Chemical Geology 363 (2014) 312–321

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

On the development of electron microprobe zircon fission-track geochronology

David J. Gombosi [a,*], John I. Garver [b], Suzanne L. Baldwin [a]

[a] *Department of Earth Sciences, Syracuse University, Syracuse, NY 13244, USA*
[b] *Geology Department, Union College, Schenectady, NY 13208, USA*

ARTICLE INFO

Article history:
Received 24 June 2013
Received in revised form 9 November 2013
Accepted 11 November 2013
Available online 18 November 2013

Editor: K. Mezger

Keywords:
Zircon
Fission-track
Electron microprobe
EPMA
ZFT
EP-FT

ABSTRACT

The fission-track method has been applied for decades to quantify rates and timing of processes in the shallow crust. The most widely used approach, the external detector method, involves counting fission-tracks, a decay product resulting from the spontaneous fission of ^{238}U, and a paired set of induced tracks (parent proxy) from the thermal neutron irradiation of ^{235}U. We propose an alternate method of dating zircons that utilizes an electron microprobe to directly measure uranium concentration [U] and image the number of spontaneous fission-tracks or etch figures that intersect the surface of the crystal using an electron backscatter detector. The electron microprobe fission-track (EP-FT) method is used to date six zircon samples, four of which are widely used as standards: Fish Canyon Tuff, Peach Springs Tuff, Buluk Member of the Bakata Formation (tuff), Tardee Rhyolite, Mt. Dromedary Complex (hypabyssal granite), and Browns Park Formation (tuff). All samples yield ages that overlap within two standard deviations of published reference ages determined using other radiometric techniques (i.e., K/Ar, ^{40}Ar/^{39}Ar, and U/Pb) and also by the traditional fission-track external detector method. To correct for poorly constrained parameters such as the spontaneous fission decay constant, weight to volume percent conversions, etching efficiency, and selection bias, we calculate a preliminary Z proportionality factor of 4469 ± 661 (1σ). The EP-FT technique avoids the hazard and expense of thermal neutron irradiation, allows simultaneous chemical compositions to be determined, removes the step of counting an external detector manually, and will likely allow much higher track densities to be counted than would be normally possible with optical microscopy. The technique is ideal for dating moderate to high U zircons (>100 ppm U).

1. Introduction

Zircon fission-track dating is one of many low temperature thermochronologic techniques applied to tectonics, landscape evolution, tephrochronology, and provenance studies (e.g., Naeser et al., 1973; Seward, 1979; Baldwin et al., 1986; Naeser et al., 1987; Brandon and Vance, 1992; Roden et al., 1993; Seward and Kohn, 1997; Brandon et al., 1998; Brix et al., 2002; Bernet et al., 2004a, 2009). In its simplest application, a zircon fission-track age constrains the time since that zircon grain cooled through a closure temperature (Dodson, 1973, 1979). The zircon fission-track closure temperatures range from ~300 °C to 180 °C (Gleadow and Brooks, 1979; Hurford, 1986; Yamada et al., 1995; Brandon et al., 1998; Tagami et al., 1998; Rahn et al., 2004; Garver et al., 2005; Bernet, 2009) and are inferred to be dependent on the amount of accumulated radiation damage in the lattice structure (Kasuya and Naeser, 1988; Garver et al., 2005). Zircon fission-track (ZFT) dating has existed for ~50 years, yet new advances in electron microbeam technology permit the extension of this technique to populations of zircon that are not dateable with traditional methods because of their high U or very old age and hence accumulated damage. The most common method, the external detector method (EDM), has the advantages of being able to detect very low (ppb) levels of U, requiring relatively little analytical equipment, but requires access to a research reactor with a high thermal/fast neutron flux for sample irradiation, and subsequent handling of radioactive materials. The electron probe fission-track (EP-FT) technique does not rely on thermal neutron irradiation (Fayon and Baird, 2005). This provides a good reason to develop the EP-FT technique as the number of research reactors is diminishing (Rogers, 2002). The EP-FT method also overcomes challenges associated with the laser ablation inductively coupled plasma mass spectrometry (LA–ICP-MS) technique in that it is non-destructive, eliminates the need for precise alignment (hence one can count tracks in a zoned zircons with great ease), and potentially allows higher track densities to be imaged than what could traditionally be counted using an optical microscope. Trace actinides that are important to determining total radiation damage and annealing behavior (i.e. U, Th) can be simultaneously measured so progress may be made in understanding the relationship between annealing and composition and/or radiation damage.

