BULLETIN DE L'ASSOCIATION MINÉRALOGIQUE DU CANADA
THE CANADIAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL ASSOCIATION OF CANADA

Volume 39 June 2001 Part 3

The Canadian Mineralogist
Vol. 39, pp. 697-715 (2001)

THE DESIGN AND EVALUATION OF NUCLEAR-WASTE FORMS: CLUES FROM MINERALOGY[¶]

RODNEY C. EWING[§]

Department of Nuclear Engineering & Radiological Sciences, Department of Materials Science & Engineering, and Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-2104, U.S.A.

ABSTRACT

The disposal of fission products and actinides generated by the nuclear-fuel cycle is one of the major challenges in Environmental Sciences of the 21st Century. Because some fission products (*e.g.*, ^{99}Tc, ^{129}I, ^{79}Se and ^{135}Cs) and actinides (*e.g.*, ^{239}Pu and ^{237}Np) are long-lived, they have a major impact on the risk assessment of geological repositories. Thus, demonstrable long-term chemical and mechanical durability are essential properties of waste forms for the immobilization and disposal of radionuclides. Mineralogical and geological studies provide excellent candidate phases for immobilization and a unique database that cannot be duplicated by a purely Materials Science approach. The "mineralogical approach" is illustrated by a discussion of zircon as a phase for the immobilization of plutonium from dismantled nuclear weapons. Other minerals, *e.g.*, monazite, apatite, pyrochlore, zirconolite and zeolites, also are important candidates for the immobilization of actinides.

Keywords: nuclear waste, nuclear waste form, nuclear weapons, plutonium, actinides, zircon, monazite, pyrochlore, zirconia, zirconolite.

SOMMAIRE

L'élimination des produits de fission et des actinides générés aux centrales d'énergie nucléaire constitue un des principaux défis environnementaux du vingt-et-unième siècle. Parce que certains des produits de fission (*e.g.*, ^{99}Tc, ^{129}I, ^{79}Se et ^{135}Cs) et certains actinides (*e.g.*, ^{239}Pu et ^{237}Np) ont de longues demi-vies, ils exercent un impact très important sur l'évaluation des risques du stockage de déchets dans un reposoir géologique. Ainsi, parmi les propriétés des média choisis pour l'immobilisation et l'enfouissement des radionucléides, une démonstration de la durabilité chimique et mécanique à long terme est essentielle. Les études minéralogiques et géologiques fournissent d'excellents candidats pour une telle immobilisation et une banque de données qu'on ne pourrait espérer trouver avec une approche typiquement utilisée en sciences des matériaux. On peut démontrer l'approche minéralogique par une discussion du zircon comme phase privilégiée pour imobiliser le plutonium d'armements nucléaires démantelés. D'autres minéraux, par exemple la monazite, l'apatite, le pyrochlore, la zirconolite et les zéolites, sont autant de candidats importants pour l'immobilisation des actinides.

(Traduit par la Rédaction)

Mots-clés: déchets nucléaires, encaissant des rebuts nucléaires, armements nucléaires, plutonium, actinides, zircon, monazite, pyrochlore, oxyde de zirconium, zirconolite.

[§] *E-mail address*: rodewing@umich.edu

[¶] This paper was presented at the17th general meeting of the International Mineralogical Association Toronto, Canada on August 14, 1998. A major portion of this paper has also been published in the *Proceedings of the National Academy of Sciences*, vol. 96, 3432-3439, as part of an NAS colloquium entitled "Geology, Mineralogy, and Human Welfare".

INTRODUCTION

The disposal of "waste" generated by the nuclear fuel cycle is among the most pressing and potentially costly environmental problems for the 21st Century, a heritage from the Atomic Age of the 20th century. Proposed disposal strategies are complicated, not only because of the large volumes and activities of waste, but also because of the political and public-policy issues associated with the long times required for containment and disposal (10^4 to 10^6 years). Furthermore, the "waste" includes fissile material, *e.g.*, ^{239}Pu, of high energy-content that may be reclaimed for use in nuclear power plants or the production of nuclear weapons. The purpose of this paper is to illustrate the unique contributions that Mineralogy and Geochemistry can make in the design and selection of durable waste-forms for the long-term disposal of actinides, particularly plutonium.

BACKGROUND INFORMATION

There are three primary sources of radioactive waste in the United States (DOE 1997).

High-level waste (HLW) resulting from reprocessing to reclaim fissile materials for weapons production

Approximately 380,000 m^3 (100 million gallons) of HLW have a total radioactivity of 960 million Curies. The greatest volumes (340,000 m^3) are stored in tanks at Hanford, Washington, and Savannah River, South Carolina. Over 99% of the present radioactivity is from non-actinide radionuclides, with half-lives of less than 50 years (reprocessing has removed much of the actinide content). After 500 years, the total activity will be substantially reduced, and the primary radionuclides will be ^{238}Pu, ^{131}Sm and ^{241}Am. After 50,000 years, most of the activity will be associated with longer-lived radionuclides such as ^{239}Pu and ^{240}Pu. Also resulting from reprocessing are the lower-activity wastes that are contaminated with transuranic elements (TRU waste). These wastes are defined as containing 100 nanocuries of alpha-emitting transuranic isotopes with half-lives greater than 20 years, per gram of waste. Over 60,000 m^3 are stored retrievably at DOE sites and are destined for disposal at the Waste Isolation Pilot Plant in New Mexico (Ahearne 1997). The estimated cost of remediation and restoration programs in the DOE complex during the next few decades is on the order of 200 billion dollars (Crowley 1997).

Used or spent nuclear fuel resulting from commercial generation of power

Just over 20% of the electricity generated in the United States is produced by nuclear power plants. In 1995, 32,200 metric tonnes of spent fuel with a total activity of 30,200 MCi were stored by the electric utilities at 70 sites (either in pools or in dry storage systems) (Ahearne 1997, Richardson 1997). By 2020, the projected inventory will be 77,100 metric tonnes of heavy metal (MTHM) with a total activity of 34,600 MCi. Although the volume of the spent fuel is only a few percent of the volume of HLW, over 95% of the total activity (defense-related plus commercially generated waste) is associated with the commercially generated spent nuclear fuel (Crowley 1997). At present, none of the spent fuel will be reprocessed; all is destined for direct disposal in a geological repository.

Dismantlement of nuclear weapons

Under the first and second Strategic Arms Reduction treaties, as well as unilateral pledges made by both the United States and Russia, thousands of nuclear weapons will be dismantled. Initially, this will result in an estimated 100 metric tonnes of weapons-related plutonium that will require long-term disposition. The strategy selected for disposition, stabilization and storage or final disposal should not only protect the public and the environment, but also must ensure that the plutonium is not readily recoverable for use in weapons (NRC 1994). Present U.S. strategy calls for "burning" the Pu as a mixed-oxide fuel in existing or modified reactors, followed by direct disposal with commercially generated spent fuel in a geological repository (NRC 1995, von Hippel 1998). A smaller portion of the Pu (tens of metric tonnes) is destined for immobilization in a durable solid followed by geological disposal. The present program has an anticipated cost of $2 billion.

Since the creation of milligram quantities of plutonium by Glenn Seaborg and colleagues in 1941, the global inventory of plutonium has reached 1,350 tonnes and continues to increase by approximately 70–100 tonnes/year (Table 1). This commercially generated plutonium is mainly in two forms: (1) still incorporated in spent nuclear fuel destined for direct geological disposal (more than 600 metric tonnes of plutonium remains in spent fuel in the U.S.), and (2) plutonium separated by

TABLE 1. ESTIMATED GLOBAL PLUTONIUM INVENTORY IN 1998

In spent fuel		Military inventories	
U.S.A.	650	Former U.S.S.R.	140
Japan	90	U.S.A.	100
France	70	France	6
Germany	50	China	5
total	**860**	Israel, India, Pakistan	1
In operating reactors	**80**	total	**252**
Separated by civilian reprocessing	**150**	Global fallout from weapons test	3
Estimated World Inventory (+70 metric tonnes/year production)			**>1,350**

Amounts of plutonium are expressed in metric tonnes. Data after Stoll (1998).

reprocessing of commercial fuel. The latter is estimated to have reached 300 metric tonnes by the year 2000, and this is greater than the amount of plutonium presently in nuclear weapons (Stoll 1998, Oversby *et al.* 1997). Considering that the bare critical mass for weapons-grade plutonium is 10 kg of metal (this number is substantially reduced in the presence of a neutron reflector), safeguarding this plutonium is essential. In fact, the need for safeguards to protect against the diversion of separated plutonium applies equally to all grades of plutonium (Mark 1993). The peaceful use of nuclear energy will inevitably require a strategy for the disposition of actinides, particularly fissile ^{239}Pu.

WHY IS THE WASTE FORM IMPORTANT?

Since the discovery of radioactivity in 1896, the technologies of the 20th Century have been dominated by developments in the nuclear sciences: production of nuclear weapons, generation of electrical power from nuclear power plants, and the medical application of radiation (Ewing 1999). The wastes from these activities were already recognized as an important issue by the middle of the 20th century, and at that time, the first proposal for the use of minerals as nuclear-waste forms was made (Hatch 1953). In the 1970s, innovative proposals were made by mineralogists, such as the tailored ceramic of Rustum Roy and colleagues at Pennsylvania State University and the Rockwell International Science Center (Roy 1975, 1977, 1979, McCarthy 1977) and the Synroc of Ted Ringwood and colleagues at the Australian National University and the Australian Nuclear Science and Technology Organisation (Ringwood 1978, 1985, Ringwood *et al.* 1979, Reeve *et al.* 1984). The use of natural glasses to evaluate nuclear-waste glasses was first proposed by Ewing (1979), and systematic compilations of potential crystalline waste-form phases were made (Haaker & Ewing 1981). During the late 1970s and early 1980s, there were extensive programs in the research and development of nuclear-waste forms; in particular, a wide variety of single and polyphase ceramics, as well as new glass compositions, were developed. Reports comparing the properties of crystalline ceramics to glass generated considerable controversy (Kerr 1979, Carter 1979). Beginning in 1978, there was a review of alternative waste-forms by a DOE panel (chaired by Larry Hench of the University of Florida), culminating in the "Atlanta Shoot-out" (Garmon 1981) and a final recommendation supporting both borosilicate glass for the Defense Waste Processing Facility (DWPF) and Synroc as a promising alternative to nuclear-waste glasses (Hench *et al.* 1981). Subsequent research activity on alternative waste-forms was severely curtailed as a result of the decision in the United States to solidify defense nuclear waste in borosilicate glass and the subsequent construction of the DWPF at Savannah River Laboratory in South Carolina. Work on nuclear-waste forms during this period was summarized by Lutze & Ewing (1988).

Most recently, there has been a resurgence of interest in crystalline nuclear-waste forms owing to the need to develop durable materials for the stabilization and disposal of "excess" plutonium that results from dismantling nuclear weapons or accumulates during the reprocessing of commercially generated nuclear fuels (Oversby *et al.* 1997, Ewing 1999). This resurgence in interest has resulted in work on minerals, such as those of the apatite group, of the monazite group, zirconolite, zircon and of the pyrochlore group, as potential nuclear-waste forms (Ewing *et al.* 1995b). A recent overview of some of the developments in waste-form research is given by Donald *et al.* (1997).

Despite the important and well-recognized advances that have been made during the past twenty-five years in the development of highly durable waste-forms, the mineralogy and materials science of this area continue to occupy a role of secondary importance in strategies concerning waste-form disposal. *It is my opinion that this secondary role is very much a result of the method of analysis used in evaluating the performance of a nuclear waste repository.*

In the United States, probabilistic assessments of performance that make extensive use of mathematical models of subsystem behavior are used to simulate the long-term behavior of the engineered and geological barriers in a nuclear waste repository (Ewing *et al.* 1999, Ewing 1999c). This highly complicated analysis tracks the fate of released radionuclides through hundreds of subsystem models that are used to describe all relevant processes, from the effects of climate change on groundwater flow and access of water to canister surfaces, through the release of radionuclides from the waste form after canister failure, through the near-field barriers of back-fill and concrete, including the processes of far-field transport, dilution and retardation, and finally to an assessment of dose and health effects to individuals at a specified locality at the boundary of the accessible environment (Fig. 1). A single assessment of performance requires thousands of input variables; some are fixed, whereas others are sampled over ranges of probable values (CRWMS 1998). In addition, expert opinion is used to establish the ranges of many of the parameters. This analysis depends heavily on assumed probabilities for events such as climate change, earthquakes and volcanic activity. These possibilities set important boundary conditions for the behavior of the total system (*e.g.,* groundwater recharge and flow rate). In addition, contrary to the linear sequence of steps portrayed in Figure 1, the subsystems are highly coupled and may be non-linear in their behavior, with extensive feedback-type interactions. The limitations of such an approach extrapolated over periods greater than 10,000 years are much debated (Ewing *et al.* 1999, Konikow & Ewing 1999). Figure 2 shows a typical assessment of dose (future prediction) compared to the geological time-scale. Typically, maximum doses occur at periods greater than 10,000 years.

