Using zircons from Hall Peninsula, Baffin Island, Nunavut to understand the effects of radiation damage on helium diffusion

A.S. Goldsmith[1], C.G. Creason[2], D.F. Stockli[3] and R.A. Ketcham[3]

[1]*Department of Geological Sciences, University of Texas at Austin, Austin, Texas, atom.goldsmith@utexas.edu*

[2]*Department of Earth Sciences, Dalhousie University, Halifax, Nova Scotia*

[3]*Department of Geological Sciences, University of Texas at Austin, Austin, Texas*

This work was part of the 2012–2014 Hall Peninsula Integrated Geoscience Program (HPIGP), led by the Canada-Nunavut Geoscience Office (CNGO) in collaboration with the Government of Nunavut, Aboriginal Affairs and Northern Development Canada, and the Geological Survey of Canada. It involved strong contributions from the universities of Alberta, Dalhousie, Laval, Manitoba, Ottawa and Saskatchewan, and the Nunavut Arctic College. It has benefited from support by local and Inuit-owned businesses and the Polar Continental Shelf Program. The focus is on bedrock (1:250 000 scale) and surficial (1:100 000 scale) geology mapping. In addition, a range of thematic studies is being conducted that includes Archean and Paleoproterozoic tectonics, geochronology, landscape uplift and exhumation, microdiamonds, sedimentary-rock xenoliths and permafrost. The goal is to increase the level of geological knowledge and better evaluate the natural-resource potential in this frontier area.

Goldsmith, A.S., Creason, C.G., Stockli, D.F. and Ketcham, R.A. 2014: Using zircons from Hall Peninsula, Baffin Island, Nunavut to understand the effects of radiation damage on helium diffusion; *in* Summary of Activities 2013, Canada-Nunavut Geoscience Office, p. 101–108.

Abstract

Zircon (U-Th)/He thermochronometry (ZHe) is a method of determining low-temperature thermal histories by measuring the concentrations of U, Th and He in zircon. Because the diffusion of He from the crystal is a function of temperature and time, the combined ratios of these elements contain valuable information about cooling of the hostrock. Helium diffusion in zircon, however, is more complex than in previous models, in that it is now well known to be significantly and systematically affected by damage to the crystal lattice caused by the á-decay of U and Th, and the spontaneous fission of ^{238}U. Therefore, a thorough and quantitative understanding of the effects of radiation damage on He diffusion kinetics is critical to the accurate modelling of thermal histories. This is particularly useful for cases in which zircons have experienced significant radiation doses, or prolonged residence at temperatures above which radiation damage is annealed. This study uses (U-Th)/He thermochronology on zircon from Hall Peninsula, Baffin Island, which displays a negative correlation with radioactive element concentration, in combination with Raman spectroscopy and laser-ablation inductively coupled plasma–mass spectrometry, to quantify the effects of radiation dose on helium diffusivity. The ages produced from this study are anticipated to show the full range of variability in He diffusivity from radiation dose. These data and others will help in identifying the thresholds of radiation dose required for significant alteration of He diffusivity, and in developing a new and more accurate model for ZHe thermochronology.

Résumé

La thermochronométrie (U/Th)/He dans les zircons est une méthode qui permet d'établir les parcours thermiques de basse-température en mesurant les concentrations en U, Th et He dans les zircons. Puisque le comportement de l'He au sein des cristaux est fonction de la température et du temps, les rapports combinés de ces éléments renferment d'importants renseignements au niveau des vitesses de refroidissement des roches encaissantes. Le comportement de l'He qui s'échappe par diffusion des zircons est cependant un processus plus complexe que ne le décrivent les modèles antérieurs; en effet, il appert maintenant que ce processus est touché considérablement, et de façon systématique, par les dégâts causés au réseau cristallin par la réaction nucléaire de désintégration alpha de l'U et du Th, ainsi que la fission spontanée de l'^{238}U. La modélisation précise des parcours thermiques exige donc une connaissance approfondie et quantitative des effets des dégâts par rayonnement sur la cinétique de l'échappement par diffusion de l'hélium. De telles connaissances se révèlent surtout utiles dans les cas où les zircons ont été exposés à de fortes doses de rayonnement, ou sont restés en place pendant une période de temps prolongée à des températures au-dessus desquelles les dégâts par rayonnement se trouvent recuits. Pour

This publication is also available, free of charge, as colour digital files in Adobe Acrobat® PDF format from the Canada-Nunavut Geoscience Office website: http://cngo.ca/summary-of-activities/2013/.

les besoins de la présente étude, on a eu recours aux résultats de la thermochronométrie (U-Th)/He dans les zircons de la péninsule Hall (île de Baffin), qui se caractérisent par une corrélation négative avec les concentrations en éléments radioactifs, combinés aux résultats provenant de la spectrométrie Raman et de l'ablation laser couplée à un spectromètre de masse à source à plasma inductif, afin de quantifier les effets de doses de rayonnement sur la diffusivité de l'hélium. Les résultats semblent indiquer que les âges obtenus et présentés dans ce rapport illustrent la gamme complète de la variabilité au niveau de la diffusion de l'He causée par les doses de rayonnement. Ces données, ajoutées à d'autres, aideront à déterminer les seuils de dose de rayonnement requis pour causer une importante altération au niveau de la diffusivité de l'He et à mettre au point de nouveaux modèles plus précis de thermochronométrie ZHe.

