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The kinetics of alpha-decay-induced amorphization in zircon and apatite containing weapons-grade plutonium or other actinides

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Abstract

Zircon and apatite form as actinide host phases in several high-level waste forms and have been proposed as host phases for the disposition of excess weapons-grade Pu and other actinides. Additionally, closely-related structure types appear as actinide-bearing phases among the corrosion products of spent nuclear fuel and high-level waste glasses. Self-radiation damage from α-decay of the incorporated Pu or other actinides can affect the durability and performance of these actinide-bearing phases. For both zircon and apatite, these effects can be modeled as functions of storage time and repository temperature and validated by comparison with data from natural occurrences. Natural zircons and apatites, with ages up to 4 billion years, provide abundant evidence for their long-term durability because of their wide spread use in geochronology and fission-track dating. Detailed studies of natural zircons and apatites, ^{238}Pu-containing zircon, a ^{244}Cm-containing silicate apatite, and ion-irradiated zircon, natural apatite and synthetic silicate apatites provide a unique basis for the analysis of α-decay effects over broad time scales. Models for α-decay effects in zircon and apatite are developed that show α-decay of Pu and other actinides will lead to a crystalline-to-amorphous transformation in zircon, but not in apatite, under conditions typical of a repository, such as the Yucca Mountain site. © 1997 Elsevier Science B.V.

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1. Introduction

A challenge facing the world community is the stabilization and immobilization of high-level radioactive waste (HLW) and special high-actinide waste streams into solid waste forms that are destined for geologic repositories. These wastes include the HLW stored in tanks at US. Department of Energy sites, an estimated 100 metric tons of weapons-grade plutonium recovered from the dismantling of several thousand nuclear weapons under the first and second Strategic Arms Reduction Treaties, several tens of tons of plutonium residues/scraps, and other high-actinide waste streams. Potential waste forms include glasses, glass-ceramics and crystalline ceramics, and in the case of glass-ceramic or crystalline-ceramic waste forms, the actinides, including plutonium, and many fission products can be stabilized in crystalline ceramic phases. Two such phases of interest are zircon [1,2] and apatite [2–6], which readily accommodate actinides and some fission products in their structures and are well-known as extremely durable mineral phases. In addition to being primary, actinide-bearing waste form phases, zircon and apatite (or closely related structure types) have been identified among the alteration (i.e. corrosion) products of HLW glasses [7–9] and the UO_2 of spent nuclear fuel [10].

Long-term durability is an important consideration in HLW and actinide disposition, but it is a particularly important consideration in Pu disposition because the fissile ^{239}Pu (half-life of 2.41×10^4 years [11]) and its fissile daughter, ^{235}U (half-life of 7.04×10^8 years [11]), present a risk of nuclear criticality (however small) for exceed-

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ingly long time periods; durability also ensures that neutron absorbers (e.g. Hf or Gd), which are also readily incorporated in the zircon and apatite structures, stay with the fissile nuclides. High Pu incorporation (5 to 20 wt%) into the waste form is desirable to minimize the total volume necessary for disposition; however, lower Pu loading (1 wt%) may be dictated by criticality concerns. In a near-surface geologic repository, temperatures are expected to decrease from initial values that could range as high as 250°C at emplacement to values less than 100°C after several hundred years [12].

Zircon ($ZrSiO_4$) forms as one of several crystalline phases in glass ceramic waste forms [13–17] and has been proposed as a durable ceramic for the immobilization and disposal of both excess weapons-grade Pu in the United States [1,2] and high-actinide wastes in Russia [18,19]. Zircon is also a prominent actinide-bearing phase formed by crystallization from the core melt at the Chernobyl Nuclear Power Plant [18,20] and has been observed as a corrosion product on HLW glass [7]. Natural zircon is an extremely durable mineral and individual grains undergo many cycles of weathering and erosion followed by transport and deposition with limited physical abrasion or dissolution. Zircons have been dated at 4.1 to 4.3 billion years [21–23], the oldest terrestrial minerals yet dated. The widespread distribution of zircon in the continental crust, its tendency to concentrate a wide variety of impurities (such as hafnium, lanthanides and actinides), the very low diffusion and loss rates of these impurities and decay products (e.g. Pb) and its resistance to chemical and physical degradation have made zircon one of the most useful accessory minerals in geologic studies. High Pu (10 wt%) [24–27] and U (> 10 wt%) [18] incorporation in zircon have been demonstrated and extensive substitution of Pu for Zr is suggested by the synthesis of isostructural $PuSiO_4$ [28].

