1)	0.692(2)	293(26)
OH5		0.212(3)	3/4	0.025(3)	420(43)
E90					
U		0.52378(8)	3/4	0.64018(9)	202(4)
Si		0.4379(8)	3/4	0.1508(9)	234(11)
CsA	0.29(2)	−0.067(1)	0.891(3)	0.262(3)	593(4)
CsB	0.16(2)	−0.045(1)	0.954(2)	0.339(4)	316(48)
O1		0.769(2)	3/4	0.667(4)	387(46)
O2		0.278(2)	3/4	0.603(3)	379(41)
O3		0.559(2)	3/4	0.986(2)	258(27)
O4		0.522(2)	0.075(1)	0.687(2)	317(24)
OH5		0.214(2)	3/4	0.029(3)	463(47)

[a] $U_{eq} = U_{eq}$ nm^2 × 10.

occupancy factors, and anisotropic-displacement parameters for all atoms resulted in R indices of 4.84% and 6.92% for observed ($|F_o| \geqslant 4\sigma_F$) reflections for crystals E185 and E90, respectively. Final difference-Fourier maps did not reveal any additional interlayer constituents. Final models are given in Table 3.

3. Results

The incorporation of Cs into the interlayers of the crystals is evident by expansion of the a unit-cell dimension (Table 2) and the large increase of the electron density in the interlayers (Fig. 2). The structure refinement indicates close to complete exchange of Cs^+ for K^+ and Na^+ with concomitant loss of interlayer (H_2O) groups from boltwoodite. Thus the structural formula for the Cs-exchanged boltwoodite is $Cs[(UO_2)(SiO_3OH)]$.

Ion exchange does not induce significant changes to the bonding within the structural sheets, as demonstrated by comparison of the polyhedral geometries of the sheets in the exchanged crystals with those of boltwoodite (Table 4). The stability of the structural sheets is also reflected in the relative insensitivity of the b and c unit-cell dimensions to the exchange of interlayer cations. Coordination polyhedra about Cs in the exchanged crystals involve seven or eight anions and are similar in both exchanged crystals: $\langle CsA\text{-}8\phi\rangle \approx 0.324$ and $\langle CsB\text{-}7\phi\rangle \approx 0.316$ nm. Bond-valence sums [21] at the cation positions are 0.95 and 0.90 for CsA and 1.13 and 1.14 for CsB in E185 and E90, respectively, consistent with the occupancy of these sites by Cs^+.

4. Discussion

This is the first demonstration of ion exchange in a single crystal of a uranyl mineral, as well as the first evidence that Cs is likely to be incorporated into the structures of uranyl phases that form under repository conditions. The ease of ion exchange in the boltwoodite structure is due to the structural stability of sheets of polyhedra of higher bond-valence [19]. Tightly bonded sheets of edge- and corner-sharing uranyl pentagonal bipyramids and silicate tetrahedra (Fig. 1) are relatively weakly linked to interlayer constituents primarily by bonds between the interlayer cations and the O atoms of the uranyl ions, which have most of their bonding requirements met by the short bond to the U^{6+} cation [22]. Ion exchange can therefore occur without significant disruption of strong bonds within the structural sheets. Several minerals have sheets of uranyl and silicate polyhedra that are topologically identical to the sheet in boltwoodite, suggesting that ion exchange is likely to be important in those structures as well. Furthermore, the structures of most uranyl phases (natural and synthetic) are dominated by sheets of uranyl polyhedra and other cation polyhedra of higher bond-valence [19], with low-valence cations occupying only interlayer positions. Therefore, ion exchange may occur in a wide variety of

