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

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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., 99Tc, 129I, 79Se and 135Cs) and actinides (e.g., 239Pu and 237Np) 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., 99Tc, 129I, 79Se et 135Cs) et certains actinides (e.g., 239Pu et 237Np) 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 un banc 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 immobiliser le plutonium d’armements nucléaires démantelé. 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.

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

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This paper was presented at the 17th 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”.

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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., 239Pu, 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 m³ (100 million gallons) of HLW have a total radioactivity of 960 million Curies. The greatest volumes (340,000 m³) 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 238Pu, 131Sm and 241Am. After 50,000 years, most of the activity will be associated with longer-lived radionuclides such as 239Pu and 240Pu. 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 m³ are stored retrievably at DOE sites and are destined for disposal at the Waste Isolation Pilot Plant in New Mexico (Ahearnre 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) (Ahearnre 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

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<th>Table 1. Estimated Global Plutonium Inventory in 1998</th>
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<td>Estimated World Inventory (+70 metric tonnes/year production)</td>
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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 timescale. 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 (\(^{137}\text{Cs}\) and \(^{90}\text{Sr}\)) and

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**Waste Package**

- Engineered Barrier
- Geosphere
- Biosphere

**Probabilistic Events**

- Climate Change
- Volcanic Activity
- Seismic Events
- Human Intrusion

**Damage Indices**

- Dose (mrem) vs Time
- Activity (\(\mu\text{Ci}\)) vs Time
- Releases at discrete times
  - Probability
    - 1
    - 2
    - 3
  - Curies
  - Risk Curves
  - Frequency of Exceedance
  - Number of Health Effects

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**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).
The long half-life of 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$_{2+}$ aqueous species, with the former predominating in oxidized natural waters. In addition, in the $3^+$, $5^+$...
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., H₂O₂), 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 137Cs and 90Sr (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 239Pu (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 239Pu decays to 235U presents an additional challenge for the durability of the waste form, but the greater critical mass of 235U combined with the possibility of dilution of 235U by 238U 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.
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 ($Ih$/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 ($HIsiO_4$), 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 $HIsiO_4$, 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 ($A^{4+}$); data from von Keller (1963) after Speer (1982).
The zircon structure is part of a larger class of ABO₃ structure types (silicates and phosphates) and is closely related to the structure of monazite, CePO₄₃, 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 (Poiri 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 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, Claué-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, Krogh et al. 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 m²s⁻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 waste-form phases, 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 periodically 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 239Pu 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, HfSiO₄. Thus, neutron-absorbing nuclides may be incorporated into the zircon structure; however, the neutron absorber must remain within atomic scale proximity of the fission radionuclide (239Pu or 235U). Recent determinations of diffusion rates for tetravalent cations (Th, U and Hf) give diffusivities in the order of 10⁻²² to 10⁻²⁰ m²s⁻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, Pu⁴⁺ is expected to have a similar diffusivity, although slightly faster diffusion is expected because of its smaller ionic radius. Thus, Pu⁴⁺ 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 m²s⁻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 10⁻⁸ moles/L (0.1 ppb) at 25°C (Tolle 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 ZrO₂ and ZrSiO₄ (Tolle 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 = 10⁻⁹ moles/m²d at 80°C, pH = 5, Tolle 1985), with the rate of long-term dissolution of a nuclear-waste borosilicate glass [R = 10⁻⁵ moles/m²d (≈ 10⁻⁷ g/m²d) 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 (Tolle 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 ZrO₂ 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·m⁻²·day⁻¹ at 250°C, 1.7 × 10⁻⁴ g·m⁻²·day⁻¹ at 200°C and 7.1 × 10⁻⁴ g·m⁻²·day⁻¹ at 120°C. The rate extrapolated to 90°C is 4.6 × 10⁻³ g·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 × 10¹ⁱ to 5 × 10¹⁵ ions/cm² (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%) (Ozkam 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 ²³⁹Pu and its daughter products (e.g., ²³⁵U) in an actinide-bearing zircon. Depending on the waste load, significant doses (>10¹⁸ α-decay events/g) accumulate, and crystalline phases become aperiodic in relatively short periods of time, 10²² 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 ²³⁸Pu or ²⁴⁴Cm (that reach α-decay doses of 10¹⁹ 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 ²³⁵U recoil from decay of ²³⁹Pu) 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 (Webber 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 10¹⁸ to 10¹⁹ 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), ²³⁸Pu-doped zircon (half-life = 87.7 a), up to doses of 0.7 dpa in 6.5 years (Webber 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
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 (HfSiO₄), thorite (tetragonal ThSiO₄) and huttonite (monoclinic ThSiO₄) 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: ZrO₂, HfO₂ or ThO₂ plus amorphous SiO₂ (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 (Fargès & Calas 1991, Fargès 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), ²⁹Si 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 SiO₄ polyhedra (Fargès 1994). The principal distortions mainly affect the ZrO₆ 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
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 ($400$–$500^\circ C$) 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 ($4 \pm 2$ 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 ($1.2 \times 10^{19}$ $\alpha$-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
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 239Pu 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 $5 \times 10^{18}$ 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. 7. Critical dose for amorphization versus storage temperature for silicate apatite and zircon containing 10 wt. % 239Pu (after Weber et al. 1997).](image_url)

![Fig. 8. Minimum temperature for storage of zircon containing 10 wt.% and 2 wt.% 239Pu, 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).](image_url)
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 SiO₂-rich and ZrO₂-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 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 UO₂ in spent nuclear fuel in connection with the problem of creating a crystalline actinide waste form for disposal. 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.

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