Natural apatites, $Ca_{10}(PO_4)_6(OH, Cl, F)_2$, are the most abundant of the phosphate minerals [29], attesting to the durability of this structure. The durability of natural apatites is also well demonstrated by apatites from the Oklo natural reactor site in the Republic of Gabon, Africa; these apatites have retained a significant ^{235}U enrichment [4] and high fission-product contributions in their structure [4,30] despite exposure to the geologic environment for nearly 2 billion years. Apatite phases, analogous to natural apatites, have been observed in glass-ceramic waste forms [31] and as recrystallized alteration products on the surfaces of HLW glasses as a result of aqueous corrosion [8,9]. The latter data indicate the inherent stability of apatite relative to HLW glasses [31]. Rare-earth silicates with the apatite structure also have been observed as actinide host phases in a devitrified borosilicate HLW glass [32], a multiphase ceramic waste form [33], a glass- ceramic waste form [34] and a cement waste form [35]. These apatites are generally of the composition $Ca_{4-x}RE_{6+x}(SiO_4)_{6-y}(PO_4)_y(F, OH, O)_2$ (where RE = La, Ce, Pr, Nd, Pm, Sm, Eu and Gd) and are isostructural with natural apatite. More recently, the apatite structure has been proposed as a host phase for the disposition of Pu and high-actinide waste [2–6].

2. Radiation effects

As actinide host phases, zircon and apatite will experience self-radiation damage from α-decay. The α-decay of U/Th impurities in natural zircon minerals [27,36–39] and of Th impurities in several natural apatite minerals, containing appreciable rare earths and silica [40,41], leads to a radiation-induced, crystalline-to-amorphous (metamict) transformation. The α-decay of ^{244}Cm incorporated into the apatite phases that formed in a devitrified HLW glass and in a multiphase ceramic waste form also resulted in the transformation of the crystalline apatite structure to an amorphous state [32,33,42]. Detailed studies of radiation effects in natural zircons [24–27,36–39] and zircon incorporating 10 wt% ^{238}Pu [24–27], as well as studies of ion-beam irradiated zircon [27] over a wide range of temperatures, have resulted in a comprehensive understanding of amorphization in zircon that provides a unique basis for long-term modeling. Likewise, studies of radiation-induced amorphization in apatite phases from the decay of incorporated ^{244}Cm [26,42–45] and from ion-beam irradiation [42,46–49] provide a similar understanding and basis for modeling long-term behavior.

Radiation-induced amorphization in zircon and apatite structures occurs only below critical temperatures that are dependent on structure, composition and irradiation conditions, as illustrated in Fig. 1 for zircon structure types [27,50] and in Fig. 2 for apatite structure types [47,48]. In general, the phosphate compositions exhibit distinctly lower critical temperatures for amorphization than for the silicates, as well as lower doses for complete amorphization at lower temperatures. Amorphization in zircon and apatite is

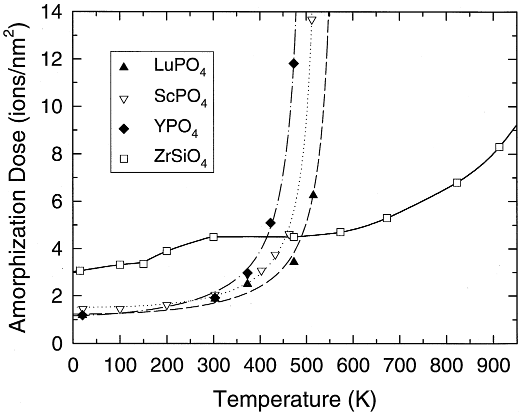

Fig. 1. Critical amorphization dose as a function of temperature for zircon [26] and three phosphate materials [49] with the zircon structure irradiated with 0.8 and 1.5 MeV Kr^+ ions.

accompanied by changes in volume [24–27,37–43], dissolution rate [39,44,51–53], mechanical properties [45,54,55] and stored energy [43,56]. Results from a study of natural zircons [57] suggest that the amorphous state is apparently stable to further radiation effects for a tenfold increase in dose over several billion years. Thus, the radiation-induced amorphous state represents the worst case condition for any performance assessment of waste form behavior. An important objective of the models developed here is to predict the time scales and temperatures over which amorphization will occur in zircon and apatite phases used for Pu disposition; however, the results are also relevant to the disposition of HLW and other high-actinide waste streams, where zircon or apatite phases may incorporate actinides.