Introduction

The technique of (U-Th)/He thermochronology of zircon ($ZrSiO_4$) is an increasingly popular method of determining low-temperature thermal histories. This approach utilizes the high concentrations of U and Th (tens to thousands of ppm) in natural zircon. As U and Th undergo radioactive decay to Pb, they implant a series of á-particles into the crystal lattice. These á-particles, consisting of two protons and two neutrons, quickly become ^{4}He by electron capture. Each decay event also causes tens of thousands of localized atomic displacements, both from the energetic ejection of the daughter á-particle and recoil of the parent nuclide. The implanted He can be lost by thermally activated diffusion, the rate of which is in part a function of temperature but also a function of the properties of the mineral lattice, particularly the extent of radiation damage. Because of the thermal component of He retention, the 'ZHe' age, calculated from the concentrations of U, Th and He, contains significant information about the cooling history of the rock. For example, in the simplest scenario of a constant cooling rate of 10°C/m.y., zircon will 'close' to He diffusion and begin to retain significant concentrations of He at approximately 170–190°C (Reiners, 2005). These cooling ages, combined with geological and/or other thermochronometric constraints, are used to produce models of thermal histories by calculating ^{4}He production and diffusion over time. Such models are of great use in understanding the timing of geological processes, including upper-crustal structural deformation, basin formation and thermal evolution, and hydrothermal activity.

The overall accuracy of these models, however, is impeded by a lack of understanding of the full complexities of He diffusion kinetics, in particular with respect to damage to the crystal lattice caused both by the á-decay of U and Th, and by the spontaneous fission of ^{238}U. The systematic effects of this damage on He diffusion have long been recognized, particularly for rocks in which populations of zircon have accumulated significant radiation doses, and that have not experienced temperatures sufficient to allow the crystal lattice to reorder, or anneal (Nasdala et al., 2004; Reiners et al., 2004; Reiners, 2005; Guenthner and Reiners, 2009; Ketcham et al., 2013). For example, ZHe ages obtained from boreholes of assorted basement rock of the Egyptian Sinai Peninsula by Pujols (2011) yield a clear negative correlation with effective uranium concentration (eU), here used as a proxy for radiation damage (Figure 1). These data are significant for several reasons, the most important of which are 1) that the variation in ages is more than 500 m.y. and their negative correlation with eU is observed in several individual samples of rock from different locations; and 2) that these ages correlate with known regional tectonic events. These relationships suggest not only that accurate modelling of thermal histories recorded by zircon (U-Th)/He requires a quantitative knowledge of the effects of radiation dose on diffusivity, but that it is possible for a rock with zircons of sufficiently variable U and Th concentrations to record multiple thermal events.

