ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Quantification of α-particle radiation damage in zircon†

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ABSTRACT

Analysis of radiation damage in natural mineral analogs such as zircon is important for the evaluation of the long-term behavior of nuclear waste forms and for geochronology. Here we present results of experiments to determine the partitioning of radiation damage due to the heavy nuclear recoil of uranium and thorium daughters and the α-particles ejected in an α-decay event in zircon. Synthetic polycrystalline zircon ceramics were doped with 10B and irradiated in a slow neutron flux for 1, 10, and 28 days to achieve the reaction ~B + n → 7Li + α (+2.79 MeV), creating an α event without a heavy nuclear recoil. The ~Li atoms produced in the nuclear reaction were directly detected by NMR “spin-counting”, providing a precise measurement of the α-dose applied to each sample. The amount of damage (number fraction and volume fraction) created by each α-event (one α-event being a ~Li + α-particle) has been quantified using radiological nuclear magnetic resonance and X-ray diffraction data. The number of permanently displaced atoms in the amorphous fraction was determined by 29Si NMR to be 252 ± 24 atoms for the 10B(n,α) event when the heavy recoil is absent, which is broadly in agreement with ballistic Monte Carlo calculations. The unit-cell swelling of the crystalline fraction, determined by X-ray diffraction, is small and anisotropic. The anisotropy is similar to that observed in ancient natural samples and implies an initial anisotropic swelling mechanism rather than an anisotropic recovery mechanism occurring over geological timescales. The small unit-cell volume swelling is only ~6% of the expansion frequently attributed to α-particles associated with an actinide α-decay event. The lattice parameters indicate a volume increase as a function of α dose of 0.21 Å/1018 α-events/g, which is significantly less than the increase of 3.55 Å/1018 α-events/g seen in Pu-doped zircon and 2.18 Å/1018 α-events/g seen in natural zircon. It is concluded that the heavy recoil plays a more important role in unit-cell swelling than previously predicted. The likely mechanism for such an effect is the rapid, and thus defect-rich, recrystallization of material initially displaced by the heavy recoil.

Keywords: Zircon, NMR spectroscopy, radiation damage, α-particle

INTRODUCTION

Radiation damage in zircon is important as a natural analog study of the behavior of nuclear waste forms over geological time periods. Zircon has a high critical amorphization temperature (Meldrum et al. 1999), which means that the structures of ancient zircons preserve, rather than recover, most of the structural disruption that occurs during α decay or spontaneous nuclear fission of actinides incorporated in the lattice. Thus, it records the scale of disruption cause by the α decay of actinides, which will be the dominant damage mechanism in spent nuclear fuel and actinide nuclear waste form materials beyond about 500 yr after emplacement in a geological repository (Bruno and Ewing 2006; Hedin 1997). The damage caused by α emitters is comprised of damage from the recoil of the heavy α-emitting nucleus (~70–100 keV) and the α-particle itself (~4.5–5.5 MeV) when the actinides uranium and thorium (and α-emitting daughters) undergo α-decay events that damage mineral structures over geological time. The response of zircon in nature is swelling and a loss of crystallinity exemplified by the seminal study by Holland and Gottfried (1955) and subsequent work (Murakami et al. 1991; Palenik et al. 2003). Zircon exposed to ion beam-induced damage (Wang and Ewing 1992; Weber et al. 1994) and plutonium doping (Weber 1990) also exhibits similar behavior. Both the crystalline and amorphous regions of the zircon swell as a result of α radiation damage. To date, there has been no experimental measure of the partitioning of the structural damage between α particle and heavy recoil and the effects of these two processes on swelling in the partially crystalline zircon in bulk materials. Such a measurement tests our understanding of the radiation damage process that applies more widely in other actinide-containing minerals and nuclear materials. Radiological nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) measurements have been applied to quantify the damage created by light, highly energetic particles generated by the nuclear reaction: ~B + n* → 7Li + α (+2.79 MeV, 2.31 MeV kinetic energy) (Fig. 1), on the crystalline structure of a synthetic