As waste forms for Pu disposition, zircon and apatite will experience self-radiation damage from the α-decay of the ^{239}Pu, which releases a 5.16 MeV α-particle and a 0.086 MeV ^{235}U recoil nucleus. The cumulative α-decay dose (i.e. α-decay events/g) in zircon or apatite for several relevant Pu loadings are calculated and shown in Fig. 3. The cumulative dose rises rapidly during the first 200 000 years of storage as the ^{239}Pu decays to the longer-lived and fissile ^{235}U. After 200 000 years, the decay of ^{239}Pu to ^{235}U will be nearly complete and the cumulative α-decay dose will achieve a temporary plateau. At longer storage times (> 10 million years), the cumulative α- decay dose again increases as the decay of the ^{235}U initiates a decay series (actinium series), which includes a sequence of seven α-decay events and results in the formation of stable ^{207}Pb.

In the α-decay of ^{239}Pu, nearly all the energy of the recoil nucleus is lost through elastic collisions with atoms in the structures of zircon and apatite, producing highly localized damage in displacement cascades, each containing about 1200 atomic displacements. The α-particle dissipates most of its energy by ionization processes, but undergoes sufficient elastic collisions along its path to produce on the order of 200 isolated atomic displacements. The interaction of the α-particles and recoil nuclei with the atomic structures of zircon and apatite can result in the simultaneous generation of both simple structural defects and amorphous (aperiodic) regions that exhibit loss of long-range order [24–27,45]. The eventual overlap of the amorphous regions leads to a completely amorphous state. Therefore, the effects of α-decay can lead to significant structural and physical changes in zircon and apatite that can impact not only their properties but the potential subsequent release of the ^{239}Pu or ^{235}U.

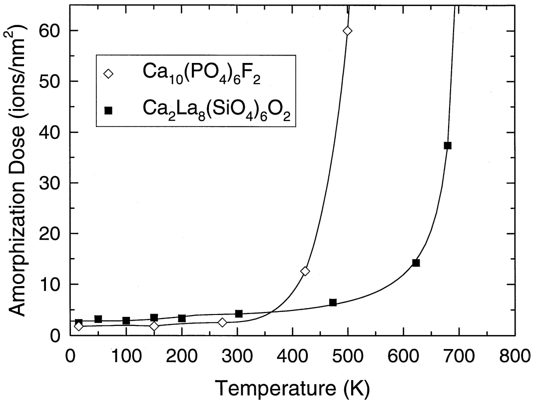

Fig. 2. Critical amorphization dose as a function of temperature in a silicate apatite [46,47] and a natural fluoroapatite (phosphate) [47] irradiated with 1.5 MeV Kr$^+$ ions.

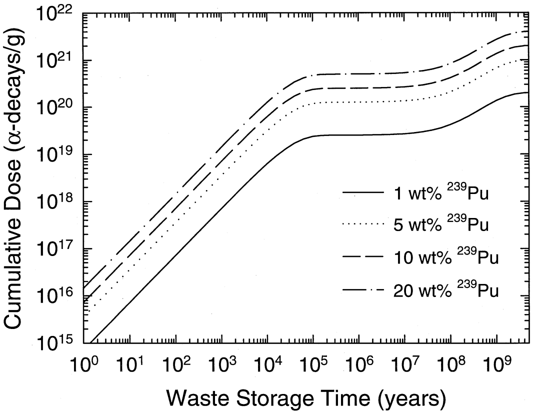

Fig. 3. Cumulative α-decay dose as a function of waste form storage time for zircon or apatite containing 1, 5, 10 and 20 wt% weapons-grade plutonium (^{239}Pu).