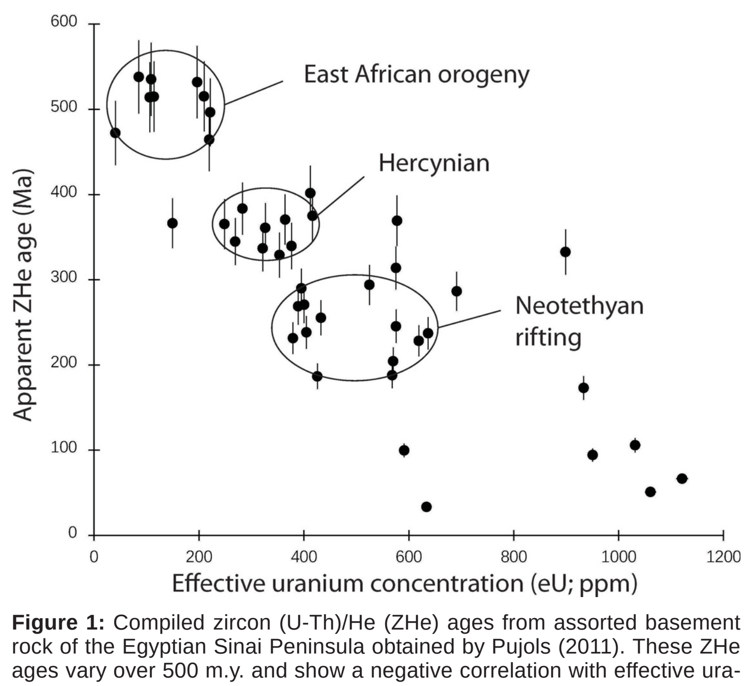

Figure 1: Compiled zircon (U-Th)/He (ZHe) ages from assorted basement rock of the Egyptian Sinai Peninsula obtained by Pujols (2011). These ZHe ages vary over 500 m.y. and show a negative correlation with effective uranium concentration (eU = [U] + 0.23[Th], which treats both elements as a single á-particle producer), here used as a proxy for radiation damage. This remarkable spread in ages is observed within individual samples of rock from various locations. Furthermore, these ages are interpreted as recording three successive tectonic events, as noted on the figure. These data provide strong evidence that zircon (U-Th)/He is a robust, dynamic thermochronometer capable of retaining significant information on complex thermal histories.

Similarly, ZHe ages from a transect of southern Hall Peninsula, collected by Creason et al. (2013) during the 2012 Hall Peninsula field season, show a strong and clear decrease in ZHe age of more than 700 m.y. with increasing eU (Creason, pers. comm., 2013). This study, and the future research described herein, utilizes further analysis of these zircons and others to understand these phenomena and develop a new model for ZHe thermochronology.

Background

Helium diffusion kinetics

Previous research

The diffusion of He from zircon is an Arrhenian process, meaning that diffusion coefficients are a function of temperature and time, for which quantitative information obtained over laboratory time scales may be extrapolated to geologically relevant settings. The He diffusion kinetics of zircon, described in detail by Reiners (2005), were primarily determined by step-heated, fractional-loss diffusion experiments on zircon from the Fish Canyon Tuff, Colorado and the rapidly exhumed Gold Butte block, Nevada (Reiners et al. 2002, 2004). One convenient method of visualizing the diffusive process is the closure temperature (T_c), generally given as the approximate temperature at which the system closes to bulk He diffusion given the simple thermal history of monotonic cooling at a rate of 10°C/m.y. (Dodson, 1973). Reiners et al. (2004) experimentally determined that zircon has a closure temperature of approximately 170–190°C. For more information on the mathematics and design of these experiments, the reader is directed to Fechtig and Kalbitzer (1966), and Harrison and Zeitler (2005).

The effects of radiation doses exceeding 2–4 × 10^{18} á-decays/g have been systematically observed to dramatically reduce the activation energy required for bulk He diffusion, leading to anomalously young ages (Nasdala et al., 2004; Reiners et al., 2004; Reiners, 2005; Guenthner and Reiners, 2009; Ketcham et al., 2013). This dosage threshold is thought to correspond to the overlapping of fission-track zones, which connect through and out of the crystal, creating low–activation energy diffusion pathways. This threshold is referred to as the fission-track percolation point, calculated by Ketcham et al. (2013) at approximately 1.9 × 10^{18} á-decays/g. Furthermore, Guenthner et al. (2013) documented an increase in diffusivity, corresponding to a decrease in T_c, of more than nine orders of magnitude at dosages exceeding this threshold, as well as a similar decrease in diffusivity of more than three orders of magnitude at lower levels of damage.

Producing a better model

The development of a newer, more accurate model for ZHe hinges not only on a quantitative understanding of the kinetics of He diffusion, but also on an understanding of the kinetics of radiation damage. The crystal lattice is affected by two distinct forms of damage: ‘fission-track damage’, caused by the spontaneous fission of ^{238}U; and ‘á-damage’, caused by the simultaneous ejection of the daughter á-particle and recoil of the parent nuclide. The accurate measurement of, and the ability to describe a model for, the accumulation and annealing of radiation damage over geological time and temperature and their evolving effects on diffusion are of critical importance to the accurate interpretation of ZHe thermochronometric data.

Although the similar radiation-damage accumulation and annealing model (RDAAM) for apatite, which describes a positive correlation between apatite closure temperature and radiation dose (Shuster et al., 2006; Flowers et al., 2009), and the new ZHe model proposed by Guenthner et al. (2013) provide an excellent framework for further research into the topic, both models are reliant on the assumption that fission-track (FT) density and/or ^{4}He concentration is an effective proxy for the α-dose present in a given grain; that is, á-recoil damage in the crystal lattice heals at approximately the same temperatures as He diffusion or fission-track annealing. While this might be an accurate proxy for apatite, the case for zircon is potentially more complex.

This study takes a different approach, focusing on datasets like those from Hall Peninsula on southern Baffin Island (Creason and Gosse, 2014, Figure 1). This study uses zircon from 16 samples collected during the Hall Peninsula field season of 2012. After standard (U-Th)/He mineral separation processes, including crushing and both magnetic and heavy liquid density separations, grains of zircon are hand selected for size and crystal quality, and analyzed using a combination of Raman spectroscopy, laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS), step-heated diffusion experiments and standard (U-Th)/He analysis. This combination of techniques will provide a dataset that will enable direct correlation between ZHe age and radiation dose, and quantitative statements about the effects of present radiation dose on diffusion constants.

