

Final Report

**Environmental Management Science Program
DE-FG07-97ER14816**

Project ID Number: 73751

Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

Rodney C. Ewing

Nuclear Engineering and Radiological Sciences
Materials Science & Engineering
Geological Sciences

University of Michigan
Cooley Bldg., 2355 Bonisteel Boulevard
Ann Arbor, Michigan 48109-2104

Field of Scientific Research: Geochemistry
Environmental Category: Spent Nuclear Fuel

Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

Rodney C. Ewing

ABSTRACT

Spent nuclear fuel (SNF), essentially UO_2 , accounts for over 95% of the total radioactivity of all of the radioactive wastes in the United States that require disposal, disposition or remediation. The UO_2 in SNF is not stable under oxidizing conditions and may also be altered under reducing conditions. The alteration of SNF results in the formation of new uranium phases that can cause the release or retardation of actinide and fission product radionuclides. Over the long term, and depending on the extent to which the secondary uranium phases incorporate fission products and actinides, *these alteration phases become the near-field source term.*

This research program has been a broadly based effort to understand the long-term behavior of SNF and its alteration products in a geologic repository.

Fortunately, our experiments and field studies have established that natural uraninite, UO_{2+x} , and its alteration products are excellent "natural analogues" for the study of the corrosion of UO_2 in SNF. This research program has addressed the following major issues:

1. What are the *long-term* corrosion products of natural UO_{2+x} , uraninite, under oxidizing and reducing conditions?
2. What is the paragenesis or the reaction path for the phases that form during alteration?
3. What is the radionuclide content in the corrosion products as compared with the original UO_{2+x} ? Do the trace element contents substantiate models developed to predict radionuclide incorporation into the secondary phases?
4. Are the corrosion products accurately predicted from geochemical codes (e.g., EQ3/6 or Geochemist's Workbench) that are used in performance assessments? Can these codes be tested by studies of natural analogue sites (e.g., Oklo, Cigar Lake or Pena Blanca).

As detailed in the summary of results, we have made substantial progress in addressing each of the above issues.

INTRODUCTION

The successful disposal of spent nuclear fuel (SNF) is one of the most serious challenges to the successful completion of the nuclear fuel cycle and the future of nuclear power generation (Ewing, 1999a, 1999b). In the United States, 21 percent of the electricity is generated by 107 commercial nuclear power plants (NPP), each of which generates 20 metric tons of SNF annually. In 1996, the total accumulation of SNF was 33,700 metric tons of heavy metal (MTHM) stored at 70 sites around the country (Richardson, 1997). The end-of-life projection for current nuclear power plants is approximately 86,000 MTHM of SNF. In the proposed nuclear waste repository at Yucca Mountain over 95% of the radioactivity originates from SNF. In 1998, approximately 130,000 MTHM of SNF have accumulated worldwide, most of it located at 236 NPP in 36 countries (Carter and Pigford, 1999). Annual production of SNF is approximately 10,000 MTHM, containing about 100 tons of “reactor grade” plutonium. Any reasonable increase in the proportion of energy production by NPP, i.e., as a substitute for hydrocarbon-based sources of energy, will significantly increase SNF production.

Spent nuclear fuel is essentially UO_2 with approximately 4-5 atomic percent actinide and fission product elements. A number of these elements have long half-lives (^{239}Pu 24,500 years; ^{237}Np 2 million years; ^{129}I 16 million years; ^{79}Se 1.1 millions years; ^{99}Tc 200,000 years); hence, ***the long-term behavior of the UO_2 is an essential concern in the evaluation of the safety and risk of a repository for SNF. One of the unique and scientifically most difficult aspects of the successful disposal of SNF is the extrapolation of short-term laboratory data (hours to years) to the long time periods (10^3 to 10^5 years)*** as required by the performance objectives set in regulations, i.e. 10 CFR 60. The direct verification of these extrapolations or interpolations is not possible, but ***methods must be developed to demonstrate compliance with government regulations and to satisfy the public that there is a reasonable basis for accepting the long-term extrapolations of spent fuel behavior.*** In recent years “natural analogues” for both the repository environment (e.g., the Oklo natural reactors) and nuclear waste form behavior (e.g., corrosion and alteration of uraninite, UO_{2+x}) have been cited as a fundamental means of achieving confirmation of long-term extrapolations (Ewing and Jercinovic, 1987; Ewing, 1991, 1992, 1993a, 1993b, 1999b). In particular, considerable effort has already been made to establish that uraninite, UO_{2+x} , with its impurities, is a good structural and chemical analogue for the analysis of the long-term behavior of the UO_2 in SNF (Fayek et al., 1997a; Janeczek and Ewing, 1991a, 1991b, 1992a, 1992b, 1995, 1996; Janeczek et al., 1993, 1996a, 1996b; Murphy, 1993; Murphy and Pabalan 1995; Murphy et al., 1995; Pearcy et al., 1994).

This proposal is based on the study of uraninite and the naturally occurring alteration products of UO_{2+x} under oxidizing and reducing conditions.

The UO_2 in SNF is not stable under oxidizing conditions. In oxic solutions, uranium has a strong tendency to exist as U^{6+} in the uranyl molecule, UO_2^{2+} . Uranyl ions react with a wide variety of inorganic and organic anions to form complexes and solid phases. Throughout most of the natural range of pH, U^{6+} forms strong complexes with oxygen-bearing ions including CO_3^{2-} , HCO_3^- , SO_4^{2-} , PO_4^{3-} , and

AsO₄³⁻, which are present in most oxidized stream and subsurface waters. In arid environments, the U⁶⁺ ion can precipitate as a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. This is well demonstrated in experimental work, e.g., in long term drip tests on UO₂ (Wronkiewicz et al., 1992, 1996, 1997; Buck et al., 1997; Wronkiewicz and Buck, 1999; Finch et al., 1999) and is confirmed by natural occurrences of UO₂ in which a wide variety of uranyl phases form as alteration products (Finch and Ewing, 1989, 1991a, 1991b, 1991c, 1992a, 1992b, 1992c, 1993, 1994, 1997; Finch et al., 1998; Pearcy et al., 1994). The most striking feature of these studies is the extremely close parallel between the paragenetic sequences (i.e. phase formation sequence) of the very long term (10 year tests) (Wronkiewicz et al., 1996, 1997; Wronkiewicz and Buck, 1999; Finch et al., 1999) and the young (therefore, low-Pb uraninites) deposits of Nopal I in Mexico (Pearcy et al., 1994). Thus, both experiments utilizing drip tests and the study of natural uranium deposits may be used to simulate the reaction progress expected for the UO₂ in spent fuel in the proposed Yucca Mountain repository (Finch and Ewing, 1992c; Wronkiewicz et al., 1996, 1997)

Under oxidizing conditions, the reaction kinetics of the conversion of UO₂ to a uranyl phase is rapid, and results in nearly complete dissolution of the original UO₂ (Murphy and Pabalan, 1995). Wronkiewicz et al. (1996) estimated that UO₂ pellets in their experiments (90°C) would have been completely altered within 660 years, concluding:

"The speed at which the UO₂ reactions occurred suggests that an advanced stage of uranyl alteration phase development can occur almost instantaneously within the constraints of the time-scale expected for repository disposal."

These results imply that alteration and subsequent trace element migration may occur simply due to the exposure of SNF to moisture in an unsaturated repository setting. The results are further supported by kinetic and thermodynamic models of UO₂ corrosion (e.g., Bruno et al., 1995; 1996, 1998) in which the final steps of the corrosion process are the precipitation and subsequent dissolution of the secondary uranyl phases.

The rapid matrix dissolution of the UO₂ in an oxidizing environment will result in a release of actinide and fission product elements, which appears to be preferentially incorporated into the structures of the uranyl phases formed during the corrosion of UO₂ (Ewing et al., 2000). Unfortunately, there are a wide variety of uranyl phases (approximately two hundred mineral names for these phases, see for example Cejka and Urbanec, 1990; Baran, 1992; Fleischer and Mandarino, 1995; Burns, 1999); and they are poorly described, their structures are often not known, and critical parameters such as their thermodynamic stability have not been determined experimentally.

Most importantly, there has been only a limited determination of the capacity of these phases to incorporate and retard the mobility of the released actinides and fission products. The fate of these radionuclides is critical to the performance assessment of a spent fuel repository in an oxidizing or reducing environment. A

basic understanding of the compositions, structures and stabilities of these phases is essential to the DOE environmental remediation program.