3. Proposed models

As discussed, α-decay in apatite and zircon generally leads to a radiation-induced, crystalline-to-amorphous transformation. In the absence of any significant recovery due to temperature or geologic time periods, the dependence of amorphous fraction, f_a, on cumulative α-decay dose, D, in silicate apatite at approximately 30°C has been previously shown [26], as illustrated in Fig. 4, to follow the direct impact model [58] for amorphization (i.e. amorphization occurring directly in a displacement cascade), which is given by the expression

$$f_a = 1 - \exp[-BD(t)], \tag{1}$$

where B is the average amorphous volume produced per decay event ($B = 4.4 \times 10^{-19}$ g). This interpretation is consistent with the changes in unit-cell volume and macroscopic swelling measured in the ^{244}Cm-doped (1.2 wt%) apatite [26]. Conventional transmission electron microscopy results of amorphization in the ^{244}Cm-doped apatite [45] and high resolution transmission electron microscopy (HRTEM) results of ion-beam-induced amorphization in apatite [49] are also consistent with direct

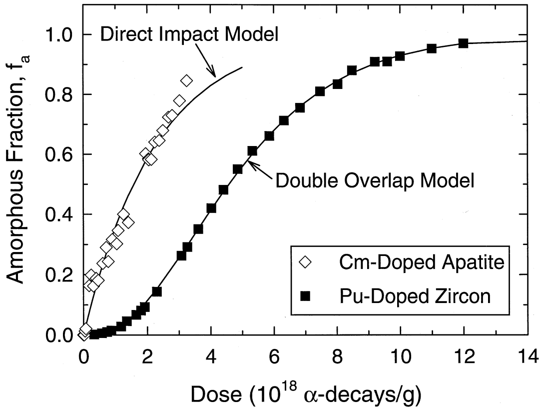

Fig. 4. Amorphous fraction as a function of cumulative α-decay dose for ^{244}Cm-doped apatite [25] and for 10 wt% ^{238}Pu zircon [23–26], along with model fits based on Eqs. (1) and (2), respectively.

impact amorphization. In the case of α-decay induced amorphization in 10 wt% ^{238}Pu zircon, the amorphous fraction, f_a, at 30°C has similarly been shown [24–27] (Fig. 4) to follow the double overlap model [58] for amorphization (i.e. amorphization occurring as a result of the local accumulation of high defect concentrations from the double overlap of displacement cascades), which is given by the expression

$$f_a = 1 - \left\{\left(1 + BD(t) + \left[BD(t)\right]^2/2\right)\exp\left[-BD(t)\right]\right\}, \tag{2}$$

where B is now related to the average damage volume per decay event ($B = 5.8 \times 10^{-19}$ g). The changes in unit-cell volume and macroscopic swelling for both natural zircons and ^{238}Pu zircon are consistent with the double overlap model [24,26]. HRTEM results of amorphization in both natural zircons and ion-irradiated zircons [27] are also consistent with amorphization occurring locally on a scale similar to cascade dimensions.

One model for the time, t, and temperature, T, dependence of direct impact amorphization has been previously derived [47] and is given by the expression

$$f_a = 1 - \exp\left[-BD(t) + K(T)t\right], \tag{3}$$

where $K(T)$ is the temperature dependent rate constant for annealing processes (e.g. epitaxial recrystallization) that decrease the size of the amorphous region produced per ion or per decay event. This model for the kinetics of direct-impact amorphization has been shown to provide a reasonable fit to the temperature dependence of amorphization in ion-irradiated apatites [47,48]. Since Eq. (3) can also be derived from Eq. (1) by including the annealing term $K(T)t$ (i.e. by substituting the term $BD(t) - K(T)t$ for $BD(t)$), we propose that a similar substitution in the expression for the double overlap model, Eq. (2), should yield a reasonable model for the kinetics of double-overlap amorphization in zircon. Such a model is given by the expression

$$f_a = 1 - \left\{\left(1 + BD(t)\ 0 - K(T)t + \left[BD(t) - K(T)t\right]^2/2\right)\exp\left[-BD(t) + K(T)t\right]\right\}, \tag{4}$$

where $K(T)$ is the rate constant for annealing processes that effectively decrease the damage volume per ion or per decay event. The temperature dependence of the dose for complete amorphization in ion-irradiated zircon [27,50] is consistent with this model. Both of the above models are based on a constant damage rate, which is rarely valid even for ion-beam irradiation. In the case of α-decay, the damage rate will decrease with time as the parent nuclei decay; however, in most cases of interest, the dose for complete amorphization due to α-decay of an actinide generally requires a time period corresponding to less than one-tenth of a half-life. Consequently, the damage rate will generally decrease by less than 7% during the time period for complete amorphization to occur. This will, of course, depend on the actual actinide content of the material, but to a first approximation, a constant damage rate is a reasonable assumption.

