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Infrared vibrational characterization and synthesis of a family of hydrous alkali uranyl silicates and hydrous uranyl silicate minerals

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ABSTRACT

Synthesis studies in the system K_2O-UO_3-SiO_2-H_2O are presented as an isothermal isobaric projection through the system at 300 °C and 30 MPa. In addition to the compatibility relationships for weeksite, boltwoodite, and soddyite, a new previously unreported hydrous alkali uranyl silicate similar in composition to weeksite was identified. Infrared spectroscopy supplemented X-ray diffraction methods to characterize the structures of the quaternary phases. It was shown by the infrared spectra that the silica in boltwoodite and soddyite are isolated tetrahedra, in confirmation of X-ray structural data. Weeksite and the newly identified phase contain sheetlike silicate units. Additionally, the H_2O of hydration of these phases was shown to be composed of two types: an ordered structural H_2O and a disordered zeolitic-type H_2O.

INTRODUCTION

Only two minerals have been identified that correspond to the set of "hydrous alkali uranyl silicate" phases: weeksite, $K_2(UO_2)_2Si_6O_{15}\cdot4H_2O$, and boltwoodite, $(H_3O)K(UO_2)(SiO_4)\cdot H_2O$. Both minerals are rare in nature. Although the synthetic preparation of these phases has been reported by Honea (1961) and Outerbridge et al. (1960), no systematic studies of the phase relations in the system K_2O-UO_3-SiO_2-H_2O have been published. The crystallography and phase relations along the UO_3-H_2O binary have been reviewed in detail by Smith et al. (1982).

Our interest in this set of unusual minerals results from their identification as alteration products of several types of simulated nuclear waste forms, notably calcine (an X-ray amorphous powder), a glass, and a tailored ceramic (McCarthy et al., 1980; Anderson, 1980; Freeborn et al., 1980). The presence of these two phases in hydrothermal experiments designed to evaluate the stability of the waste forms under conditions of temperature and pressure that represent the most plausible extreme repository-failure scenario is significant. The presence of alkali uranyl silicate phases demonstrates the mobilization of U from the waste as the hexavalent, H_2O-soluble species, thus forming a new source term for any modeling of repository behavior.

Structure determination by Stohl and Smith (1981) for boltwoodite and partial structural analyses of soddyite (a related hydrous uranyl silicate) (Stohl and Smith, 1981) and weeksite (Stohl, 1974; Anderson, 1980; Baturin and Sidorenko, 1985) provided an opportunity to augment the understanding of these partially resolved structures by means of infrared spectroscopy. This paper reports the synthesis, IR characterization, and phase relations of weeksite, boltwoodite, and related phases.

EXPERIMENTAL

Weeksite, boltwoodite, soddyite, and a previously unknown hydrous alkali uranyl silicate with a composition similar to weeksite were prepared hydrothermally at 200 and 300 °C and 30 MPa. Seventy-two compositions were prepared during the course of the study to define the compatibility relationships (Fig. 1).

The chemical reagents used as starting materials were potassium nitrate (J. T. Baker Chemical Co., reagent grade), uranyl nitrate (Research Organic Inorganic Corp., 99.5+% pure), and Ludox AS-40 colloidal silica (E. I. DuPont de Nemours & Co., Inc., technical grade). Stock solutions were made up with compositions of 0.5 *M* uranyl nitrate, 0.5 *M* Ludox, and 1.0 *M* potassium nitrate.

Individual compositions were prepared by measuring out the appropriate volumes of each stock solution in 50-mL beakers followed by dropwise addition of concentrated NH_4OH in order to form a gel where possible (Roy, 1956). An attempt was made to gel all compositions, but most mixtures would gel only to a small extent or not at all. The only solutions where gelling occurred were the ones near the silica apex. The gel precursor enhanced reactivity in the silica-rich compositions. Reaction proceeded without gel in the K_2O-UO_3-rich portions of the diagram.

