In situ $^{238}$U-$^{230}$Th disequilibrium dating of pyrochlore at sub-millennial precision

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ABSTRACT

We report the application of high-resolution in situ $^{238}$U-$^{230}$Th disequilibrium dating to pyrochlore $[(\text{Ca,Na,REE,\textbf{Th},U})_2(\text{Nb,Ti,Ta,Zr})_2\text{O}_8(\text{OH,F})]$. Compositioally zoned pyrochlore is an accessory phase in intrusive carbonatite syenites, which were ejected as cognate clasts during the eruption of the phonolitic Laacher See volcano, East Eifel, Germany, 12.9 ka ago. Separated individual pyrochlore crystals were analyzed for U-Th isotopes and elemental abundances at high spatial resolution (~25 µm) using secondary ion mass spectrometry (SIMS) with an internal precision for the $^{238}$U-$^{230}$Th isochron of ~700 a (2σ). U and Th were also analyzed by electron microprobe in SIMS spots. Instrumental mass fractionation for Th/U was corrected using an EMP vs. SIMS calibration curve, and the resulting pyrochlore isochron age of 26.1 ± 1.4 ka (including external calibration uncertainty) is concordant with the 23 +7/–6 ka U-Th zircon ages for the same sample. By contrast, AM206 pyrochlore from a Cretaceous alkali granite shows significant disequilibrium with $(^{230}\text{Th})/(^{238}\text{U}) = 0.90 ± 0.04$. The tightly defined isochron implies that U-Th in Laacher See pyrochlore remained a closed decay system during protracted residence in the magma chamber carapace, and was unaffected by hydrothermal alteration or post-eruptive weathering over time scales of tens of thousands of years. By contrast, disequilibrium in AM206 pyrochlore indicates U-Th mobilization during protracted near-surface residence.

Keywords: Pyrochlore, U-Th disequilibrium, carbonatite, radiation damage, nuclear waste

INTRODUCTION

Pyrochlore forms a chemically diverse group of accessory minerals with the general chemical formula $\text{A}_2\text{B}_2\text{O}_8\text{Z}_1+x\text{nH}_2\text{O}$. Site occupations involve large cations in eightfold coordination ($\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mn}^{2+}$, $\text{Fe}^{3+}$, $\text{Ti}^{4+}$, $\text{Nb}^{5+}$, $\text{Ta}^{5+}$, $\text{Zr}^{4+}$, $\text{Al}^{3+}$, $\text{Fe}^{2+}$, $\text{W}^{6+}$, and $\text{Zr}^{4+}$) in A, and smaller cations in sixfold coordination ($\text{Nb}^{5+}$, $\text{Ta}^{5+}$, $\text{Ti}^{4+}$, $\text{Al}^{3+}$, $\text{Fe}^{2+}$, $\text{W}^{6+}$, and $\text{Zr}^{4+}$) in B, with anions in Z comprising $\text{O}^{2–}$, $\text{OH}^–$, and $\text{F}^–$ (Hogarth et al. 2000). The pyrochlore structure is therefore a major host for REE mineralization in carbonatites, and evolved alkali rocks, and is suitable for sequestration of actinide elements in nuclear waste (Chakoumakos and Ewing 1985; Laverov et al. 2003; Ewing et al. 2004; Xu et al. 2004).

Despite high abundances of Th and U in pyrochlore—ranging from ppm to nearly 28 wt% UO$_2$ and ~4 wt% ThO$_2$, respectively (Hogarth et al. 2000)—the geochronological potential of pyrochlore and its propensity to remain a closed system over geologic time scales has only been addressed in few studies (Lumpkin and Ewing 1995; Voltaggio et al. 1997; Tappe et al. 2009). Lumpkin and Ewing (1995) tested the applicability of U-Pb dating on 1 µm-size pyrochlore crystals and detected considerable lead loss of up to 90% for altered pyrochlorites. It was therefore argued that lead is lost from pyrochlore via diffusion, while U and Th contents remain relatively stable (Lumpkin and Ewing 1995). More recently, Tappe et al. (2009) found U-Pb ages of pyrochlore from an intrusive carbonatite from Greenland to be concordant with zircon, baddeleyite, and perovskite U-Pb ages.

We present compositional and textural data of pyrochlore in plutonic clasts ejected during the 12,916 calendar years Laacher See (Germany) eruption whose age is precisely determined from varve and tree ring intercalibrations (Baales et al. 2002). This defines Laacher See as the youngest known intrusive carbonatite (Woolley and Kjarsgaard 2008). In addition, we analyzed pyrochlore from the Cretaceous Amis peralkaline granite (Namibia). The large range of U and Th concentrations within single pyrochlore crystals permits isochron dating of pyrochlore-bearing magmatic rocks at ng sampling scale. $(^{230}\text{Th})/(^{232}\text{Th})$ analysis (parentheses denoting activities) of pyrochlore by secondary ion mass spectrometry (SIMS) approaches precision similar to bulk analysis by thermal ionization mass spectrometry (TIMS) or inductively coupled plasma mass spectrometry (ICP-MS) methods.

SAMPLE SELECTION AND PREPARATION

Laacher See carbonatites with ubiquitous accessory pyrochlore occur as plutonic ejecta clasts in the Middle and Lower Laacher See tuffs (Liebsch 1996). Pyrochlore forms yellow-brownish subhedral to euhedral crystals that range in size from tens of micrometers to ~300 µm. We selected a carbonatite syenite sample [564-I; Liebsch (1996)] that yielded a U-Th zircon age of 23 +7/–6 ka (Wetzel 2009). This specimen consists of sanidine (66%), nesom (25%), and calcite (6%) with traces of magnetite and phonolitic glass (Liebsch 1996). In addition, we selected pyrochlore AM206 from the Early Cretaceous Amis Complex (Namibia; Schmitt et al. 2002) that is nominally sufficiently old to have attained secular equilibrium [i.e., $(^{230}\text{Th})/(^{232}\text{Th}) = 1$].

Samples were crushed and dry-sieved to separate the grain size fraction <500 µm. Heavy minerals were gravitationally enriched on a Wilfley table. Pyrochlores ($\rho \approx 5.3$ g/cm$^3$) were separated from lighter minerals (sanidine, nesom, calcite, and apatite) with diiodomethane ($\rho = 3.34$ g/cm$^3$). After hand-magnetic separation of magnetite ($\rho = 5.2$ g/cm$^3$), pyrochlore crystals were hand-picked and mounted on adhesive tape. Selected pyrochlore crystals that were sufficiently large and free of intergrown matrix minerals were then mounted in epoxy (564-L) or indium metal (AM206) for SIMS and electron microprobe (EMP) analyses. Secondary electron