The rate constant $K(T)$ in Eqs. (3) and (4) is the sum of temperature-dependent rate constants for irradiation-assisted and thermal annealing processes and is given by the expression

$$K(T) = \nu_{irr} \exp(-E_{irr}/kT) + \nu_{th} \exp(-E_{th}/kT), \tag{5}$$

where ν_{irr} and ν_{th} are the effective attempt frequencies and E_{irr} and E_{th} are the activation energies for the irradiation-assisted and thermal recovery processes, respectively. The activation energies for irradiation-assisted recovery processes are 0.07 [48], 0.13 [47] and 0.31 eV [27] for fluoroapatite, a rare-earth silicate apatite and zircon, respectively. The difference in the activation energies for the two apatites is due to a fundamental difference in their compositions (fluoro-phosphate system versus oxy-silicate system). For thermal recovery processes in different natural apatites, which are primarily phosphates, activation energies of 0.57 to 0.71 eV for fission track annealing have been reported [59,60] and in a rare-earth silicate apatite, an activation energy of 1.3 eV for an unidentified recovery processes has been measured by differential scanning calorimetry [46]. In zircon, thermal activation energies of 2.1, 2.9 and 3.6 eV for fission track annealing in the (001), (011) and (100) planes, respectively, have been reported [60]. In the case of zircon, the lowest activation energy (2.1 eV) for thermal recovery of track damage in the (001) plane is consistent with the observation [24–27,36] of partial recovery of the unit-cell expansion in the (001) plane of natural zircons over geologic time periods (570 million years). In studies of irradiation-as-

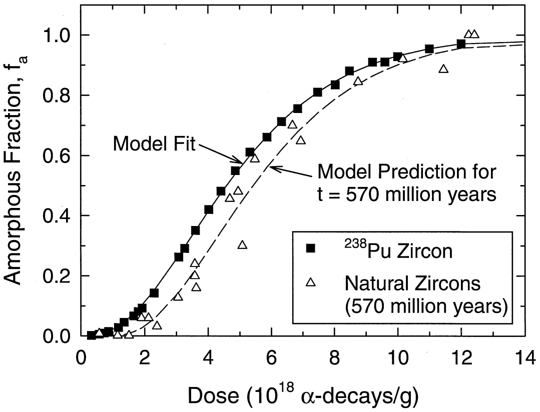

Fig. 5. Amorphous fraction as a function of cumulative α-decay dose. Comparison of experimental results for 10 wt% ^{238}Pu zircon [23–26] and for natural zircons [26,35] with the model based on Eq. (4), respectively.

sisted recrystallization in Si under high-dose-rate ion irradiation, it has been shown that ν_{irr} is proportional to the ion flux (i.e. damage rate) [61]; consequently, the first term in Eq. (5) is negligible, except under high-dose-rate ion-irradiation conditions. In the case of thermal recovery processes, which control the kinetics of radiation effects during geologic storage, ν_{th} is generally in the range of 10^{10} to 10^{14} s^{-1}.

In the case of zircon incorporating 10 wt% ^{238}Pu [24–27], $K(T)t < BD(t)$ and Eq. (4) reduces to Eq. (2), which provides an excellent fit to the Pu-doped zircon results, as shown in both Figs. 4 and 5. For natural zircons [36], where $t = 570$ million years, Eq. (4) provides an excellent fit to the data with $K(t) = 10^{-9}$ yr^{-1} (Fig. 5), which assumes E_{th} is 2.1 eV, ν_{th} is 5×10^{11} s^{-1} and an average geologic temperature of 100°C. These results provide a reasonable validation of the model for α-decay effects over geologic time periods by explicit comparison of experimental data for Pu-doped zircon taken over of 6.5 years [24–27] and the results for natural zircons self-damaged over 570 million years [36].

Complete amorphization will not occur if the damage rate, $BD(t)/t$, is less than or equal to the recovery rate, $K(T)$. Since $D(t)/t$ is just the average sample activity, A, the critical temperature, T_{c}, above which complete amorphization does not occur is defined as the temperature where $K(T) = BA$. For conditions, such as in natural minerals or for Pu disposition, where thermal recovery processes dominate, the critical temperature for amorphization is given by the expression

$$T_{\mathrm{c}} = E_{\mathrm{th}} / \left[k \ln(\nu_{\mathrm{th}}/AB) \right]. \tag{6}$$

This is identical to the equation previously derived for ion-beam irradiation from different assumptions [27,47]. Since for most cases of interest, as noted above, the dose for complete amorphization due to α-decay of an actinide generally requires a time period corresponding to less than one-tenth of a half-life, the sample activity will generally decrease less than 7% during the time period for complete amorphization to occur. For the case of α-decay in apatites and zircons, T_{c} will have a weak dependence on A (i.e. actinide content) but changes linearly with activation energy. Assuming activation energies of 0.71 and 2.1 eV for natural apatite and zircon, respectively, the corresponding values of T_{c} are -141°C and 130°C for an activity typical of that for metamict zircons [36]. The actual critical temperatures for natural apatites and zircons may differ somewhat from these predictions due to the effects of impurities, which have been shown to increase T_{c} in monazite [50].