The sample solutions were mixed, dried at 120–140 °C, scraped out of their beakers, and again thoroughly ground to a fine powder using an agate mortar and pestle. Denitration was accomplished by heating the samples at 500 °C for 4 h. After denitration, the samples were reground and placed in small plastic vials for use as starting materials for the hydrothermal experiments. X-ray diffraction patterns of a selected group of the dried gels showed recrystallization of part of the material. Charac-

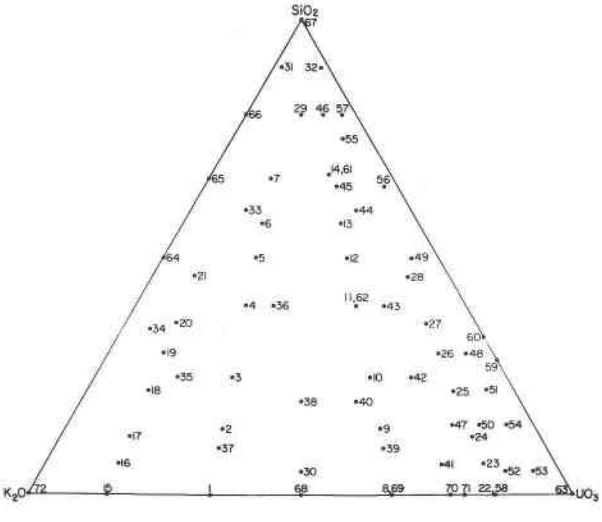


Fig. 1. Compositions prepared for phase compatibility studies. Numbers refer to Table 7 in Plesko (1981).

teristic reflections of $K_2U_2O_7$, $K_2O \cdot 6.4UO_3$, and KNO_3 were observed with $K_2U_2O_7$ as the most common product. In only one sample was there some evidence for recrystallization of the silica with the appearance of one weak peak at the expected position for the 101 reflection of quartz.

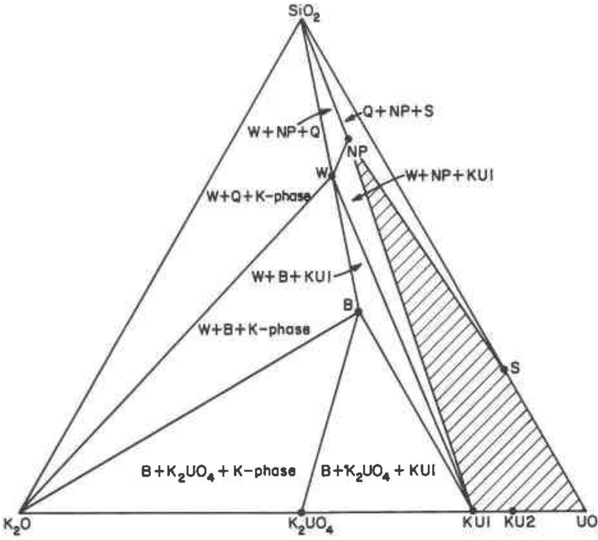
The hydrothermal experiments were conducted in Au tubes of approximately 5 mm id and 50 mm in length. Hydrogen peroxide was added to these powders in the sealed Au tubes as a mineralizing agent and to maintain an O partial pressure above the UO_2/UO_3 redox couple. The Au tubes were sealed with an oxy-hydrogen torch and their seals verified by testing in a vacuum oven at 1 torr and 100–110 °C. All phase equilibrium experiments were done in hydrothermal pressure vessels at 200 and 300 °C and 30 MPa pressure. All samples were held under isobaric conditions during initial heatup and during the time interval of the experiment. Upon completion of an experiment, the cold-seal vessel was air quenched at the reaction pressure.

The resultant reaction products were carefully examined under a binocular microscope (up to 40×), characterized by a scanning electron microscope equipped with an energy-dispersive X-ray multichannel analyzer, and analyzed by standard powder X-ray diffraction techniques. The X-ray diffraction data reported herein were collected with Ni-filtered Cu$K\alpha$ radiation using a graphite monochromator.

Samples for infrared spectroscopy were ground to fine powders, diluted 1:200 in KBr, and vacuum cold-pressed into transparent pellets. Spectra were scanned with a Perkin-Elmer model 283-B dispersive infrared spectrometer.

SYNTHESIS STUDIES

Figure 2 is an isothermal, isobaric section at 300 °C and 30 MPa projected from the H_2O apex onto the K_2O-SiO_2-UO_3 ternary. Details of the 72 compositions on which this diagram is based may be found in the thesis from which this paper is drawn (Plesko, 1981).



W = weeksite
B = boltwoodite
NP= new phase
Q = quartz
S = soddyite
K-phase = a phase now identified as being KNO_3
KU1 } unknown potassium
KU2 } polyuranate phases

Fig. 2. Isothermal, isobaric section at 300 °C and 30 MPa for the system K_2O-UO_3-SiO_2-H_2O projected onto the anhydrous base.