Inevitably, the uncertainty in such an analysis is great, with the result that the impact of important improvements in the materials properties of nuclear waste forms (*e.g.*, low rate of corrosion or high resistance to radiation damage) are lost in the uncertainty generated by the great number of variables in other parts of the repository-system analysis. Hence, there has been a tendency to rely on the geological barriers of a repository rather than the material properties of the waste form.

Despite the secondary role of waste forms as determined by total system-performance assessment, there are logical and compelling reasons for emphasizing the importance of the material properties of the waste form (Ewing 1992):

1. The strategy of radionuclide containment and isolation should emphasize near-field containment. This is primarily a function of waste form or "waste package" performance. Strategies that rely solely on long travel times, dispersal and dilution, implicitly presume release and movement of radionuclides into the environment.

2. Assessment of long-term performance of radionuclide containment requires development of deterministic models of the future physical and chemical behavior of each barrier system. Although such an assessment is challenging, it is almost certainly easier to model the chemistry and physics of corrosion and alteration of waste forms than it is to develop coupled hydrological, geochemical and geophysical models of the movement of radionuclides through the far-field of a geological repository. Both near-field and far-field assessments are necessary, and both should provide important barrier functions, but extrapolation of the corrosion behavior of the waste form over long periods can be modeled more convincingly than, as an example, hydrological systems that are site-specific and highly dependent on idealized boundary-conditions (Konikow 1986).

3. Natural phases (minerals and glasses) provide a means for testing the hypothesized long-term behavior of waste-form phases in specific geochemical environments (Ewing 1993). As an example, the mineralogical databases developed as part of the evaluation of system behavior (open *versus* closed) for radiometric dating are immediately transferable to the discussion of the release of radionuclides from actinide-bearing waste-form phases.

WHY ARE ACTINIDES IMPORTANT?

Although there are a number of fission-product radionuclides of high activity (^{137}Cs and ^{90}Sr) and

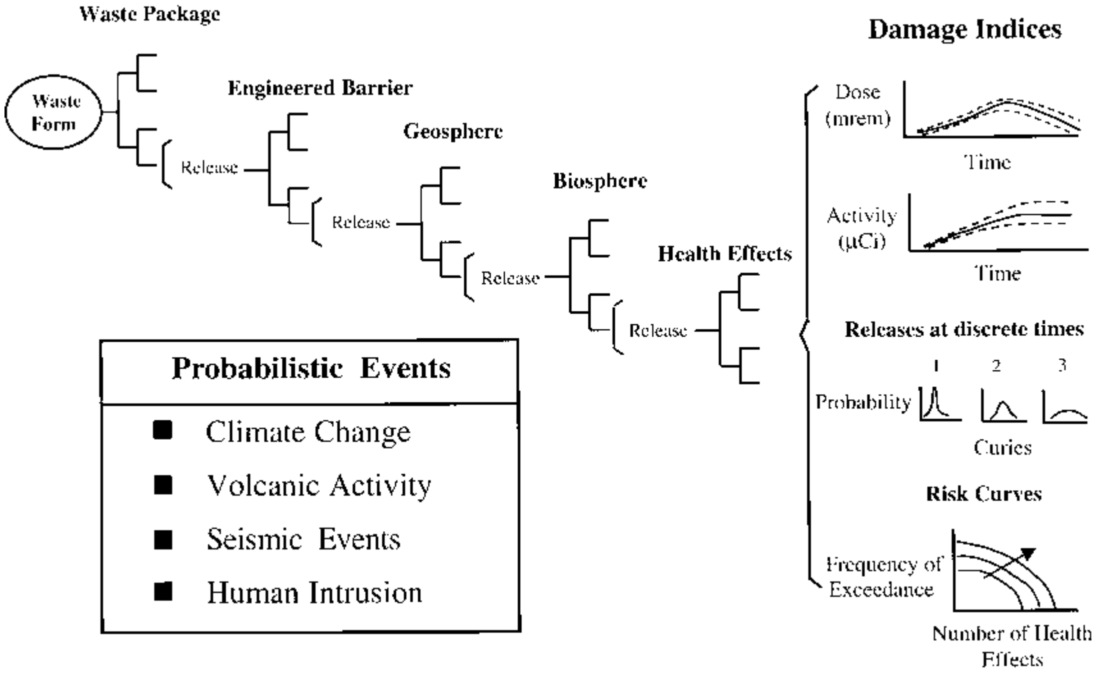

FIG. 1. Schematic representation of the steps in a probabilistic assessment of a nuclear-waste repository (after Garrick & Kaplan 1994). Depending on the type of regulation, which varies from country to country, the damage indices may vary (*e.g.*, dose to a person/critical population or fractional release of radioactivity over time or a probability of exceeding a regulatory limit plotted against the estimated effects on health).

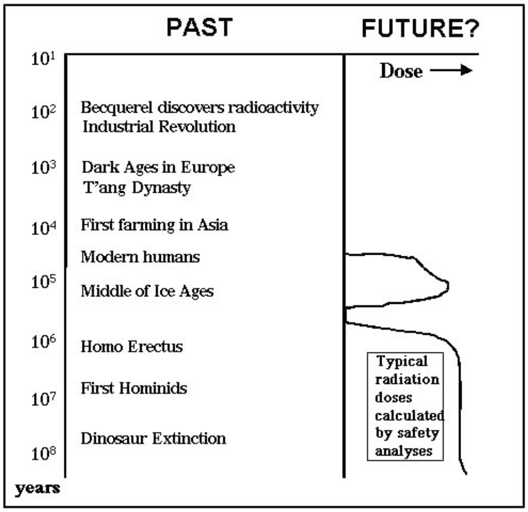

FIG. 2. Comparison of a typical dose-curve in a safety assessment of a nuclear-waste repository with the geological time-scale (after Chapman & Côme 1990). Note that the peak dose occurs well after 10,000 years.

long half-life (^{99}Tc: 200,000 a; ^{129}I: 1.6×10^7 a; ^{79}Se: 1.1×10^6 a) in spent nuclear fuel, actinides and their daughter products account for most of the radiotoxicity of nuclear waste after the first 500 years of disposal (Fig. 3). After several hundred years, radiotoxicity is dominated by ^{239}Pu (half-life = 24,100 a) and ^{237}Np (half-life = 2,000,000 a) (Hedin 1997). Thus, a major part of the long-term risk is directly related to the fate of these two actinides in the geosphere (natural, crustal concentrations of Pu are on the order of 10^{-11} ppm for ^{239}Pu). In this paper, I will focus the discussion on the design of waste forms for Pu, but in practice, equal attention should be focused on waste forms for the long-lived products of fission (Gu *et al.* 2000, Chen *et al.* 1999).

Plutonium has several important and unique properties: (1) ^{239}Pu is fissile; (2) ^{239}Pu, with a half-life of 24,100 years, decays to ^{235}U, another fissile radionuclide with a half-life of 700 million years (the bare critical mass of weapons-grade uranium is approximately 50 kg); (3) Pu has four oxidation states (3+, 4+, 5+ and 6+) in natural water–rock systems. Although crystalline PuO_2 has low solubility, Pu may exist as PuO_2^{+} or PuO_2^{2+} aqueous species, with the former predominating in oxidized natural waters. In addition, in the 3+, 5+

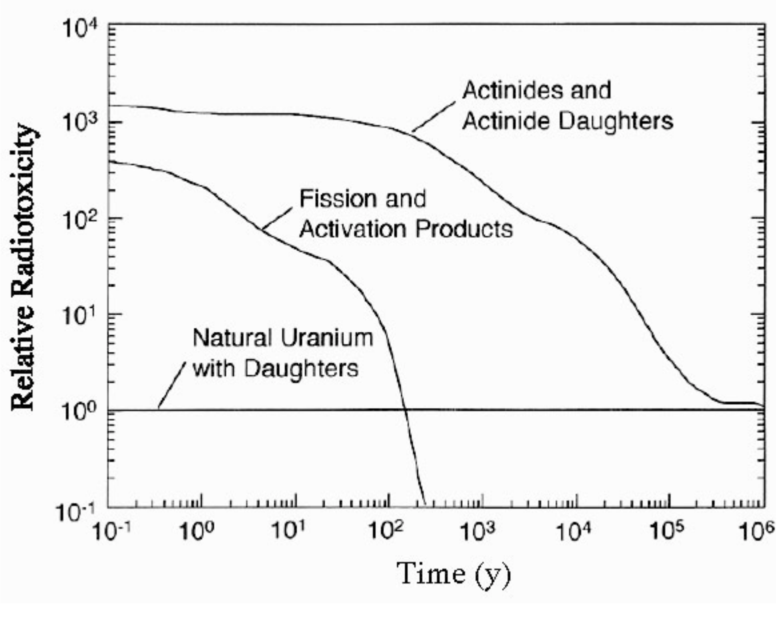

FIG. 3. Relative radiotoxicity on inhalation of spent nuclear fuel with a burnup of 38 MWd/kg U. The radiotoxicity values are relative to the radiotoxicity (horizontal line) of the quantity of uranium ore that was originally mined to produce the fuel (8 tonnes of natural uranium yields one tonne of enriched uranium, 3.5% ^{235}U) (Hedin 1997).

and 6+ oxidation states, Pu forms strong carbonate complexes at pH > 5 (Langmuir 1997). Actual concentrations of plutonium in solution are further complicated by the possibility of disproportionation among oxidation states, α-radiolysis of water to produce oxidants (*i.e.*, H_2O_2), α-decay-induced amorphization of the solid (which increases leach rates), and the formation of intrinsic actinide or actinide-bearing colloids that can increase actinide concentrations in groundwaters by several orders of magnitude (Degueldre *et al.* 2000). Thus, the geochemistry of Pu has the potential for a full range of behaviors due to dissolution, complexation, sorption, transport and precipitation mechanisms that are sensitive to redox conditions and groundwater compositions (Runde 2000). Thus, it is essential to understand the long-term behavior of Pu either as it exists in spent nuclear fuel or as it is immobilized in solid waste-forms.

DURABLE WASTE-FORMS FOR PLUTONIUM

Although the development of waste forms for plutonium poses special problems and requirements for long-term durability, weapons Pu presents special opportunities:

(a) As compared with high-level waste, the volumes are relatively small. For example, if Pu is immobilized in a typical waste-form with a waste loading of 10 wt.%, the 100 metric tonnes of weapons Pu can be immobilized in a volume of several hundred cubic meters.

(b) Weapons plutonium is remarkably pure, consisting of a Pu–Ga alloy (0.5 to 2% Ga) coated with a corrosion-resistant layer, generally Ni. This high purity provides a materials engineer with a wide range of potential techniques for processing and the possibility of producing phase-pure waste forms at prescribed levels of waste loading. The absence of highly active products of fission, such as ^{137}Cs and ^{90}Sr (the primary source of ionizing radiation), makes handling the material tractable using technologies comparable to those used to fabricate mixed-oxide reactor fuels.

(c) Although the half-life of ^{239}Pu (24,100 a) is much longer than that of the much higher-activity products of fission, a substantial amount of decay occurs over relatively short geological time-scales (*e.g.*, containment of Pu for 10 half-lives requires on the order of 241,000 a). Thus, immobilization over the time required for substantial radioactive decay is short relative to the durability of some geological materials, measured in many millions of years. The fact that ^{239}Pu decays to ^{235}U presents an additional challenge for the durability of the waste form, but the greater critical mass of ^{235}U combined with the possibility of dilution of ^{235}U by ^{238}U can provide additional barriers to the potential for a criticality event in which chain reactions are sustained.

The essential question to mineralogists thus is: Are there naturally occurring, actinide-bearing phases of *demonstrable chemical and physical durability* that can be used for the *long-term* immobilization and disposal of weapons plutonium?