For ion-beam irradiation, it has been previously shown that the relationship between amorphization dose and temperature is given by the expression [27,47]

$$D = \frac{D_0}{1 - \left[\nu_{\mathrm{irr}} / \phi\sigma \right] \exp(-E_{\mathrm{irr}}/kT)}, \tag{7}$$

where D_0 is the amorphization dose at 0 K for the high temperature recovery stage, ϕ is the ion flux and σ is the damage cross section. For 1.5 MeV Kr irradiation in La–Si apatite [47], D_0 is 0.52 dpa (displacements per atom), while in fluoroapatite, D_0 is 0.17 dpa [48]. For 1.5 MeV Kr ion irradiation in zircon [27], D_0 is 0.51 dpa. Based on a correlation between ion-beam results [47] and Cm-decay results [26] in rare-earth silicate apatites, the value of D_0 in rare-earth silicate apatite due to α-decay is 0.35 dpa, which is equivalent to 5×10^{18} α-decays/g for ^{239}Pu decay. For fluoroapatite, the D_0 of 0.17 dpa is equivalent to 2.5×10^{18} α-decays/g for ^{239}Pu. The excellent correlation previously shown between heavy ion-irradiation effects and Pu-decay effects in zircon at room temperature [27] suggests that D_0 is 0.51 dpa for heavy-ion irradiation and Pu-decay, which is equivalent to 1×10^{19} α-decays/g for ^{239}Pu.

For natural minerals and Pu-containing apatites and zircon, the temperature dependence of the critical dose for complete amorphization due to α-decay is given by an expression similar to Eq. (7),

$$D = \frac{D_0}{1 - \left[\nu_{\mathrm{th}} / AB \right] \exp(-E_{\mathrm{th}}/kT)}, \tag{8}$$

where A is the average α-activity (i.e. damage rate). For time scales less than a half-life, the activity $A = D/t$ and Eq. (8) can be simplified to the following expression:

$$D = D_0 + \left[\nu_{\mathrm{th}} t / B \right] \exp(-E_{\mathrm{th}}/kT), \tag{9}$$

which is only valid for $T < T_{\mathrm{c}}$. Predictions based on Eq. (9), using the same assumptions as for Fig. 5, can be compared with literature data on the critical dose for amorphization in ^{238}Pu-zircon ($t = 6.5$ years) [24–27] and in natural zircons as a function of zircon age [57]. The

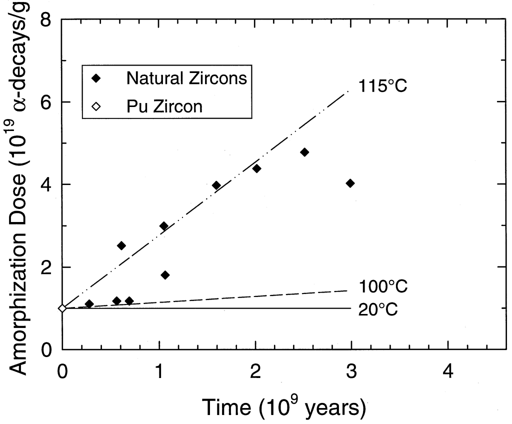

Fig. 6. Critical amorphization dose for ^{238}Pu zircon [23–26] and natural zircons [55] as a function of zircon age and model predictions at different temperatures based on Eq. (9).