The left side of the isothermal projection, from the K_2O apex to the SiO_2-K_2UO_4 join, consists largely of three compatibility triangles: weeksite + quartz + K phase, weeksite + boltwoodite + K phase, and boltwoodite + K_2UO_4 + K phase. Identification of the K phase is not completely certain; KNO_3 was the only observed crystalline phase in the region where a combination of KOH, KOH-saturated solution, and potassium silicates would be the expected phases in the K_2O-SiO_2-H_2O side of the system. Clearly some nitrate remained in the starting materials. KNO_3 was observed only on the left side of the isothermal section, most strongly near the K_2O apex.

In the quaternary system K_2O-UO_3-SiO_2-H_2O, one would expect most of the saturation surface to be located near the H_2O apex because of the limited solubility of UO_3 in H_2O and the very limited solubility of SiO_2 in H_2O. However, because of the high solubility of K_2O in H_2O, the saturation surface in this region must slope down toward the K_2O apex. The phase assemblages present on this surface consist of three solid phases coexisting with a K-rich liquid (probably KOH solution). Projecting the compositions located on this sloping saturation surface down onto the anhydrous K_2O-UO_3-SiO_2 base results in the configuration of compatibility triangles seen in Figure 2. These K-rich liquids apparently do not crystallize when the capsules are cooled to room temperature except for

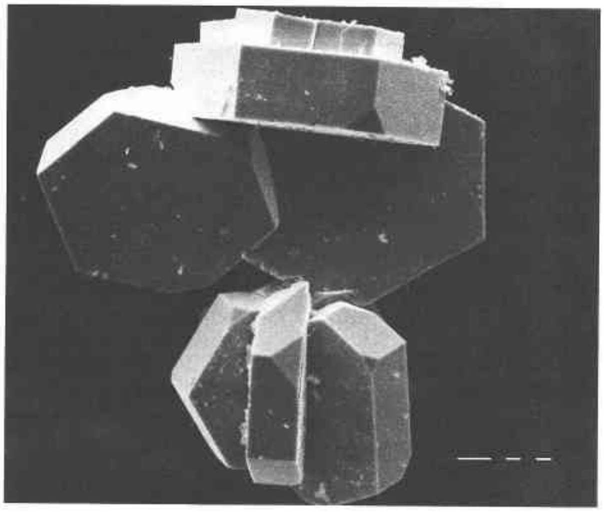


Fig. 3. Scanning electron microscope image of orange hexagonal platelets of unknown potassium uranate (OHP) phase.

the portion of the K that reacts with residual NO_3^- to form the observed KNO_3.

The right side of the isothermal projection, from the SiO_2-K_2UO_4 join to the UO_3 apex, is more complex than expected because of the presence of four previously unidentified phases (for convenience labeled KU1, KU2, OHP, and NP). This side of the diagram consists of one large compatibility triangle (boltwoodite + K_2UO_4 + KU1), four smaller compatibility triangles (weeksite + boltwoodite + KU1, weeksite + KU1 + NP, weeksite + quartz + NP, and soddyite + quartz + NP), and a region (shown cross-hatched) where it was not possible to determine the phase relations. The phases labeled KU1 and KU2 are previously unidentified potassium uranates with approximate compositions $K_2O \cdot 4UO_3$ and $K_2O \cdot 6UO_3$.

The main reason why it was not possible to determine the phase relations in the shaded region of the isothermal projection is the presence of the OHP phase (unidentified orange hexagonal platelets; Fig. 3). EDX measurements show this phase to be a potassium uranate, not a silicate. This phase appears throughout the undetermined region and does not seem to be associated with any particular composition point. Various compositions for OHP were postulated; however, none of these yielded a consistent set of phase relations. Only at the UO_3 apex was a mixture of UO_3 hydrates observed; UO_3 does not seem to extend far out into the ternary system.

INFRARED CHARACTERIZATION OF THE KNOWN PHASES

Boltwoodite

Boltwoodite was found in a number of the hydrothermal experiments as a coarse-grained powder, its color ranging from light yellow to yellow-green. In nature, boltwoodite is usually found as pale yellow, fibrous aggregates (Honea, 1961). The synthetic material gave a sharp, well-defined XRD pattern that matched well with JCPDS card no. 35-490. Boltwoodite is the only phase in the quaternary system for which a complete structural analysis has been reported (Stohl and Smith, 1981).