Significance of Research Program to the EMSP

An integral part of the performance assessment of a repository will be the interpolated behavior of UO_2 in SNF during alteration and corrosion. This research program will provide a basis for establishing the extent to which models of alteration and corrosion processes used in the performance assessment of the near-field repository environment are useful or valid. For example, it is essential that the presently large uncertainties inherent in these models be reduced (see for example the discussion by Ahn, 1996a, 1996b). Studies of natural samples of great age and appropriate geochemical environments offer a means to improve the understanding of the sources of error while decreasing uncertainties in the corrosion models.

This research focuses on near-field phenomena, that is waste form degradation. The successful understanding of relevant phenomena in the near-field reduces uncertainties in the total system performance assessment because:

- ❑ *The radionuclides are initially located within the UO_2 matrix of the spent fuel. Initially, these waste forms (spent fuel or vitrified high-level waste) are the only part of the repository that is radioactive. **The successful performance of the waste form, or subsequent incorporation of radionuclides into alteration products of the corrosion process, results in near-field containment.** This strategy is much preferred to the geologic isolation approach that presumes inherent release and movement of radionuclides, and relies on long travel times, dilution, dispersion, and sorption to restrict transport.*
- ❑ ***The chemistry and physics of the UO_2 corrosion and alteration, which lead to an understanding of subsequent release or retention of radionuclides over a given range of environmental conditions, is inherently more simply modeled and extrapolated over time** than the use of coupled hydrologic, geochemical and geophysical models of far-field radionuclide transport in of a geologic repository. That is, the extrapolation of the corrosion behavior of the UO_2 over long periods rests on a firmer scientific foundation than the extrapolated behavior of, as an example, hydrologic systems that are site specific and highly dependent on specific boundary conditions that are more difficult to model over long time periods (e.g., climate and recharge).*
- ❑ ***Naturally occurring UO_2 and its alteration products provide fundamental data for the “confirmation” of the extrapolated behavior of the UO_2 in spent fuel over long periods of time (millions to billions of years).** This approach holds great potential for the confirmation of performance assessments of near-field behavior. Uraninite provides one of the rare opportunities in which studies of a natural material can provide unambiguous data for the long-term behavior of SNF.*

Finally, we note that uranium is the most abundant actinide element in the DOE complex and the dominant element present in SNF. The results of this research

program are broadly applicable to DOE's efforts to clean up its numerous sites, such as at Fernald, Ohio, and Paducah, Kentucky, as well as dispose of defense and commercially generated SNFs. This research also provides data that are required to evaluate the long term behavior of fuel held in storage sites, both in pools or in dry casks.

RESEARCH REPORT (2000 - 2004)

The major advances resulting from this research program include:

Thermodynamic Prediction of Observed U^{6+} Phases. Analyses have shown that Blind Prediction Modelling (BPM) fails to predict the reported U^{6+} mineralogy in the weathering horizon of the 2 Ga old supergene-weathered Oklo-Okélobondo and Bangombé U-deposits and their natural fission chain reactors (Salah 2000; Jensen et al., 2002). The major problems appeared to be: 1) the lack of thermodynamic data on key uranyl phases and 2) that important species, such as SO_4^{2-} and PO_4^{3-} were not always included in the modelling. We have developed an empirical model that provides for the calculation of this much-needed thermodynamic data (Clark et al., 1998; Chen et al., 1999a). Using a method that sums the polyhedral contributions for the structural components, the thermodynamic parameters for key uranyl phases have been calculated. Based on this updated data, Eh-pH diagrams predict that coffinite and $U(HPO_4)_2 \cdot 2H_2O$ are stable U^{4+} phases under reducing conditions, and uranopilite, torbernite and bassetite will become stable as conditions become oxidizing. These phases are in accord with mineralogical observations. Previous BPM often omitted P and S and hence failed to predict the uranyl minerals observed at Bangombé. These new modelling results stress the importance of SO_4^{2-} and PO_4^{3-} resulting from dissolution of accessory apatite, monazite and sulphides in the retardation of U owing to the formation of uranyl sulphates and phosphates. This is a very specific example of the use of a natural analogue site to test conceptual models used in a performance assessment. These results have been published in *Radiochimica Acta* 90, 761-769 (2002).

In Situ Isotopic Analysis & High-Resolution Transmission Electron Microscopy (HRTEM) of UO_2 : One of the challenges in using natural uranium deposits, such as the Cigar Lake Deposit in Canada or the Oklo natural reactors in Gabon, as analogues for the long-term behavior of spent nuclear fuel has been the need to understand their complicated history of repeated alteration and criticality events (in the case of Oklo). In collaboration with Mostafa Fayek (now at Oak Ridge National Laboratory) we have used highly accurate *in situ* isotopic analyses by secondary ionization mass spectrometry (SIMS) to make measurements of the complexly intergrown uranium minerals and their alteration products. The first study was of the uranium minerals at the Cigar Lake Deposit of the Athabasca Basin in Canada. By a combination of SIMS and HRTEM, we were able to demonstrate that the nanoscale formation of alteration products, such as coffinite ($USiO_4$) and calciouranoite ($CaU_2O_7 \cdot 5H_2O$), has a profound and misleading effect on the results of conventional fluorination analyses. Using our nanoscale techniques, we were able to clearly identify 3 stages of alteration in the Cigar Lake uraninites (Fayek et al, 2002). We have extended this approach to studies of the Oklo-Okélobondo natural fission reactors in Gabon (Fayek et al., 2002). In this case, we were able to

determine the timing of separate criticality events and subsequent alteration events. Most importantly, we have been able to determine by isotopic analysis that the reactor zones nearest the surface have reacted more extensively with groundwaters of meteoric origin. We have now combined the high-resolution SIMS analysis with advanced microscopy techniques, such as high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) to put together a detailed description of the alteration processes of uraninite in the reactor cores at Oklo and Bangombé (Fayek et al. submitted).

UO₂ Incorporation of ⁹⁹Tc. ⁹⁹Tc is a long-lived radioactive fission product with a half-life of 2.13×10^5 years and a fission yield of 6.13% in nuclear reactors, making ⁹⁹Tc a prominent contributor to dose in safety assessments of nuclear waste repositories. Under Eh-pH conditions corresponding to the oxidative corrosion of SNF, which is constrained by the stability of uranyl phases relative to that of the UO_{2+x} phase, TcO₄⁻ is the predominant species of technetium with $\log [\text{TcO}_4^-]/[\text{TcO}(\text{OH})_2^0] > 2.15$ over the range of pH = 4 – 10. The low solubility of TcO₂·H₂O and high adsorption of Tc⁴⁺ by geological materials (e.g. clays), results in a groundwater concentration of Tc⁴⁺ of less than 10⁻⁸ m (Chen et al., 1999c). This implies that the incorporation of Tc⁴⁺ into alteration uranyl phases is not an important retardation mechanism. In contrast, TcO₄⁻ is highly soluble and weakly adsorbed in the near-field. Thus, the incorporation of Tc⁷⁺ into the structure of oxidized uranyl phases that might be expected to occur as an alteration product of SNF will actually result in under-bonding at the U⁶⁺ site, destabilize the structure. This suggests that significant substitution of (TcO₄⁻) will not occur in uranyl phases. These results have been published in the *Journal of Nuclear Materials* 278, 225-232 (2000).

Uraninite, UO_{2+x}, Incorporation of Trace Elements. Uraninite and associated alteration products from the Colorado Plateau were studied in detail by optical microscopy, electron microprobe analysis (EMPA), scanning electron microscopy (SEM) and backscattered electron (BSE) imaging in order to determine the behavior and fate of trace elements such as Pb, Ca, Si, Th, Zr, and REE during corrosion under oxidizing conditions. The long-term alteration products and processes of uraninite provide insight into the corrosion of UO₂ in SNF. Uraninite, schoepite, calcic uranate, uranophane, fourmarierite, a Fe-rich uranyl phase, and coffinite were identified. The primary uraninite and alteration phases generally have low trace element contents, with the exception of coffinite from Caribou Mine, Colorado. The trace element content of uraninite (Zr, Ti, Th and REEs) were in general, lower than the values measured in secondary uranyl phases, suggesting that trace elements are preferentially incorporated into the structures of the secondary uranyl phases. A compositional profile of a concentric structure in schoepite shows that alteration results in a loss of U, Pb and Zr and the incorporation of Si, Ti, Ca and P. Concentric structures are usually composed of both uraninite and uranyl phases, while microfractures are common in the secondary phases. This work has been published in *Radiochimica Acta* (Zhao and Ewing, 2000).

