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U-Th zonation-dependent alpha-ejection in (U-Th)/He chronometry

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Abstract—Both theoretical and empirical evidence shows that intracrystalline U-Th heterogeneity in zircon can lead to biases in (U-Th)/He ages if not accurately accounted for in α-ejection corrections. We present a model for age correction for U-Th zoned crystals. We apply this to spherical and prismatic grains with bipyramidal terminations. The spherical calculation is simplistic but allows rapid calculation of the approximate effects of a wide variety of U-Th zoning patterns. The bipyramidal calculation is computationally intensive but permits an more complete estimate of the combined effects of crystal morphology and source zoning as relevant to zircon. Our principle findings are: (1) the assumption of U-Th homogeneity can result in errors of up to ~30% (in rare cases, higher) for ejection-corrected ages for typical grain sizes and realistic zonation. (2) Tetragonal prisms with bipyramidal terminations, which are typical of most zircons, exhibit bulk retentivities that can differ by several percent from models considering crystals with pinacoidal terminations. When extreme cases, such as dipyramids, are considered, the bias can exceed 10% or more. (3) Morphologic effects can be accounted for to better than 1% precision by using new second-order polynomial parameters that describe retentivity as a function of surface-area-to-volume ratio calculated through more complete analysis of crystal dimensions including the height of pyramidal crystal sections. We illustrate application of our model using U-Th concentration profiles determined from single zircons by laser ablation ICP-MS from zoned Tardree Rhyolite zircons. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Since the modern resurgence of (U-Th)/He dating (Zeitler et al., 1987; Farley et al., 1996; Wolf et al., 1996), numerous studies have used (U-Th)/He thermochronometry to study a wide range of geomorphic and tectonic processes (House et al., 1998; Reiners et al., 2000; Stockli et al., 2000; House et al., 2001; Stockli et al., 2002; Armstrong et al., 2003; Ehlers et al., 2003; Reiners et al., 2003). More recent studies have exploited the relatively rapid ingrowth of He to date young volcanic deposits (Farley et al., 2002; Aciego et al., 2003; Davidson et al., 2004; Min et al., 2005), and to understand diffusive loss of He associated with wildfires (Mitchell and Reiners, 2003) and shock metamorphism of meteroites (Min et al., 2004). We address here an important source of error with (U-Th)/He dating–alpha ejection from crystals with a non-homogeneous U-Th distribution. Furthermore, we investigate age inaccuracy associated with the simplified geometries used in current bulk retentivity models (Farley, 2002).

Helium in minerals is primarily generated by radioactive decay of U and Th, and their intermediate daughter products, to Pb, and, to a lesser extent, by decay of Sm to Nd,

$$^{4}He* = 8^{238}U\left(e^{\lambda_{238}t} - 1\right) + 7^{235}\,U\left(e^{\lambda_{235}t} - 1\right) + 6^{232}\,Th\left(e^{\lambda_{232}t} - 1\right) + {}^{147}Sm\left(e^{\lambda_{147}t} - 1\right). \quad (1)$$

Each transformation in the decay chain results in the generation of an energetic alpha particle or helium nucleus. The alpha particles have sufficient kinetic energy that stopping distances are long (~15–20 μm) compared to the size of a typically analyzed grains (Farley et al., 1996). Consequently, an α-ejection correction factor (F_T) is required to account for those He atoms ejected from the crystal (Farley et al., 1996; Farley, 2002).

Farley et al. (1996) defined F_T as the fraction of radiogenic ^{4}He retained in the host grain. The He age is corrected for ejection loss of He by $t=t'/F_T$, where t' is the raw uncorrected He age, and t is the corrected age.

Monte Carlo modeling of alpha ejection from idealized crystal geometries (tetragonal prism with pinacoidal terminations for zircon and a finite cylinder for apatite) has been used to define an empiric second-order polynomial that represents F_T solely as a function of β, the surface-area-to-volume ratio of the grain (Farley et al., 1996; Farley, 2002). This analysis assumed uniform concentration of U and Th, although the effect of U-Th zonation on simplified spherical crystals was also considered. A number of studies have demonstrated that this estimated F_T provides corrected He ages that are accurate when compared with known emplacement ages for quickly-cooled zircon standards (e.g., Tagami et al., 2003), or produce compatible ages when compared with other low-temperature thermochronometers in intercalibration studies (Stockli et al., 2000; Kirby et al., 2002; Reiners et al., 2003; Reiners et al., 2004). Replicate (U-Th)/He ages have a two-sigma standard deviation of ~6%–10%, much greater than expected given typical formal analytical precision on He, U, Th, and Sm measurements, ~3%–4% (2σ). Common practice for assigning age uncertainty to unknowns is to multiply the calculated age by the relative standard deviation for replicate analyses of given mineral standard, thus precision for unknowns is limited by the reproducibility of standards.

The model presented here is motivated by the thought that grain shape and U-Th zonation may be important factors in causing overdispersion and bias in replicated He ages. Farley et al. (1996), Farley (2002), and Meesters and Dunai (2002) have considered the problem of U-Th zonation, but their work does

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not provide a full analysis of the influence of zonation and grain shape on alpha ejection. This issue may be particularly important for zircon, which commonly shows easily recognizable zoning, as indicated by cathodoluminescence (CL), backscatter electron imaging, and ion microprobe U-Pb dating (see review by Corfu et al., 2003). While CL maps do not quantitatively image U content, there is an often observed qualitative negative correlation between U content and CL intensity, likely related to CL suppression due to reduced crystallinity in high-U, radiation damaged domains (Nasdala et al., 2003). U-Th inhomogeneity is recognized in apatite as well (Boyce and Hodges, 2001; Dempster et al., 2003; Boyce and Hodges, 2005), but is less well documented in the literature.

