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**Direct Investigations of the Immobilization of Radionuclides in the
Alteration Products of Spent Nuclear Fuel**

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EXECUTIVE SUMMARY

Safe disposal of the nation's nuclear waste in a geological repository involves unique scientific and engineering challenges owing to the very long-lived radioactivity of the waste. The repository must retain a variety of radionuclides that have vastly different chemical characters for several thousand years. Most of the radioactivity that will be housed in the proposed repository at Yucca Mountain will be associated with spent nuclear fuel, much of which is derived from commercial reactors [about 70,000 tons of UO_2 (LWR) spent fuel by the year 2010]. DOE is custodian of approximately 8000 tons of spent nuclear fuel that is also intended for eventual disposal in a geological repository. Unlike the spent fuel from commercial reactors, the DOE fuel is diverse in composition with more than 250 varieties. Safe disposal of spent fuel requires a detailed knowledge of its long-term behavior under repository conditions, as well as the fate of radionuclides released from the spent fuel as waste containers are breached. Nine radionuclides are of special concern because of their long half-lives, radiological toxicities, and potential mobilities under repository conditions: Np-237, Pu-239, Pu-242, U-234, Pa-231, Tc-99, I-129, Se-79, and C-14. In addition, Am-241 is important because it is a parent of Np-237. An understanding of the behaviors of each of these elements under repository-relevant conditions is essential to safe disposal.

Laboratory-scale experiments using UO_2 spent fuel, unirradiated UO_2 , and uranium metal indicate that spent fuels are unstable under the moist oxidizing conditions expected in the proposed repository at Yucca Mountain. The experimental results are consistent with studies of natural analogues that show significant alteration of uraninite (the mineral analogue of UO_2 in spent fuel) under conditions similar to those expected in the proposed repository. Both vapor hydration and hydrologically unsaturated drip tests involving spent fuel have demonstrated that the alteration rates of the spent fuel will be appreciable under repository conditions, with the alteration products being mainly uranyl (U^{6+}) phases owing to the dominance of U in spent fuel. The results of our research have demonstrated that it is likely that the uranyl phases forming due to the alteration of spent fuel will incorporate many of the radionuclides contained in the spent fuel, thus having a profound impact upon the mobility of the radionuclides.

Our research involved several thrusts designed to provide an understanding of the impact of uranyl phases on radionuclide mobility in a geological repository: (1) we have characterized the crystal structures and chemistries of more than 75 uranyl phases that are likely to form due to the alteration of spent fuel in the proposed repository, and developed a structural hierarchy for uranyl phases that aids prediction of their impact upon radionuclide mobility, (2) we have developed theoretical predictions of incorporation mechanisms for various radionuclides into uranyl phases that are likely to form under repository conditions, (3) we have verified selected predicted incorporation mechanisms by synthesis of uranyl phases containing the radionuclide of interest, (4) we have demonstrated ion exchange of radionuclides into the structures of single crystals of uranyl phases expected to form in the proposed repository, (5) we have measured the heats of formation of uranyl phases important for repository performance, (6) we have studied the structures and stabilities of various neptunyl and neptunyl-uranyl phases by phase synthesis and synchrotron experiments, (6) we have developed the bent-Laue X-ray analyzer for studying trace transuranium elements in U solids, (7) we have used synchrotron techniques to examine spent fuel and its corrosion products, (8) we have developed synthesis methods for uranyl phosphate phases, and (9) we have conducted corrosion testing on simulated five-metal Epsilon particles.

These components, taken together, provide an enhanced understanding of the impact of uranyl phases on the release of radionuclides during the corrosion of spent fuel under the conditions of the proposed repository. We have demonstrated that uranyl alteration phases may significantly retard radionuclide migration from waste forms in the proposed repository.

RESEARCH OBJECTIVES

The safe disposal of the nation's nuclear waste in a geologic repository is one of the most significant and difficult scientific endeavors of the twenty-first century. Unique scientific challenges are posed by the very long-lived radioactivity of nuclear waste. Many radionuclides of vastly different chemical character must be retained by the repository for several thousand years. Some with longer half-lives, such as Np-237, Pu-239 and Tc-99, need to be isolated for periods approaching a million years. In order to ensure the safety of a geologic repository, a detailed understanding of the mobility of radionuclides in complex natural systems is essential.

It is well-established that spent nuclear fuel is chemically unstable under the moist oxidizing conditions expected in Yucca Mountain, and that the most abundant phases formed during alteration of spent fuel following container failure will be uranyl compounds. Prior to the beginning of our EMSP research, laboratory simulations (e.g., Wronkiewicz et al. 1992, 1996; Finn et al. 1996) and studies of natural occurrences (e.g., Frondel 1958; Smith 1984; Finch & Ewing 1992; Finch & Murakami 1999) provided insight into the types of uranyl phases that might form in Yucca Mountain. Studies of natural analogues (i.e., oxidized U deposits) revealed that uranyl phases that may form in Yucca Mountain may persist for many thousands of years (e.g., Finch et al. 1996). Burns et al. (1997) proposed that radionuclides contained in spent nuclear fuel may be incorporated into uranyl alteration phases that form in the repository, thereby possibly substantially reducing their mobility. The final report of the Yucca Mountain Total Systems Performance Assessment Peer Review Panel (Whipple et al. 1999) emphasized the need for systematically evaluating the potential of incorporation of radionuclides into uranyl compounds that may form in Yucca Mountain. Such studies are essential to assess the importance of this mechanism of radionuclide retention on repository performance.

Knowledge of the crystal structures, chemistries, stabilities and paragenesis of uranyl minerals lag far behind most other mineral groups, owing in large part to the occurrence of these minerals as complex intergrowths of multiple phases, making routine analysis very difficult. Studies of natural analogues and laboratory simulations have left little doubt that uranyl minerals will be very important alteration phases of spent nuclear fuel in the proposed repository at Yucca Mountain. As we have argued in many publications (see Literature Cited below), a detailed understanding of all aspects of these minerals is key to assessing their impact upon the release of radionuclides from the waste forms. Our research objectives include detailed characterization (structural and chemical) of uranyl compounds that are likely to form under repository conditions, the prediction of possible mechanisms of incorporation of radionuclides into their structures, and experimental verification of such incorporation.

This report summarizes work conducted under DOE grant DE-FG07-97ER14820, which was funded from September, 1997 to September, 2004. Our research combines basic and applied studies of the crystal chemistry of U^{6+} and other actinides, with emphasis on the long-term performance of the proposed geological repository at Yucca Mountain. In addition to significantly improving our understanding of factors impacting the mobility of radionuclides in Yucca Mountain, our research is important for understanding the mobility of actinides in the vadose zone, in altered U mine and mill tailings, and in soils contaminated by U.