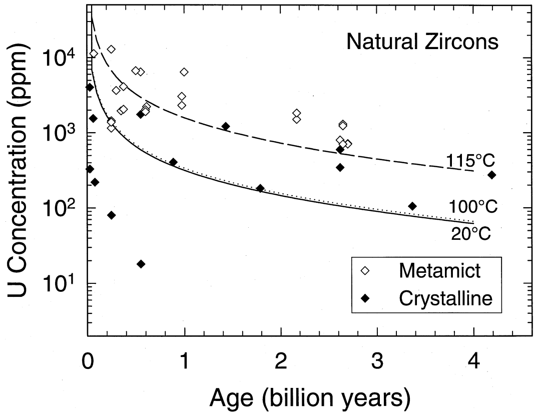

Fig. 7. Uranium content for crystalline and metamict zircons of different age [20,49,60–71] and model predictions at different temperatures based on Eqs. (10) and (11).

results are shown in Fig. 6 for several temperatures and indicate that Eq. (9) reasonably brackets the critical amorphization dose observed in natural zircons over geologic time scales. The results in Fig. 6 also suggest that many of the older zircons were at temperatures close to or above T_c sometime in their history.

The critical radionuclide (U, Th, Pu, or other actinides) concentration, N_0, necessary at the time of formation ($t = 0$) to induce amorphization over time, t, at temperature, T, is easily derived from Eq. (8) and is given by the expression

$$N_0\ (\mathrm{ppm}) = \frac{10^6 D_0/(n_\mathrm{d} m)}{[1 - [\nu_\mathrm{th}/AB]\exp(-E_\mathrm{th}/kT)][1 - \exp(-\lambda t)]}, \tag{10}$$

where n_d is the number of displacements per α-decay, m is the number of α-decays in the decay chain (primarily for natural minerals where the half-lives of the daughters are much shorter than the parent) and λ is the decay constant of the parent radionuclide. Eq. (10) defines the critical concentration boundary between partially crystalline and fully amorphous states as a function of age and can be validated against natural mineral data, as discussed previously [50]. For natural minerals, the present day critical concentration, $N_c(t)$, in minerals of age, t, is given by

$$N_c(t) = N_0 \exp(-\lambda t). \tag{11}$$

Eq. (11) is plotted in Fig. 7 for the case of natural zircons at several temperatures, using the same assumptions as in Fig. 5, along with data for natural zircons [21,50,62–73] representing a wide range of age and present-day uranium content. In general, Eq. (11) provides a reasonable delineation of the crystalline-amorphous boundary in natural zircons. Some of the older zircons that fall above this boundary are known to have experienced more elevated temperatures due to a metamorphic event that would have resulted in annealing.

Since only natural apatites containing silica appear to be susceptible to amorphization over geologic time periods and then only partial amorphization is observed, there is no way to validate the above models for apatite as has been done for zircon. However, the predicted behavior for most natural apatites (i.e. T_c is less than ambient temperature) is consistent with literature observations [29].

4. Model calculations

The predicted amorphization dose as a function of temperature is shown in Fig. 8 for rare-earth silicate apatite and zircon phases containing 1 and 10 wt% weapons

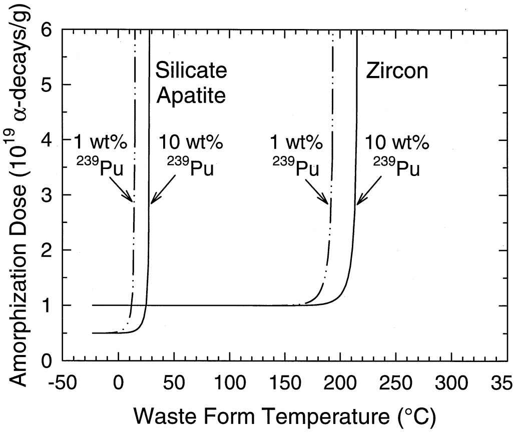

Fig. 8. Critical amorphization dose as a function of storage temperature for silicate apatite and zircon phases containing 1 and 10 wt% ^{239}Pu.

^{239}Pu. The effect of damage rate or α-activity (i.e., actinide content) on the temperature dependence is clearly evident and is consistent with the calculated values of T_c, based on Eq. (6), which for silicate apatite containing 1 and 10 wt% ^{239}Pu are 15 and 29°C, respectively, and for zircon are 196 and 218°C, respectively, for 1 and 10 wt% ^{239}Pu loadings. These results suggest that apatite phases containing excess weapons Pu will remain crystalline, due to high thermal recovery rates, under conditions expected for a near-surface repository, such as at the Yucca Mountain site. In the case of zircon containing excess weapons Pu, the results suggest that the dose required to cause amorphization will rise rapidly at temperatures above 160 to 200°C, depending on Pu content and amorphization will be significantly reduced or even suppressed. Thus, the incorporation of ^{239}Pu into zircon will lead to a crystalline-to-amorphous transformation at conditions expected in a near-surface repository (i.e. temperatures falling below 150°C after several hundred years). Although the initial elevated temperatures in a geologic repository may retard amorphization, eventually zircons containing Pu will undergo a radiation-induced, crystalline-to-amorphous transition in a time that will depend on the Pu loading. Under deep borehole conditions (i.e. temperatures exceeding 160°C), the amorphization of Pu-containing zircons would be much reduced or even suppressed due to simultaneous annealing processes.