Retardation of Radionuclides in the Oklo Natural Reactors. The natural fission reactors in Gabon have been studied in detail by optical microscopy, BSE, and EMPA to determine the source term, extent of uraninite alteration, and the means of retardation of nuclear reaction products during their 2 Ga year long

geological history. A detailed study of the recently excavated Okélobondo reactor zone was conducted. This reactor zone consists of a ~ 55 cm thick reactor core overlain by a typically less than 60 cm thick hydrothermal alteration halo, *argile de pile*. The reactor core mainly consists of uraninite (≤ 90 vol.%), galena, illite, and minor chlorite. The *argile de pile* consists mainly of chlorite cut by fine illite veinlets. The uraninite has been subjected to minor degree of coffinitization ($\text{UO}_2 \rightarrow \text{USiO}_4 \cdot n\text{H}_2\text{O}$). Several accessory phases occur in the reactor zone of which U-Zr-silicate, monazite, sulfides, and sulfur-arsenides are particularly important with respect to retardation of fissiogenic elements. The “unaltered” uraninite is relatively pure and consists of 87.01 ± 0.72 to 91.24 ± 0.91 wt.% UO_2 and 5.66 ± 0.61 to 7.22 ± 0.53 wt.% PbO . The major impurities are SiO_2 ($\leq 0.78 \pm 0.11$ wt.%), CaO ($\leq 1.84 \pm 0.09$ wt.%), and FeO ($\leq 0.55 \pm 0.04$ wt.%). The concentration of fissiogenic trace elements is low: $\text{ZrO}_2 \leq 0.09 \pm 0.04$ wt.%, $\text{ThO}_2 \leq 0.20 \pm 0.11$ wt.%, $\text{Ce}_2\text{O}_3 \leq 0.09 \pm 0.02$ wt.%, and $\text{Nd}_2\text{O}_3 \leq 0.10 \pm 0.06$ wt.%, but showed a distinct variation with location in the reactor zone. The concentration of the fissiogenic trace elements was higher ($\text{ZrO}_2 \leq 24.29$ wt.%, $\text{ThO}_2 \leq 0.31$ wt.%, $\text{Ce}_2\text{O}_3 \leq 0.75$ wt.%, and $\text{Nd}_2\text{O}_3 \leq 0.50$ wt.%) in U-Zr-silicate observed in fracture veinlets and mineral coatings in the reactor zone. Inferred from mineral chemistry, the fissiogenic Zr (including $^{90}\text{Sr} \rightarrow ^{90}\text{Zr}$), Ce, Nd, and Th (daughter of $^{238}\text{U}(\text{n},\gamma,2\beta)^{239}\text{Pu}(\text{n},\gamma)^{240}\text{Pu}$ and $^{235}\text{U}(\text{n},\gamma)^{236}\text{U}$) are well-retained in uraninite and retarded by the U-Zr-silicate during migration. Fissiogenic LREE may also have been incorporated into rare monazite. Fissiogenic Ru, including ^{99}Ru a daughter of ^{99}Tc , was mainly retained in ruthenium sulfur-arsenides ($\pm \text{Pb}$, Co , and Ni), such as ruthenarsenite and ruarsite. This work was published in the *Bulletin of the Geological Society of America* (Jensen and Ewing, 2001).

PUBLICATIONS (2000-2004)

*student authors:

- L.F. Konikow and R.C. **Ewing** (2000) Reply to Comments by B. Sagar on “Is a probabilistic performance assessment enough?” in Ground Water, vol. 38(1), 2-3.
- F. Chen, P.C. Burns and R.C. **Ewing** (2000) Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. Journal of Nuclear Materials 278, 225-232.
- M. Fayek, Peter Burns, Young-Xiang Guo and R.C. **Ewing** (2000) Micro-structures associated with uraninite alteration. Journal of Nuclear Materials 277, 204-210.
- D. Zhao and R.C. **Ewing** (2000) Alteration products of uraninite from the Colorado Plateau. Radiochimica Acta 88, 739-749.
- K.A. Jensen and R.C. **Ewing** (2000) Microtexture and chemistry of “unaltered” uraninite in the Oklo, Okélobondo, and Bangombé Natural Fission Reactors. Proceedings of the second joint EC-CEA workshop of the OKLO-natural analogue Phase II project. Nuclear Science and Technology, EUR 19116, 61-91.
- K.A. Jensen*, J. Janeczek, R.C. **Ewing**, P. Stille, and F. Gauthier-Lafaye, (2000) Crandallites and coffinite: retardation of nuclear reaction products at the Bangombé natural fission reactor, Scientific Basis for Nuclear Waste Management XXII. J. Shoesmith and R.W. Smith, Eds., Materials Research Society Symposium Proceedings, vol. 608, 525-532.
- K.A. Jensen*, J. Janeczek, R.C. **Ewing**, P. Stille, F. Gauthier-Lafaye, S. Salah* (2000) Crandallites and coffinite: Retardation of nuclear reaction products at the Bangombé natural fission reactor. Proceedings of the Materials Research Society, vol. 608, 525-532.
- R.C. **Ewing** (2001) Ageing studies of nuclear waste forms. In *Ageing Studies & Lifetime Extension of Materials*, edited by L.G. Mallinson (Kluwer Academic/Plenum Publishers, New York) 15-22.
- R.C. **Ewing** (2001) Nuclear waste forms: The evaluation of very long-term behavior. Materials Technology, vol. 16(1), 30-36.
- K.A. Jensen* and R.C. **Ewing** (2001) The Okélobondo natural fission reactor, southeast Gabon: Geology, mineralogy and retardation of nuclear reaction products. Geological Society of America Bulletin 113, 32-62.
- R.C. **Ewing** (2001) The design and evaluation of nuclear waste forms: Clues from mineralogy. Canadian Mineralogist, vol. 39, 697-715. This paper received the Hawley Medal of the Mineralogical Association of Canada.
- R.C. **Ewing** (2002) Plutonium: The nuclear fuel cycle & the environment. Facets, 1(2), 11-14.
- R.C. **Ewing**, Fanrong Chen and S. B. Clark (2002) An empirical method for calculating thermodynamic parameters for U(VI) phases, applications to performance assessment calculations. Proceedings of a workshop on “The Use of Thermodynamic Databases in Performance Assessment”, Nuclear Energy Agency (OECD), 93-102.
- R.C. **Ewing** (2002) Materials research in nuclear waste management: Reflections on twenty-five MRS symposia. (invited) Eds. B.P. McGrail and G.A. Cragolino, Scientific Basis for Nuclear Waste Management XXV, Proceedings of the Materials Research Society, vol. 713, 3-14.