We emphasize the publication of the results of our EMSP-funded research in excellent journals. A summary of publications that present results of our EMSP research is at the end of this report.

METHODS AND RESULTS

Structures and Chemistry of U⁶⁺ Compounds Relevant to Yucca Mountain (Notre Dame)

At the beginning of our EMSP research, understanding of the crystal structures, chemistries, stabilities and occurrences of the uranyl compounds relevant to Yucca Mountain performance was entirely insufficient, from the perspective of understanding their potential impact on repository performance. The crystal structures were unknown for most of these phases, and even many of their chemical formulae were in doubt. Detailed structural analysis of uranyl phases relevant to repository performance has therefore been a high priority of our research. Suitable natural crystals have never been found for many of the compounds of interest, so we invested considerable effort in developing synthesis procedures for growth of crystals ~100 µm in dimension. We have now published the detailed structures and chemistries of more than 75 uranyl compounds that may be relevant to Yucca Mountain (Table 1).

Table 1. Incomplete listing of published structural studies of uranyl minerals and compounds		
Mineral name	Formula	
Studtite	$[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$	$\text{Na}_6[(\text{UO}_2)_2\text{O}(\text{MoO}_4)_4]$
Fontanite	$\text{Ca}[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2](\text{H}_2\text{O})_6$	$\text{Na}_6[(\text{UO}_2)(\text{MoO}_4)_4]$
Autunite	$\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$	$\text{K}_6[(\text{UO}_2)_2\text{O}(\text{MoO}_4)_4]$
Uranosphaerite	$\text{Bi}(\text{UO}_2)\text{O}_2\text{OH}$	$\text{Cs}[(\text{UO}_2)_6(\text{MoO}_4)_7(\text{H}_2\text{O})_2]$
Becquerelite	$\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_8$	$\text{NH}_4[(\text{UO}_2)_6(\text{MoO}_4)_7(\text{H}_2\text{O})_2]$
Haiweeite	$\text{Ca}[(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2](\text{H}_2\text{O})_3$	$\text{Na}_2[(\text{UO}_2)(\text{MoO}_4)_2]$
Weeksite	$\text{K}_2(\text{UO}_2)_2\text{Si}_6\text{O}_{15}(\text{H}_2\text{O})_4$	$\text{K}_2[(\text{UO}_2)(\text{MoO}_4)_2](\text{H}_2\text{O})$
Boltwoodite	$(\text{K}_{0.56}\text{Na}_{0.42})[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_{1.5}$	$\text{Cs}_4[(\text{UO}_2)_3\text{O}(\text{MoO}_4)_2(\text{MoO}_5)]$
Compreignacite	$\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$	$\text{Cs}_6[(\text{UO}_2)(\text{MoO}_4)_4]$
Agriuerite	$\text{K}_2(\text{Ca},\text{Sr})[(\text{UO}_2)_3\text{O}_3(\text{OH})_2] \cdot 2.4\text{H}_2\text{O}$	$[(\text{UO}_2)\text{Mo}_2\text{O}_7(\text{H}_2\text{O})_2]$
Wyartite	$\text{CaU}^{5+}(\text{UO}_2)_2(\text{CO}_3)_4(\text{OH})(\text{H}_2\text{O})_7$	$\text{Na}_3\text{Ti}_3[(\text{UO}_2)(\text{MoO}_4)_2](\text{H}_2\text{O})_4$
Bijvoetite	$[(\text{Y}, \text{REE})_8^{3+}(\text{UO}_2)_{16}(\text{CO}_3)_{16}\text{O}_8(\text{OH})_8(\text{H}_2\text{O})_{25}](\text{H}_2\text{O})_{14}$	$\text{Na}_{13-x}\text{Ti}_{3+x}[(\text{UO}_2)(\text{MoO}_4)_3]_4(\text{H}_2\text{O})_{6+x}$
Grimsilite	$\text{K}_3\text{Na}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})$	$\text{Na}_3\text{Ti}_5[(\text{UO}_2)(\text{MoO}_4)_3]_2$
Uranopilite	$[(\text{UO}_2)_6(\text{SO}_4)_2(\text{OH})_6(\text{H}_2\text{O})_6](\text{H}_2\text{O})_8$	$\text{Na}_2[(\text{UO}_2)(\text{MoO}_4)_2](\text{H}_2\text{O})_4$
Zippeite	$\text{K}_3(\text{H}_2\text{O})_3[(\text{UO}_2)_4(\text{SO}_4)_2\text{O}_3(\text{OH})]$	$(\text{C}_6\text{H}_{14}\text{N}_2)_3[(\text{UO}_2)_5(\text{MoO}_4)_8](\text{H}_2\text{O})_4$
Mg zippeite	$\text{Mg}(\text{H}_2\text{O})_{3.5}[(\text{UO}_2)_2(\text{SO}_4)_2\text{O}_2]$	$(\text{C}_2\text{H}_{10}\text{N}_2)[(\text{UO}_2)(\text{MoO}_4)_2]$
Zn zippeite	$\text{Zn}(\text{H}_2\text{O})_{3.5}[(\text{UO}_2)_2(\text{SO}_4)_2\text{O}_2]$	$\text{Li}_2[(\text{UO}_2)(\text{MoO}_4)_2]$
Na zippeite	$\text{Na}_5(\text{H}_2\text{O})_{12}[(\text{UO}_2)_8(\text{SO}_4)_4\text{O}_5(\text{OH})_3]$	$\text{Rb}_6[(\text{UO}_2)(\text{MoO}_4)_4]$
Co zippeite	$\text{Co}(\text{H}_2\text{O})_{3.5}[(\text{UO}_2)_2(\text{SO}_4)_2\text{O}_2]$	$\text{Rb}_6[(\text{UO}_2)_2\text{O}(\text{MoO}_4)_4]$
Umohoite	$[(\text{UO}_2)\text{MoO}_4(\text{H}_2\text{O})](\text{H}_2\text{O})$	$\text{Rb}_2[(\text{UO}_2)(\text{MoO}_4)_2]$
Irginite	$[(\text{UO}_2)\text{Mo}_2\text{O}_7(\text{H}_2\text{O})_2](\text{H}_2\text{O})$	$\text{Rb}_2[(\text{UO}_2)_2(\text{MoO}_4)_3]$
$\text{Rb}_2[(\text{UO}_2)_6(\text{MoO}_4)_7(\text{H}_2\text{O})_2]$	$\text{Cs}_3[(\text{UO}_2)_{12}\text{O}_7(\text{OH})_{13}](\text{H}_2\text{O})_3$	$\text{Na}_2[(\text{UO}_2)_3\text{O}_3(\text{OH})_2]$
$\text{Ag}_6[(\text{UO}_2)_3\text{O}(\text{MoO}_4)_5]$	$\text{K}_5[(\text{UO}_2)_{10}\text{O}_8(\text{OH})_9](\text{H}_2\text{O})$	$\text{Pb}_2(\text{H}_2\text{O})[(\text{UO}_2)_{10}\text{UO}_{12}(\text{OH})_6(\text{H}_2\text{O})_2]$
$\alpha\text{-Cs}_2[(\text{UO}_2)_2(\text{MoO}_4)_3]$	$\text{Sr}_{2.84}[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]_2(\text{H}_2\text{O})_2$	$\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$
$\beta\text{-Cs}_2[(\text{UO}_2)_2(\text{MoO}_4)_3]$	$\text{Na}[(\text{UO}_2)_4\text{O}_2(\text{OH})_5](\text{H}_2\text{O})_2$	$\text{Ca}_5[(\text{UO}_2)(\text{CO}_3)_3]_2(\text{NO}_3)_2(\text{H}_2\text{O})_{10}$
$\text{Ti}_2[(\text{UO}_2)_2\text{O}(\text{MoO}_5)]$	$\text{Ca}[(\text{UO}_2)_4\text{O}_3(\text{OH})_4](\text{H}_2\text{O})_2$	$\text{Ca}_6[(\text{UO}_2)(\text{CO}_3)_3]_2\text{Cl}_4(\text{H}_2\text{O})_{19}$
$\text{Na}_6(\text{UO}_2)(\text{SO}_4)_4(\text{H}_2\text{O})_2$	$(\text{NH}_4)_2[(\text{UO}_2)_2(\text{SO}_4)_2\text{O}_2]$	$\text{Ca}_{12}[(\text{UO}_2)(\text{CO}_3)_3]_4\text{Cl}_8(\text{H}_2\text{O})_{47}$
$\text{Ca}_2\text{Ba}_4[(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2]_3(\text{H}_2\text{O})_{16}$	$(\text{NH}_4)_4(\text{H}_2\text{O})[(\text{UO}_2)_2(\text{SO}_4)_2\text{O}_2]_2$	$\text{Na}_4(\text{UO}_2)_2(\text{Si}_4\text{O}_{10})_2(\text{H}_2\text{O})_4$
$(\text{UO}_2)_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$	$\text{K}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$	$\text{KNa}_3(\text{UO}_2)_2(\text{Si}_4\text{O}_{10})_2(\text{H}_2\text{O})_4$
$\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$	$\text{Na}_{10}(\text{UO}_2)(\text{SO}_4)_4(\text{SO}_4)_2(\text{H}_2\text{O})_3$	$[\text{Co}(\text{H}_2\text{O})_6]_3[(\text{UO}_2)_5(\text{SO}_4)_8(\text{H}_2\text{O})](\text{H}_2\text{O})_5$
$\text{Rb}_2(\text{UO}_2)[(\text{UO}_2)(\text{PO}_4)]_4(\text{H}_2\text{O})_2$	$\text{KNa}_5[(\text{UO}_2)(\text{SO}_4)_4](\text{H}_2\text{O})$	$(\text{NH}_4)_3(\text{H}_2\text{O})_2\{[(\text{UO}_2)_{10}\text{O}_{10}(\text{OH})][(\text{UO}_4)(\text{H}_2\text{O})_2]\}$