Methodology

Raman spectroscopy

Raman spectroscopy is a technique that observes shifts in energy of a high-energy monochromatic laser resulting from low-frequency vibrations of molecular bonds due to inelastic collisions between photons and electron clouds. It has been well documented as an effective, nondestructive means of measuring radiation damage in zircon (Nasdala et al., 1995; Geisler et al., 2001; Geisler, 2002; Geisler and Pidgeon, 2002; Nasdala et al., 2003; Nasdala et al., 2004; Geisler et al., 2005; Marsellos and Garver, 2010). In this technique, the frequency and full width at half maximum

(FWHM) of the í 3 [SiO_4] antisymmetric stretching peak are measured. The í 3 stretching peak in highly crystalline zircon occurs at a frequency of approximately 1008 cm^{-1} and has an FWHM of approx. 1.2 cm^{-1} (Nasdala et al., 1995; Zhang et al., 2000a; Nicola and Rutt, 2001; Marsellos and Garver, 2010). With increasing radiation doses, the frequency decreases and the FWHM increases nearly linearly (Figure 2), reaching a limit at which the crystalline structure of the mineral is thought to be totally amorphous, or metamict, corresponding to a frequency of approximately 975–985 cm^{-1} and an FWHM of 25–38 cm^{-1} (Nasdala et al., 1995; Zhang et al., 2000b; Nasdala et al., 2001). For more information on this technique, the reader is directed to Nasdala et al. (1995) and Nasdala et al. (2004).

The majority of studies that use Raman spectroscopy to estimate zircon radiation doses do so on polished grain mounts, so that grains with a heterogeneous U and Th distribution can be identified prior to analysis by cathodoluminescence or back-scattered electron imaging. However, calculation of the á-ejection correction in (U-Th)/He, which estimates the amount of ^{4}He ejected outside the grain boundary by actinides near the grain boundary (Farley et al., 1996), is vastly simpler for whole grains; therefore, this study used whole grains rather than polished. This approach raises several potential issues, the most prominent of which is the commonly heterogeneous distribution of U and Th, which causes a similarly heterogeneous distribution of radiation dose. If a zircon's surface is enriched or depleted in U and/or Th with respect to the rest of the grain, Raman spectra taken on the surface will respectively over- or underestimate the radiation dose; likewise, due to anomalously high or low He ejection outside of the grain from near the grain boundary, the apparent ZHe age of the grain will be anomalously old or young, respectively. Another significant issue raised by the methodology of whole-grain Raman analyses is the effect of chemistry on the í 3 peak, typically measured by electron microprobe, which has been documented by several researchers (Hurley and Fairbairn, 1953; Geisler et al., 2001; Kolesov et al., 2001; Nicola and Rutt, 2001; Geisler et al., 2005; Marsellos and Kidd, 2008; Marsellos and Garver, 2010). These issues are addressed by the use of LA-ICP-MS, described in the next section.

Measurements of Raman spectra were taken in the Mineral Physics Lab at the University of Texas at Austin with a 532 nm laser operating at 30–70 mW, and measured by an Andor Technology plc. spectrometer at 1800 grooves/mm. Calibrations were performed at the beginning of each experiment using a combination of a Si wafer and a polished mount of well-characterized Mud Tank zircon; the Mud Tank zircon was remeasured every 30 measurements to check for machine drift. Results from current Raman measurements and their respective radiation-dose estimates, calculated with equations from Nasdala et al. (2001), are given in Table 1.

Zircons were hand selected for size and quality to ensure that no features such as fractures or broken edges would affect the He measurements. For further information on selection of suitable grains for (U-Th)/He analysis, see Farley et al. (1996). Each grain was measured by Raman spectroscopy in at least three spatially separate, 25 µm spots on a crystalline surface; the spectra, such as those in Figure 2,