- M. Fayek, K.A. Jensen*, R.C. **Ewing** and L.R. Riciputi (2002) In situ isotopic analysis of uraninite microtextures from the Oklo and Okélobondo natural fission reactors. Eds. B.P. McGrail and G.A. Cragolino, Scientific Basis for Nuclear Waste Management XXV, Proceedings of the Materials Research Society, vol. 713, 849-856.
- R.C. **Ewing** and L.M. Wang (2002) “Phosphates as Nuclear Waste Forms” in Reviews in Mineralogy & Geochemistry, vol. 48, M.J. Kohn, J. Rakovan and J.M. Hughes (Editors) 673-699.
- K.A. Jensen*, C.S. Palenik*, and R.C. **Ewing** (2002) U^{6+} -phases in the weathering zone of the Bangombe U-deposit: Observed and predicted mineralogy. Radiochimica Acta 90, 761-769.
- M. Fayek, M. T. Harrison, R.C. **Ewing**, Marty Grove and Chris D. Coath (2002) O and Pb isotopic analyses of uranium minerals by ion microprobe and U-Pb ages from the Cigar Lake deposit. Chemical Geology, 185, 205-225.
- R.C. **Ewing** (2002) Atomaffald – løsninger fra mineralogien. Geologisk Nyt, no. 5, 4-8 (in Danish).
- S. Utsunomiya, K.A. Jensen, G.J. Keeler and R.C. **Ewing** (2002) Uraninite and fullerene in atmospheric particulates. Environmental Science & Technology 36, 4943-4947.
- S. Utsunomiya, L.M. Wang, M. Douglas, S.B. Clark and R.C. **Ewing** (2003) The effect of ionizing radiation on uranophane. American Mineralogist 88, 159-166.
- S. Utsunomiya and R.C. **Ewing** (2003) Application of high-angle dark field scanning transmission electron microscopy, energy dispersive x-ray spectrometry, and energy-filtered transmission electron microscopy to the characterization of nanoparticles in the environment. Environmental Science & Technology 37, 786-791.
- M. Douglas*, S.B. Clark, Satoshi Utsunomiya and R.C. **Ewing** (2002) Trace metal incorporation into uranophane $[Ca(UO_2)(SiO_3OH)]_2 \cdot 5H_2O$. Journal of Nuclear Technology, vol. 3, 504-507.
- F. Chen and R.C. **Ewing** (in press) Structure-configurational entropy and its effect on the thermodynamic stability of uranyl phases: With special application for the geological disposal of nuclear waste. Science (China).
- S. Utsunomiya, L. Wang, M. Douglas*, S.B. Clark and R.C. **Ewing** (2003) The effect of ionizing radiation on uranophane. American Mineralogist, 88, 159-166.
- S. Utsunomiya and R.C. **Ewing** (2003) Application of high-angle annular dark field scanning transmission electron microscopy, scanning transmission electron microscopy-energy dispersive x-ray spectrometry, and energy-filtered transmission electron microscopy to the characterization of nanoparticles in the environment. Environmental Science & Technology, 37, 786-791.
- Fanrong Chen and R.C. **Ewing** (2003) Structure-configurational entropy and its effect on the thermodynamic stability of uranyl phases: With special application for the geological disposal of nuclear waste. Science (China, Series D), 46(1), 39-49.
- P. Stille, F. Gauthier-Lafaye, K.A. Jensen, S. Salah, G. Bracke, R.C. **Ewing** and D. Louvat (2003) REE migration in groundwaters close the natural fission reactor of Bangombé (Gabon). Chemical Geology, 198, 289-304.
- M. Fayek, S. Utsunomiya, R.C. **Ewing**, L.R. Riciputi and K.A. Jensen (2003) Oxygen isotopic composition of nano-scale uraninite at the Oklo-Okélobondo natural fission reactors, Gabon. American Mineralogist, 88, 1583-1590.

- K.A. Traexler*, S. Utsunomiya, A.B. Kersting and R.C. **Ewing** (2004) Colloid transport of radionuclides: Yucca Mountain performance assessment. Eds. V.M. Oversby and L.O. Werme, Scientific Basis for Nuclear Waste Management XXVII, Proceedings of the Materials Research Society, vol. 807, 653-658.
- S. Utsunomiya, S.C. Peters, J.D. Blum and R.C. **Ewing** (2003) nanoscale mineralogy of arsenic in a region of New Hampshire with elevated As-concentrations in the groundwater. American Mineralogist, 88, 1844-1852.
- H. Hidaka, J. Janeczek, F.N. Skomurski, R.C. **Ewing** and F. Gauthier-Lafaye (in press) Geochemical fixation of rare earth elements into secondary minerals in sandstones beneath a natural fission reactor at Bangombé, Gabon. Geochimica et Cosmochimica Acta.
- L.Z. Evins, K.A. Jensen, and R.C. **Ewing** (in press) Uraninite recrystallization and Pb-loss in the Oklo and Bangombé natural fission reactors, Gabon. Geochimica et Cosmochimica Acta.
- F. Chen, P.C. Burns and R.C. **Ewing** (in preparation) Retention of ^{129}I in the near-field of nuclear waste repositories. Journal of Nuclear Materials.

SUMMARY OF IMPACTS OF THE RESEARCH PROGRAM

Impact on International Programs. During the past three years, my research group at the University of Michigan has had an active program of research on uranium-bearing phases, the corrosion products of uraninite, and the UO_2 in SNF. The work has benefited from numerous collaborations, many of them international. As an example, Professor Ewing was a participant in the European Union project to study radionuclide migration around the Oklo reactors in Gabon. The EU program supported collaborations with scientists in Denmark, Poland, France, Spain and Japan. He participates in a new European initiative to study radionuclide release from the Bangombé reactor under oxidizing conditions. As a result of this collaboration, Professor Ewing now has an extensive research collection of Oklo samples that provide the basis for future work. Through a NATO program there is an active collaboration with Russian colleagues at the Khlopin Radium Institute in St. Petersburg and through a BES/DOE program we collaborate with the IGEM of the Russian Academy of Science in Moscow in studies of minerals suitable for use as actinide waste forms. We are continuing our collaboration with Dr. F. Chen at the Guangzhou Institute of Geochemistry of the Chinese Academy of Sciences.

Impact on Review and Advisory Committees. Within the United States, Professor Ewing serves on many committees associated with DOE projects. He served as a member of the Committee for the “Peer Review of the Total System Performance Assessment – Viability Assessment of the Yucca Mountain Repository”, as a member of the National Research Council’s committee on “Alternative High-Level Waste Treatments at the INEEL Site”, and on the NSF committee for “Opportunities in Mineral and Rock Physics and Chemistry.” He has been a member of the program committees for the Materials Research Society symposium, “Scientific Basis for Nuclear Waste Management”, a consultant for the Advisory Committee on Nuclear Waste of the Nuclear Regulatory Commission, and

serves on an international review committee of the waste form development program in France (VESTALE Program) . He is presently a member of the Board of Radioactive Waste Management of the National Research Council. Professor Ewing received a Guggenheim Fellowship (2002) for to study the impact of the nuclear fuel cycle on the environment. Since 2000, Professor Ewing has given 27 invited presentations on various aspects of nuclear waste management. All of these activities have provided opportunities to present the results of this EMSP-supported program.

Impact on Education & Infrastructure. Most important to the long-term impact of the EMSP-supported program is the training of graduate students and post-doctoral fellows in the field of radioactive waste management. Professor Ewing's group has trained a number of scientists who are now prominent in the nuclear waste management field (e.g., G. Lumpkin at Cambridge University in the U.K., W. Gong at the Vitreous State Laboratory at Catholic University, R. Finch at ANL, Peter Burns at Notre Dame, Mostafa Fayek at ORNL, Kate Helean at UC-Davis, Julia McAnallen at the Nuclear Regulatory Commission, Janusz Janeczek at the University of Silesia, and Keld Jensen at the National Institute of Occupational Health in Denmark). The present EMSP program at the University of Michigan supports or has supported: C. Palenik (Ph.D. candidate in Geological Sciences, recipient of Office of Civilian Radioactive Waste Management Fellowship); K. Traexler (Ph.D. candidate in Nuclear Engineering and Radiological Sciences), F. Skomurski (Ph.D. candidate in Geological Sciences), Keld Jensen (Ph.D. candidate and post-doctoral fellow), Farong Chen (post-doctoral fellow), Satoshi Utsunomiya (post-doctoral fellow).

COLLABORATIVE INTERACTIONS

Because of our long involvement in this field, particularly with international scientists, the EMSP program allowed us to maintain long-term collaborations with colleagues working on various aspects of uranium chemistry. .

The main collaborations are listed below:

Dr. Peter Burns	Notre Dame University structural studies and refinements of uranium minerals
Professor Udo Becker	University of Michigan surface science studies
Dr. Jordi Bruno	QuantiSci, Barcelona, Spain leaching studies of uranium minerals; solution chemistry of actinides
Dr. Ignasi Casas	Department of Chemistry UPC, Barcelona, Spain leaching studies of uranium minerals
Dr. Fanrong Chen	Guangzhou Institute of Geochemistry Chinese Academy of Sciences, Wushan, P.R. China geochemical modeling of uranium-phase dissolution
Professor Sue Clark	Department of Chemistry

Dr. Mostafa Fayek	Washington State University structure-based models of solubility
Professor Frank Hawthorne	Center of Isotope Geochemistry Oak Ridge National Laboratory isotopic studies of uranium deposits
Professor Janusz Janeczek	Department of Geological Sciences University of Manitoba crystal structure refinements of uranium minerals
Dr. Keld Jensen	Faculty of Earth Sciences University of Silesia mineralogy and geochemistry of the Oklo reactors
Dr. Gregory Lumpkin	National Institute of Occupational Health, Denmark mineralogy and geochemistry of Oklo natural reactors
Professor Takashi Murakami	Cambridge University, United Kingdom structural and TEM studies of waste forms and U^{6+} phases
Professor Alex Navrotsky	Mineralogical Institute, Tokyo University studies of uranium phases by FEG-TEM and x-ray diffraction analysis
Dr. Juan de Pablo	University of California, Davis Calorimetric studies of waste forms and U^{6+} phases
	Department of Chemical Engineering UPC, Barcelona, Spain leaching studies of uranium minerals

REFERENCES CITED

The principal investigator's name (this proposal) is indicated in **bold type** in the list of cited references.