The predicted amorphization behavior for rare-earth silicate apatite and zircon containing 10 wt% ^{239}Pu is shown in Figs. 9 and 10, respectively, as a function of time for several temperatures. These results are consistent with the results in Fig. 8; the amorphization rate for silicate apatite decreases rapidly above 10°C and for zircon decreases rapidly above 190°C. At the higher temperatures, the amorphization rate is decreased even further due to both an increase in the recovery rate and a decrease in the actual α-activity, $A(t)$, (nearly a factor of 2) due to the longer time scales (approaching one half-life). At this temperature, the amorphization rate is only slightly greater than the recovery rate. As the α-activity decreases with time, the recovery rate becomes dominant, and the amorphous fraction decreases as the amorphous regions recrystallize.

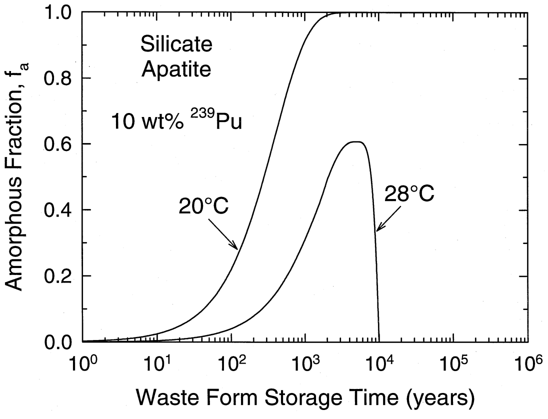

Fig. 9. Predicted amorphous fraction at several temperatures as a function of waste storage time for a silicate apatite phase containing 10 wt% ^{239}Pu.

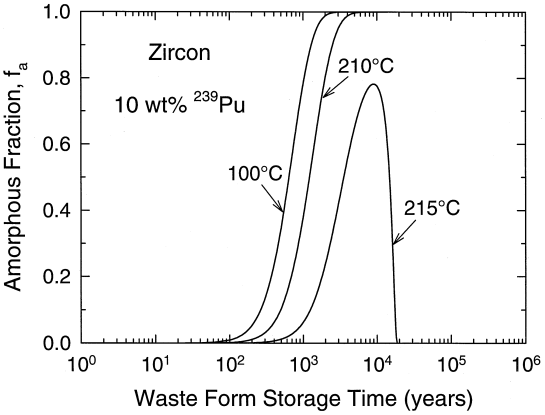

Fig. 10. Predicted amorphous fraction at several temperatures as a function of waste storage time for a zircon phase containing 10 wt% ^{239}Pu.

Actual behavior for Pu containing apatites and zircons may differ slightly from that shown in Figs. 8–10 due to compositional variations, as suggested in Figs. 1 and 2, and due to impurities, which have been shown to increase T_c in monazite [50]. Clearly, the effect of Pu and rare-earth content on the kinetics requires further investigation. Ideally, temperature dependent studies of Pu containing specimens would provide further validation of the models and data on the effects of compositional variations on the kinetic parameters.

5. Conclusions

The models presented here demonstrate that apatite incorporating ^{239}Pu will remain crystalline, despite self-radiation effects, because of the high thermal recovery rates. The incorporation of ^{239}Pu into zircon, however, will lead to a crystalline-to-amorphous transformation at conditions expected in a near surface repository, such as Yucca Mountain. The initial elevated temperatures in a geologic repository may retard amorphization in zircon, but eventually zircons containing Pu will undergo a radiation-induced crystalline-to-amorphous transition in a time that will depend on the Pu loading. Under deep borehole conditions (i.e. temperatures exceeding 160°C), the amorphization of zircon would be much reduced or even suppressed due to simultaneous annealing processes. However, even in the event of complete amorphization, zircon is much more durable than borosilicate glass or the UO_2 in spent fuel under oxidizing conditions (the primary waste forms presently proposed for Pu [74]).

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