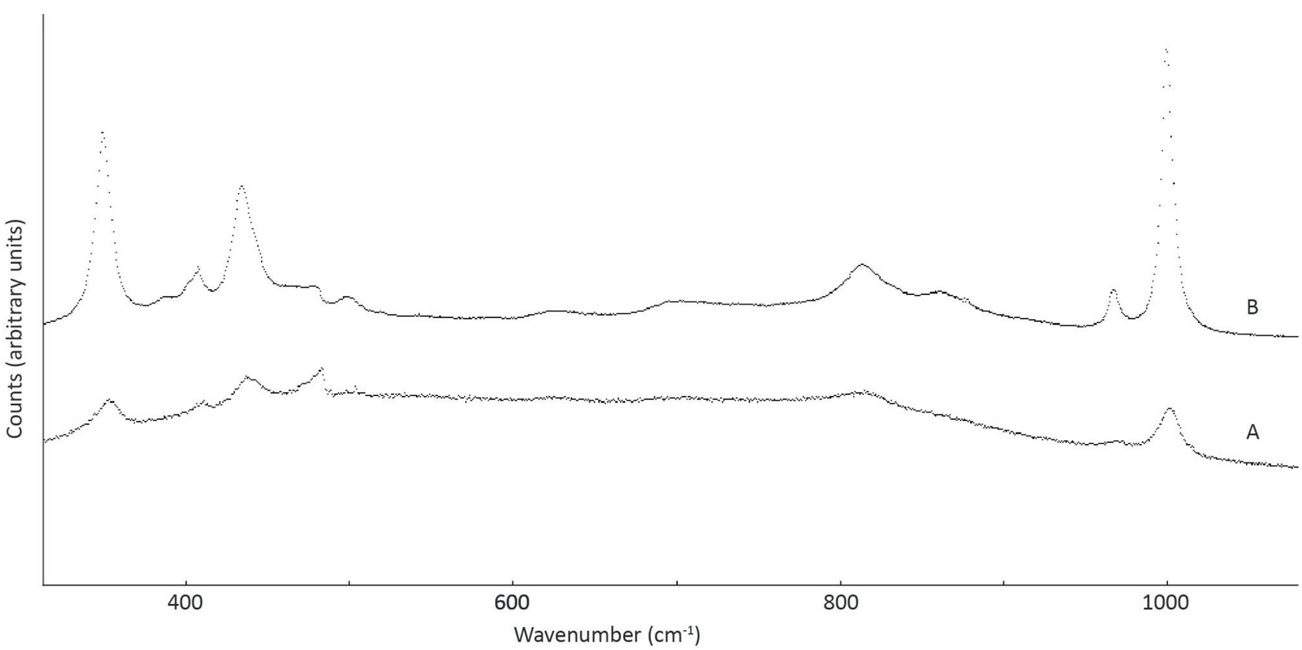

Figure 2: Raman spectra of two zircon grains from Hall Peninsula, southern Baffin Island, Nunavut. The í 3 peak, from which radiation damage is estimated, occurs at approximately 1000 cm^{-1}. Spectrum A is significantly more damaged than spectrum B, as indicated by the shorter, wider peak of A and the higher signal-to-noise ratio.

Table 1: Frequency and FWHM measurements of zircon from Hall Peninsula, southern Baffin Island, Nunavut, corrected for apparatus function, and the estimated radiation doses. Each value is the average of a minimum of three measurements taken at spatially separate points on a crystalline surface of the grain, together with the standard deviation. These data highlight the wide range of radiation doses experienced by the zircon. Abbreviations: FWHM, full width at half maximum; σ, standard deviation.