- T.M. Ahn (1996a) Long-Term Kinetic Effects and Colloid Formations in Dissolution of LWR Spent Fuels. Office of Nuclear Regulatory Commission, NUREG-1564, 45 pp.
- T.M. Ahn (1996b) Dry Oxidation and Fracture of LWR Spent Fuels. Office of Nuclear Regulatory Commission, NUREG-1565, 29 pp.
- F. d'Annuncci, C. Sari, and G. Schumacher (1977) Migration of metallic fission products in reactor oxide fuels. Nuclear Technology, 35, 80-86.
- V. Baran (1992) Uranium(VI) = Oxygen Chemistry Uranyl hydroxo complexes, uranate, oxides. Nuclear Research Institute, 250 68 Rez, Czechoslovakia, 135 pp.
- U. Becker, K. Rosso, M.F. Jr. Hochella (2001) The proximity effect on semiconducting mineral surfaces: A new aspect of mineral surface reactivity and surface complexation theory? Geochimica et Cosmochimica Acta, 65, 2641-2649.
- V. Bouska (1978) Davnoveky prirodni uranovy reaktor: Geologicky Pruzkum. 20/4, p. 121.
- H. Brabryn (1972) A Precambrian nuclear reactor. New Scientist, 56, 342-343.
- D.G. Brookins (1990) Radionuclide behavior at the Oklo nuclear reactor, Gabon. Waste Management, 10, 285-296.
- R. Bros, J. Carpéne, V. Seré, and A. Beltritti (1996) Occurrence of Pu and fissiogenic REE in hydrothermal apatites from the fossil nuclear reactor 16 at Oklo (Gabon). Radiochimica Acta, 74, 277-282.
- R. Bros, P. Andersson, P. Roos, S. Claesson, E. Holm, and J. Smellie (1998) Swedish investigations on the Bangombé reactor zone U-series disequilibrium and time-scale of radionuclide mobilization processes. Oklo Working Group – Proceedings of the first joint EC-CEA workshop on the Oklo- Natural Analogue Phase II project held in Sitjes, Spain, from 18 to 20 June, 1997. Nuclear Science and Technology, EUR 18314 EN, 187-195.
- J. Bruno, I. Casas, and I. Puigdomenech (1988) The kinetics of dissolution of UO_2 (s) under reducing conditions. Radiochimica Acta, 44/45, 11-16.
- J. Bruno, I. Casas, E. Cera, R.C. **Ewing**, R.J. Finch and L.O. Werme (1995) The assessment of the long-term evolution of the spent nuclear fuel matrix by kinetic, thermodynamic and spectroscopic studies of uranium minerals. Scientific Basis for Nuclear Waste Management XVIII T. Murakami and R.C. **Ewing**, Eds., Materials Research Society Symposium Proceedings, 353, 633-639.
- J. Bruno, E. Cera, L. Duro, T.E. Eriksen and L.O. Werme (1996) A kinetic model for the stability of spent fuel matrix under oxic conditions. Journal of Nuclear Materials, 238, 110-120.
- C.J. Bruton and H.F. Shaw (1988) Geochemical simulation of reaction between spent fuel waste form and J-13 water at 25°C and 95°C. Scientific Basis for Nuclear Waste Management XI. M.J. Apted and R.E. Westermann, Eds., Materials Research Society Symposium Proceedings, 112, 485-494
- E.C. Buck, D. Wronkiewicz, P.A. Finn, and J.K. Bates (1997) A new uranyl oxide hydrate phase derived from spent fuel alteration. Journal of Nuclear Materials, 249, 70-76.

- P.C. Burns, M.L. Miller and R.C. **Ewing** (1996) U^{6+} minerals and inorganic phases: A comparison and hierarchy of crystal structures. Canadian Mineralogist, 34, 845-880.
- P.C. Burns, R.C. **Ewing** and F.C. Hawthorne (1997) The crystal chemistry of hexavalent uranium: Polyhedral geometries, bond-valence parameters, and polyhedral polymerization. Canadian Mineralogist, 35, 1551-1570.
- P.C. Burns (1999) The crystal chemistry of uranium. Uranium: Mineralogy, Geochemistry and the Environment. P. Burns and R. Finch, Eds., Reviews in Mineralogy, 38, 23-90
- L.J. Carter and T.H. Pigford (1999) The world's growing inventory of civil spent fuel. Arms Control Today, 29(1), 8-14.
- I. Casas, J. Bruno, E. Cera, R.J. Finch and R.C. **Ewing** (1994) Kinetic and thermodynamic studies of uranium minerals. Swedish Nuclear Fuel and Waste Management Co., SKB Technical Report 94-16, 73 pp.
- I. Casas, J. Bruno, E. Cera, R.J. Finch and R.C. **Ewing** (1997) Characterization and dissolution behavior of a becquerelite from Shinkolobwe (Zaire). Geochimica et Cosmochimica Acta, 61(18), 3879-3884.
- I. Casas, J. de Pablo, J. Giménez, M.E. Torrero, J. Bruno, E. Cera, R. Finch, and R.C. **Ewing**, (1998) The role of pe, pH, and carbonate on the solubility of UO_2 and uraninite under nominally reducing conditions. Geochimica et Cosmochimica Acta, 62, 2223-2231.
- J. Cejka and Z. Urbanec (1990) Secondary Uranium Minerals. Rozprawy Cechoslovenske Akademie Ved (Academia Praha) 91 pp.
- F. Chen, R.C. **Ewing** and S.B. Clark (1999a) The Gibbs free energies and enthalpies of formation of uranium (VI) phases: An empirical method of prediction. American Mineralogist 84(4), 650-654.
- F. Chen, P.C. Burns and R.C. **Ewing** (1999b) ^{79}Se : geochemical and crystallo-chemical retardation mechanisms. Journal of Nuclear Materials 275, 81-94.
- F. Chen, P.C. Burns and R.C. **Ewing** (1999c) Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. Journal of Nuclear Materials 278, 225-232.
- S.B. Clark, R.C. **Ewing**, and J.C. Schaumlöffel (1998) A method to predict free energies of formation of mineral phases in the $U(VI)-SiO_2-H_2O$ system. Journal of Alloys and Compounds, 271, 189-193.
- G.A. Cowan, (1976) A natural fission reactor. Scientific American, 235, 36-47.
- D. Curtis, T. Benjamin, and A. Gancarz (1989) Fission product retention in the Oklo natural fission reactors. Applied Geochemistry, 4, 49-62.
- M.C. Duff, D B. Hunter, I. R. Triay, P. Bertsch, J. Kitten and D. T. Vaniman (2001). Comparison of two micro-analytical methods for detecting the spatial distribution of sorbed Pu on geologic materials. Journal of Contaminant Hydrology 47(2-4): 211-218.
- M.C. Duff, D. B. Hunter, I. R. Triay, P. M. Bertsch, D. T. Reed, S. R. Sutton, G. Shea-McCarthy, J. Kitten, P. Eng, S. J. Chipera and D. T. Vaniman (1999). Mineral associations and average oxidation states of sorbed Pu on tuff. Environmental Science and Technology 33(13 1999): 2163-2168.

