Why natural monazite never becomes amorphous: Experimental evidence for alpha self-healing

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ABSTRACT

Monazite, a common accessory rare-earth orthophosphate mineral in the continental crust widely used in U-Pb geochronology, holds promise for (U-Th)/He thermochronology and for the immobilization of Pu and minor actinides (MA) coming from spent nuclear fuel reprocessing. Previous results obtained on natural and plutonium-doped monazite have demonstrated the ability of this structure to maintain a crystalline state despite high radiation damage levels. However, the low critical temperature (~180 °C), above which amorphization cannot be achieved in natural monazite under ion irradiation, does not explain this old and unsolved paradox: why do natural monazites, independent of their geological history, remain crystalline even when they did not experience any thermal event that could heal the defects? This is what the present study aims to address. Synthetic polycrystals of LaPO4-monazite were irradiated sequentially and simultaneously with α particles (He) and gold (Au) ions. Our results demonstrate experimentally for the first time in monazite, the existence of the defect recovery mechanism, called α-healing, acting in this structure due to electronic energy loss of α particles, which explains the absence of amorphization in natural monazite samples. This mechanism is critically important for monazite geo- and thermochronology and to design and predictively model the long-term behavior of ceramic matrices for nuclear waste conditioning.

Keywords: Monazite, α self-healing, in situ TEM irradiation, dual-ion beam irradiation, helium, geochronology, thermochronology, nuclear waste

INTRODUCTION

Monazite (APO4, A = LREE, Th, U, Ca; Clavier et al. 2011) is a common accessory rare-earth orthophosphate mineral in the continental crust widely used in U-Pb geochronology (Parrish 1990). It is also a promising candidate for the immobilization of Pu (for countries that are not actively reusing Pu in MOX fuel) and minor actinides (MA) coming from spent nuclear fuel reprocessing (Boatner and Sales 1988; Weber et al. 1998), due to its high structural flexibility that can accommodate high concentrations of actinides in its structure, its high chemical durability, and its apparent high-radiation resistance (e.g., Ewing and Wang 2002; Seydoux-Guillaume et al. 2004; Lumpkin 2006; Oelkers and Montel 2008; Dacheux et al. 2013). However, this last point, demonstrated in natural crystals (Seydoux-Guillaume et al. 2004), is still not understood. During an α-decay event, an α-particle (4–8 MeV) and a recoil nucleus (70–165 keV) are released. The kinetic energy of these two particles is deposited in the host material by two distinct processes, ballistic (S_{ball}) and electronic (S_{elec}). The ballistic process corresponds to elastic collisions between atom nuclei, and the electronic process corresponds to ionization resulting in a local temperature rise in

the material. Most of the atomic displacements that can result in amorphization of the crystal lattice are caused by the recoil nuclei (e.g., 1000–2000 atomic displacements) due to intense elastic collision cascades (Ewing et al. 2000). In contrast to its U-Pb geochronological concurrent zircon—which commonly contains U in the hundreds of parts per million range, has received α-decay doses on the order of 10^{18}–10^{19} α/g, and is easily amorphized (Ewing et al. 2000)—even very old (up to 2 Ga) monazite crystals, containing high concentrations of actinides (up to 10 wt% ThO2 and ~1 wt% UO2) and thus sustaining high irradiation doses [(up to 1.7 × 10^{20} α/g that should induce up to 14 displacements per atom (dpa)], are not amorphous; evidence of radiation damage is limited to isolated nanometer-sized domains within the crystal, corresponding to strain in the lattice (Seydoux-Guillaume et al. 2004). Similarly, Pu-doped monazite remains crystalline even after an irradiation dose of 7.5 × 10^{18} α/g (0.8 dpa; Deschanels et al. 2014), which is well above the critical amorphization doses (~0.3 dpa) determined using external heavy-ion irradiation experiments (Meldrum et al. 1996). The reason for this apparent resistance has remained an enigma until today. It is well known that the critical amorphization temperature, for natural monazite under ion irradiation is relatively low (180 °C; Meldrum et al. 1997a) compared to other minerals (e.g., 830 °C).