Sample no.	Rock type	Frequency (cm^{-1})	Frequency σ	FWHM (cm^{-1})	FWHM σ	Estimated dose (10^{16} α/mg)
zR-C012-1	Biotite granite	1000.1	0.27	7.1	0.4	7.1
zR-C012-2	Biotite granite	1002.4	0.40	7.3	0.5	7.3
zR-C012-3	Biotite granite	1002.8	0.57	10.3	2.0	10.3
zR-C012-4	Biotite granite	1000.6	1.98	11.4	2.2	11.4
zR-C012-5	Biotite granite	992.8	4.77	7.1	0.3	7.1
zR-C013-1	Biotite granite	1003.8	0.40	6.5	0.1	6.5
zR-C013-2	Biotite granite	1003.8	0.32	7.8	0.5	7.8
zR-C013-3	Biotite granite	1003.1	0.75	12.7	0.9	12.7
zR-C013-4	Biotite granite	998.0	0.1	8.8	0.7	8.8
zR-C013-5	Biotite granite	1003.1	0.2	7.2	0.7	7.2
zR-C015-1	Biotite granite	1001.4	0.35	11.3	1.1	11.3
zR-C015-2	Biotite granite	1003.0	1.41	8.3	1.9	8.3
zR-C015-3	Biotite granite	1002.9	0.16	8.2	0.4	8.2
zR-C015-4	Biotite granite	1001.7	1.44	9.5	1.6	9.5
zR-C015-5	Biotite granite	997.5	0.89	12.5	0.5	12.4
zR-C016-1	Biotite granite	1002.3	1.68	6.9	1.9	6.9
zR-C016-2	Biotite granite	1001.3	2.04	9.0	2.1	9.0
zR-C016-3	Biotite granite	999.9	0.17	10.2	0.6	10.2
zR-C016-4	Biotite granite	1000.0	0.67	10.9	0.5	10.9
zR-C016-5	Biotite granite	1003.9	0.49	7.4	0.1	7.4
zR-Y080-1	Magnetite monzogranite	995.8	5.60	10.2	2.7	10.2
zR-Y080-2	Magnetite monzogranite	991.1	5.15	12.9	2.2	12.9
zR-Y080-3	Magnetite monzogranite	1001.7	1.65	9.1	1.6	9.1
zR-Y080-4	Magnetite monzogranite	998.0	2.46	12.3	2.6	12.3
zR-Y080-5	Magnetite monzogranite	998.8	1.76	9.5	1.5	9.5
zR-B099-1	Biotite tonalite	1002.3	1.13	9.1	0.6	9.1
zR-B099-2	Biotite tonalite	1001.2	1.08	9.0	2.3	9.0
zR-B099-3	Biotite tonalite	1000.5	0.61	11.1	0.2	11.1
zR-B099-4	Biotite tonalite	1001.1	1.16	9.6	0.9	9.6
zR-B099-5	Biotite tonalite	1001.3	0.52	11.1	0.8	11.1
zR-B102-1	Biotite diorite	1002.6	0.78	8.8	1.2	8.8
zR-B102-2	Biotite diorite	996.6	1.80	14.8	2.1	14.8
zR-B102-3	Biotite diorite	1002.2	0.56	11.6	2.5	11.6
zR-B102-4	Biotite diorite	999.2	1.76	11.3	1.3	11.3
zR-B102-5	Biotite diorite	996.0	0.78	13.7	1.8	13.7
zR-B106-1	Monzogranite	993.8	0.55	17.7	0.3	17.6
zR-B106-3	Monzogranite	999.9	1.62	13.6	0.4	13.6
zR-B106-4	Monzogranite	992.7	0.80	18.8	1.6	18.8
zR-B106-5	Monzogranite	997.2	1.24	13.9	1.0	13.9
zR-B106-7	Monzogranite	996.8	1.00	14.7	2.1	14.7

are averages collected over a minimum of five sequential, 10-second accumulation periods. Data were fitted and corrected for apparatus function using techniques described in Nasdala et al. (2001).

Laser-ablation inductively coupled plasma–mass spectrometry

Once characterized by Raman spectroscopy, zircon grains were placed on double-sided taped epoxy mounts and analyzed by laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS). This technique involves an excimer laser that ablates a pit 16–20 µm deep and 40 µm wide into the surface of the zircon, measuring concentrations of trace elements—most importantly U, Th and Hf—and the results are calibrated against National Institute of Standards and Technology glass of known concentration. These data, which have been collected and are currently being evaluated, will

- ensure that Raman measurements made on the surface of the grain are estimating a relevant radiation dose. These measurements will allow comparison of the eU concentration used to calculate the grain's (U-Th)/He age with the eU value on the surface of the grain and help evaluate whether the Raman measurement is a reasonable estimation or an over/underestimate of the radiation dose.
- ensure that the He age is accurate. Natural zircon commonly has complex growth zoning or other chemical

heterogeneity. In the case of a grain that has a rim enriched or depleted in U or Th relative to the rest of the grain, a disproportionate amount of ^{4}He is either ejected from or not produced at the grain boundary, and the resulting age will be anomalously young or old, respectively. Therefore, LA-ICP-MS measurements of U and Th at the grain surface allow determination of whether the ZHe measured is over- or underestimated.

- facilitate corrections to shifts in the Raman spectrum caused by elements, such as Hf (which occurs in natural zircon up to 10 wt. %), U and Th, that have been noted by several researchers (Hurley and Fairbairn, 1953; Geisler et al., 2001, 2005; Kolesov et al., 2001; Nicola and Rutt, 2001; Marsellos and Kidd, 2008; Marsellos and Garver, 2010).

(U-Th)/He analysis and diffusion experiments

Following LA-ICP-MS analysis, whole-grain He, U and Th concentrations are measured at the (U-Th)/He Lab of the University of Texas at Austin. This is done via fractional-loss diffusion experiments, and by standard (U-Th)/He analysis. Although a limited number of these data have been collected, the bulk of these analyses are ongoing.

The first technique, step-heated fractional-loss diffusion experiments, are performed on zircons selected on the basis of chemical homogeneity, as measured by LA-ICP-MS, and radiation doses, as estimated by Raman spectroscopy. In these experiments, individual zircons are placed inside Pt foil capsules, wrapped in a Cu foil packet and placed in ultrahigh vacuum, wherein they are heated by a halogen bulb; heating takes place in a series of increasing and then decreasing temperatures for specified durations of time. The volume of ^{4}He released during each step is spiked with a known volume of ^{3}He, cryogenically purified and measured by quadrupole mass spectrometry (QMS). The Raman spectrum of each grain is remeasured after the experiment is complete to ensure that no significant annealing has occurred during exposure of the grain to high temperatures. Grains are then subjected to standard (U-Th)/He laser heating to ensure that >99% of the gas has been diffused from the grain.