Structures we have reported (incomplete listing in Table 1) include those of studtite, becquerelite, haiweeite, weeksite, boltwoodite and compreignacite, all of which have been identified as alteration phases on spent fuel and UO₂ in laboratory experiments (e.g., Finch et al.

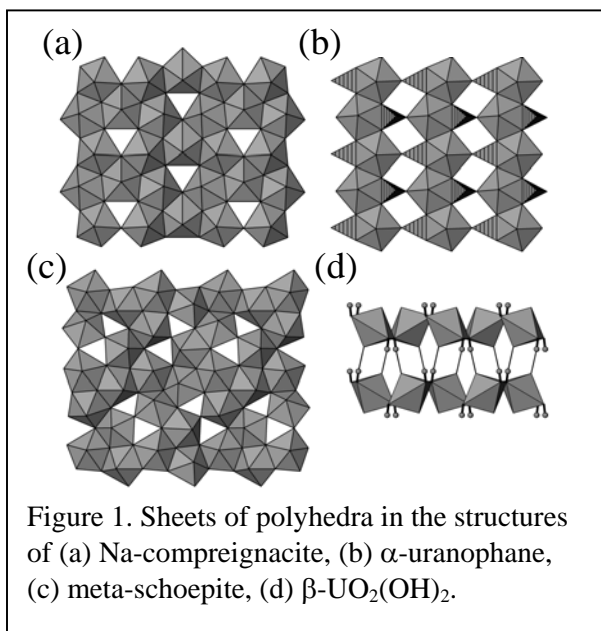
1999; Finn et al. 1996; McNamara et al. 2003; Amme 2002; Amme et al. 2002; Sattonnay et al. 2001).

Our structure studies have focused on several important chemical classes of U^{6+} compounds, and include detailed structural analysis, chemical characterization, and in many cases, discovery of new phases. Structures have been categorized according to the hierarchy of structures (Burns et al. 1996, Burns 1999), which serves as the basis of predicting radionuclide incorporation mechanisms (Burns et al. 1997, Chen et al. 1999, 2000). Our results have also been published in Russian (Burns 2004). References for each are provided below.

Predicting Incorporation of Radionuclides into Uranyl Compounds (Notre Dame)

The structural hierarchy of uranyl compounds (Burns et al. 1996, Burns 1999) has been continuously extended by our studies. The hierarchy is exceedingly important to our understanding of the structural relationships of these complex materials, and is the foundation of predicting incorporation mechanisms of radionuclides into their structures. Likely sites for incorporating radionuclides such as ^{135}Cs and ^{90}Sr have been established (Burns 1999; Burns & Li 2002). Burns et al. (1997) predicted incorporation mechanisms for Np and Pu into uranyl compounds, and Chen et al. (1999, 2000) considered the cases of Se and Tc. We have extended the approach of Burns et al. (1997) to include prediction of Np and Pu incorporation into compounds with newly determined structures.

Experimental Studies of Np^{5+} Incorporation into Uranyl Compounds (Notre Dame)



The long half-life of Np-237 (2.14×10^6 years) and potential high mobility of Np^{5+} in chemically oxidizing groundwater make it one of the most important radionuclides for the long-term performance of the proposed repository at Yucca Mountain. Burns et al. (1997) predicted that Np^{5+} may be incorporated into uranyl compounds. Because recent experimental evidence for Np incorporation into uranyl compounds is limited and contradictory (Buck et al. 1998; Fortner et al. 2004), one of our major objectives was to determine whether selected uranyl compounds can incorporate Np^{5+} into their structures.

