Rare-earth elements in synthetic zircon: Part 2. A single-crystal X-ray study of xenotime substitution

ROBERT J. FINCH,1,* JOHN M. HANCHAR,1† PAUL W. O. HOSKIN,2‡ AND PETER C. BURNS3

1Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, U.S.A.
2Research School of Earth Sciences, Institute of Advanced Studies, The Australian National University, Canberra ACT 0200, Australia
3Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556-0767, U.S.A.

ABSTRACT

Zircon crystals synthesized in a Li-Mo oxide melt and doped with trivalent lanthanides and Y (REE), both with and without P, were examined by single-crystal X-ray diffraction (XRD). REE are incorporated into the Zr site in the zircon structure, and some Zr appears to be displaced to the Si site. Crystals doped with middle REE (MREE, Sm to Dy) and Y, plus P follow the xenotime substitution (REE3+ + P5+ = Zr4+ + Si4+) rather closely, whereas crystals doped with heavy REE (HREE, Er to Lu) deviate from the xenotime substitution, having REE:P atomic ratios significantly greater than one. Xenotime substitution requires that P5+ replace Si4+, but this substitution becomes limited by strain at the Si site in HREE-doped crystals. As Si sites become saturated with P5+, additional charge balance in synthetic zircon crystals may be provided by Mo6+ and Li+ from the flux entering interstitial sites, accounting for an additional 0.3 to 0.6 at% HREE beyond that balanced by P5+ ions. Heavy REE are more compatible in the zircon structure than are LREE and MREE, and HREE substitution is ultimately limited by the inability of the zircon structure to further accommodate charge-compensating elements. Thus the limit on REE concentrations in zircon is not a simple function of REE3+ ionic radii but depends in a complex way on structural strain at Zr and Si sites, which act together to limit REE and P incorporation. The mechanisms that limit the coupled xenotime substitution change from LREE to HREE. This change means that REE fractionation in zircon may vary according to the availability of charge-compensating elements. REE partition coefficients between zircon and melt must also depend in part on the availability of charge-compensating elements and their compatibility in the zircon structure.

INTRODUCTION

Zircon is a ubiquitous accessory mineral in nature. The ability of zircon to retain chemical and isotopic information has led to its use in a wide range of geochemical investigations. Isotopic data gleaned from zircon can provide fundamental information about the evolution of the crust and differentiation of the mantle (Hanchar et al. 1994; Buick et al. 1995; Bowring 1995; Vervoot et al. 1996). U-Pb dating of zircon has long been used to unravel the timing of tectonic events and related processes, including orogenic episodes (Solar et al. 1998) and regional metamorphism (Gibson and Ireland 1995), even to constrain the duration of the Permian mass extinction (Bowring et al. 1998). The use of zircon as a dating tool is so well established that zircon ages have been used to support isotopic ages determined by other methods (Stein et al. 1998). The widespread use of zircon in geochronology reflects the exceptional durability of zircon under diverse geochemical conditions. For example, detrital zircons have been used to date processes such as river-basin development and provenance (Riggs et al. 1996) and sedimentation rates (Altermann and Nelson 1998).

In addition to its use as a geochronometer, zircon is an important geochemical indicator. For example, zircon crystals may preserve oxygen isotopic information through metasomatic events that disrupt oxygen isotopic ratios in other minerals (King et al. 1998; Taylor and Huston 1998). The extraordinary chemical durability of zircon is a critical factor in it being proposed as a candidate waste form for the geologic disposal of weapons-grade Pu (Ewing and Lutze 1997; Ewing 1999).

Although a minor constituent of most rocks in which they occur, accessory minerals such as zircon, monazite, xenotime, and apatite commonly account for most trace elements in felsic igneous and aluminous metamorphic rocks (Bea 1996a, 1996b). The extent to which an element becomes incorporated into a mineral that crystallizes from a liquid is expressed as a partition coefficient, $D = [M]_{\text{mineral}}/[M]_{\text{liquid}}$. Often, the only remnants of ancient liquids are the minerals left behind, and partition coefficients may provide the only information available about the composition of the parent liquid. Thus we hope to better