Rather than selecting a specific waste-form in preference to others for immobilization of Pu, I will illustrate the contribution that "mineralogical thinking" can bring to the table of such a discussion. The critical aspects of the question are the determination *of "demonstrable, long-term physical and chemical durability"*. Durability refers to a wide variety of properties: mechanical strength, thermodynamic stability, slow kinetics for corrosion processes, retention of trace elements (in this case, actinides and neutron absorbers, such as Gd and Hf) due to low diffusivity.

The qualitative geological answer to such a question is obvious; that is, the suite of heavy minerals that survive weathering, erosion, transport and deposition (in some cases many cycles) and persist as placer deposits in stream beds. The classic paper on heavy detrital minerals by Hutton (1950) provides a detailed list of heavy minerals from which actinide-bearing phases may be identified (Table 2). Other important actinide-bearing phases (pyrochlore, zirconolite and baddeleyite) that were not included by Hutton have been added to Table 2. The second issue is what geological and mineralogical data exist for these phases? Table 2 gives the number of citations for these phases taken from the GeoRef database in 2001. The result is not surprising; those phases that are important for geochronology (zircon, apatite and monazite) account for a major part (95%) of the published literature. These studies are of two types: (1) laboratory studies used to determine the ability of the minerals to retain isotopic signatures as result of their physical and chemical durability in a variety of geological environments, and (2) age-dating studies that essentially confirm the results of the laboratory studies

TABLE 2. ACTINIDE-BEARING PHASES THAT ARE CONSIDERED FOR IMMOBILIZATION OF PLUTONIUM

phase	ideal formula	GeoRef citations (2001)	durable?[1]
pyrochlore[2]	$(Ca,REE)Ti_2O_7$	374	
zirconolite	$CaZrTi_2O_7$	77	
apatite	$Ca_{4-x}\mathit{REE}_{6+x}(SiO_4)_{6-y}(PO_4)_y(O,F)_2$	6,470	yes
zircon	$ZrSiO_4$	10,479	yes
monazite	$CePO_4$	2,256	yes
baddeleyite[3]	ZrO_2	320	

[1] Heavy minerals identified and discussed in a monograph on heavy-mineral occurrences (Hutton 1950). Heavy minerals that were noted, but not included in this table are: gadolinite, allanite, thorite, titanite and xenotime. Thorite ($ThSiO_4$) and xenotime (YPO_4) are isostructural with zircon; gadolinite, allanite and titanite are either relatively rare or less durable than the minerals listed in the table.

[2] Presently receiving the greatest attention within the U.S. program for the disposition of fissile materials.

[3] Cubic and tetragonal polymorphs of ZrO_2 have been considered as waste-form phases; however, naturally occurring ZrO_2 is most commonly monoclinic baddeleyite. Although not cited in Hutton (1950), it is included in this list because of its known durability and because it is considered both as a waste form and as inert-fuel matrix for "burning" plutonium (Oversby *et al.* 1997, Sickafus *et al.* 1999).

in actual, long-term geological environments. *Both types of studies provide the essential data required for waste-form design and selection.*

Present research on waste forms for immobilization of Pu includes a relatively short list of phases (Table 2). In the U.S., most of the effort within the Materials Disposition program of DOE focuses on immobilization in a ceramic (Cochran *et al.* 1997), particularly an isometric titanate, pyrochlore, and its monoclinic derivative, zirconolite, as there are considerable data on these materials as waste-form phases (Ewing *et al.* 1995b). However, the DOE evaluation and selection process (Cochran *et al.* 1997) is very different from the mineralogical approach presented in this paper.

In order to illustrate the mineralogical approach, I review relevant work on zircon, drawn mainly from the mineralogical and geochemical literature, in order to show the utility of the "mineralogical approach", as well as the extensive amount of data that are already available in the literature. Although the structure of zircon (Robinson *et al.* 1971) and those of actinide orthosilicates (Taylor & Ewing 1978, von Keller 1963) have been known for thirty years, I focus on studies applicable to the analysis of zircon as an actinide nuclear-waste form. Many of the required data have been in the published literature for many years.

ZIRCON AS A WASTE FORM FOR ACTINIDES

Zircon ($I4_1/amd$, $Z = 4$) has U and Th concentrations typically up to 5,000 ppm, but reaching 10 wt.%. Zircon is an extremely durable mineral (Hanchar & Miller 1993). Commonly found as a heavy mineral in stream sediments, zircon shows limited chemical alteration or physical abrasion after transport over great distances (Hutton 1950, Riggs *et al.* 1996). The widespread distribution of zircon in the continental crust, its tendency to concentrate trace elements (lanthanides and actinides), its use in age dating, and its resistance to chemical and physical degradation (Pidgeon *et al.* 1966, Craig 1968, Krogh & Davis 1975, Suzuki 1987) have made zircon probably the most useful accessory mineral in geological studies.

Zircon has been identified as an actinide-bearing phase in polyphase ceramic waste-forms (Harker & Flintoff 1990). Zircon also occurs in the Chernobyl lavas as an important actinide-bearing phase (6 to 12 atomic % U) (Anderson *et al.* 1993a). Its propensity to incorporate actinides and its durability have led to the suggestion that zircon be used to immobilize actinides (Burakov 1993, Anderson *et al.* 1993b, Ewing *et al.* 1995c). On the basis of the ability of natural zircon to retain Pb, Gentry *et al.* (1982) suggested that materials like zircon could effectively retain radioactive waste. This early suggestion was prescient, but did not evaluate the extent of solid solution of actinides in zircon and did not consider the much greater radiation-induced damage that would occur in such a radioactive waste-form (Ludwig *et al.* 1984).

Structure

The structure of zircon consists of ZrO_8 triangular dodecahedral groups that form edge-sharing chains parallel to the *a* axis and SiO_4 tetrahedra that form edge-sharing chains with alternating ZrO_8 groups parallel to the *c* axis (Robinson *et al.* 1971, Taylor & Ewing 1978). Uranium and Th replace Zr in low concentrations; however, compositions of ASiO$_4$, in which A^{4+} represents Zr, Hf, Th, Pa, U, Np, Pu and Am, have been synthesized (von Keller 1963). The regular increase in the unit-cell volume with the increasing ionic radius of the *A*-site cation confirms that these compounds are isostructural (Fig. 4). Four of these compositions, hafnon ($HfSiO_4$), zircon, coffinite ($USiO_4$) and thorite ($ThSiO_4$) occur as minerals. Structure refinements (von Keller 1963, Speer 1982, Speer & Cooper 1982) suggest complete miscibility between $ZrSiO_4$ and $HfSiO_4$, but there are miscibility gaps on the $ZrSiO_4 – USiO_4$ and $ZrSiO_4 – ThSiO_4$ joins (Mumpton & Roy 1961). Zircon with 9.2 atom % Pu (8.1% ^{238}Pu; 1.1% ^{239}Pu) substituting for Zr has been synthesized (Weber 1991). This is equal to a waste load of 10 wt.% Pu, but the maximum extent of the solubility of Pu in zircon has not been determined. Synthesis of a pure $PuSiO_4$ (von Keller 1963) suggests that extensive substitution of Pu for Zr is possible (Speer & Cooper 1982).

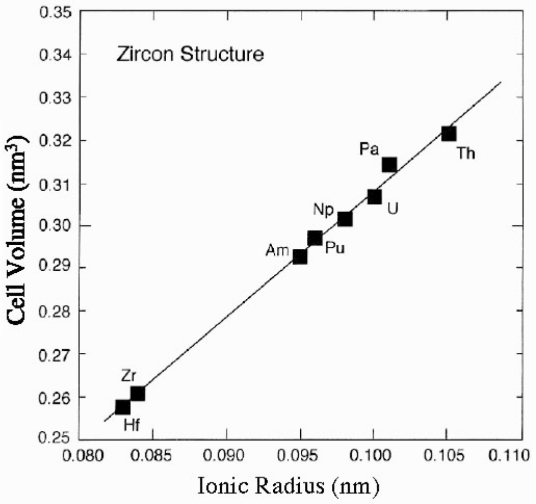

FIG. 4. Variation in unit-cell volume of actinide silicates, ASiO$_4$, with the zircon structure as a function of ionic radius ($^{[8]}A^{4+}$); data from von Keller (1963) after Speer (1982).

The zircon structure is part of a larger class of ABO_4 structure types (silicates and phosphates) and is closely related to the structure of monazite, $CePO_4$, another durable phase commonly used in geological age-dating. Numerous *A*-site compositions (La, Pr, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu Sc and Y) with the zircon and monazite structure-types have been synthesized, and their structures, refined. These synthesized materials have provided the basis for detailed optical-absorption spectroscopy and paramagnetic resonance studies of U, Pu, Cm, Np and Gd incorporation into the zircon structure-type (Poirot *et al.* 1988, 1989).

Geochronology

Recent progress in the use of zircon in age dating has involved a sensitive high-resolution ion microprobe (SHRIMP), a method that allows measurement of isotopic ratios on areas as small as 20–30 μm, thus providing age dates on separate zones within single crystals of zircon. Cores of a detrital zircon in a quartzite at Mount Narryer, Western Australia, have been dated at 4,100–4,300 million years ago (Ma), until recently the oldest terrestrial mineral yet found (Froude *et al.* 1983). In Western Australia, the Jack Hills contain slightly younger (3,900–4,270 Ma) detrital zircon (Compston & Pidgeon 1986, Maas *et al.* 1992). The zircon crystals in Australia are individual, recycled grains in a younger (3,500 Ma) sequence of metamorphosed sedimentary rocks, as are similarly dated crystals of zircon from the Sino-Korean craton in northeastern China (3,800 Ma) (Liu *et al.* 1992). The oldest so-called intact crust is found in the early Archean (3,800–3,960 Ma) granitic basement in northwestern Canada (Bowring *et al.* 1989) and western Greenland (Nutman *et al.* 1993). Most recently, Wilde *et al.* (2001) have dated zircon from the Jack Hills at 4,404 Ma, 130 million years older than any previously identified on Earth. The oldest crystals of zircon in the solar system are found as rare inclusions in meteorites and were dated at 4,560 Ma (Ireland & Wlotzka 1992). There are many hundreds of papers that can be cited to illustrate the use of zircon in dating very old rocks, but of greater importance is the establishment through field studies of the effects of geological processes on the durability of zircon either under surface conditions of sedimentary transport (Riggs *et al.* 1996) or at much higher temperatures, *e.g.*, granulite-facies metamorphism (Roberts & Finger 1997), extremely high metamorphic pressures (Deutsch & Schärer 1990, Claoué-Long *et al.* 1991, Wayne & Sinha 1988, 1992) or meteorite impact (Bohor *et al.* 1993). Such geochronological studies provide a valuable source of information on the long-term behavior of zircon under a variety of geochemical conditions.

The most recent and dramatic example of the extraordinary ability of zircon to retain its U–Pb systematics comes from studies of zircon from the Chicxulub impact structure of the Yucatán Peninsula (Bohor *et al.* 1993, Krogh *et al.* 1993, Kamo & Krogh 1995). The shocked crystals of zircon were exhumed from the Chicxulub basement rock during meteorite impact and dispersed in the fine dust of the impact cloud. Discordances in the U–Pb systematics (*e.g.,* Pb loss) are proportional to the extent of impact-induced shock textures, and isotopic resetting is consistent with partial lead-loss at the time of impact (65 Ma), providing convincing support for the meteorite impact origin of the Chicxulub crater and its being the source of ejected material found at the Cretaceous–Tertiary (K–T) boundary in North America. Uranium–lead dating studies show that shocked zircon in the fine-grained ejecta, deposited in areas as far apart as Colorado, Saskatchewan and Haiti at the Cretaceous–Tertiary boundary, has a predominant age of 545 Ma, in agreement with dates for shocked zircon from the Chicxulub crater (Krogh *et al.* 1993, Kamo & Krogh 1995). Only a material of remarkable durability, such as zircon, could preserve the isotopic signature of an event of such extreme conditions (Kamo & Krogh 1995).