Our studies of Np^{5+} incorporation into uranyl compounds have focused on four phases: the Ca uranyl silicate α -uranophane, $Ca[(UO_2)_2(SiO_3OH)_2](H_2O)_5$, and the uranyl

oxide hydrates meta-schoepite, $UO_3 \cdot 2H_2O$, Na-compreignacite, $Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$, and β - $UO_2(OH)_2$ (Burns et al. 2004). α -uranophane, meta-schoepite and Na-compreignacite have each been found as alteration products of spent nuclear fuel under simulated Yucca Mountain conditions (Finch et al. 1999, Finn et al. 1996). Owing to the similarities between the crystal chemistry of Np^{5+} and U^{6+} (Burns et al. 1997), it is likely that Np^{5+} will substitute for U^{6+} in some crystal structures. However, in order for this substitution to occur, a charge-balance mechanism

is essential and local modifications of bonding must occur. Thus, although it is possible to predict that Np^{5+} should be incorporated into some phases, experimental verification is essential. The phases selected for our study provide considerable structural diversity, which is important to probe the structural controls on Np^{5+} incorporation. α -uranophane contains sheets of uranyl pentagonal bipyramids and silicate tetrahedra, with Ca and H_2O located in the interlayers. Na-compreignacite and meta-schoepite contain topologically distinct sheets of uranyl pentagonal bipyramids. The interlayer of Na-compreignacite contains Na and H_2O , whereas the sheets of uranyl polyhedra in meta-schoepite are electroneutral, and the interlayer contains only H_2O . In the case of $\beta\text{-UO}_2(\text{OH})_2$, uranyl square bipyramids are linked through vertex-sharing to give sheets, and the sheets are linked directly by hydrogen bonds; there are no interlayer constituents in this structure (Fig. 1).

We conducted >100 synthesis experiments to optimize our synthesis approaches, which included a double-containment method because of the radiological hazards of Np^{5+} . We then synthesized each compound at either 70°C or 100°C from solutions containing from 10 to ~450 ppm Np^{5+} . Products were recovered and washed with boiling water, and aliquots of the mother solutions were taken before and after the synthesis experiments. Portions of each powder were also washed in acetic acid to strip any Np^{5+} that may have been sorbed to the surface of the crystals. Products were confirmed by X-ray powder diffraction, and products and solutions were analyzed using ICP-AES for U, Na and Ca, and ICP-MS for Np.

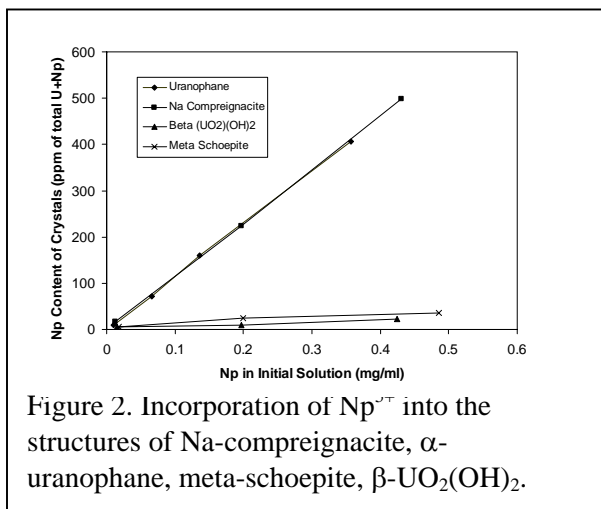


Figure 2. Incorporation of Np^{5+} into the structures of Na-compreignacite, α -uranophane, meta-schoepite, $\beta\text{-UO}_2(\text{OH})_2$.

Results of the Np^{5+} incorporation experiments are given in Figure 2 (Burns et al. 2004). Neither meta-schoepite or $\beta\text{-UO}_2(\text{OH})_2$ incorporated more than a few ppm Np^{5+} . In contrast, Na-compreignacite and α -uranophane incorporated Np^{5+} in proportion to the Np^{5+} concentration in the mother solution, and crystals of each containing more than 400 ppm Np^{5+} (of total $\text{Np} + \text{U}$) were obtained. The Np^{5+} concentration in the crystals was not significantly reduced by washing in acid, thereby demonstrating incorporation, rather than sorption onto the mineral grains.

Cation substitution in the interlayer of the structures is the likely charge-balance mechanism that permits Np^{5+} substitution for U^{6+} within the sheets. XAS was used to demonstrate that Np incorporated into powders of Na-compreignacite remains in the pentavalent oxidation state (Skanthakumar et al. 2004). This study indicates that Np^{5+} is likely to be incorporated into uranyl compounds that form in Yucca Mountain, and that this incorporation may have a significant impact upon the mobility of Np.

Ion Exchange of Cs and Sr into Uranyl Compounds (Notre Dame)

Prior to the current research, ion exchange had not been demonstrated for single crystals of any U^{6+} compound. Using single crystals of natural boltwoodite, Burns (1999) demonstrated the exchange of Cs into the interlayer. These experiments were done using a few crystals with maximum dimensions of ~200 μm . The crystals were recovered after treatment with a concentrated CsCl solution at 90°C (14 days) and 180°C (24 hours). The crystals remained intact, with well-defined faces and sharp edges, thereby ruling out a solution-reprecipitation

mechanism of exchange. Single-crystal structure determinations for crystals before and after the experiments showed that essentially all of the Na and K contained in the interlayer of the crystals was replaced by Cs, as demonstrated by the substantial increase in the electron density in the interlayer. Additional experiments performed using synthetic boltwoodite demonstrated ion exchange of Cs into the structure where Cs was present in solution at concentrations of ~100 ppm (Hill & Burns 1999). Burns & Li (2002) demonstrated the ion exchange of Sr into the structure of becquerelite from concentrated solutions of SrCl_2 , and Hoskin & Burns (2002) showed that Cs readily exchanges into the structure of compreignacite from concentrated solutions. Hoskin & Burns (2003) also demonstrated exchange of Cs into the structure of compreignacite from solutions that contained only 100 ppm Cs. In these experiments, crystals were treated for 14 days at 90°C, followed by analysis using an electron microprobe.