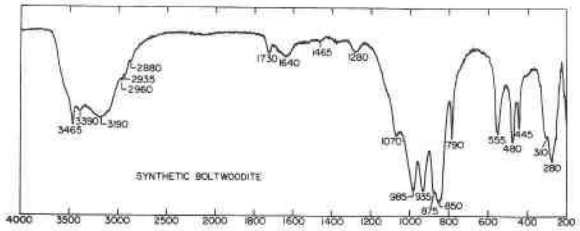


Fig. 4. Infrared spectrum of synthetic boltwoodite.

The infrared spectrum of boltwoodite is presented in Figure 4. Two sharp bands at 985 and 935 cm^{-1} are in the spectral region indicative of orthosilicate structures such as garnet and olivine (Lyon, 1962). The structure determination of boltwoodite shows that the SiO_4 tetrahedra are isolated and unpolymerized as they are in orthosilicates.

The spectrum of boltwoodite in the 3500-cm^{-1} region suggests that several kinds of H-bearing species are present. This region contains the characteristic O-H stretching modes (Ryskin, 1974). The sharp bands at 3465, 3390, and 1730 cm^{-1} are indicative of H_2O molecules located on ordered sites. The H_2O bending mode at 1730 cm^{-1} argues for H_2O (or H_3O^+) rather than OH. The broad band at 3190 cm^{-1} and the broad 1640-cm^{-1} bending mode are indicative of H_2O molecules having a disordered arrangement (White, 1971). The structure determination shows that H_2O occurs as H_2O of crystallization (in the first coordination sphere around the cation), as OH or hydronium ions to balance the electric charge of the uranyl silicate, or as zeolitic H_2O (Stohl and Smith, 1981). The zeolitic H_2O could be responsible for the broad bands at 3190 and 1640 cm^{-1}, whereas the sharp bands indicate that the remaining H_2O is located in an ordered arrangement in the structure.

Weeksite

Weeksite was one of the more frequently occurring phases present in the system. It usually appeared as small, yellow, needlelike crystals in radiating clusters (Fig. 5), just as it does in nature (Outerbridge et al., 1960) and in waste/rock interaction products (Freeborn et al., 1980). It gave a sharp, well-defined XRD pattern that matched well with JCPDS card no. 12-462.

The infrared spectrum of weeksite is presented in Figure 6. This spectrum can be divided into three regions: a high-wavenumber region that contains the stretching vibrations of H_2O molecules and OH ions, a midrange region that contains the stretching vibrations of silicate tetrahedra and uranyl ions, and a low-wavenumber region that contains the complex vibrations associated with the bending and twisting of the crystal structure.

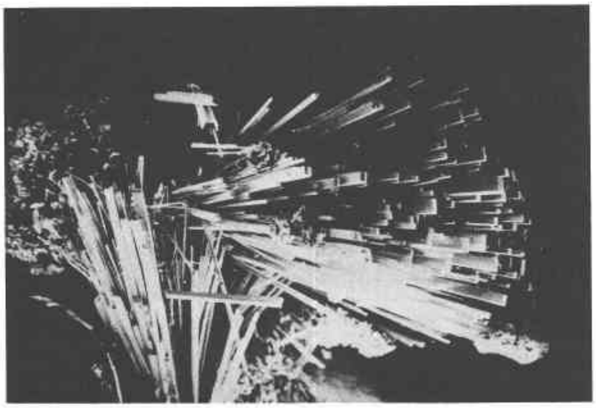


Fig. 5. Scanning electron microscope image of synthetic weeksite crystals.

The position of the Si-O antisymmetric stretching modes in the midrange infrared have long been known to indicate the degree of polymerization of the silica tetrahedra (e.g., Launer, 1952). To obtain a calibration curve for the relations between band position and number of nonbridging O atoms, data were plotted for a large number of silicate minerals (Fig. 7). Figure 6 suggests that the main weeksite bands at 1125 and 1055 cm^{-1} are due to silica tetrahedra with one nonbridging O atom per tetrahedron. A partial structure determination (Anderson, 1980; Stohl and Smith, 1981) and a later investigation of the structure (Baturin and Sidorenko, 1985) agree that the main silicate structural units are sheetlike, but one-third of the silica in the structure has not yet been located. The bands at 915 and 870 cm^{-1} can most reasonably be assigned to the antisymmetric stretching mode of the UO_2^{2+} ion.