Alteration and disturbed U/Pb systematics

Any process that can disturb the U/Pb isotopic systematics of zircon crystals has an important effect on whether the radiometrically determined dates are concordant or discordant. There is an extensive literature about this type of alteration (Pidgeon *et al.* 1966, Craig 1968, Krogh & Davis 1975, Davis *et al.* 1968). Discordant ages are common and are mainly due to Pb loss and, less commonly, due to U loss. Discordant ages are usually attributed to episodic loss of Pb or U during thermal events (Davis *et al.* 1968) and are enhanced by: (1) physical degradation due to an increase in surface area caused by microfracturing that is the result of volume expansion associated with α-decay damage (Wayne & Sinha 1992, Chakoumakos *et al.* 1987, Holland & Gottfried 1955), and (2) chemical alteration caused by radiation-induced amorphization that creates damaged aperiodic domains in which diffusion of Pb is enhanced (Davis & Krogh 2000) and for which rates of bulk leaching increase. Thus, discordant ages are generally the result of the accumulation of highly damaged regions resulting from α-decay damage. More accurate U/Pb dates may be obtained by removing the radiation-damaged regions by physical abrasion or etching (Krogh 1995). Differential etching (using 48% HF) has shown that removal of radiation-damaged zones improves concordance of U/Pb ages in the remaining unaltered material (Krogh & Davis 1975).

Recently, Watson *et al.* (1997) have investigated the incorporation of Pb into zircon, and Lee (1993) evaluated the mechanisms by which Pb may be lost. The loss of Pb by diffusion is an extremely slow process (at 1000°C, the diffusivity of Pb in zircon is 10^{-25} m^2s^{-1}).

Such low diffusivities confirm Pb closure temperatures in excess of 900°C (Cherniak & Watson 2000), implying that U/Th/Pb isotopic ages are unlikely to be reset by thermal events alone, except under the most extreme geological conditions (*i.e.*, partial melting or granulite-grade metamorphism: Lee 1993). In addition, under extreme geological conditions (*e.g.*, zircon deformed in shear zones and altered by hydrothermal solutions), U/Pb systematics are disturbed. Detailed experimental studies (Sinha *et al.* 1992) have shown that experimentally induced U/Pb isotopic discordance in zircon is a complex function of the amount of radiation damage and thermal annealing (Meldrum *et al.* 1998b).

In summary, there are abundant data from geochronological studies to show that natural zircon can quantitatively retain Pb for billions of years in the absence of episodic thermally induced loss of Pb (Ludwig *et al.* 1984): however, radiation damage (discussed in a later section) may lead to a significant increase in diffusional loss of Pb (Cherniak & Watson 2000, Davis & Krogh 2000). Furthermore, minor alteration of zircon over long periods of time and under extreme conditions stands in contrast to the observations of other potential ceramic nuclear-waste forms, such as pyrochlore (Lumpkin & Ewing 1996), for which data of the type summarized above are simply not presently available.

Diffusion of tetravalent cations and rare-earth elements (REE)

Even though diffusion rates for Pb are low, the diffusivities of U and Th in zircon at 1100°C are orders of magnitude lower (Cherniak & Watson 2000), suggesting complete containment of actinides for billions of years. The principal process by which diffusion rates might increase is through damage due to α-decay events (Ludwig *et al.* 1984). Elements may preferentially segregate into aperiodically damaged regions that have inherently higher solubilities than crystalline ceramics (McLaren *et al.* 1994); subsequent annealing of the sample can substantially change the microstructure of the damaged zircon (Cherniak *et al.* 1991).

Development of a waste form for weapons ^{239}Pu requires knowledge of diffusion rates of the actinides, as well as elements with high neutron-capture cross-sections (*e.g.*, Hf and Gd) in order to prevent criticality events. Natural zircon can contain up to several thousand ppm of rare earths, including up to 500 ppm Gd, and zircon exhibits nearly complete solid-solution with hafnon, $HfSiO_4$. Thus, neutron-absorbing nuclides may be incorporated into the zircon structure; however, the neutron absorber must remain within atomic scale proximity of the fissile radionuclide (^{239}Pu or ^{235}U). Recent determinations of diffusion rates for tetravalent cations (Th, U and Hf) give diffusivities in the order of 10^{-22} to 10^{-20} m^2s^{-1} in the temperature range 1400 to 1650°C (Cherniak *et al.* 1997a, Lee *et al.* 1997). On the basis of similarities in ionic radii, Pu^{4+} is expected to have a similar diffusivity, although slightly faster diffusion is expected because of its smaller ionic radius. Thus, Pu^{4+} is essentially immobile under all but the most extreme geological conditions. The very low mobility of Pu in the zircon structure is also supported by the preservation of fine-scale chemical zoning and isotopic signatures in the inherited cores of zircon crystals even though they have experienced protracted thermal events. In contrast, the *REE* diffuse at rates four to five orders of magnitude faster than tetravalent cations (Cherniak *et al.* 1997b). The diffusion rates vary among the *REE* in a systematic manner as a function of ionic radius; thus for Gd, the estimated activation energy and diffusivity in zircon at 1000°C are 189 kcal/mol and 3.2×10^{-26} m^2s^{-1}, respectively. Again, the closure temperature of zircon for *REE* is quite high (>1000°C) for all but the smallest grains. Other phases that have been suggested as waste-form phases (*e.g.*, titanite and apatite) have closure temperatures many hundreds of degrees lower than those of zircon.

Dissolution studies

Studies of zircon under extreme laboratory conditions have confirmed the loss of U, Th and Pb (Pidgeon *et al.* 1966, Craig 1968, Sinha *et al.* 1992). Loss of Pb can be the result of grain-boundary or volume diffusion (in which there is no dissolution of the zircon), or bulk dissolution of zircon. However, at lower temperature (< 80°C) and near-neutral pH values (*i.e.*, conditions more pertinent to nuclear-waste disposal), zircon is extremely insoluble in typical groundwater compositions equilibrated with granitic bedrock. Unfortunately, there is much less information on leaching of zircon in the literature than is necessary for its full evaluation as a waste form.

Crystalline zircon is stable to such an extent that the equilibrium concentrations of Zr and Si are in the order of 10^{-9} moles/L (0.1 ppb) at 25°C (Tole 1985). Dissolution of highly damaged zircon follows a first-order reaction, on the basis of Si concentrations. Concentrations of Zr remain below 0.05 ppm (the instrument's detection-limit) owing to precipitation of ZrO_2 and $ZrSiO_4$ (Tole 1985). The leach rate of zircon increases with α-decay damage on the order of one to two orders of magnitude (Ewing *et al.* 1982). Comparing the dissolution rate for metamict zircon ($R = 10^{-7}$ moles/m^2/d at 80°C, pH = 5, Tole 1985), with the rate of long-term dissolution of a nuclear-waste borosilicate glass [$R = 10^{-5}$ moles/m^2/d (= 10^{-3}g/m^2/d) in water at 98°C, Werme *et al.* 1990] shows that the dissolution rate of radiation-damaged zircon is still considerably lower than that of glass in stagnant silica-saturated solutions. In an open system (*e.g.*, moving groundwater where solubility limits are not reached), the leach rate for zircon (Tole 1985) used in this comparison does not increase; however, the leach rate of borosilicate glass may increase by three orders of magnitude until the final rate of reaction is reached (Lutze & Ewing 1988).

Thus, one of the main advantages of zircon may be its high durability in an open system where groundwaters are present, as this characteristic allows considerably greater flexibility in disposal strategy (*e.g.,* deep borehole). For this reason, it is essential to determine the maximum forward rate of the dissolution reaction. This is particularly challenging, as the dissolution rate for zircon is low, and precipitation of ZrO_2 removes Zr from the leaching solution. Recently, a high-temperature Soxhlet extractor was designed to measure the forward rate of dissolution of zircon in the range of 120 to 250°C. The measured rates are as follows: 4.1×10^{-4} $g{\bullet}m^{-2}$ day^{-1} at 250°C, 1.7×10^{-4} $g{\bullet}m^{-2}$ day^{-1} at 200°C and 7.1×10^{-5} $g{\bullet}m^{-2}$ day^{-1} at 120°C. The rate extrapolated to 90°C is 4.6×10^{-5} $g{\bullet}m^{-2}$ day^{-1}; therefore, in an open system and in the absence of a solubility-limiting phase, a 100 μm crystal of zircon would require 150,000 years for complete dissolution (Helean 1997, Helean *et al.* 1999). Under static conditions, the dissolution rate is substantially reduced. The experimental results are consistent with the high chemical durability of zircon in a wide range of geological environments.

Physical properties

The mechanical properties of zircon change with increasing α-decay dose (Chakoumakos *et al.* 1991) and as a result of implantation by Pb ions (540 keV) up to fluences of 3.3×10^{11} to 5×10^{15} $ions/cm^2$ (a dose range that spans the crystalline-to-amorphous transition: Oliver *et al.* 1994). The α-decay-induced softening leads to a decrease in hardness (40%) and bulk elastic modulus (70%) (Özkan 1976), but there is an increase in fracture toughness, probably caused by crack-tip blunting owing to aperiodic domains (Chakoumakos *et al.* 1991). The ion-beam irradiation resulted in softening (70%) and a decrease in bulk modulus (42%). The principal effect of the changes in mechanical properties is the formation of a pronounced system of fractures (Chakoumakos *et al.* 1987) due to differential volume-expansion in zones of different α-decay dose. A model has been developed that describes the sets of radial and concentric fractures that are characteristic of zircon, principally a function of the degree of damage (*e.g.,* the amorphous fraction), zone thickness, and the confining pressure (Lee & Tromp 1995). This type of analysis is required in order to evaluate the development of microfractures as a function of radiation damage, and is particularly useful in considering disposal in a deep borehole.

Radiation damage

Radiation damage from incorporated actinides and their daughter products can have a profound effect on the physical properties and chemical durability of minerals and ceramics (Ewing *et al.* 2000). This is especially true for the α-decay of ^{239}Pu and its daughter products (*e.g.,* ^{235}U) in an actinide-bearing zircon. Depending on the waste load, significant doses ($>10^{18}$ α-decay events/g) accumulate, and crystalline phases become aperiodic in relatively short periods of time, 10^3 years (Fig. 5) (Ewing *et al.* 1995a, Weber *et al.* 1998). Note that zircon crystals can accumulate relatively high doses of α-decay (horizontal line in Fig. 5). This allows a comparison of data from accelerated-irradiation techniques, either actinide-doping with short-lived α-decay nuclides such as ^{238}Pu or ^{244}Cm (that reach α-decay doses of 10^{19} α-decay event/g) or ion-beam irradiation experiments (Ewing *et al.* 2000).

In an α-decay event, the α-particle dissipates most of its energy (4.5 to 5.8 MeV for actinides) by ionization processes over a range of 16 to 22 μm, but undergoes enough elastic collisions along its path to produce several hundred isolated atomic displacements. The largest number of displacements occur near the end of the α-particle range. The more massive, but lower energy, α-recoil (86 keV ^{235}U recoil from decay of ^{239}Pu) dissipates nearly all of its energy in elastic collisions over a very short range, 30 to 40 nm, causing ~1,000 atomic displacements. The density of energy deposited into the cascade is high (up to 1 eV/atom) and occurs over an extremely short time ($<10^{-12}$ s). Thus, a single α-decay event generates approximately 1200 atomic displacements, significantly more than the 0.1 displacements generated per β-decay event. Because of the large number of atomic displacements during an α-decay event, there is a profound effect on the structure and properties of crystalline solids that incorporate actinides. The cumulative effect of dose will be time- and temperature-dependent because of annealing and recrystallization of damaged areas (Weber *et al.* 1997).