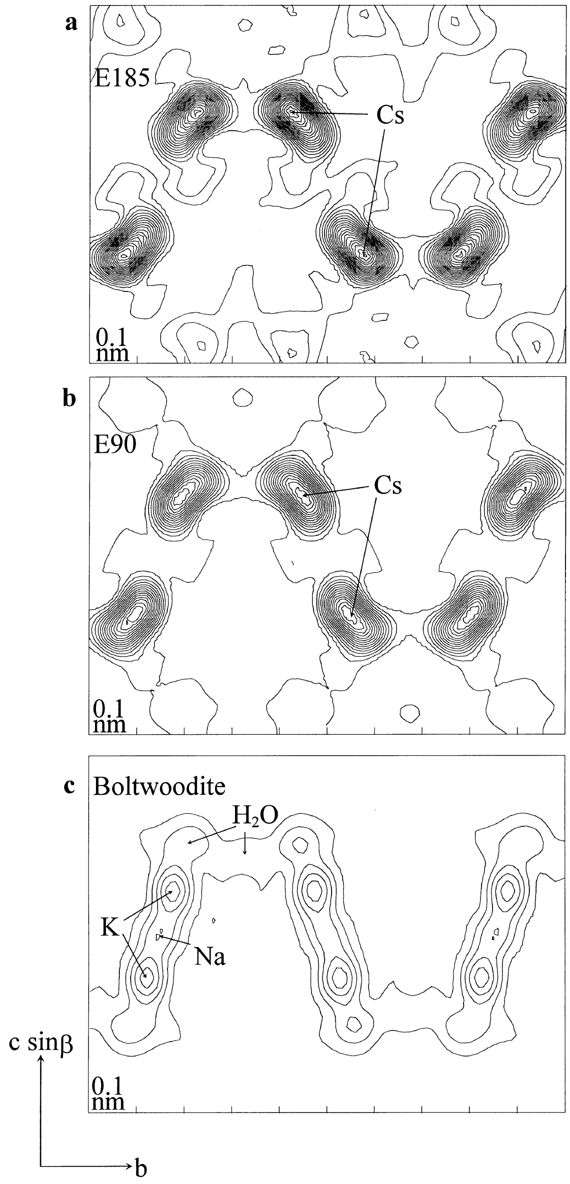

Fig. 2. Difference-Fourier maps through the interlayer of Cs-exchanged boltwoodite and boltwoodite. The maps were calculated perpendicular to [1 0 0] at $x = 0$. (a) Cs-exchanged boltwoodite obtained by treatment at 185°C for 24 h. (b) Cs-exchanged boltwoodite obtained by treatment at 90°C for 14 days. (c) natural boltwoodite from Namibia [16]. The first contour line in each plot is 1 $e/0.001$ nm^3 and the contour interval is 2 $e/0.001$ nm^3. Note that the interlayer in the structures of E185 and E90 contains many more electrons than the interlayer in boltwoodite.

Table 4
Selected interatomic distances (nm) and angles (°) for Cs-exchanged boltwoodite and boltwoodite [16]

	Interlayer			Uranyl silicate sheet		
	E185	E90		E185	E90	Boltwoodite
CsA-OH5	0.301(2)	0.307(2)	U-O2	0.179(1)	0.179(2)	0.1802(9)
CsA-O3^{a}	0.306(2)	0.311(2)	U-O1	0.179(2)	0.180(2)	0.1812(9)
CsA-O2	0.311(2)	0.315(2)	U-O3	0.224(1)	0.226(1)	0.2270(8)
CsA-OH5^{b}	0.323(1)	0.322(1)	U-O4^{g,h}	0.2330(9) × 2	0.232(1)	0.2315(5) × 2
CsA-O2^{c}	0.329(2)	0.323(2)	U-O4^{i,j}	*0.2478(9)* × 2	*0.246(1)*	0.2449(6) × 2
CsA-O1^{d}	0.336(2)	0.333(2)	⟨U-O$_{Ur}$⟩	0.179	0.1795	0.1807
CsA-O1^{e}	0.339(2)	0.338(2)	⟨U-O$_{eq}$⟩	0.2371	0.2364	0.2358
CsA-O4^{f}	0.351(1)	*0.354(2)*	O2-U-O1	177.6(6)	177.8(7)	177.8(4)
⟨CsA-ϕ⟩	0.324	0.325				
			Si-O3^{k}	0.159(1)	0.158(1)	0.1596(9)
CsB-O2^{c}	0.285(2)	0.281(2)	Si-OH5	0.166(2)	0.167(2)	0.161(1)
CsB-O1^{d}	0.296(2)	0.295(2)	Si-O4^{i,j}	*0.1598(9)* × 2	*0.163(1)* × 2	0.1625(6) × 2
CsB-O2	0.297(2)	0.299(2)	⟨Si-O⟩	0.1611	0.1627	0.1614
CsB-OH5^{b}	0.319(2)	0.324(2)				
CsB-O1^{e}	0.322(2)	0.321(2)				
CsB-OH5	0.340(3)	0.347(3)				
CsB-O4^{f}	0.351(1)	*0.354(2)*				
⟨CsB-ϕ⟩	0.316	0.317				

Note: a = $x-1, y, z-1$; b = $-x, 2-y, -z$; c = $-x, 2-y, 1-z$; d = $1-x, 2-y, 1-z$; e = $x-1, y, z$; f = $-x, 1-y, 1-z$; g = $x, \frac{1}{2}-y, z$; h = $x, y+1, z$; i = $1-x, 1-y, 1-z$; j = $1-x, \frac{1}{2}+y, 1-z$; k = $x, y, z-1$.

uranyl minerals, many of which are likely to form as corrosion products of spent fuel in a geologic repository.