Zircons not selected for diffusion experiments also undergo standard (U-Th)/He analysis. Single grains are placed in a Pt foil packet, placed in ultrahigh vacuum and laser heated until >99% of the total gas has been extracted. The resulting ^{4}He is spiked with a known quantity of ^{3}He, cryogenically purified and measured by QMS.

Following measurements of ^{4}He concentration, each grain is placed in a Teflon vial and spiked with a ^{235}U/^{230}Th tracer. Grains are dissolved in acid, in high-pressure digestion vessels over the course of one week, after which U and Th concentrations are measured by solution ICP-MS.

Preliminary results and future work

Although the dataset is thus far incomplete, it is expected that these data will clearly continue and elaborate on the trend observed in earlier Hall Peninsula ZHe results. Results from this study will both highlight the threshold at which radiation dose begins to affect He diffusion kinetics, and the threshold at which radiation dose is too high to permit systematic He retention by the grain (Creason, pers. comm., 2013). Once fully evaluated, LA-ICP-MS trace-element concentration data will allow identification of zonation and verify the relevance of the Raman measurement to the grain as a whole, as well as allow estimation of present radiation dose and back-calculation to the radiation dose at the time of the closure of He diffusion for that particular grain. Understanding radiation dose threshold at which He diffusivity begins to change is critical for obtaining accurate thermal histories from ZHe models.

These data will provide a critical piece of the puzzle. Ultimately, however, without an accurate model of the kinetics of radiation damage and accumulation and annealing as a function of temperature and time, it is impossible to truly accurately model how the evolving radiation dose changes He diffusivity over time. Perhaps even more critical is the lack of an independent measurement of the low-temperature thermal history of Hall Peninsula, without which it is impossible to develop a model that relates the thresholds provided by these data to temperature. Although step-heated fractional-loss diffusion experiments are helpful in relating diffusive constants to radiation dose, an independent measurement of thermal history is paramount to establish full confidence in these data. To the best of the authors' knowledge, no zircon fission-track (ZFT) or apatite fission-track (AFT) cooling ages are available for Hall Peninsula; however, it is possible that ZFT and AFT ages from these samples and others would provide the data necessary to derive a functional model.

Economic considerations

This study will yield better constraints on the effects of radiation dose on He diffusion kinetics and a better method of modelling thermal histories. Although Hall Peninsula perhaps represents a simple case of exceptionally slow cooling of crystalline rock (Stockli and Creason, pers. comm., 2013), the results of this study will provide a basis for addressing the more complex situation of the thermal history of sedimentary basins. The development of such a technique would be particularly useful in old basins in which zircons have experienced significant accumulation of damage, or basins that have complex thermal histories, consisting of multiple thermal events that could affect the presence, quality and maturation of hydrocarbon reserves. Therefore, the most significant economic contribution of this project is the improved ability to evaluate the provenance and time-temperature evolution of economic sedimentary basins and associated structural deformation.

Conclusions

An understanding of the full complexity of He diffusion in zircon is critical to its use as a thermochronometer capable of recording a wide range of thermal events in a region. The development of a new model for ZHe that accounts for these complexities is particularly important for cases in which the zircons have accumulated significant amounts of radiation damage and have experienced slow cooling, such as on Hall Peninsula of Baffin Island, or complex cooling histories that involve multiple events at successively lower temperatures, as seen in the Egyptian Sinai Peninsula. The models for ZHe by Reiners (2005) and Guenthner et al. (2013) are an excellent beginning, but, as evidenced by the data presented herein, much work remains to be done.

Acknowledgments

The authors thank E.J. Pujols for providing the first set of data needed to get this project off the ground, and the rest of the team at the(U-Th)/He Lab of the University of Texas at Austin for their friendship and support. The authors also thank J.C. Gosse, the Hall Peninsula Integrated Geoscience Program and the Canada-Nunavut Geoscience Office for allowing the use of their very interesting and helpful zircons. This manuscript has also benefitted from excellent suggestions and revision by N.M. Rayner.

References

Creason, C.G. and Gosse, J.C. 2014: Preliminary characterization of the Mesozoic–Cenozoic exhumation history of Hall Peninsula, Baffin Island, Nunavut, based on apatite and zircon (U-Th)/He thermochronology; *in* Summary of Activities 2013, Canada-Nunavut Geoscience Office, p. 93–100.

Creason, C.G., Gosse, J.C. and Young, M.D. 2013: Rift flank uplift and landscape evolution of Hall Peninsula, Baffin Island, Nunavut: an exhumation model based on low-temperature thermochronology; *in* Summary of Activities, 2012, Canada-Nunavut Geoscience Office, p. 75–84.