Studies of radiation effects in zircon have a long history (Vance 1975, Ewing 1994, Murakami *et al.* 1991, Wang & Ewing 1992a, Nasdala *et al.* 1996, Farges & Calas 1991, Woodhead *et al.* 1991, Farges 1994, Weber *et al.* 1994, Salje *et al.* 1999, Meldrum *et al.* 1999a, b, Begg *et al.* 2000, Capitani *et al.* 2000). Zircon undergoes a radiation-induced transformation from the periodic to aperiodic (metamict) state at doses over 10^{18} to 10^{19} α-decay events/g (= 0.2 to 0.6 dpa, displacements per atom) with a corresponding decrease in density and volume expansion of 18%. Previous studies include the analysis of zircon crystals that have accumulated α-decay-event damage up to doses of nearly 0.7 dpa over 550 million years (Holland & Gottfried 1955, Murakami *et al.* 1991, Nasdala *et al.* 1996), ^{238}Pu-doped zircon (half-life = 87.7 a), up to doses of 0.7 dpa in 6.5 years (Weber 1991, Weber *et al.* 1994, Weber & Maupin 1988) and heavy-ion-beam irradiated zircon using 2 MeV He^+, 0.8 MeV Ne^+, 1.5 MeV Ar^+, 0.7–1.5 MeV Kr^+ and 1.5 MeV Xe^+ to doses of 0.2 to 2.3 dpa in times of less than one hour (Wang & Ewing 1992b, Weber *et al.* 1994, Wang *et al.* 1993). All three types of damage

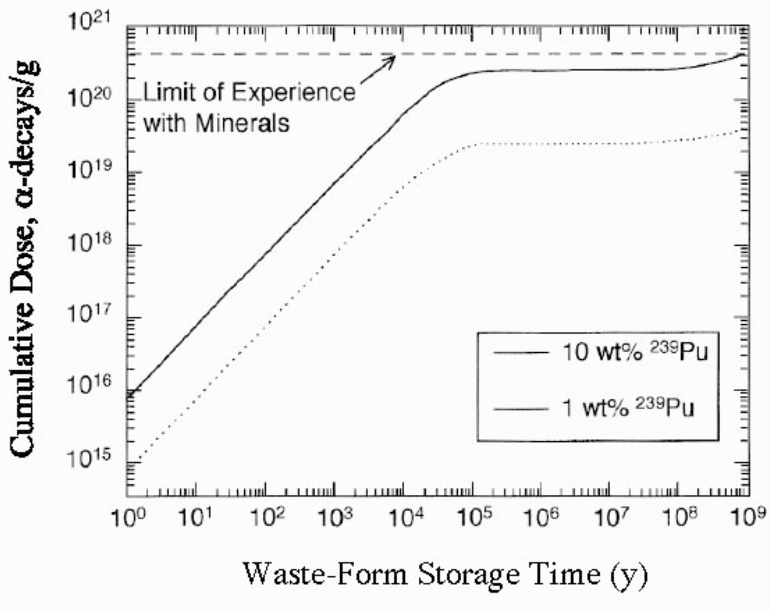

FIG. 5. Cumulative α-decay dose as a function of waste-form storage time for a ceramic (*e.g.*, zircon) containing 1 wt.% and 10 wt.% loading of ^{239}Pu (after Weber *et al.* 1997). The dashed horizontal line indicates maximum doses reached in zircon from decay of U and Th and daughter products.

experiments include detailed studies of annealing kinetics. Zircon studies (*e.g.*, of samples that are 550 million years in age) and the experimental results for ion-beam irradiation of less than one hour result in a range of dose rate of over eight orders of magnitude. *In situ* ion-beam irradiation combined with high-resolution transmission electron microscopy have shown that damage-induced microstructures and ingrowth of damage with increasing dose can be simulated using heavy-ion irradiation (Fig. 6). Thus, there is a firm basis for predicting the microstructure of radiation-damaged zircon as a function of dose, temperature, and type of radiation (Ewing 1993, Wang *et al.* 1993, Weber *et al.* 1994, Ewing *et al.* 2000). Systematic studies have been done for monazite- and zircon-structure orthophosphates with a wide variety of *A*-site end-member compositions (Meldrum *et al.* 1997a, b) and orthosilicates (Meldrum *et al.* 1998a, b,1999a, b). Zircon, hafnon ($HfSiO_4$), thorite (tetragonal $ThSiO_4$) and huttonite (monoclinic $ThSiO_4$) become amorphous in a two-stage process with increasing temperature when irradiated with 800 keV Kr^+ or Xe^+ ions in the temperature range of 20 to 1100 K. The temperature at which amorphization does not occur (*i.e.*, the temperature when the rate of simultaneous annealing is equal to the rate of damage accumulation) increases in the order: huttonite, zircon, hafnon, thorite. When irradiated with heavy ions, all four orthosilicates may decompose into crystalline oxides: ZrO_2, HfO_2 or ThO_2 plus amorphous SiO_2 (Meldrum *et al.* 1998a). Ion-beam irradiation of synthetic and natural zircon and monazite (with impurities) showed that impurities lower the dose required for amorphization and correspondingly increase the temperature above which a material cannot be amorphized. This finding suggests that impurities increase susceptibility to amorphization and inhibit annealing, particularly when coupled charge-balance substitutions are required (Meldrum *et al.* 1997b, 1999b).

Atomic-scale descriptions of structural rearrangements during damage accumulation and annealing have been obtained by EXAFS studies of metamict zircon (Farges & Calas 1991, Farges 1994), X-ray-diffraction refinements of the structure (Ríos & Salje 1999, Ríos *et al.* 2000a, b), Raman spectroscopy (Zhang *et al.* 2000), infrared spectroscopy (Zhang *et al.* 2001), ^{29}Si nuclear magnetic resonance (Farnan & Salje 2001) and transmission electron microscopy (Murakami *et al.* 1991, Capitani *et al.* 2000). Metamictization is accompanied by major atomic reorganization: loss of well-defined medium-range order, disruption of the immediate environment of Zr, decrease of the average coordination number of Zr, and tilting and distortion of SiO_4 polyhedra (Farges 1994). The principal distortions mainly affect the ZrO_8 polyhedra (Ríos *et al.* 2000b). The damage-ingrowth process is heterogeneous, essentially the result of overlapping cascades that form by direct impact (Salje *et al.* 1999, Ríos *et al.* 2000a), and the

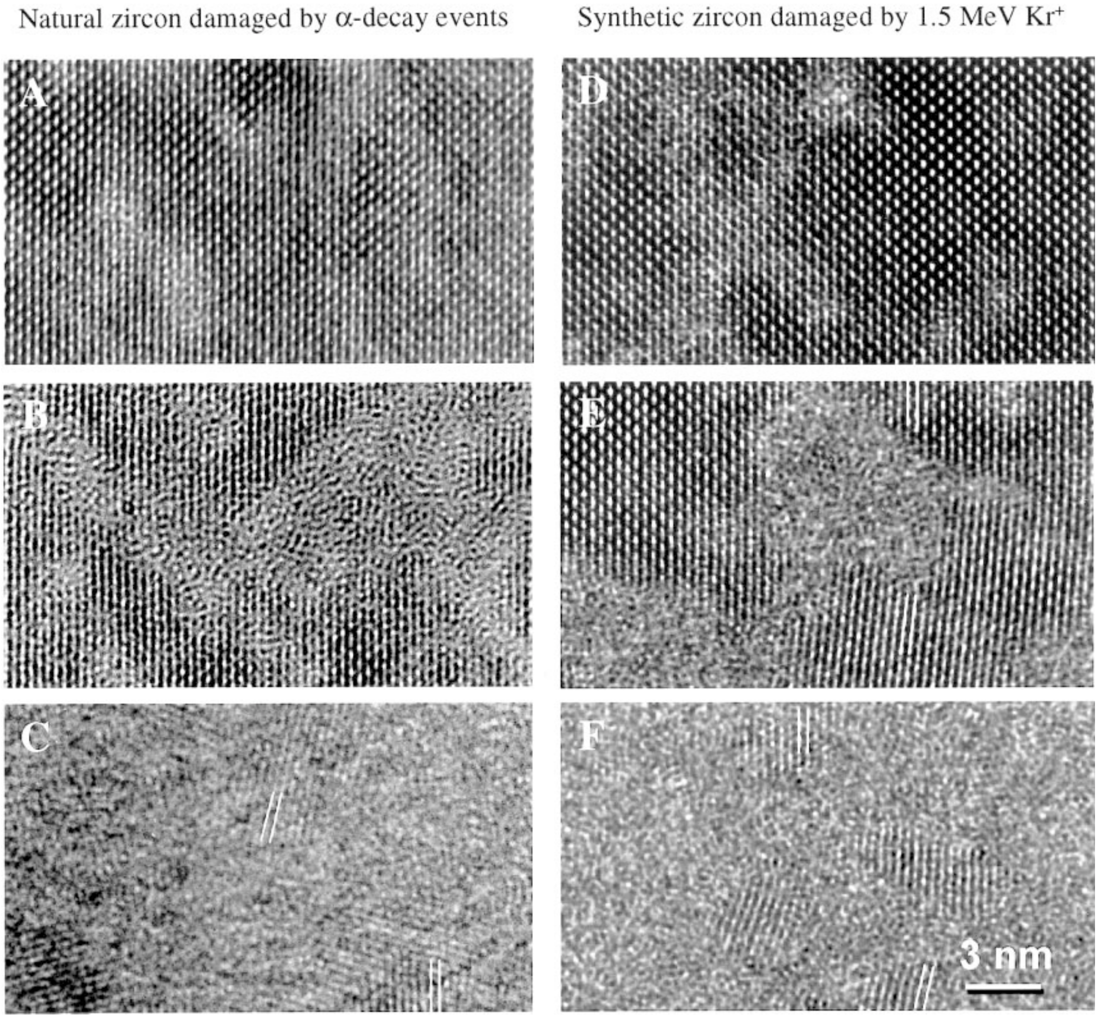

FIG. 6. Comparison of radiation damage in zircon (A–C) and 1.5 MeV Kr^+ irradiated synthetic zircon (D–F): (A) 5×10^{13} α-decay events/mg (0.003 dpa); (B) 1.8×10^{15} α/mg (0.091 dpa); (C) 6.4×10^{15} α/mg (0.32 dpa); (D) 5×10^{13} Kr^+/cm^2 (0.057 dpa); (E) 1.5×10^{14} Kr^+/cm^2 (0.17 dpa); (F) 3×10^{14} Kr^+/cm^2 (0.34 dpa). Complete amorphization in both was observed after 0.5–0.55 dpa. Figure courtesy of Lu-min Wang (Murakami *et al.* 1991, Weber *et al.* 1994).

damage accumulation can be described as a percolation-type process (Trachenko *et al.* 2000). The aperiodic structure changes with increasing dose, with the polymerization of SiO_4 tetrahedra being greatest at the highest dose (Farnan & Salje 2001). A two-stage thermal-annealing process was observed; that at lower temperature (400–500°C) resulted in the formation of minor Zr-rich domains (Farges 1994).

Finally, transmutation effects (^{239}Pu decays to ^{235}U) are important in crystalline materials, as they may lead to phase instability. The solubility of U in zircon is only known approximately (4 ± 2 mole %) (Mumpton & Roy 1961); thus, for higher concentrations of U, one might expect the formation of $USiO_4$ (also with the zircon structure) and UO_2.

There are few crystalline ceramics for which such a wide variety of data on radiation damage is available. On the basis of these data, for a waste load of 10 wt.% of ^{239}Pu under ambient conditions, zircon will reach the saturation dose of damage (1.2×10^{19} α-decay events/g or 0.8 dpa) in less than 2,000 years (Fig. 7); thus, the properties of zircon must be considered in light of its radiation-damaged, aperiodic state. The extensive database make it possible to model damage accumulation (*e.g.,* proportion of the amorphous fraction) as a function of dose and temperature, and compare the results to

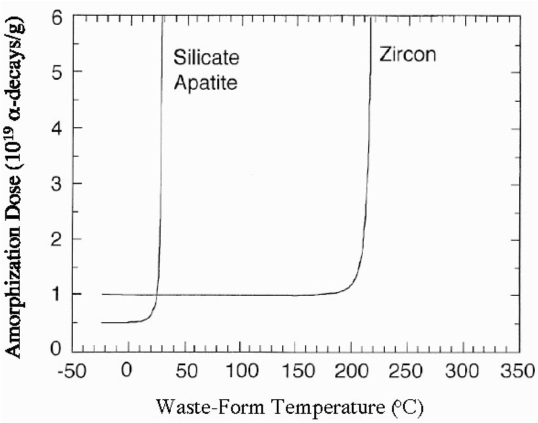

FIG. 7. Critical dose for amorphization *versus* storage temperature for silicate apatite and zircon containing 10 wt. % ^{239}Pu (after Weber *et al.* 1997).

those for other phases (*e.g.,* apatite: Weber *et al.* 1997). Figure 7 shows the critical dose for the amorphization of zircon as compared to a synthetic silicate apatite (data for both phases are based on ion-beam irradiation experiments). Above 225°C, zircon with a 10 wt.% loading of ^{239}Pu will remain in the crystalline state owing to thermal annealing. In contrast, synthetic silicate apatite anneals readily and will remain in the crystalline state at ambient temperature. Such models are very sensitive to the activation energies for thermal annealing (Meldrum *et al.* 1998b). More recent work has suggested that temperatures as high as 400°C are required to maintain the crystallinity of zircon containing 10 wt. % Pu (Meldrum *et al.* 1998a). Modeled results were compared to zircon crystals of known thermal history and are in good agreement, except in those cases where there has been episodic thermal annealing (Meldrum *et al.* 1998b). The same type of analysis allows one to calculate the minimum temperature of storage required to maintain the crystallinity of any actinide-bearing waste form (Fig. 8). At present, sufficient data for this type of analysis are available only for zircon.

