Dissolution of radiation-damaged zircon in lateritic soils

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ABSTRACT

Zircon crystals from lateritic soils at Nsimi, Cameroon, were investigated using electron microprobe analysis (EMPA), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Raman spectroscopy to determine the extent of radiation damage from alpha-decay events. The soils belong to a small watershed developed on granitic rocks of the Congo craton (2.9 Ga). Interactions with fluids are evidenced by significant CaO (up to 1.5 wt%), Al2O3 (up to 2.9 wt%), and Fe2O3 (up to 2.9 wt%) concentrations in UO2 rich regions (0.05 to 1 wt%) of the zircon. Regional heating up to 500 °C, related to the Pan-African orogeny about 0.6 Ga ago, has lead to the recrystallization of the radiation-damaged grains and the formation of a nanoporous microstructure. The correlation observed between the presence of dissolution features and the actual damage state of zircon shows that zircon dissolution occurs under tropical weathering conditions and with preferential dissolution of the highly radiation-damaged regions. Congruent dissolution of zircon and the limited mobility of Zr are supported by the absence of zirconium oxide precipitates in the fractures of weathered grains of zircon.

Keywords: Zircon, Nsimi, laterite, nanopore, zirconium, metamict, radiation damage, TEM

INTRODUCTION

The relation between the chemical and physical durability of zircon and radiation damage from alpha-decay of uranium and thorium has been the focus of considerable attention because of the wide use of zircon to investigate various geological processes, including the petrogenesis of igneous and metamorphic rocks (Hoskin and Schaltegger 2003), hydrothermal alteration (Geisler et al. 2003a, 2003b), and weathering and evolution of soils (Hallsworth et al. 2000; Balan et al. 2001a). In addition, the long-term behavior of an actinide-containing mineral, such as zircon, may be used to evaluate the long-term stability of nuclear waste forms for actinides in different geologic environments (Ewing et al. 1995a, 1999, 2001).

Radiation damage in zircon is primarily related to the recoil of heavy nuclei during alpha-decay processes, which leads to the formation of nanometer-size amorphous domains (Weber et al. 1994; Salje et al. 1999; Ewing et al. 2003). The accumulation and overlap of these domains ultimately lead to a macroscopic amorphous state (Murakami et al. 1991; Rios et al. 2000), referred to as the metamict state. At an atomic scale, metamict zircon displays an increased polymerization of [SiO4]-tetrahedra inferred from the results of NMR spectroscopy (Farnan et al. 2003) and by ab initio molecular dynamics simulations (Balan et al. 2003), together with an overall decrease of Zr-coordination (Farges and Calas 1991) related to the formation of Zr-O-Zr linkages (Meldrum et al. 1998). At the nanoscale, metamict zircon is often heterogeneous consisting of a low-density amorphous phase and less damaged high-density domains. There are preferential diffusion paths through the mixed-domain zircon that can be described by percolation theory (Rios et al. 2000). Macroscopic properties such as density and elastic moduli (Chakoumakos et al. 1987), formation enthalpy (Ellsworth et al. 1994), and dissolution rate (Ewing et al. 1982) are significantly modified by radiation-induced amorphization. Metamictization of zircon is often accompanied by significant enrichments in Ca and Al, as evidenced in experimentally and naturally altered metamict zircons (Geisler et al. 2003a, 2003b). The structural effects of radiation damage in zircon must be considered when using zircon for age-dating or thermochronology applications (Utsunomiya et al. 2007). Isotopic dating of damaged zircon most often provides discordant ages because of severe lead loss (Geisler and Schleicher 2000). The decreased stability of amorphous zircon may also contribute to Zr mobility in hydrothermal alteration and weathering environments (Balan et al. 2001a). However, the amorphization of zircon is often offset by thermal annealing, which contributes to the recovery of the crystalline structure (Nasdala et al. 2001). The amorphous domains of metamict minerals may be annealed not only at high temperature, but also under low-temperature hydrothermal conditions, as water efficiently catalyzes the recrystallization of zircon. The temperature above which recrystallization prevails over dissolution in wet environ-