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 K₂O-UO₃-SiO₂-H₂O 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. Weeksie and the newly identified phase contain sheetlike silicate units. Additionally, the H₂O of hydration of these phases was shown to be composed of two types: an ordered structural H₂O and a disordered zeolitic-type H₂O.

INTRODUCTION

Only two minerals have been identified that correspond to the set of "hydrous alkali uranyl silicate" phases: weeksite, K₄(UO₂)₂Si₆O₁₈·4H₂O, and boltwoodite, (H₂O)K(UO₂)₃(SiO₂)·H₂O. 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 K₂O-UO₃-SiO₂-H₂O have been published. The crystallography and phase relations along the UO₃-H₂O 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, H₂O-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 NH₄OH 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 K₂O-UO₃-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-
teristic reflections of K$_2$U$_2$O$_7$, K$_2$O-6.4UO$_3$, and KNO$_3$ were observed with K$_3$U$_3$O$_8$ 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 CuKα 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$_2$O apex onto the K$_3$O-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).

The left side of the isothermal projection, from the K$_3$O apex to the SiO$_2$-K$_3$O$_4$ join, consists largely of three compatibility triangles: weeksite + quartz + K phase, weeksite + boltwoodite + K phase, and boltwoodite + K$_2$UO$_4$ + 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$_3$O-SiO$_2$-H$_2$O 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$_3$O apex.

In the quaternary system K$_3$O-UO$_3$-SiO$_2$-H$_2$O, one would expect most of the saturation surface to be located near the H$_2$O apex because of the limited solubility of UO$_3$ in H$_2$O and the very limited solubility of SiO$_2$ in H$_2$O. However, because of the high solubility of K$_3$O in H$_2$O, the saturation surface in this region must slope down toward the K$_3$O 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$_3$O-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
the portion of the K that reacts with residual NO₃⁻ to form the observed KNO₃.

The right side of the isothermal projection, from the SiO₂-K₂UO₄ join to the UO₃ 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 + K₂UO₄ + KU₁), four smaller compatibility triangles (weksite + boltwoodite + KU₁, weksite + KU₁ + NP, weksite + 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 K₂O·4UO₃ and K₂O·6UO₃.

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 (unknown 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 UO₃ apex was a mixture of UO₃ hydrates observed; UO₃ 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).

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 SiO₄ 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 H₂O molecules located on ordered sites. The H₂O bending mode at 1730 cm⁻¹ argues for H₂O (or H₂O⁺) rather than OH. The broad band at 3190 cm⁻¹ and the broad 1640-cm⁻¹ bending mode are indicative of H₂O molecules having a disordered arrangement (White, 1971). The structure determination shows that H₂O occurs as H₂O 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 H₂O (Stohl and Smith, 1981). The zeolitic H₂O could be responsible for the broad bands at 3190 and 1640 cm⁻¹, whereas the sharp bands indicate that the remaining H₂O 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 H₂O 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.
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\(^{2+}\) ion.

The spectrum shows that two types of H\(_2\)O are present. As discussed in connection with the boltwoodite spectrum, the sharp bands at 3605, 3504, and 1625 cm\(^{-1}\) are indicative of H\(_2\)O molecules located in ordered sites, whereas the broad band at 3420 cm\(^{-1}\) is indicative of H\(_2\)O molecules or OH ions having a disordered arrangement. The structure determination shows that H\(_2\)O can occur as H\(_2\)O 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\(_2\)O. It is very likely that the zeolitic H\(_2\)O 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\(_2\)O is located in an ordered arrangement in the structure, but whether this is H\(_2\)O 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.

**Soddyite**

Soddyite, \((\text{UO}_2)_3(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}\), 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 unpolymorized. Although a complete structure determination has not yet been made,
The NP phase
dence that NP is a distinct phase and not a mixture comes
alkali silicate minerals could be easily overlooked. Evi-
believed to be a hydrated alkali uranyl silicate.
ural occurrence in association with weeksite and other
cause the NP phase is such a nondescript material, a nat-
earthy masses with a particle size less than 10 μm. Be-
noimal composition point of weeksite, the new phase is
position of KrO.4UO3·11SiO2, plus an undetermined
from the other. The composition that gave the strongest
occurred as powders it was not possible to separate one
phase because it was not possible to synthesize it phase-
thing listed in the JCPDS files. The powder data listed in
phases in Table 2.

New phases in the system K2O-UO3-SiO2-H2O
The NP phase
A previously unreported phase was observed near the
SiO2 apex, near the nominal composition point for
weksite. 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 any-
thing 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 oc-
curred 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 com-
position of K2O·4UO3·11SiO2 plus an undetermined
amount of H2O. 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. Be-
cause the NP phase is such a nondescript material, a nat-
ural occurrence in association with weeksite and other
alkali silicate minerals could be easily overlooked. Ev-
dence that NP is a distinct phase and not a mixture comes

from its X-ray powder diffraction pattern, its IR absorp-
tion spectrum, and its persistence over a wide range of
bulk compositions in proportions that point to a distinct
composition as shown in Figure 2.

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 si-
licates (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 alkali uranyl silicate, NP

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

The potassium uranates, KU1 and KU2

The phase KU1 has a nominal composition based on EDX data of K2O·4UO3. 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 K2O·6UO3. The X-ray diffraction data (Table 5) could be indexed on an orthorhombic cell with the parameters listed in Table...
2. The pattern is not similar to that given in JCPDS card no. 28-836 for a phase listed as K₂O-6.4UO₃.

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 K₂O-UO₃-SiO₂-H₂O 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 K₂O·4UO₃·1.5SiO₂ plus an unknown amount of H₂O (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 H₂O. The infrared spectra of these phases show the presence of at least two types of H₂O: a structural H₂O located on specific sites and loosely bound, zeolite type of H₂O that is much more disordered.

ACKNOWLEDGMENTS

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