Previous experiments provided limited evidence of ion exchange in uranyl phases [23–27]; however, these experiments were done on powdered specimens, and dissolution–reprecipitation cannot be ruled out. In the current study, essentially complete exchange of Cs^+ for K^+ and Na^+ in the interlayer sites of single crystals of boltwoodite occurred within 14 days at 90°C and required less than 24 h at 185°C, without loss of structural integrity. The ease of Cs exchange into boltwoodite has implications for the mobility of Cs in a repository containing spent nuclear fuel. Boltwoodite will likely form in close proximity to corroded spent oxide fuel [7], and may be abundant [6]. If Cs is in the water from which boltwoodite crystals nucleate and grow, boltwoodite will incorporate Cs directly into its structure, thereby inhibiting the release of radioactive Cs from the repository. In addition, contact of Cs-rich solutions with pre-existing boltwoodite may result in Cs exchange into the boltwoodite crystals, also reducing Cs mobility. Alternatively, subsequent interaction of Cs-poor solutions with Cs-containing boltwoodite could *liberate* Cs by ion exchange, thereby increasing its mobility. It is likely that additional radionuclides can be exchanged into uranyl minerals, and this has serious implications for the long-term evolution of a geological repository containing spent nuclear fuel.

The demonstration of ion exchange in uranyl minerals impacts upon our understanding of uranyl mineral paragenesis in nature because it reveals that early formed uranyl minerals may be converted to new species, via ion exchange, when crystals come in contact with solutions containing dissolved cations. Thus, the current mineral assemblage may not be representative of the assemblage that was thermodynamically favored at the time of mineral precipitation.

Acknowledgements

This research was funded by the Environmental-Management Sciences Program of the United States Department of Energy (DE-FG07-97ER14820). I thank Dr Robert Finch and Dr Dave Wronkiewicz for comments and suggestions for improvement of the manuscript.

References

[1] Site characterization plan, US Department of Energy, Office of Civilian Radioactive Waste Management, Report DOE/RW-0199 (1988).
[2] T. Wadsten, J. Nucl. Mater 64 (1977) 315.
[3] R. Wang, Y.B. Katayama, Nucl. Chem. Waste Management 3 (1982) 83.
[4] C.N. Wilson, Pacific Northwestern Laboratory Report PNL-7170 (1990).
[5] D.J. Wronkiewicz, J.K. Bates, T.J. Gerding, E. Veleckis, B.S. Tani, J. Nucl. Mater 190 (1992) 107.
[6] P. A Finn, J.C. Hoh, S.F. Wolf, S.A. Slater, J.K. Bates, Radiochim. Acta 74 (1996) 65.

[7] D.J. Wronkiewicz, J.K. Bates, S.F. Wolf, E.C. Buck, J. Nucl. Mater 238 (1996) 78.

[8] C. Frondel, US Geological Survey Bulletin 1064 (1958).

[9] R.J. Finch, R.C. Ewing, J. Nucl. Mater 190 (1992) 133.

[10] E.C. Pearcy, J.D. Prikryl, W.M. Murphy, B.W. Leslie, Appl. Geochem. 9 (1994) 713.

[11] P.C. Burns, R.C. Ewing, M.L. Miller, J. Nucl. Mater 245 (1997) 1.

[12] E.C. Buck, R.J. Finch, P.A. Finn, J.K. Bates, Mater Res. Soc. Symp. Proc. 506 (1998) 94.

[13] J.R. Smyth, A.T. Spaid, D.L. Bish, Am. Mineral. 75 (1990) 522.

[14] P. Yang, J. Stolz, T. Armbruster, M.E. Gunter, Am. Mineral. 82 (1997) 517.

[15] S. Staunton, M. Roubaud, Clay Mineral. 45 (1997) 251.

[16] P.C. Burns, Can. Mineral. 36 (in press).

[17] P.C. Burns, Can. Mineral. 36 (in press).

[18] F.V. Stohl, D.K. Smith, Am. Mineral. 66 (1981) 610.

[19] P.C. Burns, M.L. Miller, R.C. Ewing, Can. Mineral. 34 (1996) 845.

[20] P.C. Burns, Can. Mineral. 36 (1998) 847.

[21] N.E. Brese, M. O'Keeffe, Acta Crystallogr. B 47 (1991) 192.

[22] P.C. Burns, R.C. Ewing, F.C. Hawthorne, Can. Mineral. 35 (1997) 1551.

[23] B.G. Bilgin, Chim. Acta Turcica 17 (1989) 109.

[24] B.G. Bilgin, Chim. Acta Turcica 17 (1989) 205.

[25] M.C.A. Sandino, B. Grambow, Radiochim. Acta 66/67 (1994) 37.

[26] M.E. Torrero, I. Casas, B.A. Grambow, Radiochim. Acta 66&67 (1994) 29.

[27] R. Vochten, N. Blaton, O. Peters, K. Van Spriegel, L.A. Van Haverbeke, Can. Mineral. 35 (1997) 735.