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Influence of temperature and uranium on the radiation stability of zircon

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Abstract

The influence of temperature and uranium on the zircon ($ZrSiO_4$) radiation stability has been studied. The results show that zircon clusterization (formation of $USiO_4$ clusters) may influence appreciably the radiation stability of zircon. However, the temperature also exerts an effect on the zircon radiation stability and may decrease the effective α-dose. In case of $USiO_4$ cluster formation, the dependence of the undamaged part of the mineral on the quantity of uranium atoms per cluster has been derived.

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1. Introduction

In the context of the geological time scale, self-irradiation due to the α-decay of incorporated actinide elements may transform initially crystalline minerals into an amorphous state that is called 'metamict'. The α-decay has two damage sources:

(a) He-ions (α-particles), which have an energy of 4.2–5.5 MeV and show mainly electronic stopping, producing about 100 displacements. Most of the displaced atoms are isolated defects, which arise for the most part at the end of the path of α-particles having the range 10–20 μm [1].
(b) Heavy recoil atoms, which have a recoil energy of about 0.1 MeV. The recoil atoms show predominantly nuclear stopping and give rise to a dense collision cascade with typically 800 displacements in case of zircon, $ZrSiO_4$ [2] within a short distance of about 20 nm [1].

Natural actinide-bearing minerals such as zircon [3,4] may cover a full range from being little damaged by radiation to become entirely metamict. However, some authors [5,6] have indicated that the calculated self-irradiation dose does not correlate with the zircon metamictization level.

Thus, some zircons have a higher degree of metamictization than other zircons, but have a lower

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self-irradiation dose (α-events/g). Until now there has been no satisfactory explanation of this fact in the literature. So, the determination of reasons for the radiation stability of zircon is subject of the present investigation. In this paper we concentrate the attention on the temperature factor and the uranium distribution.

It has been shown in Refs. [7,8] that the radiation stability of the layer and island U-, Th- minerals may be due to the presence of water molecules or nanochannels. In the structure of crystalline zircon there are no water molecules and nanochannels. So, the radiation stability of zircon may be stimulated only by the temperature factor. But, apart from a uniform distribution of uranium atoms, sometimes nonuniform distributions exist. The degree of clusterization (the relative uranium part with a nonuniform distribution) depends on the thermodynamic conditions of mineral formation. It has been shown in Ref. [2] that the maximum activation energy for point defects in zircon is 1 eV, and the critical temperature T_c, above which such defects are not induced, is about −100 °C. On the other hand, Meldrum et al. indicate [2] that in the case of zircon, the critical temperature for dense collision cascades induced by recoil atoms is equal to $T_c \approx 360$ °C. So, the main factor of amorphization must be connected with recoil atoms. As it is well known, the recoil atoms cover a distance of about 20 nm. But in the case of uranium clusterization, the distance between the clusters may be about 200 nm, and the most part of the mineral will remain in the crystalline state. Hence, the main factors of the radiation stability in zircon are the nonuniform uranium distribution and the temperature factor.

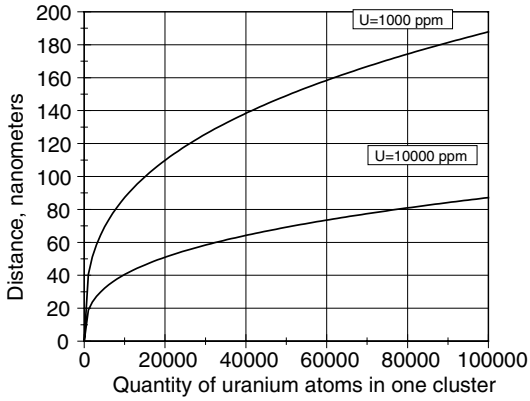

Fig. 1. Distance between two nearest-neighbor clusters versus the quantity of uranium atoms in one cluster.

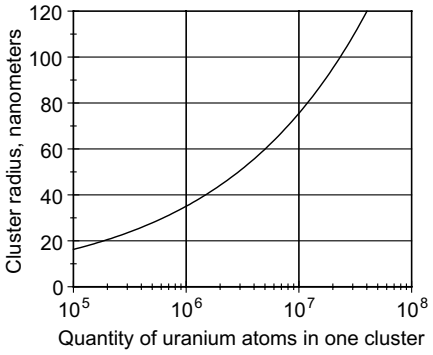

Fig. 2. Cluster radius versus the quantity of uranium atoms in one cluster.

2. Modelling and discussion

Let us assume that zircon ($U_xZr_{1-x}SiO_4$) contains 10 000 at. ppm of uranium atoms ($x = 0.01$). If the uranium atoms are distributed uniformly in the structure, then the distance between the two nearest uranium atoms (r_{01}) will be about 2 nm. In this case, the recoil atoms amorphize all volume of zircon. But if the uranium atoms are distributed nonuniformly due to their clusterization, then the distance between the two nearest clusters is higher than r_{01}.