The exchange of Cs into boltwoodite and compreignacite, and Sr into uranophane (Burns 1999, Burns & Li 2002, Hoskin & Burns 2003) have significant implications for the mobility of Cs, Sr and other radionuclides under repository conditions. These results indicate that uranyl compounds can exchange lower-valence radionuclides with solutions after they grow, and that they can incorporate such radionuclides during growth. These phases may either sequester radionuclides or release them, depending upon the relative activities of different ions in the solution.

XANES and EXAFS Studies of Uranyl Compounds (Notre Dame)

X-ray absorption spectroscopy (XANES and EXAFS) can provide a wealth of information concerning the oxidation states and coordination environments of U and Np in samples of environmental interest. However, a basic understanding of the relationships between XAS (X-ray Absorption Spectroscopy) spectra for structures containing actinides has not been fully developed. We therefore undertook a systematic study of the U L_{III} -edge XANES and EXAFS spectra for a series of crystalline uranium compounds that have well-refined structures, known valence states and that display a range of coordination environments about U^{6+} . We selected structures that contain the uranyl ion in a variety of coordination environments, as well as structures that have been reported to contain U^{6+} in unusual 6-fold coordination geometry, such as the 4+2 geometry in Li_4UO_5 .

Spectra were collected using the BESSRC beam line at the Advanced Photon Source. We studied 13 compounds that included uranyl silicates, uranyl carbonates, uranyl phosphates, uranyl sulfates, and uranyl oxide hydrates, several of which may form in Yucca Mountain once containers are breached. XANES spectra of the 13 compounds are consistent with hexavalent uranium (E_0 onset at 17.173 keV). The XANES spectra of the first 11 compounds (chernikovite to KUCrO_6) are similar – each contain uranyl ions. Delta- UO_3 has U^{6+} in regular octahedral coordination, whereas Li_4UO_5 has U^{6+} in an unusual six-fold geometry, and these differences are manifested by differences in their XANES spectra. Extended X-ray absorption fine structure spectra were processed in k-space using parameters from the crystal structure refinements and fixed coordination numbers.

Thermochemistry of U^{6+} Compounds (Notre Dame)

Recent advances in the understanding of the crystal chemistry and structures of U^{6+} compounds important for repository performance provide the foundation for studies of their thermodynamics. However, there is a dearth of material and much of what is available in nature consists of intergrown phases. We have studied selected U^{6+} phases in order to further establish the thermodynamic properties of these compounds, which should provide an underpinning for

development of methods to predict thermodynamic parameters based upon structural connectivity.

We have conducted high temperature oxide melt drop-solution calorimetry to measure drop solution enthalpies (ΔH_{ds}) of select U^{6+} carbonate, oxyhydrate, and phosphate phases. Experiments were done, with the assistance of Prof. Alexandra Navrotsky, using a Calvet-type high temperature custom-built calorimeter located at the University of California-Davis. Sodium molybdate at 976 K was used as the solvent. Previous calorimetric experiments demonstrate that these are ideal conditions for UO_3 as it promoted rapid dissolution of uranium-bearing compounds. Results of this research are in Hughes et al. (2004, 2005).

Studies of neptunium geochemistry (Argonne)

Because of its long half life (2.14 Ma), radiotoxicity and potential mobility, neptunium-237 is an isotope of significant concern at many contaminated DOE sites. It is also a major dose contributor according to current performance-assessment models for the potential repository at Yucca Mountain, Nevada. Work at Argonne National Laboratory during this project focused on incorporating Np into synthetic U oxides and hydroxides and examining the fate of Np during the aqueous corrosion of Np-doped U oxides, as well as developing enhanced capabilities for analyzing samples containing multiple actinides by using EXAFS. As part of this effort, Np-doped U_3O_8 ($Np_xU_{3-x}O_8$) was synthesized with Np concentrations ranging from 0.5 to 9.4 wt% Np, corresponding to Np:U ratios from 1:160 to 1:8. Although not a naturally occurring mineral, U_3O_8 bears structural similarities to many uranyl compounds with both known and potential importance as radionuclide hosts in the environment. The success of this synthesis will be helpful in achieving our proposed goal to synthesize Pu and Am-bearing U oxides and hydroxides by using similar synthesis techniques. Np-bearing uranium compounds were characterized by X-ray diffraction and X-ray absorption spectroscopy.

Development of a bent-Laue X-ray analyzer for resolving XAS data for trace transuranium actinides in U solids (Argonne)

Collecting high-quality X-ray absorption spectra of low levels of Np in U compounds required that we develop a special detector for our XAS (X-ray Absorption Spectroscopy) data collection. Because the Np-L α fluorescence ($L\alpha_1 = 13.944$ keV, $L\alpha_2 = 13.760$ keV) is very close in energy to the U-L α fluorescence ($L\alpha_1 = 13.615$ keV, $L\alpha_2 = 13.439$ keV) and occurs at higher energy (i.e., just above the absorption edge of U), the use of standard fluorescence detectors is precluded. Employing a bent Laue analyzer, which provides superior energy discrimination, isolates the signal of the relatively small amount of Np in our samples by removing the large contribution for uranium. Several reports and one journal paper reporting this work have been published.

Characterizing Np-doped U_3O_8 (Argonne)

The successful synthesis of a series of Np-bearing U_3O_8 is the strongest evidence to date for the direct structural incorporation of Np into U sites in a uranium oxide. Analyses of Np-doped U_3O_8 by XANES indicates that Np occupies distorted U sites in U_3O_8 and most likely occurs as Np(IV). As Np(IV) replaces U in U_3O_8 , the ratio of U(VI) to U(V) must increase until all U is hexavalent in $Np_xU_{3-x}O_8$. Charge balance, therefore, requires that the value of x not exceed one in $Np_xU_{3-x}O_8$. Powder X-ray diffraction analyses of Np-doped U_3O_8 indicates that it

forms a homogeneous solid solution from approximately 0.1 wt.% Np up to 9.5 wt. % Np, and that the dependence of the lattice parameters on Np concentration suggests that a complete solid solution may be possible for values of x in $\text{Np}_x\text{U}_{3-x}\text{O}_8$ from zero to one; that is, between end-member compositions U_3O_8 and NpU_2O_8 . The substitution of Np(IV) for U in U_3O_8 imparts significant strain to the structural sheets, although the distortion to the sheets appears to reach a maximum for x of 0.3 and above; in fact, Np-doped U_3O_8 exhibits nearly isovolumetric strain, with the a and b cell parameters changing in a complementary fashion, such that the area defined by the a - b plane remains nearly constant (the c cell dimension changes only slightly). As noted, Np(IV) occupies six-coordinated U sites in $\text{Np}_x\text{U}_{3-x}\text{O}_8$, such as occur in beta- U_3O_8 , and Finch & Kropf (2003) suggest that NpU_2O_8 may be isostructural, or nearly so, with beta- U_3O_8 .