- Y. Dymkov, P. Holliger, M. Pagel, A. Gorshkov, and A. Artyukhina, (1997) Characterization of a La-Ce-Sr-Ca aluminous hydroxy phosphate in nuclear zone 13 in the Oklo uranium deposit (Gabon). Mineralium Deposita, 32, 617-620.
- S. Eklund, (1975) Oklo, a natural reactor 1800 my ago. Canadian Mining Journal, 96, 35-36.
- R.C. **Ewing** and M. J. Jercinovic (1987) Natural analogues: Their application to the prediction of the long-term behavior of nuclear waste forms (invited paper). Scientific Basis for Nuclear Waste Management X, J. K. Bates and W. B. Seefeldt, Eds., Materials Research Society Proceedings, 84, Pittsburgh, Pennsylvania, 84, 67-86.
- R.C. **Ewing** (1991) The use of natural systems to predict radionuclide migration. Proceedings of the Third International Symposium on Advanced Nuclear Energy Research, Global Environment and Nuclear Energy, organized by the Japan Atomic Energy Research Institute, 167-175.
- R.C. **Ewing** (1992) The role of natural analogues in performance assessment: Applications and limitations. Proceedings of the Third International Conference on High Level Radioactive Waste Management, James S. Tulenko, Ed., (American Nuclear Society) 1429-1436.
- R.C. **Ewing** (1993a) Long-term predictions using natural analogues. The Role of Natural Analogs in Geologic Disposal of High-Level Nuclear Waste, Proceedings of symposium sponsored by the Nuclear Regulatory Commission W.M. Murphy and K.A. Kovach, Eds., Center for Nuclear Waste Regulatory Analyses, Report 93-020, 29-35.
- R.C. **Ewing** (1993b) The long-term performance of nuclear waste forms: The use of natural materials – Three case studies. Scientific Basis for Nuclear Waste Management XVI, C.G. Interrante and R.T. Pabalan, Eds., Materials Research Society Symposium Proceedings, 294, 559-568.
- R.C. **Ewing** (1999a) Radioactivity and the 20th Century. Reviews in Mineralogy, 38, 1-22.
- R.C. **Ewing** (1999b) Less Geology in the Geological Disposal of Nuclear Waste. Science 286, 415-417.
- R.C. **Ewing**, M.S. Tierney, L.F. Konikow and R.P. Rechard (1999) Performance Assessments of Nuclear Waste Repositories: A Dialogue on Their Value and Limitations. Risk Analysis 19, 933-958.
- R.C. **Ewing**, A. Meldrum, L.M. Wang and S.X. Wang (2000) Radiation-Induced Amorphization. Reviews in Mineralogy & Geochemistry, vol. 39, 317-361.
- R. Evron, G. Kimmel, and Y. Eyal (1994) Thermal recovery of self-radiation damage in uraninite and thorinite. Journal of Nuclear Materials, 217(1-2), 54-55.
- M. Fayek, J. Janeczek and R.C. **Ewing** (1997a) Mineral chemistry and oxygen isotopic analyses of uraninite, pitchblende and uranium alteration minerals from the Cigar Lake Deposit, Saskatchewan, Canada. Applied Geochemistry 12, 549-565.
- M. Fayek, T.K. Kyser, and R.C. **Ewing** (1997b) Uraninite-water interactions in an oxidizing environment. Scientific Basis for Nuclear Waste Management XX, W.J. Gray and I. Triay, Eds., Materials Research Society Symposium Proceedings, 465, 1201-1208.
- M. Fayek, P.C. Burns, Y.X. Guo and R.C. **Ewing** (2000) Micro-structures and geochemical consequences associated with uraninite alteration. Journal of Nuclear Materials, 277, 204-210.
- M. Fayek, K.A. Jensen, R.C. **Ewing**, L.R. Riciputi (2002) In situ isotopic analysis of uraninite microstructures from the Oklo-Okélobondo natural fission reactors, Gabon. Mat. Res. Soc. Symp. Proc., vol. 713, 849-856.

- M. Fayek, T.M. Harrison, R.C. **Ewing**, M. Grove and C.D. Coath (2002) O and Pb isotopic analyses of uranium minerals by ion microprobe and U-Pb ages from the Cigar Lake deposit. Chemical Geology 185, 205-225.
- M. Fayek, S. Utsunomiya, R.C. **Ewing**, K.A. Jensen, and L.R. Riciputi, (submitted) The oxygen isotopic composition of nano-scale uraninite at Oklo natural fission reactors, Gabon: American Mineralogist.
- M. Fayek, S. Utsunomiya, S.M. Pfiffner, L. Anovitz, Y.A. Gorby, D.C. White, L.R. Riciputi, R.C. **Ewing** and F.J. Stadermann (submitted) Predicting the stability of nano-scale bio-precipitated uranium phases. Nature.
- R.J. Finch and R. C. **Ewing** (1989) Alteration of natural UO₂ under oxidizing conditions from Shinkolobwe, Katanga, Zaire: A natural analogue for the corrosion of spent fuel. Final report to Swedish Nuclear Fuel and Waste Management Co. SKB 89-37, 31 pages.
- R.J. Finch and R.C. **Ewing** (1991a) Uraninite alteration products in an oxidizing environment and their relevance to the disposal of spent nuclear fuel. Swedish Nuclear Fuel and Waste Management Co. , SKB 91-15, 124 pages.
- R.J. Finch and R. C. **Ewing** (1991b) Alteration of natural uraninite under oxidizing conditions from Shinkolobwe, Katanga, Zaire: A natural analogue for the corrosion of spent fuel. Radiochimica Acta, 52/53, 395-401.
- R.J. Finch and R.C. **Ewing** (1991c) Phase relations of the uranyl oxide hydrates and their significance to the disposal of spent fuel. Scientific Basis for Nuclear Waste Management XIV. T. Abrajano, Jr. and L.H. Johnson, Eds., Materials Research Society, Pittsburgh, Pennsylvania, 241-246.
- R.J. Finch and R.C. **Ewing** (1992a) Alteration of natural uranyl oxide hydrates in Si-rich groundwaters: Implications for uranium solubility. Scientific Basis for Nuclear Waste Management XV. C. Sombret, Ed., Materials Research Society, Pittsburgh, Pennsylvania, vol 257, 465-472.
- R.J. Finch and R.C. **Ewing** (1992b) Uranyl oxide hydrates and uraninite corrosion: relevance to "Natural Analogue" studies of spent fuel corrosion. Proceedings of the Third International Conference on High Level Radioactive Waste Management, James S. Tulenko, Ed., (American Nuclear Society) 332-337.
- R.J. Finch and R.C. **Ewing** (1992c) Corrosion of uraninite under oxidizing conditions. Journal of Nuclear Materials, 190, 133-156.
- R.J. Finch, M.L. Miller, and R.C. **Ewing** (1992) Weathering of natural uranyl oxide hydrates: Schoepite polytypes and dehydration effects. Radiochimica Acta, 58/59, 433-443.
- R.J. Finch and R.C. **Ewing** (1993) The alteration of uraninite to clarkeite. Scientific Basis for Nuclear Waste Management XVI. C.G. Interrante and R.T. Pabalan, Eds., Proceedings of the Materials Research Society, 294, Pittsburgh, Pennsylvania, 513-520.
- R.J. Finch and R.C. **Ewing** (1994) Formation, oxidation and alteration of ianthinite. Scientific Basis for Nuclear Waste Management XVII. A. Barkatt and R.A. Van Konynenburg, Eds., Proceedings of the Materials Research Society, 333, Pittsburgh, Pennsylvania, 625-630.
- R.J. Finch, J. Suksi, K. Rasilainen and R.C. **Ewing** (1995a) The long-term stability of becquerelite. Scientific Basis for Nuclear Waste Management XVIII, T. Murakami and R.C. **Ewing**, Eds., Proceedings of the Materials Research Society, 353, 647-652.