The spectrum shows that two types of H_2O are present. As discussed in connection with the boltwoodite spectrum, the sharp bands at 3605, 3504, and 1625 cm^{-1} are indicative of H_2O molecules located in ordered sites, whereas the broad band at 3420 cm^{-1} is indicative of H_2O molecules or OH ions having a disordered arrangement. The structure determination shows that H_2O can occur as H_2O of crystallization (in the first coordination sphere around the cation), as OH or hydronium ions to balance the electric charge of the uranyl silicate, or as zeolitic H_2O. It is very likely that the zeolitic H_2O gives rise to the broad band at 3420 cm^{-1}. The sharp bands at 3605, 3540, and 1625 cm^{-1} indicate that the remaining H_2O is located in an ordered arrangement in the structure, but whether this is H_2O in the first coordination sphere of the cation or whether it is the OH or hydronium ions balancing the electric charge of the uranyl silicate sheet cannot be determined from the spectrum.

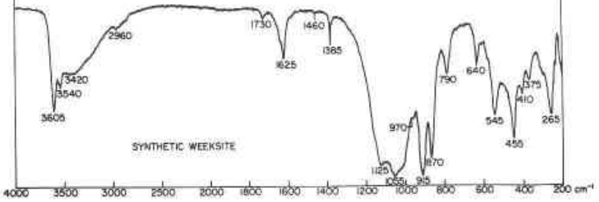


Fig. 6. Infrared spectrum of synthetic weeksite.

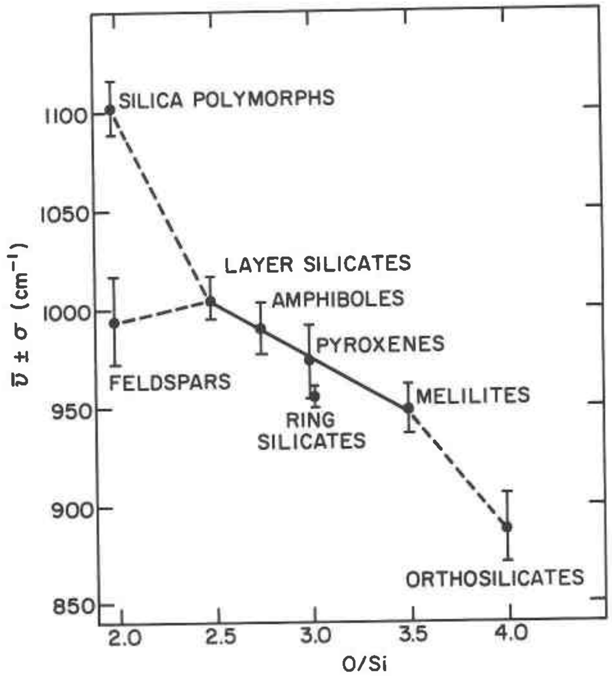


Fig. 7. The relationship between wavenumber of the antisymmetric Si-O stretching modes and the O/Si ratio for some common silicates. The solid circles represent the mean wavenumber of this group of bands for published spectra of the families of silicates. The bars indicate 1 sd on either side of the mean. The plot is based on IR spectra of powdered silicates in KBr matrices published by Lyon (1962).

Soddyite

Soddyite, $(UO_2)_5(SiO_4)_2(OH)_2 \cdot 5H_2O$, another naturally occurring compound, was found in many of the hydrothermal experiments. In one experiment, which had the nominal composition of soddyite, the phase appeared as long, yellow, columnar crystals embedded in a fine-grained yellow powder. In all the other hydrothermal experiments in which it occurred, soddyite appeared as a fine-grained powder ranging in color from yellow to lime green. In nature, soddyite occurs as flat-bladed crystals or fibers having a color from greenish yellow to canary yellow (Gorman, 1962). The synthetic phase gave a sharp, well-defined XRD pattern that matched well with JCPDS card no. 35-491.