Synthesis of uranyl oxyhydroxides from Np-bearing U_3O_8 (Argonne)

Exposure of Np-bearing U_3O_8 to humid air (100% relative humidity) at 90° and 150°C under nominally oxidizing conditions produces a variety of U(VI), Np(V) and Np(IV) solids. The primary sink for Np during corrosion of $\text{Np}_{0.33}\text{U}_{2.67}\text{O}_8$ at 150° C is crystalline NpO_2 ; whereas, corrosion of $\text{Np}_{0.33}\text{U}_{2.67}\text{O}_8$ at 90° C produces approximately equal proportions of crystalline NpO_2 and Np_2O_5 . Dehydrated schoepite, $(\text{UO}_2)\text{O}_{0.25-z}(\text{OH})_{1.5+2z}$ ($0 \leq z \leq 0.15$), is the predominant U(VI) compound formed in these experiments and does not appear to incorporate measurable amounts of Np (a previous report that Np was incorporated into in this solid were the result of an interference inherent to the analytical technique used (EELS) see Fortner et al. 2004]). Results of this work have been presented at several conferences (Finch 2002, Finch et al. 2002, Finch & Kropf 2003).

XAS examinations of spent fuel and its corrosion products (Argonne)

Detailed understanding of the structural roles that Np, Pu and Am play in spent fuel and uranyl compounds formed as fuel-corrosion products is an important part of understanding the crystal-chemical and potential geochemical behaviors of these actinides. As part of this effort, we have conducted the first-ever EXAFS examinations of fully radioactive spent nuclear fuel. Owing to our development of the bent-Laue detector for XAS (see above), we have been able to obtain high-quality EXAFS spectra from Pu, and Np in unaltered spent fuel at concentrations of 1.3 and 0.08 wt.%, respectively. Preliminary analyses indicate that both Np and Pu are tetravalent and substitute for U in the UO_2 fuel. Similar high-precision EXAFS analyses of uranyl oxyhydroxides (dehydrated schoepite) formed during the oxidative alteration of spent fuel after more than eight years (104 months) in humid air have demonstrated that Np is not incorporated into these solids, a result consistent with the results reported by Burns et al. (2004), which also found that Np was not incorporated into metaschoepite (see above).

EXAFS of lanthanide-bearing silicates and effects of lanthanide substitutions on physical properties (Argonne)

Lanthanides are useful, non-radioactive chemical analogues of many actinides of environmental concern, so we have also been examining solid-state structural effects of lanthanide substitutions in synthetic crystals of zircon (ZrSiO_4). A major part of this effort is aimed at developing our capabilities for collecting EXAFS data from compounds with elements that may experience absorption-edge interferences caused by signal overlap from neighboring elements, as is the case for many actinides and lanthanides. Furthermore, non-radioactive lanthanides provide useful surrogates for examining structural changes induced by substitutions into crystalline materials, such as ZrSiO_4 . Recent efforts at Argonne have focused on examining

REE substitutions by XRD and XAS. Results of these studies indicate that coupled substitutions of REE and P into zircon induces substantial strain at the *Si* site, limiting the degree of solid solution between zircon and xenotime (YPO_4). EXAFS analyses indicate that REE occupy Zr sites rather than interstitial sites, as has been proposed. A recent compressibility study of REE- and P-doped zircon demonstrates that REE-doped ZrSiO_4 is “softer” (has lower compressibility), which acts to delay the onset of the high-pressure phase transformation to riedite (also ZrSiO_4). Such changes to the physical properties of zircon (a notably durable mineral) suggests that substitutions of actinides and lanthanides into waste forms and uranyl alteration products may impact the long-term durability of substituted solids.

Synthesis of uranyl phosphates (Missouri - Rolla)

Naturally occurring uranyl phosphates (e.g., meta-autunite, sodium autunite, etc.) and vanadates display an enhanced stability in near-surface oxidizing environments relative to other uranyl phases. The potential mobility of radionuclides may be retarded if they can become incorporated into these phases. Uranyl phosphates may be induced to form by using phosphate-rich backfill material in a near-field spent fuel disposal vault or they may occur following the corrosion of phosphate-rich waste forms (Haworth et al., 2003). Synthetic phosphuranylite, $\text{Ca}(\text{UO}_2)[(\text{UO}_2)_3(\text{OH})_2(\text{PO}_4)_2]_2 \cdot 12\text{H}_2\text{O}$ was synthesized in seven and 35 day experiments at 90°C , but was replaced by meta-autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$) after 182 days (Turner and Wronkiewicz, 2003; Turner, 2003). Both phases displayed a strong affinity for incorporating cesium (experimental K_d s ranged from ~ 100 to 1000). The Cs content in these crystals was also relatively unaffected by washing in a mild acetic acid solution, suggesting that the Cs is incorporated within the crystalline structure rather than being loosely adsorbed to the surface. By contrast, Re^{7+} (surrogate for Tc^{7+}) was only weakly sorbed to the Ca-phosphates (experimental K_d s < 0.005) and was easily desorbed by washing in the acetic acid. Surrogate radionuclide sorption tests conducted with sodium autunite ($\text{NaUO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) displayed similar results as noted in the Ca-phosphate experiments.

Incorporation of lanthanide elements in uranyl phases (Missouri - Rolla)

The potential for incorporating radionuclides into a uranyl hydroxide ($\text{UO}_2(\text{OH})_2$) was evaluated by precipitating uranyl phases from aqueous solutions containing dissolved lanthanide elements (2.1 ppm Ce^{4+} , 4.6 ppm Ce^{4+} , or 286 ppm Nd^{3+}). These elements are used to both evaluate the potential behavior of lanthanide radionuclides and as surrogate elements for the actinides (e.g., Ce^{4+} and Nd^{3+} for Pu^{4+} and Am^{3+} , respectively). An analysis of the crystalline products indicate a progressive decrease in concentration of cerium; from 26, to 20, and finally 11 ppm for crystals produced in 7-, 35-, and 190-day tests, respectively ($K_d = 14, 11, 3$, respectively; Kim et al., 2000, 2002). Results with neodymium display a similar trend, with concentrations in the solid decreasing from 1240 to 922 ppm between 7 and 35 days of reaction ($K_d = 14$ and 11, respectively). The decreasing concentration of lanthanides in the uranyl crystals can be correlated with a coarsening in crystal size, decrease in the concentration of dissolved uranium, and decrease in the ratio of surface area/volume of the crystals.