- R.J. Finch, F.C. Hawthorne and R.C. **Ewing** (1995b) Prediction of unknown uranyl oxide hydrate structure types: Comparison of calculated and measured XRD powder patterns. Scientific Basis for Nuclear Waste Management XVIII, T. Murakami and R.C. **Ewing**, Eds., Proceedings of the Materials Research Society, 353, 653-660.
- R.J. Finch, F.C. Hawthorne and R.C. **Ewing** (1996a) Schoepite and dehydrated schoepite. Scientific Basis for Nuclear Waste Management XIX, W.M. Murphy and D.A. Knecht, Eds., Proceedings of the Materials Research Society, vol. 412, 361-368.
- R.J. Finch, M.A. Cooper, F.C. Hawthorne and R.C. **Ewing** (1996b) The crystal structure of schoepite, $[(\text{UO}_2)_8 \text{O}_2 (\text{OH})_{12}](\text{H}_2\text{O})_{12}$. Canadian Mineralogist, 34, 1071-1088.
- R.J. Finch, J. Suksi, K. Rasilainen and R.C. **Ewing** (1996c) Uranium-series ages for secondary uranium minerals with applications to the long-term evolution of spent nuclear fuel. Scientific Basis for Nuclear Waste Management XIX, W.M. Murphy and D.A. Knecht, Eds., Proceedings of the Materials Research Society, vol. 412, 823-830.
- R.J. Finch and R.C. **Ewing** (1997) Clarkeite: new chemical and structural data. American Mineralogist, 82, 607-619.
- R.J. Finch, F.C. Hawthorne, and R.C. **Ewing** (1998) Crystallographic relations among schoepite, metaschoepite and dehydrated schoepite. Canadian Mineralogist, 36, 831-845.
- R.J. Finch, P.A. Finn, E.C. Buck, and J.K. Bates (1999) Oxidative corrosion of spent fuel in vapor and dripping groundwater at 90°C. Scientific Basis for Nuclear Waste Management XXI, D.J. Wronkiewicz and J.H. Lee, Eds., Materials Research Society Symposium Proceedings, 556, 431-438.
- P.A. Finn, J.C. Hoh, S.F. Wolf, S.A. Slater and J.K. Bates (1996) The release of U, Pu, Cs, Sr, Tc and I from spent fuel under unsaturated conditions. Radiochimica Acta, 74, 65-71.
- M. Fleischer and J.A. Mandarino (1995) Glossary of Mineral Species. Mineralogical Record Inc, Tucson, Arizona.
- F. Gauthier-Lafaye, F. Weber, and H. Ohmoto (1989) Natural Fission Reactors of Oklo. Economic Geology, 84, 2286-2295.
- F. Gauthier-Lafaye, P. Holliger, P., and P.-L. Blanc (1996) Natural fission reactors in the Franceville basin, Gabon: A review of the conditions and results of a "critical event" in a geological system. Geochimica et Cosmochimica Acta, 60, 4831-4852.
- J. Geoffroy and J. Lissilour (1975) Microscopic study of the Oklo uranium-bearing ores, in proceedings, Le Phénomène d'Oklo, International Atomic Energy Agency, Vienna, p. 132-157.
- B. George-Aniel, J.L. Leroy, and B. Poty (1991) Volcanogenic uranium mineralization in the Sierra Peña Blanca District, Chihuahua, Mexico: three genestic models. Economic Geology, 86, 233-248.
- P.C. Goddell (1981) Geology of the Peña Blanca uranium deposits. Uranium in Volcanic and Volcanoclastic Rocks – AAPG Studies in Geology No 13, P.C. Goddell and A.C. Waters, Eds., American Association for Petroleum Geologists, El Paso, Texas, 275-291.
- B.X. Gu, L.M. Wang, and R.C. **Ewing** (2000) The effect of amorphization on the Cs ion exchange and retention capacity of zeolite-NaY. Journal of Nuclear Materials 278, 64-72.
- J.M. Haschke, T.H. Allen, L.A. Morales (2001) Reactions of plutonium dioxide with water and hydrogen-oxygen mixtures: mechanisms for corrosion of uranium and plutonium. Journal of Alloys and Compounds, 314, 78-91.

- M.N. Heldhili, B.V. Yakshinskiy, T.E. Madey (2000) Interaction of water vapor with $\text{UO}_2(001)$. Surface Science, 445, 512-525.
- H. Hidaka, K. Takahashi, and P. Holliger (1994a) Migration of fission products into micro-minerals of the Oklo natural fission reactors. Radiochimica Acta 66/67, 573-578.
- H. Hidaka, T. Sugiyama, M. Ebihara, and P. Holliger (1994b) Isotopic evidence for the retention of ^{90}Sr inferred from ^{90}Zr in the Oklo natural fission reactors: Implication for geochemical behavior of fissiogenic Rb, Sr, Cs, and Ba. Earth and Planetary Science Letters, 122, 173-182.
- H. Hidaka and P. Holliger (1998) Geochemical and neutronic characteristics of the natural fission reactors at Oklo and Bangombé (Gabon). Geochimica et Cosmochimica Acta, 60, 4831-4852.
- H. Hidaka, P. Holliger, F. Gauthier-Lafaye (1999) Tc/Ru fractionation in the Oklo and Bangombé natural fission reactors, Gabon. Chemical Geology, 155, 323-333.
- H. Hidaka and F. Gauthier-Lafaye (submitted) Redistribution of fissiogenic and non-fissiogenic REE, Th and U in and around natural fission reactors at Oklo and Bangombé, Gabon. Geochimica Cosmochimica Acta.
- P. Holliger (1991) The new Oklo reaction zones: U-Pb dating and in situ characterization of fission products by ion analysis. Report on Progress. Technical Note DEM No 01/92. 36p.
- H. Isobe, T. Murakami and R.C. **Ewing** (1992) Alteration of uranium minerals in the Koongarra deposit, Australia: Unweathered zone. Journal of Nuclear Materials 190, 174-187.
- J. Janeczek and R.C. **Ewing** (1991a) High-temperature annealing of natural UO_2 . Scientific Basis for Nuclear Waste Management XIV. T. Abrajano, Jr. and L.H. Johnson, Eds., Materials Research Society, Pittsburgh, Pennsylvania, 235-240.
- J. Janeczek and R.C. **Ewing** (1991b) X-Ray powder diffraction study of annealed uraninite. Journal of Nuclear Materials, 185, 66-77.
- J. Janeczek and R.C. **Ewing** (1992a) The structural formula of uraninite. Journal of Nuclear Materials, 190, 128-132.
- J. Janeczek and R.C. **Ewing** (1992b) Corrosion and alteration of uraninite under reducing conditions. Journal of Nuclear Materials, 192, 157-173.
- J. Janeczek, R.C. **Ewing** and L.E. Thomas (1993) Oxidation of uraninite: Does tetragonal U_3O_7 occur in nature?. Journal of Nuclear Materials, 207, 176-191.
- J. Janeczek and R.C. **Ewing** (1995) Mechanisms of lead release from uraninite in the natural fission reactors in Gabon. Geochimica et Cosmochimica Acta, 59 (10), 1917-1931.
- J. Janeczek and R.C. **Ewing** (1995) Mechanism of lead-release from uraninite in the natural fission reactors in Gabon. Geochimica et Cosmochimica Acta, 59, 1917-1932.
- J. Janeczek and R.C. **Ewing** (1996a) Phosphatian coffinite with rare earth elements and Ce-rich françoisite-(Nd) from sandstone beneath a natural fission reactor at Bangombé, Gabon. Mineralogical Magazine, 60, 665-669.
- J. Janeczek and R.C. **Ewing** (1996b) Florencite-(La) with fissiogenic REEs from the natural fission reactor at Bangombé, Gabon. American Mineralogist, 81, 1263-1269.
- J. Janeczek, R.C. **Ewing**, V.M. Oversby and L.O. Werme (1996) Uraninite and UO_2 in spent nuclear fuel: A comparison. Journal of Nuclear Materials, 238, 121-130.

- J. Janeczek (1999) Mineralogy and geochemistry of natural fission reactors in Gabon. Uranium: Mineralogy, Geochemistry and the Environment. P. Burns and R. Finch, Eds., Reviews in Mineralogy, 38, 321-392.
- K. A. Jensen, R.C. **Ewing**, and F. Gauthier-Lafaye, (1997) Uraninite: a 2 Ga spent nuclear fuel from the natural fission reactor at Bangombe in Gabon, West-Africa. Scientific Basis for Nuclear Waste Management XX. W.J. Gray and I.R. Triay, Eds., Materials Research Society Symposium Proceedings, 465, 1209-1218.
- K.A. Jensen and R.C. **Ewing** (1999) Microtexture and chemistry of “unaltered” uraninite in the Oklo, Okélobondo, and Bangombé natural fission reactors. In Louvat, D., Michaud, V. and von Marevic, H., eds., Oklo Working Group, Proceedings of the second EC-CEA workshop on the Oklo-natural analogue Phase II project held in Helsinki, Finland, from 16-18 June 1998, Nuclear Science and Technology, EUR 19116 EN, 61-91.
- K.A. Jensen, J. Janeczek, R.C. **Ewing**, P. Stille, F. Gauthier-Lafaye, and S. Salah (2000) Crandallites and coffinite: retardation of nuclear reaction products at the Bangombé natural fission reactor. Scientific Basis for Nuclear Waste Management XXII. D. Shoesmith and Smith, R.W., Eds., Materials Research Society Symposium Proceedings, 608, 525-532.
- K.A. Jensen and R.C. **Ewing** (2001) The Okélobondo natural fission reactor, SE-Gabon: Geology, mineralogy and retardation of nuclear reaction products: Geological Society of America – Bulletin, 113, 32-62.
- K.A. Jensen, C.S. Palenik, and R.C. **Ewing** (2002) U⁶⁺-phases in the weathering zone of the Bangombe U-deposit: Observed and predicted mineralogy. Radiochimica Acta 90, 761-769.
- A.B. Kersting, D.W. Efurd, D.L. Finnegan, D.K. Smith, J. Thompson (1999) Migration of plutonium in ground water at the Nevada Test Site. Nature, 396, 6714: 56-59.
- J.I. Kim, G. Buckau, and R. Klenze (1987) Natural colloids and generation of actinide pseudocolloids in natural groundwater. Natural Analogues in Radioactive Waste Disposal, B. Come and N.A. Chapman, Eds., 289-299
- J.I. Kim (1991) Actinide colloid generation in groundwater. Radiochimica Acta, 52-3, 71-81.
- H. Kleykamp (1985) The chemical state of the fission products in oxide fuels. Journal of Nuclear Materials, 131, 221-246.
- P. Liu, T. Kendelewicz, G.E. Jr. Brown, G.A. Parks (1998a) Reaction of water with MgO(100) surfaces. Part I: synchrotron X-ray photoemission studies of low-defect surfaces. Surface Science, 412-413, 287-314.
- P. Liu, T. Kendelewicz, G.E. Jr. Brown (1998b) Reaction of water with MgO(100) surfaces. Part II: synchrotron photoemission studies of defective surfaces. Surface Science, 412-413, 315-332.
- R.D. Loss, K.J.R. Rosman, J.R. de Laeter, D.B. Curtis, T.M. Benjamin, A.J. Gancarz, W.J. Maeck, and J.E. Delmore (1989) Fission product retentivity in peripheral rocks at the Oklo natural fission reactors, Gabon. Chemical Geology, 76, 71-84.
- Hj. Matzke (1987) Atomic transport properties in UO₂ and mixed oxides (U,Pu)O₂. Journal of the Chemical Society, Faraday Transactions, 2, 1121-1142.
- C. Menet, M.-T. Ménager, and J.-C. Petit (1992) Migration of radioelements around the new nuclear reactors at Oklo: Analogies with a high-level waste repository. Radiochimica Acta, 58/59, 395-400.
- M.L. Miller, R.J. Finch, P.C. Burns and R.C. **Ewing** (1996a) Description and classification of uranium oxide hydrate sheet topologies. Journal of Materials Research, 11(12), 3048-3056.