Like boltwoodite, the sharp bands at 980 and 910 cm^{-1} (Fig. 8) are indicative of a structure in which the SiO_4 tetrahedra are isolated and unpolymerized. Although a complete structure determination has not yet been made,

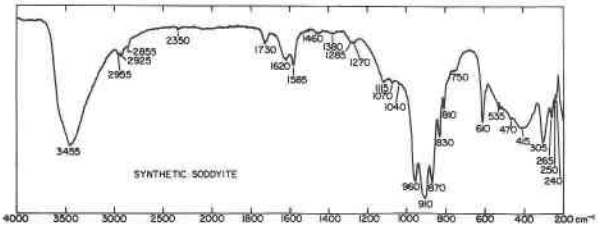


Fig. 8. Infrared spectrum of synthetic soddyite.

soddyite has been shown to be isostructural with a synthetic uranyl germanate (Legros et al., 1972; Stohl and Smith, 1981). In this structure, the GeO_4 tetrahedra are isolated and shared between two uranyl germanate chains that lie 90° to each other (Stohl and Smith, 1981). The large, broad band at 3455 cm^{-1} suggests a disordered arrangement for the H_2O in this structure. This is consistent with the proposed three-dimensional structure with large channels running between uranyl silicate chains (Stohl, 1974). The H_2O is located within the channels (Smith, 1983). H_2O molecules randomly oriented within these large, open channels could give rise to the absorption at 3455 cm^{-1} (Ryskin, 1974).

NEW PHASES IN THE SYSTEM K_2O-UO_3-SiO_2-H_2O

The NP phase

A previously unreported phase was observed near the SiO_2 apex, near the nominal composition point for weeksite. This phase, designated NP in Figure 2, usually appeared as a fine-grained, lime green material with a coarse-grained, granular, white phase embedded in it (probably quartz). The X-ray diffraction peaks of the new phase are sharp and well defined but do not match anything listed in the JCPDS files. The powder data listed in Table 1 were indexed on a triclinic cell using the Visser indexing program. The cell constants are compared with those of the known phases in Table 2.

It was difficult to obtain chemical information on this phase because it was not possible to synthesize it phase-pure. It was always found in association with soddyite, weeksite, or quartz, and because these phases usually occurred as powders it was not possible to separate one from the other. The composition that gave the strongest and sharpest XRD peaks for the new phase and that had the least interference from other phases had a bulk composition of $K_2O \cdot 4UO_3 \cdot 15SiO_2$ plus an undetermined amount of H_2O. The actual composition point for this phase is probably located within a few mole percent of this bulk composition. Because of its proximity to the nominal composition point of weeksite, the new phase is believed to be a hydrated alkali uranyl silicate.

SEM images of the NP phase showed only fine-grained, earthy masses with a particle size less than 10 μm. Because the NP phase is such a nondescript material, a natural occurrence in association with weeksite and other alkali silicate minerals could be easily overlooked. Evidence that NP is a distinct phase and not a mixture comes from its X-ray powder diffraction pattern, its IR absorption spectrum, and its persistence over a wide range of bulk compositions in proportions that point to a distinct composition as shown in Figure 2.

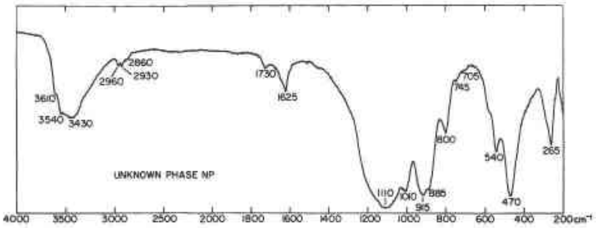


Fig. 9. Infrared spectrum of new alkali uranyl silicate (NP) phase.

The infrared spectrum of the NP phase (Fig. 9) is very similar to that of weeksite. The large, broad band at 1110 cm^{-1} and the smaller band at 1010 cm^{-1} are similar to the weeksite bands at 1125 and 1055 cm^{-1}. These bands are characteristic of cross-linked chains of sheetlike silicates (Fig. 7). The uranyl bands at 915 and 885 cm^{-1} for the NP phase are also similar to those of weeksite that occur at 915 and 870 cm^{-1}. Many similarities can also