---

* Corresponding author at: ExxonMobil Upstream Research Company, Houston, TX 7725277098, USA. Tel.: +1 781 789 9718.
E-mail address: djgombos@syr.edu (D.J. Gombosi).

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.11.005

The recent development of LA–ICP-MS FT dating (Svojtka and Kosler, 2002; Hasebe et al., 2004; Donelick et al., 2006; Hadler et al., 2009; Hasebe et al., 2009, 2011), chemical isochron U/Pb dating (e.g. Suzuki and Adachi, 1991; Kato et al., 1997; Suzuki and Kato, 2008) and chemical U/Pb dating (Williams et al., 1999; Pyle et al., 2002; Spear and Pyle, 2002; Goncalves et al., 2005; Jercinovic and Williams, 2005; Pyle et al., 2005; Spear et al., 2009; Sánchez et al., 2011) are utilized in the EP-FT technique as we are able to adapt and modify relevant procedures associated with each of these methods. In this paper we develop the basis for EP-FT dating through a robust treatment of the analytical conditions, decay constant biases, and statistics required for the development of the electron microprobe zircon fission track technique.

2. Background: fission-track dating

Fission-track dating relies on counting linear damage zones within geologic insulator materials such as glass, apatite, titanite, or zircon (Price and Walker, 1962; Fleischer and Price, 1964a,b; Fleischer et al., 1964) formed from the spontaneous fission of ^{238}U. Damaged regions are etched with a chemical etchant (KOH:NaOH for zircon) (Gleadow et al., 1976; Garver, 2003) to make the tracks larger, and hence visible using an optical microscope at high magnification (1000–2000×). The fission-tracks, produced naturally as the result of radioactive decay, can be counted once etched. There are several variations on the technique used determine the ratio of ^{238}U (parent) to the number of tracks including the EDM, population, re-etch, and LA–ICP-MS methods (e.g., Naeser, 1976; Gleadow, 1981; Jonckheere et al., 2003; Hasebe et al., 2004). All except the LA–ICP-MS method involve irradiation of the sample with thermal neutrons in a nuclear reactor (Price and Walker, 1962) which induce fission of ^{235}U but not of ^{238}U.

The EDM technique, however, can introduce errors that arise from poor contact between the external detector and the crystal during irradiation and in misalignments, which may occur while counting the number of spontaneous and induced tracks, or even accidentally cleaving of the external detector if mica is used. In order to calculate an age the EDM also calls for understanding thermal neutron fluence in the reactor, the thermal neutron capture cross-section for ^{235}U, and the spontaneous fission decay constant of ^{238}U.

Historically these parameters either have large uncertainty in their measurement or are poorly known, so a method of correction using a proportionality factor zeta (ζ) with reference to a standard of known age (Fleischer and Hart, 1972; Hurford and Green, 1983) was recommended by the IUGS (Hurford, 1990) to overcome these inherent complexities. Today the majority of laboratories still use the standards based ζ approach, although with better measurements of the decay constant (Holden and Hoffman, 2000) and irradiation parameters (Van den Haute et al., 1988; Jonckheere, 1995) using an absolute approach where the age is not calibrated to a standard is now routinely applied in several laboratories.

