Radiation damage and uranium concentration in zircon as assessed by Raman spectroscopy and neutron irradiation

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ABSTRACT

Radiation damage of natural and synthetic zircon grains is evaluated by Raman spectroscopy to understand annealing and stability of fission tracks. Analyses focus on a suite of 338 Paleozoic detrital zircon grains from metamorphosed strata in the Hellenic forearc that were variably annealed by a Miocene thermal event, as well as a suite of 97 synthetic zircon grains. The Raman wavenumber shift of ν₁[SiO₄] reveals that radiation damage and damage distribution in this suite mainly depends on uranium concentration. In zircon with similar uranium concentration, the Raman wavenumber shift allows for the determination of radiation damage in different crystals, which is a function of effective accumulation time. Nine detrital zircons grains with moderate radiation damage were stepwise annealed at 1000 and 1400 °C, which resulted in progressive removal of radiation damage revealed in an increase of ν₁[SiO₄] peak positions. For a partly reset sample that was brought to temperatures of ~350 °C in a geologic setting (Hellenic forearc), we use the Raman measurements and uranium determination to estimate a Zircon Damage Discrimination Factor (Z₃₀₃₀), which is our attempt to estimate only radiation damage in single grains by accounting for affects of the uranium atom in the Raman wavenumber. This discrimination allows for a separation of zircon fission track (ZFT) ages of single ages based on grains that have a low track retention (high damage, fully reset grain), thus refining the age determination of cooling in a rock that shows variable resetting.

Keywords: Geochronology, zircon fission track, radiation damage, uranium content, Raman spectroscopy

INTRODUCTION

Radiation damage in zircon is manifested by a decrease in crystallinity, the production of color, a decrease in density, an increase in water, and volume expansion (Ewing et al. 2003 and references therein). Because zircon is so widely used in geochronology, understanding the relationship of crystallinity to radiation damage is very important, and in the case of fission track dating, crystallinity or lack of crystallinity is inferred to be the primary factor that affects track retention and annealing (Kasuya and Naeser 1988). Therefore, radiation damage in zircon is central to understanding the kinetics of track formation and stability, the bounds of closure temperature, and the environmental conditions of track fading or annealing at elevated temperatures.

For this work, we are primarily interested in how radiation damage affects the material properties of zircon that we routinely analyze using fission-track dating (Garver 2008). There are two primary effects that are of concern. One is that radiation damage increases the chemical reactivity of a zircon, and this affect facilitates etching and track revelation in the lab: fission tracks in damaged grains etch easily and quickly. The other is that radiation damage changes the annealing and closure temperature in zircon. Damaged grains are easily annealed when brought to elevated temperatures (~200 °C and greater), and damaged grains appear to have a lower closure temperature compared to grains with little or no damage (see Garver et al. 2005 and references therein). As such, we measured radiation damage and crystallinity in a zircon using Raman spectroscopy to aid our understanding of fission tracks in zircon.

Trace concentrations of U⁴⁺ and/or Th⁴⁺ substitute for Zr⁴⁺ in natural zircons (ZrSiO₄), and the radioactive decay of U and Th causes internal radiation damage in the crystal that increases with accumulation time (e.g., Holland and Gottfried 1955; Ahrens 1965; Ahrens et al. 1967). Due to similarities in the ionic radius of U⁴⁺ and Th⁴⁺ (1.00–1.05 Å) (Shannon 1976), these elements replace Zr⁴⁺ and occur in zircon with abundances typically ranging from tens to thousands of parts per million (Speer 1980). The emission of an α-particle during decay causes the displacement of several hundred atoms, and the recoil of the radiogenic atom (uranium and its prompt daughter isotopes) produces several thousand atomic displacements within the lattice (e.g., Weber et al. 1994; Farman and Salje 2001; Fleischer 2003). Zircon grains with higher U and Th (e.g., 1000 ppm) contain more radiation damage than those with lower uranium (e.g., 200 ppm) given a comparable effective accumulation time of radiation damage (i.e., similar thermal history). Although this observation seems intuitively obvious, the difference in radiation damage from crystal to crystal in the same rock can have profound implications for the geochronologic systematics of that sample (i.e., see discussion in Bernet and Garver 2005).

When a zircon grain is analyzed in the laboratory, one would like to know the total amount of accumulated radiation damage...