Stored energy

Values for stored energy have been carefully determined (Ellsworth *et al.* 1994) by transposed-temperature drop calorimetry over the range of the periodic-to-aperiodic transition on a suite of zircon crystals from Sri Lanka (550 million years). The energy released during annealing varies sigmoidally as a function of α-decay-event dose, reaching a saturation value of 322 ± 16 J/g at doses greater than 5×10^{18} α-decay events/g. This is greater than values typical of nuclear-waste glasses, which are generally less than 150 J/g and which saturate at a dose of 10^{18} α-decay events/g; however, sudden release of this energy is not anticipated to cause a significant rise in temperature for either the glass or

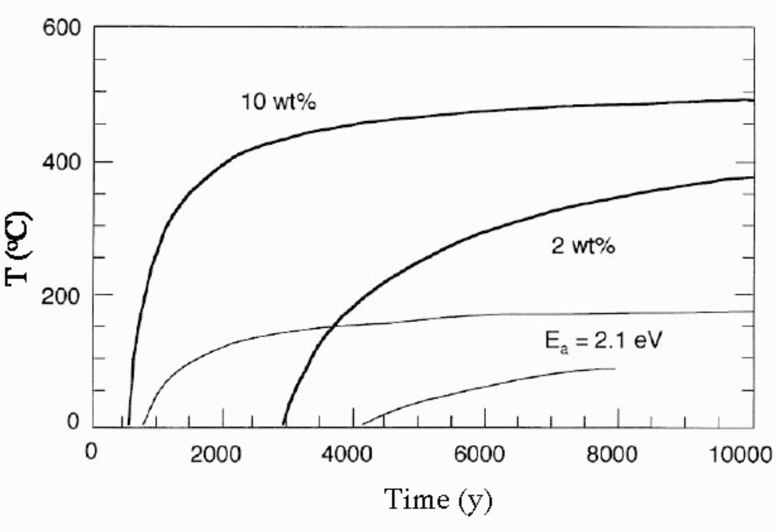

FIG. 8. Minimum temperature for storage of zircon containing 10 wt.% and 2 wt.% ^{239}Pu, respectively, *versus* storage time in order to ensure complete crystallinity of zircon. Such model calculations are very sensitive to activation energy. The dark solid line is for an activation energy of 3.6 eV, the lower, thinner line for 2.1 eV (Meldrum *et al.* 1998b).

zircon. The magnitude of the enthalpy of annealing suggests that radiation damage is pervasive on the scale of fractions of nanometers, perhaps leading to the formation of microdomains of amorphous SiO_2-rich and ZrO_2-rich regions in the metamict state. This suggestion is consistent with observations made by secondary-ion mass spectrometry and high-resolution transmission electron microscopy (McLaren *et al.* 1994), extended X-ray absorption fine-structure spectroscopy of annealed zircon (Farges 1994) and Raman spectroscopy (Zhang *et al.* 2000).

SUMMARY

The database for a mineral such as zircon provides a compelling case for its long-term chemical and mechanical durability as an actinide waste-form. The database for zircon is extensive and provides ample opportunity to confirm experimental and modeled results against actual behavior in a wide range of geological environments. If the issue is one of long-term verification of materials performance, there is no other comparable database for an actinide-bearing phase. Having said this, I emphasize that the use of zircon as a waste form for actinides is not the only or necessarily the best choice. Are there others? The answer is most definitely yes, and prominent among them are monazite (Boatner *et al.* 1980) and the polymorphs of zirconia (Sickafus *et al.* 1999). Important work on the use of cubic zirconia as an inert-fuel matrix and a nuclear-waste form (Oversby *et al.* 1997, Gong *et al.* 2000, in press) can fundamentally change important aspects of the treatment and processing of actinides in the nuclear-fuel cycle. More recently, zirconate pyrochlore compositions have been identified as being entirely radiation-resistant (Wang *et al.* 1999, Sickafus *et al.* 2000). The presently proposed ceramic for Pu disposal in the United States is a titanate pyrochlore that becomes amorphous at relatively low doses (Weber & Ewing 2000); in contrast, the zirconate pyrochlore will remain crystalline for tens of millions of years.

I believe that we have only just scratched the surface of mineralogical applications to issues related to nuclear-waste disposal. As an example, much can be learned about the alteration of UO_2 in spent nuclear fuel by studying the products of secondary alteration of uraninite, UO_{2+x} (Finch & Ewing 1992, Janeczek *et al.* 1996, Burns *et al.* 1997a, b). Mineralogical studies provide abundant information and insight into the results of long-term corrosion and alteration processes, and these are the essential data required for the design, evaluation and selection of materials used in the disposal of nuclear waste.

ACKNOWLEDGEMENTS

I have benefitted greatly from collaborations with Werner Lutze over the past twenty years. Our collaboration has provided many examples of the dictum that a good argument (with a good wine) can lead to good Science. I am also indebted to colleagues who have made important contributions to my thinking on this subject: Lynn Boatner, Boris Burakov, B. Grambow, Janusz Janeczek, Takashi Murakami, Jean-Claude Petit, Lu-min Wang, and Bill Weber. Students and post-doctoral fellows have done the hard work in the laboratory: Peter Burns, Robert Finch, Mike Jercinovic, Gregory Lumpkin, Binxi Gu, Kate Helean, Al Meldrum and Shixin Wang. I thank John Hanchar for very useful discussions about diffusion in zircon. The manuscript was substantially improved by the detailed reviews by Frank Hawthorne, Peter Burns and Chris Palenik, as well as careful editing by Bob Martin. This work has been sustained by support by Basic Energy Research Sciences of the Department of Energy (#DE–FG02–97ER45656).

REFERENCES

AHEARNE, J.F. (1997): Radioactive waste: the size of the problem. *Physics Today* **50**(6), 24-29.

ANDERSON, E.B., BURAKOV, B.E. & PAZUKHIN, E.M. (1993a): High-uranium zircon from "Chernobyl lavas". *Radiochimica Acta* **60**, 149-151.

________, ________ & VASILIEV, V.G. (1993b): Creation of a crystalline matrix for actinide waste at the Khlopin Radium Institute. *Proc. SAFE WASTE 93* **2**, 29-33.

BEGG, B.D., HESS, N.J., WEBER, W.J., CONRADSON, S.D., SCHWEIGER, M.J. & EWING, R.C. (2000): XAS and XRD study of annealed ^{238}Pu- and ^{239}Pu-doped zircons ($Zr_{0.92}Pu_{0.08}SiO_4$). *J. Nucl. Mater.* **278**, 212-224.

BOATNER, L.A., BEALL, G.W., ABRAHAM, M.M., FINCH, C.B., HURAY, P.G. & RAPPAZ, M. (1980): Monazite and other lanthanide orthophosphates as alternative actinide waste forms. *In* Scientific Basis for Nuclear Waste Management **2** (C.J.M. Northrup, Jr., ed.). Plenum Press, New York, N.Y. (289-296).

BOHOR, B.F., BETTERTON, W.J. & KROGH, T.E. (1993): Impact-shocked zircons: discovery of shock-induced textures reflecting increasing degrees of shock metamorphism. *Earth Planet. Sci. Lett.* **119**, 419-424.

BOWRING, S.A., WILLIAMS, I.S. & COMPSTON, W. (1989): 3.96 Ga gneisses from the Slave Province, Northwest-Territories, Canada. *Geology* **17**, 971-975.

BURAKOV, B.E. (1993): A study of high uranium technogeneous zircon (Zr,U)SiO_4 from Chernobyl "lavas" in connection with the problem of creating a crystalline matrix for high level waste disposal. *Proc. SAFE WASTE 93* **2**, 19-28.

BURNS, P.C. EWING, R.C. & MILLER, M.L. (1997a): Incorporation mechanisms of actinide elements into the structures of U^{6+} phases formed during the oxidation of spent nuclear fuel. *J. Nucl. Mater.* **245**, 1-9.

________, Finch, R.J., Hawthorne, F.C., Miller, M.L. & Ewing, R.C. (1997b): The crystal structure of ianthinite, $[U_2^{4+}(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$: a possible phase for Pu^{4+} incorporation during the oxidation of spent nuclear fuel. *J. Nucl. Mater.* **249**, 199-206.

Capitani, G.C., Leroux, H., Doukhan, J.C., Ríos, S., Zhang, M. & Salje, E.K.H. (2000): A TEM investigation of natural metamict zircons: structure and recovery of amorphous domains. *Phys. Chem. Minerals* **27**, 545-556.

Carter, L.J. (1979): Academy squabbles over radwaste report. *Science* **205**, 287-289.

Chakoumakos, B.C., Murakami, T., Lumpkin, G.R. & Ewing, R.C. (1987): Alpha-decay-induced fracturing in zircon: the transition from the crystalline to the metamict state. *Science* **236**, 1556-1559.

________, Oliver, W.C., Lumpkin, G.R. & Ewing, R.C. (1991): Hardness and elastic modulus of zircon as a function of heavy-particle irradiation dose. I. In-situ α-decay event damage. *Radiation Effects and Defects in Solids* **118**, 393-403.

Chapman, N.A. & Côme, B. (1990): Long-term predictions: making proper use of geological evidence *In* Safety Assessment of Radioactive Waste Repositories. OECD Press, Paris, France (1-6).

Chen, Fanrong, Burns, P.C. & Ewing, R.C. (1999): ^{79}Se: geochemical and crystallo-chemical retardation mechanisms. *J. Nucl. Mater.* **275**, 81-94.

Cherniak, D.J., Hanchar, J.M. & Watson, E.B. (1997a): Diffusion of tetravalent cations in zircon. *Contrib. Mineral. Petrol.* **127**, 383-390.

________, ________ & ________ (1997b): Rare-earth diffusion in zircon. *Chem. Geol.* **134**, 289-301.

________, Lanford, W.A. & Ryerson, F.J. (1991): Lead diffusion in apatite and zircon using ion implantation and Rutherford backscattering techniques. *Geochim. Cosmochim. Acta* **55**, 1663-1673.

________ & Watson, E.B. (2000): Pb diffusion in zircon. *Chem. Geol.* **172**, 5-24.

Claoué-Long, J.C., Sobolev, N.V., Shatsky, V.S. & Sobolev, A.V. (1991): Zircon response to diamond-pressure metamorphism in the Kokchetav massif, USSR. *Geology* **19**, 710-713.

Cochran, S.G., Dunlop, W.H., Edmunds, T.A., MacLean, L.M. & Gould, T.H. (1997): *Fissile Material Disposition Program Final Immobilization Form Assessment and Recommendation. Lawrence Livermore National Laboratory, Rep.* **UCRL-ID-128705**.

Compston, W. & Pidgeon, R.T. (1986): Jack Hills, evidence of more very old detrital zircons in Western Australia. *Nature* **321**, 766-769.

Craig, H. (1968): Zircon lead loss: a kinetic model. *Science* **159**, 447.

Crowley, K.D. (1997): Nuclear waste disposal: the technical challenges. *Physics Today* **50**(6), 32-39.

CRWMS M&O, Civilian Radioactive Waste Management System, Management and Operating Contractor (1998): *Total System Performance Assessment, Viability Assessment of a Repository at Yucca Mountain* **3**. TRW Environmental Safety Systems, Inc., Las Vegas, Nevada.

Davis, D.W. & Krogh, T.E. (2000) Preferential dissolution of ^{234}U and radiogenic Pb from α-recoil-damaged lattice sites in zircon: implications for thermal histories and Pb isotopic fractionation in the near surface environment. *Chem. Geol.* **172**, 41-58.

Davis, G.L., Hart, S.R. & Tilton, G.R. (1968): Some effects of contact metamorphism on zircon ages. *Earth Planet. Sci. Lett.* **5**, 27-34.

Degueldre, C., Triay, I., Kim, J.I., Vilks, P., Laaksoharju, M. & Miekeley, N. (2000): Groundwater colloid properties: a global approach. *Appl. Geochem.* **15**, 1043-1051.

Department of Energy (1997): *Linking Legacies: Connecting the Cold War Nuclear Weapons Production Processes to Their Environmental Consequences* (1997). Office of Environmental Management 0319 , Washington, D.C.