TABLE 1. X-ray data for the new alkyl uranyl silicate, NP

2θ (Cu$K\alpha$)	d-values$_{obs}$ (Å)	d-values$_{calc}$ (Å)	I/I_0	hkl
14.83	5.97	5.97	75	$\bar{2}00$
16.55	5.36	5.35	8	$\bar{2}01$
17.30	5.13	5.12	10	220
20.95	4.24	4.24	30	201
22.75	3.91	3.91	36	$\bar{1}02$
23.40	3.80	3.80	14	231
25.05	3.56	3.55	100	$\bar{1}40$
25.35	3.51	3.51	96	240
26.60*	3.35	3.35	20	$\bar{3}20$
27.53	3.24	3.24	6	$\bar{2}\bar{2}2$
29.43	3.035	3.032	74	$\bar{4}01$
30.43	2.937	2.938	9	$\bar{4}20$
30.60	2.922	2.917	7	$\bar{2}\bar{3}2$
33.08	2.708	2.706	15	$\bar{2}42$
34.45	2.603	2.601	26	242
36.20	2.481	2.478	30	411
37.63	2.390	2.389	69	$\bar{5}00$
40.60B	2.222	2.221	8	$\bar{3}\bar{5}2$
43.12	2.098	2.096	15	$\bar{3}61$
44.45	2.038	2.037	57	$\bar{5}51$
45.62	1.989	1.985	18	$\bar{6}31$
48.10B	1.892	1.890	8	$\bar{6}40$
51.00	1.791	1.789	36	512
51.95	1.760	1.759	52	$7\bar{2}1$
53.20	1.722	1.720	35	$\bar{7}11$
54.43	1.686	1.684	15	182
55.30	1.661	1.660	8	382
56.62	1.626	1.623	4	$7\bar{4}2$
57.78	1.596	1.594	6	731

Note: B indicates a broadened peak.
* May be a quartz peak.

TABLE 2. Unit-cell parameters for phases in the system K_2O-UO_3-SiO_2-H_2O

Name	a_0 (Å)	b_0 (Å)	c_0 (Å)	α	β	γ
Soddyite*	8.32	11.21	18.71	—	—	—
Boltwoodite*	27.40	7.02	6.65	—	—	—
Weeksite*	14.26	35.88	14.2	—	—	—
NP	12.38	15.86	7.88	96.04	102.73	96.91
OHP	8.15	8.75	24.39	—	96.92	—
KU2	13.96	12.39	7.02	—	—	—

* Data taken from JCPDS files.

be seen in the low-wavenumber region of both spectra (600 to 200 cm^{-1}). Yet despite their similarities, the two spectra are different enough to show that the NP phase is indeed a new phase and not weeksite. The spectrum also shows that, like weeksite, the NP phase contains two types of H_2O.

The OHP phase

The orange hexagonal platelets (OHP) get their name from their color and the well-developed pseudohexagonal morphology (Fig. 3). X-ray powder data obtained by the Gandolfi method for the OHP phase are given in Table 3. The diffraction pattern could be indexed on a monoclinic cell to yield the parameters listed in Table 2. An energy-dispersive X-ray analysis showed that the two primary constituents of this phase are K and U. Based on the absence of Si lines in the EDX spectrum, the OHP phase appears to be a uranate rather than a silicate, but no sample was prepared with sufficient phase purity to determine the composition.

TABLE 3. X-ray data for phase OHP

2θ (Cu$K\alpha$)	d-values$_{obs}$ (Å)	d-values$_{calc}$ (Å)	I	hkl
11.06	8.0	7.97	mw	$\bar{1}01$
14.52	6.1	6.09	m	$\bar{1}03$
20.18	4.4	4.39	m	$\bar{1}05$
25.08	3.55	3.55	ms	024
27.02	3.30	3.30	ms	$\bar{2}14$
29.28	3.05	3.05	w	$\bar{2}06$
31.62	2.83	2.83	vw	222
35.92	2.50	2.50	vw	035
36.68	2.45	2.45	vw	$\bar{1}28$
41.42	2.18	2.18	vw	041
45.83	1.98	1.98	vw	$\bar{3}31$
47.35	1.92	1.92	vw	$\bar{2}42$
49.25	1.85	1.85	vw	047
53.26	1.72	1.72	mw	336
54.28	1.69	1.69	mw	$\bar{3}43$
55.71	1.65	1.65	w	431
56.83	1.62	1.62	vw	500
57.61	1.60	1.60	w	$\bar{5}13$
58.82	1.57	1.57	vw	$\bar{5}15$
61.85	1.50	1.50	vw	428
65.25	1.430	1.429	vw	$\bar{1}62$
66.56	1.405	1.403	vw	$\bar{1}64$
69.06	1.360	1.359	vw	$\bar{6}02$
72.10	1.310	1.308	vw	612
73.40	1.290	1.288	vw	$\bar{5}45$
75.10	1.265	1.264	vw	537
77.25	1.235	1.233	vw	538
81.58	1.180	1.179	vw	458

Note: Pattern obtained using single-crystal Gandolfi method by Christine A. Anderson, Department of Geosciences, Crystallography Laboratory, The Pennsylvania State University. Abbreviations: ms = moderate strong, m = moderate, mw = moderately weak, w = weak, vw = very weak.