In the cubic symmetry approximation, we have calculated the distance between two nearest-neighbor clusters (r_0) versus the quantity of uranium atoms per cluster (N) (Fig. 1). Suggesting that a cluster has a spherical form and its chemical composition is $USiO_4$, the radius of the cluster (r_1) has been calculated (Fig. 2). During nuclear decay, one uranium atom will undergo eight α-decays. In this case, the maximum length between the cluster center and the end of the path of the recoil atom will be equal to $L = (160 + r_1)$ nm. So, the part of the zircon structure (in percent) which cannot be amorphized is equal to $(1 - (4\pi L^3/3r_0{}^3)) \cdot 100\%$. The dependence of the undamaged part of mineral (in percent) versus N is shown in Fig. 3. If $x = 0.01$, then the undamaged part of zircon is equal to 17% for $N = 10^7$ ($r_1 = 76$ nm) and is equal to 59% for $N = 3 \times 10^7$

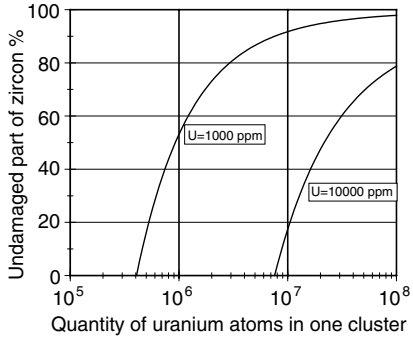

Fig. 3. The undamaged part of zircon (in wt.%) versus the quantity of uranium atoms in one cluster.

($r_1 = 109$ nm). In the case $x = 0.001$, the undamaged part of zircon is equal to 16% for $N = 5 \times 10^5$ ($r_1 = 28$ nm) and is equal to 60% for $N = 1.2 \times 10^6$ ($r_1 = 37$ nm).

Another factor, which reduces the degree of radiation damage, is the temperature. In Refs. [2,9] Meldrum et al. show that the radioactive stability of a mineral depends on the exposure temperature. If $T > T_c$ (T_c is the critical temperature), then the mineral cannot be amorphized. Meldrum et al. [10] have deduced the following formula for the critical temperature:

$$T_c = \frac{E_a}{k \cdot \ln\left[\frac{Af_a}{P(1-\varepsilon)(1-f_a)}\right]}, \quad (1)$$

where A is the lattice vibration frequency ($\approx 10^{13}$ Hz), E_a is the activation energy for a dense collision cascade, f_a is the amorphous fraction of the mineral, P is the dose rate (dpa/s), ε is the relative quantity of point defects, which arise from heavy ion irradiation.

Note that formula (1) has been deduced for synthetic zircons which were irradiated with 1.5 MeV Kr^+ or 800 keV Kr^+ at an ion flux of about 10^{14} m^{-2} s^{-1}. While the dose rate P is equal to about 10^{-3} dpa/s for syntetical zircons, the dose rate P is equal to about 10^{-19} dpa/s for natural zircons.

The critical amorphization dose for ^{238}Pu-substituted zircon was found to be 1.4×10^{19} α-decays/g ($D \approx 0.57$ dpa) [11], Nasdala et al. investigated the metamict zircon with the critical amorphization dose equal to 1.06×10^{19} α-decays/g ($D \approx 0.43$ dpa) [6], Geisler investigated the metamict zircon with the critical amorphization dose equal to 4.8×10^{18} α-decays/g ($D \approx 0.19$ dpa) [12]. However, it has been shown in [12] that mainly fully metamict zircons (the fraction of the amorphous phase being more than 90%) are characterized by the critical amorphization dose equal to $(1.3–1.5) \times 10^{19}$ α-decays/g ($D \approx 0.53–0.6$ dpa). So, as indicated in [13], the critical amorphization dose D for synthetical zircon is nearly equal to the critical amorphization dose for natural zircons ($D \approx 0.55$ dpa).

Assuming that $D = 0.5$ dpa, Meldrum et al. have derived the following expression that relates the present-day concentration of equivalent uranium for metamictization, N_c (expressed in atomic ppm), to the age t (expressed in years), of the given mineral grain as a function of temperature T (in Kelvin scale) [2]:

$$N_c\,(\text{ppm}) = \frac{470}{(1-\exp[14.5(1-523/T)]) \cdot (\exp[1.55 \times 10^{-10} \cdot t]-1)}. \quad (2)$$

If a temperature of 100 °C is assumed for the Sri Lanka specimens of zircon, which have an age of 570 Ma, then expression (2) gives $N_c = 5100$ ppm. This is in good agreement with Nasdala's et al. data [6] for the Sri Lanca zircons (Nasdala et al. investigated highly metamict Sri Lanca zircons with U ≈ 6000 ppm).

A study of two other zircons (K1 and K2) gave contradictory results [6]. Zircon K1 has a moderate degree of metamictization and an age of 324 ± 4 Ma. Zircon K2 has a lower degree of metamictization and an age of 552 ± 5 Ma. Nasdala et al. have calculated α fluences to be 3.1×10^{18} α/g and 4.3×10^{18} α/g for zircons K1 and K2, respectively. It is possible that the temperature for zircon K2 was higher than for zircon K1, or the clusterization occurs in zircon K2 and does not occur in zircon K1.

3. Conclusions

The uranium distribution in zircon exerts a substantial effect on its radioactive stability. According to the calculations, in the case of uniform distribution of uranium in zircon, the critical uranium concentration makes U ≈ 5100 at. ppm (0.66 wt.%). At the same time, with a nonuniform uranium distribution in zircon, the latter will stay in a nonmetamict state (provided the clusters are rather large in size) at least, up to uranium concentrations U ≈ 10 000 at. ppm (1.29 wt.%). However, the temperature also influences the zircon radiation stability and may decrease the effective α-dose even at higher uranium concentrations in the sample irrespective of the uranium distribution in the sample structure. So, the two main reasons for the radioactive stability of zircon are the temperature factor and the nonuniform uranium distribution in zircon.

Acknowledgements

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