Deutsch, A. & Schärer, U. (1990): Isotope systematics and shock-wave metamorphism. I. U–Pb in zircon, titanite, and monazite, shocked experimentally up to 59 GPa. *Geochim. Cosmochim. Acta* **54**, 3427-3434.

Donald, I.W., Metcalfe, B.L. & Taylor, R.N.J. (1997): Review: the immobilization of high level radioactive wastes using ceramics and glasses. *J. Mater. Sci.* **32**, 5851-5887.

Ellsworth, S., Navrotsky, A. & Ewing, R.C. (1994): Energetics of radiation damage in natural zircon ($ZrSiO_4$). *Phys. Chem. Minerals* **21**, 140-149.

Ewing, R.C. (1979): Natural glasses: analogues for radioactive waste forms. *In* Scientific Basis for Nuclear Waste Management **1** (G.J. McCarthy, ed.). Plenum Press, New York, N.Y. (57-68).

________ (1992): Preface – Thematic issue on nuclear waste. *J. Nucl. Mater.* **190**, vii-ix.

________ (1993): The long-term performance of nuclear waste forms: natural materials – three case studies. *In* Scientific Basis for Nuclear Waste Management XVI (C.G. Interrante & R.T. Pabalan, eds.). *Mater. Res. Soc. Proc.* **294**, 559-568.

________ (1994): The metamict state: 1993 – the centennial. *Nucl. Instrum. Methods Phys. Res.* **B91**, 22-29.

________ (1999a): Nuclear waste forms for actinides. *Proc. Natl. Acad. Sci. USA* **96**, 3432-3439.

________ (1999b): Radioactivity in the 20th Century. *In* Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R.J. Finch, eds.). *Rev. Mineral.* **38**, 1-21.

________ (1999c): Less geology in the geological disposal of nuclear waste. *Science* **286**, 415-417.

___________, HAAKER, R.F. & LUTZE, W. (1982): Leachability of zircon as a function of alpha dose. *In* Scientific Basis for Nuclear Waste Management **V** (W. Lutze, ed.). *Mater. Res. Soc., Symp. Proc.* **11**, 389-397.

________, LUTZE, W. & WEBER, W.J. (1995c): Zircon: a host-phase for the disposal of weapons plutonium. *J. Mater. Res.* **10**, 243-246.

________, MELDRUM, A., WANG, LU-MIN & WANG, SHI-XIN (2000): Radiation-induced amorphization. *In* Transformation Processes in Minerals (S.A.T. Redfern & M.A. Carpenter, eds.). *Rev. Mineral. Geochem.* **39**, 317-361.

________, TIERNEY, M.S., KONIKOW, L.F. & RECHARD, R.P. (1999): Performance assessments of nuclear waste repositories: a dialogue on their value and limitations. *Risk Analysis* **19**, 933-958.

________, WEBER, W.J. & CLINARD, F.W., JR. (1995a): Radiation effects in nuclear waste forms for high-level radioactive waste. *Progress in Nuclear Energy* **29**, 63-127.

________, ________ & LUTZE, W. (1995b): Crystalline ceramics: waste forms for the disposal of weapons plutonium. *In* Disposal of Weapon Plutonium Approaches and Prospects (E.R. Merz & W.J. Walter, eds.). Kluwer Academic Publishers, Dordrecht, The Netherlands (65-83).

FARGES, F. (1994): The structure of metamict zircon: a temperature-dependent EXAFS study. *Phys. Chem. Minerals* **20**, 504-514.

________ & CALAS, G. (1991): Structural analysis of alpha-radiation damage in zircon and thorite: a X-ray absorption study. *Am. Mineral.* **76**, 60-73.

FARNAN, I. & SALJE, E.K.H. (2001): The degree and nature of radiation damage in zircon observed by ^{29}Si nuclear magnetic resonance. *J. Appl. Phys.* **89**, 2084-2090.

FINCH, R.J. & EWING, R.C. (1992): The corrosion of uraninite under oxidizing conditions. *J. Nucl. Mater.* **190**, 133-156.

FROUDE, D.O., IRELAND, T.R., KINNY, P.D., WILLIAMS, I.S., COMPSTON, W., WILLIAMS, I.R & MYERS, J.S. (1983): Ion microprobe identification of 4,100–4,200 Myr-old terrestrial zircons. *Nature* **304**, 616-618.

GARMON, L. (1981): The box within a box within a box. *Science News* **120**, 396-399.

GARRICK, B.J. & KAPLAN, S. (1994): Quantitative performance assessment of nuclear waste repositories. *U.S. Nuclear Waste Technical Review Board, Tech. Note.*

GENTRY, R.V., SWORSKI, T.J., MCKOWN, H.S., SMITH, D.H., EBY, R.E. & CHRISTIE, W.H. (1982): Differential lead retention in zircons: implications for nuclear waste containment. *Science* **216**, 296-298.

GONG, W.L., LUTZE, W. & EWING, R.C. (2000): Zirconia ceramics for excess weapons plutonium waste. *J. Nucl. Mater.* **277**, 239-249.

________, NAZ, S., LUTZE, W., BUSCH, R., PRINJA, A. & STOLL, W. (2001): Safe disposal of surplus plutonium. *J. Nucl. Mater.* **279** (in press).

GU, BINXI, WANG, LU-MIN & EWING, R.C. (2000): Effect of amorphization on the Cs ion exchange and retention capacity of zeolite-NaY. *J. Nucl. Mater.* **278**, 64-72.

HAAKER, R.F. & EWING, R.C. (1981): Naturally occurring crystalline phases: analogues for radioactive waste forms. *Pacific Northwest Lab.* (*Richland, Washington*), **PNL-3505/UC-70**.

HANCHAR, J.M. & MILLER, C.F. (1993): Zircon zonation patterns as revealed by cathodoluminescence and backscattered electron images: implications for interpretation of complex crustal histories. *Chem. Geol.* **110**, 1-13.

HARKER, A.B. & FLINTOFF, J.F. (1990): Polyphase ceramic for consolidating nuclear waste compositions with high Zr–Cd–Na content. *J. Am. Ceram. Soc.* **73**, 1901-1906.

HATCH, L.P. (1953): Ultimate disposal of radioactive wastes. *American Scientist* **41**, 410-421.

HEDIN, A. (1997): Spent nuclear fuel – how dangerous is it? *SKB Tech. Rep.* **97-13**.

HELEAN, K.B. (1997): *Zircon Dissolution*. M.S. thesis, Univ. New Mexico, Albuquerque, New Mexico.

________, LUTZE, W. & EWING, R.C. (1999): Dissolution studies of inert materials. In Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries **IV** (J.C. Marra & G.T. Chandler, eds.). *Am. Ceram. Soc., Ceram. Trans.* **93**, 297-304.

HENCH, L.L., CHARLES, R.J., COOPER, A.R., EWING, R.C., HUTCHINS, J.R., READEY, D.W., VERSNYDER, F.L. & WIDERHORN, S.M. (1981): The evaluation and selection of candidate high level waste forms. Alternative waste form peer review panel. *Nat. Tech. Information Serv., Rep.* **3**, **USDOE/TIC-11472**.

VON HIPPEL, F.N. (1998): How to simplify the plutonium problem. *Nature* **394**, 415-416.

HOLLAND, H.D. & GOTTFRIED, D. (1955): The effect of nuclear radiation on the structure of zircon. *Acta Crystallogr.* **8**, 291-300.

HUTTON, C.O. (1950): Studies of heavy detrital minerals. *Geol. Soc. Am., Bull.* **61**, 635-716.

IRELAND, T.R. & WLOTZKA, F. (1992): The oldest zircons in the solar system. *Earth Planet. Sci. Lett.* **109**, 1-10.

JANECZEK, J., EWING, R.C., OVERSBY, V.M. & WERME, L. (1996): Uraninite and UO_2 in spent nuclear fuel: a comparison. *J. Nucl. Mater.* **238**, 121-130.

KAMO, S.L. & KROGH, T.E. (1995): Chicxulub crater source for shocked zircon crystals from the Cretaceous–Tertiary boundary layer, Saskatchewan: evidence from new U–Pb data. *Geology* **23**, 281-284.

VON KELLER, C. (1963): Unteruchungen über die Germanate und Silikate des Typs ABO_4 der vierwertigen Elemente Thorium bis Americium. *Nukleonik* **5**, 41-48.

KERR, R.A. (1979): Nuclear waste disposal: alternatives to solidification in glass proposed. *Science* **204**, 289-291.

KONIKOW, L.F. (1986): Predictive accuracy of a groundwater model – lessons from a postaudit. *Ground Water* **24**, 173-184.

________ & EWING, R.C. (1999): Is a probabilistic performance assessment enough? *Ground Water* **37**, 481-482.

KROGH, T.E. (1995): Dating polymetamorphic rocks. *Geotimes* **40**, 20-22.

________ & DAVIS, G.L. (1975): Alteration in zircons and differential dissolution of altered and metamict zircon. *Carnegie Inst. Wash., Year Book* **74**, 619-623.

________, KAMO, S.L., SHARPTON, V.L., MARIN, L.E. & HILDEBRAND, A.R. (1993): U–Pb ages of single shocked zircons linking distal K/T exjecta to the Chicxulub crater. *Nature* **366**, 731-734.

LANGMUIR, D. (1997): *Aqueous Environmental Geochemistry*. Prentice Hall, Upper Saddle River, New Jersey.

LEE, J.K.W. (1993): Problems and progress in the elucidation of U and Pb transport mechanisms in zircon. *In* Defects and Processes in the Solid State: Geoscience Applications: The McLaren Volume (J.N. Boland & J.D. Fitz Gerald, J.D., eds.). Elsevier, Amsterdam, The Netherlands (423-446).

________ & TROMP, J. (1995): Self-induced fracture generation in zircon. *J. Geophys. Res.* **100**, 17,753-17,770.

________, WILLIAMS, I.S. & ELLIS, D.J. (1997): Pb, U and Th diffusion in natural zircon. *Nature* **390**, 159-161.

LIU, D.Y., NUTMAN, A.P., COMPSTON, W., WU, J.S. & SHEN, Q.H. (1992): Remnants of $\geq$3800 Ma crust in the Chinese part of the Sino-Korean craton. *Geology* **20**, 339-342.

LUDWIG, K.R., ZARTMAN, R.E. & GOLDICH, S.S. (1984): Lead retention in zircons. *Science* **223**, 835.

LUMPKIN, G.R. & EWING, R.C. (1996): Geochemical alteration of pyrochlore group minerals: betafite subgroup. *Am. Mineral.* **81**, 1237-1248.

LUTZE, W. & EWING, R.C., eds. (1988): *Radioactive Waste Forms for the Future.* North-Holland, Amsterdam, The Netherlands.

MAAS, R., KINNY, P.D., WILLIAMS, I.S., FROUDE, D.O. & COMPSTON, W. (1992): The Earth's oldest known crust: a geochronological and geochemical study of 3900–4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Australia. *Geochim. Cosmochim. Acta* **56**, 1281-1300.

MARK, J.C. (1993): Explosive properties of reactor-grade plutonium. *Science & Global Security* **4**, 111-128.

MCCARTHY, G.J. (1977): High level waste ceramics: materials considerations, process simulation and product characterization. *Nuclear Technology* **32**, 92-105.

MCLAREN, A.C., FITZ GERALD, J.D. & WILLIAMS, I.S. (1994): The microstructure of zircon and its influence on the age determination from Pb/U isotopic ratios measured by ion microprobe. *Geochim. Cosmochim. Acta* **58**, 993-1005.

MELDRUM, A., BOATNER, L.A. & EWING, R.C. (1997b): Displacive radiation effects in the monazite- and zircon-structure orthophosphates. *Phys. Rev. B* **56**, 13805-13814.

________, ________, WANG, LU-MIN & EWING, R.C. (1997a): Ion-beam-induced amorphization of $LaPO_4$ and $ScPO_4$. *Nucl. Instrum. Methods Phys. Res.* **B127/128**, 160-165.

________, ________, WEBER, W.J. & EWING, R.C. (1998b): Radiation damage in zircon and monazite. *Geochim. Cosmochim. Acta* **62**, 2509-2520.

________, ________, ZINKLE, S.J., WANG, SHI-XIN, WANG, LU-MIN & EWING, R.C. (1999b): Effects of dose rate and temperature on the crystalline-to-metamict transformation in the ABO_4 orthosilicates. *Can. Mineral.* **37**, 207-221.

________, ZINKLE, S.J., BOATNER, L.A. & EWING, R.C. (1998a): A transient liquid-like phase displacement-cascades of zircon, hafnon, and thorite. *Nature* **395**, 56-58.