Corrosion testing of a simulated five-metal Epsilon Particle (Missouri - Rolla)

Non-radioactive metal powders were mixed and arc melted in an atomic percent ratio of 40% Mo, 30% Ru, 15% Pd, 10% Re, and 5% Rh (Re used as a surrogate for Tc); a composition that attempted to simulate epsilon particles in spent reactor fuel. Scanning electron microscopy images of the as-cast samples denote sample heterogeneities with Mo, Mo-Ru-Re, and Mo-Ru-Pd rich zones (Wronkiewicz et al., 2002). Results from vapor hydration tests (200°C) for time periods up to 35 days indicate the formation of Mo- and Re-enriched alteration phases. Phase growth was enhanced when air was periodically replenished in the test vessels suggesting that oxide and/or hydroxide alteration phases may play a role in the corrosion process. MCC-1 corrosion tests (90°C) were conducted for time periods up to 182 days in solutions of either a) deionized water or b) deionized water acidified with nitric acid to a pH of 3.0. The deionized water tests progressively decreased in pH with increasing reaction time (5.5 to 4.0), while the pH remained at a near-constant value of 3.0 in the nitric acid solutions. Normalized Re/Mo release ratios varied from 0.20 to 0.86, and increased as a function of reaction time and acidity. Release of the platinum group metals (Pd, Rh, and Ru) was insignificant in comparison to Mo and Re.

Contributions to the Education of Tomorrow's Scientists

This EMSP research program has been very active in educating the scientists of tomorrow. As with any successful research program in a university setting, students have been extensively involved with all aspects of this project. At the University of Notre Dame, undergraduates, graduate students, and post-doctoral fellows have been given many unique opportunities in research by this funding (summarized in Table 2). Students have been given the opportunity to work with sophisticated techniques and facilities, and to gain expertise in the areas of actinide mineralogy and geochemistry. Eight undergraduates have been involved in this project. For example, Ms. Rebecca Glatz worked on this project as an undergraduate from her sophomore through senior years, and published a major paper concerning the results of her study. She then won a National Science Foundation Graduate Fellowship and is now working towards her Ph.D. degree at Stanford University. Ms. Kathryn Deely, also an undergraduate, worked on this project for two years. This EMSP project provided Kathryn the opportunity to gain experience at Argonne National Laboratory in the hot labs managed by Dr. Lynda Soderholm. Kathryn completed Radworker II training at Argonne, and worked extensively with Np. She is a co-author on three archival journal papers, and won the best undergraduate paper award at the Notre Dame Environmental Research Symposium last fall, where about 80 students presented results of their research. Two undergraduate students were supported by EMSP funded research at the University of Missouri – Rolla. Chase Watkins and Andrew Baughman contributed to the understanding of corrosion processes affecting the epsilon phase in spent nuclear fuel and published their research findings at the annual Materials Research Society Meeting in Boston. Chase Watkins also received the Oliver Rudolph Grawe Award for top Geology undergraduate student in Missouri in 2001.

Table 2. Contributions to the education of tomorrow's scientists

University of Notre Dame		
Francis Hill	Post-doctoral Fellow	Post-doctoral fellow at Rutgers University
Christopher Cahill	Post-doctoral Fellow	Assistant Professor, George Washington University
Paul Hoskin	Post-doctoral Fellow	Assistant Professor at Frieburg University
Sergey Krivovichev	Post-doctoral Fellow	Professor at St. Petersburg State University
Robert Shuvalov	Post-doctoral Fellow	
Yaping Li	Ph.D. (2002)	Post-doctoral fellow at IPNS, Argonne National Lab
Jennifer Jackson	M.S. (2000)	Now a Ph.D. student at University of Illinois-Urbana
Andrew Locock	Ph.D. 2004	Mineral Curator at Royal Ontario Museum
Karrie-Ann Hughes	Ph.D.(expected 2005)	Current
Amanda Klingensmith	Ph.D. (expected 2007)	Current
Paul Geisting	Ph.D. (expected 2006)	Current
Bridget McCollam	M.S. 2005	Ph.D. student at SUNY
Kathryn Deely	Undergraduate	
Leslie Hayden	Undergraduate	Ph.D. student at RPI
Kara Tholen	Undergraduate	
Alex Garza	Undergraduate	
Rebecca Glatz	Undergraduate	NSF Graduate Fellow, Ph.D. student at Stanford
Aaron Martin	Undergraduate	
Andrew Irvine	Undergraduate	Business school at Colorado School of Mines
Erin Keppel	Undergraduate	School teacher in St. Louis
University of Missouri-Rolla		
Cheol Woon Kim	Ph.D. (2001)	Assistant Research Professor, Univ. Missouri Rolla
Andrew Turner	M.S. (2003)	Working in private sector
Hillary Hayworth	M.S. (expected 2005)	Working in private sector
Chase Watkins	Undergraduate	Working in private sector
Andrew Baughman	Undergraduate	MS student at University of Missouri - Rolla

PERSONNEL SUPPORTED (1997-2004)

PIs:

Prof. Peter C. Burns, University of Notre Dame
 Prof. David J. Wronkiewicz, University of Missouri-Rolla
 Dr. Robert Finch, Argonne National Laboratory

Post-Doctoral Fellows

University of Notre Dame

Dr. Frances Hill (1997-1999)
 Dr. Christopher Cahill (1999-2000)
 Dr. Sergey Krivovichev* (1999-2000)
 Dr. Paul W.O. Hoskin (2000-2001)
 Dr. Robert Shuvalov (2003-2004)

Graduate Students

University of Notre Dame

Ms. Jennifer Jackson (M.S. 2000)
 Mr. Yaping Li (Ph.D. 2001)
 Mr. Andrew Locock (Ph.D. 2004)
 Ms. Karrie-Ann Hughes (Ph.D. expected 2005)
 Ms. Amanda Klingensmith (Ph.D. expected 2007)
 Mr. Paul Giesting (Ph.D. expected 2006)
 Ms. Bridget McCollam (M.S. 2005)

University of Missouri-Rolla

Mr. C.W. Kim. (Ph.D. 2001)
 Mr. Andrew Turner (M.S. 2003)
 Ms. Hillary Hayworth (M.S. expected 2005)

Undergraduate Students

University of Notre Dame

Ms. Kathryn Deely
 Ms. Leslie Hayden
 Ms. Kara Tholen
 Mr. Alex Garza
 Ms. Rebecca Glatz
 Mr. Aaron Martin
 Mr. Andrew Irvine
 Ms. Erin Keppel

University of Missouri-Rolla

Mr. Chase Watkins
 Mr. Andrew Baughman

*Dr. Krivovichev's and Dr. Shuvalov's stipends were provided by an NSF-NATO fellowship to work on the project; their research expenses were supported from the EMSP grant.