Some recent studies have shown that U-Th zonation does produce significant age bias in (U-Th)/He dating. For example, Tagami et al. (2003) reported zircon He ages for the rapidly cooled Tardee Rhyolite. The reported mean ejection-corrected age 78.8 ± 7.0 Ma is much older than the U/Pb zircon crystallization age 58.4 ± 0.7 Ma (Gamble et al., 1999). In contrast, the uncorrected He age 56.2 ± 5.4 Ma agrees well with the emplacement age. Tagami et al. (2003) showed that Tardree Rhyolite zircons commonly have U-rich cores and U-poor rims (imaged by intracrystalline spontaneous fission-track distributions) which produce nearly complete ^{4}He retention. Thus, the standard F_T correction overestimates the ^{4}He ejected resulting in "too-old" ages. In another example, single-grain zircon He dating of slowly cooled plutons by Reiners et al. (2004) showed that zircons with tips and rims enriched by a factor of 30 in U produced ages that were "too-young" compared with ages from non-zoned zircons. The accuracy of ejection corrected He ages from non-zoned grains was inferred using time-temperature curve determined from ^{40}Ar/^{39}Ar multi-diffusion-domain analysis of K-feldspar. Reiners et al. (2004) showed that by using an α-ejection correction that accounted for the zoning, the He ages for the zoned and unzoned zircons could be brought into agreement.

In this paper, we use a numerical model to evaluate the relationships between helium retentivity and U-Th distributions for styles of zonation typical for zircon. We consider spherical grains and also bipyramidal prisms; however, the model calculation can be easily extended to other grain shapes, and thus could be used to estimate α-ejection corrections for other commonly dated minerals, such as apatite and titanite. In some cases (e.g., commonly with titanite), a breakage correction may need to be added to deal with the fact that these phases are commonly fragmented (Farley et al., 1996; Reiners and Farley, 1999; Stockli and Farley, 2004). Our model deals solely with α-ejection for quickly cooled zoned samples and does not treat the combined effects of α-ejection and helium diffusion (e.g., Meesters and Dunai, 2002).

Routine use of our model requires a minimally destructive methodology for analyzing U-Th distribution that can be easily applied to individual crystals before dating. Preliminary work indicates that 213 nm laser ablation ICP-MS depth profiling on unmodified whole grains does not significantly disturb the He systematics. We present here modeling results and corrected ages based U-Th zonation depth-profiles of Tardree Rhyolite zircons to illustrate the technique. A future paper will provide a more complete report on this methodology.

Table 1. Summary of abbreviations and symbols used in the text.

$\vec{A}$	Final alpha resting position vector
$\vec{P}$	Parent nuclide position vector
$\vec{S}$	Alpha-particle trajectory vector
F_T	Homogeneous bulk retentivity
F_{ZAC}	Zonation-dependent bulk retentivity
m	Subscript representing mth isotope
$f_m(\vec{P})$	Local retentivity, continuous form
$f_m(x_i, y_j, z_k)$	Local retentivity of m, discrete form
$a_m(x_i, y_j, z_k)$	Alpha-productivity
i, j, k	Matrix indices in x, y, and z
Δ	Isotropic computational grid spacing
C_m	Concentration of isotope m
α_m	Alphas produced in decay chain of m
λ_m	Decay constant for m
r_i	Discrete radial position
R	Spherical grain radius
τ	Growth-progress variable
γ	Age bias
$\hat{N}_n$	Unit normal vector for nth crystal face
d_n	Distance of nth crystal face to the origin
β	Surface-area-to-volume ratio
L	Crystal length
W_1, W_2	Crystal widths
h	Average pyramid height

1.1. General Method

Consider a U or Th atom at position $\vec{P}$ (Table 1). Radioactive decay produces an alpha particle that moves in direction $\vec{S}$. The alpha particle comes to rest at

$$\vec{A} = \vec{P} + \vec{S} \tag{2}$$

The direction of $\vec{S}$ is random but its magnitude S, is the constant alpha stopping distance as specified by the average kinetic energy for all decays (Farley et al., 1996) (Table 2). In the absence of diffusion, ignoring nm-scale displacement of intermediate daughter products, and given sufficient time, spontaneous decay would result in a set of alpha particles uniformly distributed at a distance S around $\vec{P}$. If $\vec{P}$ lies in close proximity to a grain boundary some of these positions may fall outside of the host grain (i.e., α-ejection). We define the local retentivity $f(\vec{P})$ as the fraction of alpha particles generated at $\vec{P}$ that remain in the host grain. $f(\vec{P})$ can be determined by analytical integration for some simple grain geometries (e.g., Farley et al., 1996; Meesters and Dunai, 2002) but more complex grain shapes require solutions by numerical integration or Monte Carlo modeling (Farley et al., 1996; Farley, 2002).

In our model the bulk ^{4}He retentivity for an entire grain is given by integration over a three-dimensional grid. The nodes of the grid are defined by $x_i = \Delta i$, $y_j = \Delta j$, and $z_k = \Delta k$, where x, y and z are continuous Cartesian coordinates, and x_i, y_j and z_k are discrete positions within an isotropic grid with node spacing defined by Δ. The retention F_{ZAC} for an entire grain is defined by the weighted average

$$F_{ZAC} = \frac{\sum f_m(x_i, y_j, z_k) a_m(x_i, y_j, z_k)}{\sum a_m(x_i, y_j, z_k)}. \tag{3}$$