________, ________, ________ & ________ (1999a): Heavy-ion irradiation effects in the ABO_4 orthosilicates: decomposition, amorphization, and recrystallization. *Phys. Rev. B* **59**, 3981-3992.

MUMPTON, F.A. & ROY, R. (1961): Hydrothermal stability studies of the zircon–thorite group. *Geochim. Cosmochim. Acta* **21**, 217-238.

MURAKAMI, T., CHAKOUMAKOS, B.C., EWING, R.C., LUMPKIN, G.R. & WEBER, W.J. (1991): Alpha-decay event damage in zircon. *Am. Mineral.* **76**, 1510-1532.

NASDALA, L., PIDGEON, R.T. & WOLF, D. (1996): Heterogeneous metamictization of zircon on a microscale. *Geochim. Cosmochim. Acta* **60**, 1091-1097.

NATIONAL RESEARCH COUNCIL (1994): *Management and Disposition of Excess Weapons Plutonium*. National Academy of Sciences, Washington, D.C.

NATIONAL RESEARCH COUNCIL (1995): *Management and Disposition of Excess Weapons Plutonium: Reactor-Related Options*. National Academy of Sciences, Washington, D.C.

NUTMAN, A.P., FRIEND, C.R.L., KINNY, P.D. & MCGREGOR, V.R. (1993): Anatomy of an Early Archean gneiss complex: 3900 to 3600 Ma crustal evolution in southern West Greenland. *Geology* **21**, 415-418.

OLIVER, W.C., MCCALLUM, J.C., CHAKOUMAKOS, B.C. & BOATNER, L.A. (1994): Hardness and elastic modulus of zircon as a function of heavy-particle irradiation dose. II. Pb-ion implantation damage. *Radiation Effects and Defects in Solids* **132**, 131-141.

OVERSBY, V.M., MCPHEETERS, C.C., DEGUELDRE, C. & PARATTE, J.M. (1997): Control of civilian plutonium inventories using burning in a non-fertile fuel. *J. Nucl. Mater.* **245**, 17-26.

ÖZKAN, H. (1976): Effect of nuclear radiation on the elastic moduli of zircon. *J. Appl. Phys.* **47**, 4772-4779.

PIDGEON, R.T., O'NEIL, J.R. & SILVER, L.T. (1966): Uranium and lead isotopic stability in a metamict zircon under experimental hydrothermal conditions. *Science* **154**, 1538-1540.

POIROT, I.S., KOT, W.K., EDELSTEIN, N.M., ABRAHAM, M.M., FINCH, C.B. & BOATNER, L.A. (1989): Optical study and analysis of Pu^{4+} in single crystals of $ZrSiO_4$. *Phys. Rev. B* **39**, 6388-6394.

________, ________, SHALIMOFF, G, EDELSTEIN, N., ABRAHAM, M.M., FINCH, C.B. & BOATNER, L.A. (1988): Optical and EPR investigations of Np^{4+} in single crystals of $ZrSiO_4$. *Phys. Rev. B* **37**, 3255-3264.

REEVE, D.D., LEVINS, D.M., WOOLFREY, J.L. & RAMM, E.J. (1984): Immobilisation of high-level radioactive waste in SYNROC. *In* Advances in Ceramics **8** (G.G. Wicks & W.A. Ross, eds.). American Ceramic Society, Columbus, Ohio (200-208).

RICHARDSON, J.A. (1997): United States high-level radioactive waste management programme: current status and plans. *Proc. Instn. Mech. Engrs.* **211 A**, 381-392.

RIGGS, N.R., LEHMAN, T.M., GEHRELS, G.E. & DICKINSON, W.R. (1996): Detrital zircon link between headwaters and terminus of the Upper Triassic Chinle–Dockum paleoriver system. *Science* **273**, 97-100.

RINGWOOD, A.E. (1978): *Safe Disposal of High-Level Nuclear Reactor Wastes: a New Strategy*. Australian National University Press, Canberra, Australia.

________ (1985): Disposal of high-level nuclear wastes: a geological perspective. *Mineral. Mag.* **49**, 159-176.

________, KESSON, S.E., WARE, N.G., HIBBERSON, W. & MAJOR, A. (1979): Immobilisation of high level nuclear reactor wastes in SYNROC. *Nature* **278**, 219-223.

RÍOS, S., MALCHEREK, T., SALJE, E.K.H. & DOMENEGHETTI, C. (2000b): Localized defects in radiation-damaged zircon. *Acta Crystallogr.* **B56**, 947-952.

________ & SALJE, E.K.H. (1999): Diffuse X-ray scattering from weakly metamict zircon. *J. Phys.: Condensed Matter* **11**, 8947-8956.

________, ________, ZHANG, M. & EWING, R.C. (2000a): Amorphization in zircon: evidence for direct impact damage. *J. Phys.: Condensed Matter* **12**, 2401-2412.

ROBERTS, M.P. & FINGER, F. (1997): Do U–Pb zircon ages from granulites reflect peak metamorphic conditions? *Geology* **25**, 319-322.

ROBINSON, K., GIBBS, G.V. & RIBBE, P.H. (1971): The structure of zircon: a comparison with garnet. *Am. Mineral.* **56**, 782-790.

ROY, R. (1975): Ceramic science of nuclear waste fixation. *Am. Ceram. Soc., Bull.* **54**, 459 (abstr.).

________ (1977): Rational molecular engineering of ceramic materials. *J. Am. Ceram. Soc.* **60**, 358-359.

________ (1979): Science underlying radioactive waste management: status and needs. *In* Scientific Basis for Nuclear Waste Management **1** (G.J. McCarthy, ed.). Plenum Press, New York, N.Y. (1-20).

RUNDE, W. (2000): The chemical interactions of actinides in the environment. *Los Alamos Science* **26**, 338-357.

SALJE, E.K.H., CHROSCH, J. & EWING, R.C. (1999): Is "metamictization" of zircon a phase transition? *Am. Mineral.* **84**, 1107-1116.

SICKAFUS, K.E., HANRAHAN, R.J., JR., MCCLELLAN, K.J., MITCHELL, J.N., WETTELAND, C.J., BUTT, D.P., CHODAK, P., III, RAMSEY, K.B., BLAIR, T.H., CHIDESTER, K., MATZKE, H., YASUDA, K., VERRALL, R.A. & YU, NING (1999): Burn and bury option for plutonium. *Am. Ceram. Soc. Bull.* **78**(1), 69-74.

________, MINERVINI, L., GRIMES, R.W., VALDEZ, J.A., ISHIMARU, M., LI, F., MCCLELLAN, K.J. & HARTMANN, T. (2000): Radiation tolerance of complex oxides. *Science* **289**, 748-751.

SINHA, K.A., WAYNE, D.M. & HEWITT, D.A. (1992): The hydrothermal stability of zircon: preliminary experimental and isotopic studies. *Geochim. Cosmochim. Acta* **56**, 3551-3560.

SPEER, J.A. (1982): Zircon. *In* Orthosilicates (2nd edition; P.H. Ribbe, ed.). *Rev. Mineral.* **5**, 67-135.

________ & COOPER, B.J. (1982): Crystal-structure of synthetic hafnon, $HfSiO_4$, comparison with zircon and the actinide orthosilicates. *Am. Mineral.* **67**, 804-808.

STOLL, W. (1998): What are the options for disposition of excess weapons plutonium? *Mater. Res. Bull.* **23**(3), 6-16.

SUZUKI, K. (1987): Discordant distribution of U and Pb in zircon of Naegi granite: a possible indication of Rn migration through radiation damage. *Geochem. J.* **21**, 173-182.

TAYLOR, M. & EWING, R.C. (1978): The crystal structures of the $ThSiO_4$ polymorphs: huttonite and thorite. *Acta Crystallogr.* **B34**, 1074-1079.

TOLE, M.P. (1985): The kinetics of dissolution of zircon ($ZrSiO_4$). *Geochim. Cosmochim. Acta* **49**, 453-458.

TRACHENKO, K., DOVE, M.T. & SALJE, E.K.H. (2000): Modelling the percolation-type transition in radiation damage. *J. Appl. Phys.* **87**, 7702-7707.

VANCE, E.R. (1975): α-recoil damage in zircon. *Radiation Effects* **24**, 1-6.

WANG, LU-MIN & EWING, R.C. (1992a): Detailed in situ study of ion beam-induced amorphization of zircon. *Nucl. Instrum. Methods Phys. Res.* **B65**, 324-329.

________ & ________ (1992b): Ion beam induced amorphization of complex ceramic materials – minerals. *Mater. Res. Soc. Bull.* **XVII**, 38-44.

________, ________, WEBER, W.J. & EBY, R.K. (1993): Temperature and ion-mass dependence of amorphization dose for ion beam irradiated zircon ($ZrSiO_4$). *In* Beam–Solid Interactions: Fundamentals and Applications (M. Nastasi, L.R. Harriott, N. Herbots & R.S. Averback, eds.). *Mater. Res. Soc., Proc.* **279**, 451-456.

WANG, SHI-XIN, BEGG, B.D., WANG, LU-MIN, EWING, R.C., WEBER, W.J. & GOVIDAN KUTTY, K.V. (1999): Radiation stability of gadolinium zirconate: a waste form for plutonium disposition. *J. Mater. Res.* **14**, 4470-4473.

WATSON, E.B., CHERNIAK, D.J., HANCHAR, J.M., HARRISON, T.M. & WARK, D.A. (1997): The incorporation of Pb into zircon. *Chem. Geol.* **141**, 19-31.

WAYNE, D.M. & SINHA, A.K. (1988): Physical and chemical response of zircons to deformation. *Contrib. Mineral. Petrol.* **98**, 109-121.

________ & ________ (1992): Stability of zircon U–Pb systematics in a greenschist-grade mylonite: an example from the Rockfish Valley fault zone, central Virginia, USA. *J. Geol.* **100**, 593-603.

WEBER, W.J. (1991): Self-radiation damage and recovery in Pu-doped zircon. *Radiation Effects and Defects in Solids* **115**, 341-349.

_______ & EWING, R.C. (2000): Plutonium immobilization and radiation effects. *Science* **289**, 2051-2052.

________, ________, CATLOW, C.R.A., DIAZ DE LA RUBIA, T., HOBBS, L.W., KINOSHITA, C., MATZKE, H., MOTTA, A.T., NASTASI, M., SALJE, E.K.H., VANCE, E.R. & ZINKLE, S.J. (1998): Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium. *J. Mater. Res.* **13**, 1434-1484.

________, ________ & MELDRUM, A. (1997): The kinetics of alpha-decay-induced amorphization in zircon and apatite containing weapons-grade plutonium or other actinides. *J. Nucl. Mater.* **250**, 147-155.

________, ________ & WANG, LU-MIN (1994): The radiation-induced crystalline-to-amorphous transition in zircon. *J. Mater. Res.* **9**, 688-698.

________ & MAUPIN, G.D. (1988): Simulation of radiation-damage in zircon. *Nucl. Instrum. Methods Phys. Res.* **B32**, 512-515.

WERME, L.O., BJÖRNER, I.K., BART, G., ZWICKY, H.-U., GRAMBOW, B., LUTZE, W., EWING, R.C. & MAGRABI, C. (1990): Chemical corrosion of highly radioactive borosilicate nuclear waste glass under simulated repository conditions. *J. Mater. Res.* **5**, 1130-1146.

WILDE, S.A., VALLEY, J.W., PECK, W.H. & GRAHAM, C.M. (2001): Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409**, 175-178.

WOODHEAD, J.A., ROSSMAN, G.R. & SILVER, L.T. (1991): The metamictization of zircon: radiation dose-dependent structural characteristics. *Am. Mineral.* **76**, 74-82.

ZHANG, M., SALJE, E.K.H., EWING, R.C., FARNAN, I., RÍOS, S., SCHLÜTER, J. & LEGGO, P. (2001): Alpha-decay damage and recrystallization in zircon: evidence for an intermediate state from infrared spectroscopy. *J. Phys.: Condensed Matter* **12**, 5189-5199.

________, ________, FARNAN, I., GRAEME-BARBER, A., DANIEL, P., EWING, R.C., CLARK, A.M. & LEROUX, H. (2000): Metamictization of zircon: Raman spectroscopic study. *J. Phys.: Condensed Matter* **12**, 1915-1925.

Received June 15, 1999, revised manuscript accepted March 10, 2001.