PUBLISHED OF RESULTS OF EMSP-FUNDED RESEARCH

We have placed significant emphasis on publishing the results of our EMSP-funded research in well-respected, peer-reviewed journals and symposia proceedings. The following three sections provide a listing of publications funded by EMSP from Notre Dame, University of Missouri-Rolla, and Argonne National Laboratory; in those cases where more than one of the investigators was an author of a publication, the publication is included in both lists.

Publications funded by EMSP Grant DE-FG07-97ER14820: University of Notre Dame

Bold = PI, PD = Post-Doc, GS = Graduate Student, US = Undergraduate Student

Listed below are archival journal publications only.

- Hughes Kubatko^{GS}, K.-A., Helean, K.B., Navrotsky, A. & **Burns, P.C.** (2005): Thermodynamics of uranyl minerals: Enthalpies of formation of uranyl oxide hydrates. *American Mineralogist* (submitted).
- Hughes Kubatko^{GS}, K.-A., Helean, K.B., Navrotsky, A. & **Burns, P.C.** (2004): Thermodynamics of uranyl minerals: Enthalpies of formation of rutherfordine, UO_2CO_3 , andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})_5$, and grimselite, $\text{K}_3\text{NaUO}_2(\text{CO}_3)_3\text{H}_2\text{O}$. *American Mineralogist* (submitted).
- Locock^{GS}, A.J., **Burns, P.C.**, Duke, M.J.M. & Flynn^{UG}, T.M. (2004): Monovalent cations in structures of the meta-autunite group. *Canadian Mineralogist* 42, 973-996.
- Hughes Kubatko^{GS}, K.A. & **Burns, P.C.** (2004): The crystal structure of a novel uranyl tricarbonatite, $\text{K}_2\text{Ca}_3[(\text{UO}_2)(\text{CO}_3)_3]_2(\text{H}_2\text{O})_6$. *Canadian Mineralogist* 42, 997-1004.
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- Locock^{GS}, A.J. & **Burns, P.C.** (2004): Revised Tl(I)-O bond valence parameters and the structures of thallos dichromate and thallos uranyl phosphate hydrate. *Zeitschrift für Kristallographie* 219, 1-8.
- Krivovichev^{PD}, S.V. & **Burns, P.C.** (2004): Gamma- UMo_2O_8 as a new polymorph of uranium dimolybdate containing tetravalent uranium. *Doklady Physics* 49, 76-77.
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- Burns, P.C.**, Alexopoulos^{GS}, C.M., Hotchkiss^{UG}, P.J., Locock^{GS}, A.J. (2004): An unprecedented uranyl phosphate framework in the structure of $[(\text{UO}_2)_3(\text{PO}_4)\text{O}(\text{OH})(\text{H}_2\text{O})_2](\text{H}_2\text{O})$. *Inorganic Chemistry* 43, 1816-1818.
- Krivovichev^{PD} S.V. & **Burns, P.C.** (2004): Synthesis and crystal structure of $\text{Cs}_4(\text{UO}_2)(\text{CO}_3)_3$. *Radiochemistry (in Russian)* 46, 12-15.
- Krivovichev^{UG} S.V. & **Burns, P.C.** (2004): Crystal structure of $\text{K}(\text{UO}_2)(\text{NO}_3)_3$ and some features of the $\text{M}(\text{UO}_2)(\text{NO}_3)_3$ compounds ($\text{M} = \text{K}, \text{Cs}, \text{NH}_4$). *Radiochemistry* 46, 16-19.
- Hughes Kubatko^{GS}, K.A. & **Burns, P.C.** (2003): The Rb-analogue of grimselite, $\text{Rb}_6\text{Na}_2[(\text{UO}_2)(\text{CO}_3)_3]_2(\text{H}_2\text{O})$. *Acta Crystallographica* C60, i25-i26.
- Krivovichev^{PD} S.V. & **Burns, P.C.** (2003): Crystal chemistry of uranyl molybdates. X. The crystal structure of $\text{Ag}_{10}[(\text{UO}_2)_8\text{O}_8(\text{Mo}_5\text{O}_{20})]$. *Canadian Mineralogist* 41, 1455-1462.
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- Krivovichev^{PD}, S.V. & **Burns, P.C.** (2003): The first sodium uranyl chromate, $\text{Na}_4[(\text{UO}_2)(\text{CrO}_4)_3]$: Synthesis and crystal structure determination. *Z Anorg Allg Chem* 629, 1965-1968.

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- Krivovichev^{PD}, S.V. & **Burns**, P.C. (2003): Geometrical isomerism in uranyl chromates II. Crystal structures of $\text{Mg}_2[(\text{UO}_2)_3(\text{CrO}_4)_5](\text{H}_2\text{O})_{17}$ and $\text{Ca}_2[(\text{UO}_2)_3(\text{CrO}_4)_5](\text{H}_2\text{O})_{19}$. *Zeitschrift für Kristallographie* 218, 683-702.
- Locock^{GS}, A.J. & **Burns**, P.C. (2003): Structures and synthesis of framework triuranyl diarsenate hydrates. *Journal of Solid State Chemistry* 176, 18-26.
- Locock^{GS}, A.L. & **Burns**, P.C. (2003): Structures and synthesis of framework Rb and Cs uranyl arsenates and their relationships with their phosphate analogues. *Journal of Solid State Chemistry* 175, 372-379.
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- Krivovichev^{PD}, S.V. & **Burns**, P.C. (2003): Crystal chemistry of uranyl molybdates. VIII. Crystal structures $\text{Na}_3\text{Ti}_3[(\text{UO}_2)(\text{MoO}_4)_4]$, $\text{Na}_{13-x}\text{Ti}_{3+x}[(\text{UO}_2)(\text{MoO}_4)_3]_4(\text{H}_2\text{O})_{6+x}$ ($x = 0.1$), $\text{Na}_3\text{Ti}_5[(\text{UO}_2)(\text{MoO}_4)_3]_2(\text{H}_2\text{O})_3$ and $\text{Na}_2[(\text{UO}_2)(\text{MoO}_4)_2](\text{H}_2\text{O})_4$. *Canadian Mineralogist* 41, 707-719.
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Volume Editor

- (1999) Editor for *Scientific Basis for Nuclear Waste Management XXII* (David J. **Wronkiewicz** and Joon Lee editors), volume 556, The Materials Research Society, Pittsburgh, PA. This volume contains 162 peer-reviewed papers, in 1331 pages, related to various aspects of nuclear waste disposal.

Student Theses/Dissertations

- Turner, A.S. (2003): Synthesis of uranium phosphate phases and potential retardation effects on spent fuel radionuclides. University of Missouri – Rolla MS Thesis, 130 p.
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