- M.L. Miller, R.J. Finch, P.C. Burns, and R.C. Ewing (1996b) Description and classification of uranium oxide hydrate sheet topologies: Toward the development of a structural model for the estimation of thermodynamic parameters. Scientific Basis for Nuclear Waste Management XIX, W.M. Murphy and D.A. Knecht, Eds., Proceedings of the Materials Research Society, vol. 412, 369-376.
- J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben (1992) Handbook of X-ray Photoelectron Spectroscopy. J. Chastain, Ed., Perkin-Elmer Corporation.
- W.M. Murphy (1993) Site characterization and model validation. Focus '93 Topical Meeting, Las Vegas, Nevada, page 115.
- W.M. Murphy and R.T. Pabalan (1995) Review of empirical thermodynamic data for uranyl silicate minerals and experimental plan. Center for Nuclear Waste Regulatory Analyses, Report 95-014, 21 pp.
- W.M. Murphy, R.T. Pabalan and C.J. Goulet (1995) High-level waste near-field processes and variations. Center for Nuclear Waste Regulatory Analyses. Report CNWRA 95-01S, 10-10.
- C. Muggelberg, M.R. Castell, G.A.D. Briggs, D.R. Goddard (1998) The atomic structure of the $\text{UO}_{2+x}(110)$ surface and the effects of interstitial oxygen: an elevated-temperature STM study. Surface Science, 402-404, 673-677.
- M. Neuilly, J. Bussac, C. Frejacques, G. Nief, G. Vendryes, and J. Yvon, (1972) Sur l'existence dans un passe recule d'une reaction de chaine naturelle de fissions, dans le gisement d'uranium d'Oklo (Gabon). Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences, Serie D., Sciences Naturelles, 275, 1847-1849.
- K. Nogita, and K. Une, (1997) High-resolution TEM of high burnup fuel. Journal of Nuclear Materials, 250, 244-249.
- Pearcy, E.C., J.D. Prikryl, W.M. Murphy and B.W. Leslie (1994) Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Chihuahua, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. Applied Geochemistry, 9, 713-732 .
- L. Pourcelot and F. Gauthier-Lafaye (1998) Mineralogical, chemical, and isotope data on uraninites from natural fission reactors (Gabon): effects of weathering conditions. Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences. Paris, 326, 485-492.
- C.N.R. Rao, G.U. Kulkarni, P.J. Thomas, and P.P. Edwards, (2002) Size-dependent chemistry: Properties of nanoparticles. Chemistry-A European Journal, 8, 29-35.
- I.L.F. Ray, H. Thiele, and H.J. Matzke (1992) Transmission electron microscopy study of fission product behavior in high burnup UO_2 . Journal of Nuclear Materials, 188, 90-95.
- J.A. Richardson (1997) United States high-level radioactive waste management programme: current status and plans. Proceedings of Instn. Mechanical Engineers 211(A), 381-392.
- V. Savery and M. Pagel (1997) The effects of water radiolysis on local redox conditions in the Oklo, Gabon, natural fission reactors 10 and 16. Geochimica et Cosmochimica Acta, 61, 4479-4494.
- D.W. Shoesmith (2000) Fuel corrosion processes under waste disposal conditions. Journal of Nuclear Materials, 282, 1-31.
- A.A. Solomon (1973) Radiation-induced creep of UO_2 . Journal of the American Ceramic Society, 56/3, 164-171.

- E. Swissa, I. Jacob, U. Atzmony, N. Shamir, M.H. Mintz (1989) Hydrogen-oxygen accumulation on polycrystalline uranium surfaces. Surface Science, 223, 607-620.
- Total System Performance Assessment, Viability Assessment of a Repository at Yucca Mountain (TRW Environmental Safety Systems, Las Vegas, NV, 1998).
- S. Utsunomiya, L.M. Wang, M. Douglas, S.B. Clark and R.C. **Ewing** (2003) The effect of ionizing radiation on uranophane. American Mineralogist 88, 159-166.
- S. Utsunomiya and R.C. **Ewing** (2003) Application of high-angle dark field scanning transmission electron microscopy, energy dispersive x-ray spectrometry, and energy-filtered transmission electron microscopy to the characterization of nanoparticles in the environment. Environmental Science & Technology 37, 786-791.
- S. Utsunomiya, L.M. Wang and R.C. Ewing (submitted) Radiation-induced formation of UO_2 . Nature.
- S. Utsunomiya, S.C. Peters, J.D. Blum and R.C. Ewing, Nano-scale mineralogy of Arsenic phases by HAADF-STEM, American Mineralogist, Submitted.
- K. Winer, C.A. Colmenares, R.L. Smith, F. Wooten (1987) Interaction of water vapor with clean and oxygen-covered uranium surfaces. Surface Science, 183, 67-99.
- D.J. Wronkiewicz, J.K. Bates, T.J. Gerding, E. Veleckis and B.S. Tani (1992) Uranium release and secondary phase formation during unsaturated testing of UO_2 at 90°C. Journal of Nuclear Materials, 190, 107-127.
- D.J. Wronkiewicz, J.K. Bates, S.F. Wolf and E.C. Buck (1996) Ten-year results from unsaturated drip tests with UO_2 at 90°C: implications for the corrosion of spent nuclear fuel. Journal of Nuclear Materials, 238, 78-95.
- D.J. Wronkiewicz, E.C. Buck, and J.K. Bates (1997) Grain boundary corrosion and alteration phase formation during the oxidative dissolution of UO_2 pellets. Scientific Basis for Nuclear Waste Management XII, W.J. Gray and I. Triay, Eds., Materials Research Society Symposium Proceedings, 465, 519-526.
- D.J. Wronkiewicz and E.C. Buck (1999) Uranium mineralogy and the disposal of spent nuclear fuel. In Uranium: Mineralogy, Geochemistry and the Environment. P. Burns and R. Finch, Eds., Reviews in Mineralogy, 38, 475-497.
- H. Xu and Y. Wang (1999) Electron energy-loss spectroscopy (EELS) study of oxidation states of Ce and U in pyrochlore and uraninite – natural analogues for Pu- and U-bearing waste forms. Journal of Nuclear Materials, 265, 117-123.
- D. Zhao, Donggao and R.C. **Ewing** (1999) Zirconium-rich uraninite from the Central City District, Gilpin County, Colorado. Annual meeting of the Geological Society of America, p. A135.
- D. Zhao, Donggao and R.C. **Ewing** (2000) Alteration products of uraninite from the Colorado Plateau. Radiochimica Acta, 88, 739-749.