2.1. LA–ICP-MS fission-track dating

In the past decade, direct measurement of [U] through the use of LA–ICP-MS in fission-track dating has been under development (Svojtka and Kosler, 2002; Hasebe et al., 2004, Donelick et al., 2006; Hadler et al., 2009; Hasebe et al., 2009, 2011). The primary advantage in using LA–ICP-MS is that it eliminates the need to irradiate samples with thermal neutrons. This in turn eliminates the need to handle radioactive materials and improves turnaround time for dating material. Additionally, any irradiation variables are also eliminated and other elements of interest (i.e., Hf, Th, and REEs in zircon) can be simultaneously measured. A possible drawback when using fission-track LA–ICP-MS dating is the assumption that there is no variability in [U] between the volume the laser ablates and the integrated volume from which tracks emerge. This assumption limits the ability to quantify zonation at depth within the grain. The technique is also destructive on the scale of the laser spot, so alternative methods of capturing stacks of images prior to LA–ICP-MS are beginning to be used to retain information about the tracks (Gleadow et al., 2007). Depending on how the LA–ICP-MS analysis is performed an assumption is commonly made that an isotope of one of the major elements in the matrix mineral (e.g., ^{29}Si in zircon) has a fixed abundance, and this major element isotope is used as an internal standard (Hasebe et al., 2009, 2011). To our knowledge, no studies have been published to substantiate the assumption of major element homogeneity across all zircons.

2.2. The fission-track age equation

The density (ρ) of tracks is related to the area (A) in cm^2, and the total number of tracks (N) by:

$$\rho = \frac{N}{A}. \tag{1}$$

By measuring two sets of tracks (ρ_s/ρ_i) as a proxy for the daughter/parent ratio ($\rho_s/^{238}$U) the EDM avoids the need to explicitly calculate the number of ^{238}U atoms represented by the subsurface volume which contains surface-intersecting fission-fragments.

We use a simplified form of the fission-track age equation (Gleadow, 1974; Wagner and Van den Haute, 1992) which removes any terms typically associated with irradiation and assumes direct measurement of ^{238}U concentrations.

$$t = \frac{1}{\lambda_\alpha} \ln\left(\frac{\lambda_\alpha}{\lambda_{sf}} \frac{\rho_s}{N_{238U}} QG + 1\right). \tag{2}$$

Where ρ_s is the density (Eq. (1)) of natural spontaneous tracks intersecting the surface of the crystal over the count area, t is the fission-track age, N_{238U} is the number of ^{238}U atoms in the volume below the surface sampled by surface-intersecting tracks, G is a geometry factor, where 0.5 is the value for an internal surface (4π geometry), and λ_{sf} and λ_α are the ^{238}U spontaneous fission and alpha decay constants. The variable Q is a procedural factor, a combined term describing both the etching efficiency of a material and the observational variance of the operator (Jonckheere and Van den Haute, 2002).

When using Eq. (2), three major sources of uncertainty are introduced: the λ_{sf} value, counting uncertainty in measuring ρ_s, and ascertaining the number of ^{238}U atoms.

In previous decades the correct value of the spontaneous fission decay constant (λ_{sf}) has been the largest source of uncertainty. To reduce uncertainties associated with the decay constant, etching efficiency, and irradiation parameters (in the EDM method), the concept of a Z factor was introduced (Fleischer and Hart, 1972; Hurford and Green, 1983). The Z factor serves as a proportionality constant determined by using a sample of known age and treating it in the exact same manner as the unknown. The Z factor differs from the better known ζ factor in that it does not integrate irradiation factors within the value and the ζ factor accounts for differences between irradiations using a standard U glass as a neutron flux monitor.

$$Z = \frac{e^{\lambda_\alpha t_{std}} - 1}{\lambda_\alpha \frac{\rho_s}{N_{238U\,std}} G}. \tag{3}$$

Where t_{std} is the age of a well-constrained standard determined using another geochronologic technique (most often K–Ar or ^{40}Ar/^{39}Ar). Substituting Z into Eq. (2) this becomes:

$$t = \frac{1}{\lambda_\alpha} \ln\left(\frac{\rho_s}{N_{238U}} G\hat{Z}\lambda_\alpha + 1\right). \tag{4}$$