TABLE 4. X-ray data for KU1 phase

2θ (Cu$K\alpha$)	d-values (Å)	I/I_0
14.00	6.33	51
20.30	4.38	11
23.98	3.71	20
25.38	3.51	86
27.52	3.24	100
28.15	3.17	13
30.62	2.920	33
33.78	2.653	25
34.35B	2.611	15
34.70	2.585	20
35.70	2.515	19
37.98	2.369	10
40.45	2.230	7
41.23	2.190	5
42.20	2.141	5
43.40	2.085	24
44.32	2.044	14
45.78	1.982	24
46.38	1.958	24
47.02	1.933	39
48.82	1.865	14
50.18	1.818	15
50.75	1.799	15
52.35	1.748	31

The potassium uranates, KU1 and KU2

The phase KU1 has a nominal composition based on EDX data of $K_2O \cdot 4UO_3$. The X-ray diffraction pattern (Table 4) could not be indexed, and it is not certain, therefore, that some of the lines listed are not due to impurities.

The phase KU2 has a nominal composition $K_2O \cdot 6UO_3$. The X-ray diffraction data (Table 5) could be indexed on an orthorhombic cell with the parameters listed in Table

TABLE 5. X-ray data for KU2 phase

2θ (Cu$K\alpha$)	d-values$_{obs}$ (Å)	d-values$_{calc}$ (Å)	I/I_0	hkl
12.63	7.01	7.01	33	001
17.92	4.95	4.95	8	201
22.90	3.88	3.88	6	301
25.38	3.51	3.51	100	002
26.39	3.38	3.37	43	012
28.43	3.14	3.13	42	202
29.32	3.046	3.040	99	420
36.12	2.487	2.478	30	050
37.10	2.423	2.419	11	341
41.02	2.200	2.199	11	441
45.23	2.005	2.002	23	152
47.05	1.931	1.930	75	532
51.98	1.759	1.757	20	433
54.12	1.695	1.693	20	801
55.85	1.646	1.644	7	533

2. The pattern is not similar to that given in JCPDS card no. 28-836 for a phase listed as $K_2O \cdot 6.4UO_3$.

Both KU1 and KU2 seem to be uranates and not silicates. EDX spectra show no evidence for Si, and the IR spectra show the strong uranyl bands but do not show any evidence for silicate absorption.

CONCLUSIONS

This study has shown that both weeksite and boltwoodite can be synthesized at temperatures up to at least 300 °C. These two hydrous alkali uranyl silicates occupy a significant portion of the K_2O-UO_3-SiO_2-H_2O system, thus explaining the ubiquitous occurrence of these phases in nuclear waste-form stability experiments.

The presence of vibrational bands in the infrared spectrum of boltwoodite that correspond to the symmetric stretching and antisymmetric stretching modes of isolated silica tetrahedra support their existence in the boltwoodite structure as determined by Stohl and Smith (1981). Further, the infrared spectrum obtained for soddyite also indicates the presence of isolated silica tetrahedra, as reported by Stohl and Smith (1981).

The structural determinations of both a synthetic and natural weeksite (Anderson, 1980, and Stohl, 1974, respectively) were only successful in identifying two-thirds of the silica in the phase. These silica tetrahedra link with uranyl groups to form parallel chains in the *bc* plane. Although not confirmed, it is believed that the remaining third of the silica bridges these chains to form a sheetlike silicate structure. The sheetlike nature of the structure is supported by the observed IR bands at 1124 and 1055 cm^{-1}.

As a consequence of the synthesis study, a new, previously unrecognized potassium uranyl silicate phase was identified with a composition similar to weeksite. No precise chemical analyses were obtained, but a nearly pure phase (by XRD characterization) was obtained from material with bulk composition $K_2O \cdot 4UO_3 \cdot 15SiO_2$ plus an unknown amount of H_2O (identified in the IR spectrum). The vibrational spectrum obtained for this phase suggests that it has the sheetlike silicate structure recognized in weeksite.

All of the phases described contain appreciable H_2O. The infrared spectra of these phases show the presence of at least two types of H_2O: a structural H_2O located on specific sites and loosely bound, zeolite type of H_2O that is much more disordered.

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