Dodson, M.H. 1973: Closure temperature in cooling geochronological and petrological systems; Contributions to Mineralogy and Petrology, v. 40, p. 259–274.

Farley, K., Wolf, R. and Silver, L. 1996: The effects of long alpha-stopping distances on (U · Th)/He ages; Geochimica et Cosmochimica Acta, v. 60, no. 21, p. 4223–4229.

Fechtig, H. and Kalbitzer, S. 1966: The diffusion of argon in potassium-bearing solids; *in* Potassium Argon Dating, O.A. Schaeffer and J. Zahringer (ed.), Springer-Verlag, p. 68–107.

Flowers, R.M., Ketcham, R.A., Shuster, D.L. and Farley, K.A. 2009: Apatite (U-Th)/He thermochronometry using a radiation damage accumulation and annealing model; Geochimica et Cosmochimica Acta, v. 73, no. 8, p. 2347–2365.

Geisler, T. 2002: Isothermal annealing of partially metamict zircon: evidence for a three-stage recovery process; Physics and Chemistry of Minerals, v. 29, no. 6, p. 420–429.

Geisler, T. and Pidgeon, R.T. 2002: Raman scattering from metamict zircon: comments on "Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage" by L. Nasdala, M. Wenzel, G. Vavra, G. Irmer, T. Wenzel and B. Kober (Contributions to Mineralogy and Petrology, v. 141, p. 125–144); Contributions to Mineralogy and Petrology, v. 143, no. 6, p. 750–755.

Geisler, T., Burakov, B.E., Zirlin, V., Nikolaeva, L. and Philipp, P. 2005: A Raman spectroscopic study of high-uranium zircon from the Chernobyl 'lava'; European Journal of Mineralogy, v. 17, no. 6, p. 883–894.

Geisler, T., Pidgeon, R.T., van Bronswijk, W. and Pleysier, R. 2001: Kinetics of thermal recovery and recrystallization of partially metamict zircon: a Raman spectroscopic study; European Journal of Mineralogy, v. 13, no. 6, p. 1163–1176.

Guenthner, W. and Reiners, P. 2009: He diffusion in zircon: observations from (U-Th)/He age suites and ^{4}He diffusion experiments and implications for radiation damage and anisotropic effects; American Geophysical Union, Fall Meeting, 2009, abstract V52C-06.

Guenthner, W., Reiners, P., Ketcham, R.A., Nasdala, L. and Giester, G. 2013: Helium diffusion in natural zircon: radiation damage, anisotropy, and the interpretation of zircon (U-Th)/He thermochronology; American Journal of Science, v. 313, p. 145–198.

Harrison, T.M. and Zeitler, P.K. 2005: Fundamentals of noble gas thermochronometry; Reviews in Mineralogy and Geochemistry, v. 58, p. 123–149.

Hurley, P.M. and Fairbairn, H. W. 1953: Radiation damage in zircon: a possible age method; Geological Society of America Bulletin, v. 64, no. 6, p. 659–673.

Ketcham, R.A., Guenthner, W.R. and Reiners, P.W. 2013: Geometric analysis of radiation damage connectivity in zircon, and its implications for helium diffusion; American Mineralogist, v. 98, no. 2–3, p. 350–360.

Kolesov, B.A., Geiger, C.A. and Armbruster, T. 2001: The dynamic properties of zircon studied by single-crystal X-ray diffraction and Raman spectroscopy; European Journal of Mineralogy, v. 13, no. 5, p. 939–948.

Marsellos, A.E. and Garver, J.I. 2010: Radiation damage and uranium concentration in zircon as assessed by Raman spectroscopy and neutron irradiation; American Mineralogist, v. 95, no. 8–9, p. 1192–1201.

Marsellos, A. and Kidd, W. 2008: Extension and exhumation of the Hellenic forearc ridge in Kythera; Journal of Geology, v. 116, no. 6, p. 640–651.

Nasdala, L., Irmer, G. and Wolf, D. 1995: The degree of metamictization in zircon: a Raman spectroscopic study; European Journal of Mineralogy, v. 7, p. 471–478.

Nasdala, L., Reiners, P.W., Garver, J.I., Kennedy, A.K., Stern, R.A., Balan, E. and Wirth, R. 2004: Incomplete retention of radiation damage in zircon from Sri Lanka; American Mineralogist, v. 89, no. 1, p. 219–231.

Nasdala, L., Wenzel, M., Vavra, G., Irmer, G., Wenzel, T. and Kober, B. 2001: Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage; Contributions to Mineralogy and Petrology, v. 141, no. 2, p. 125–144.

Nasdala, L., Zhang, M., Kempe, U., Panczer, G., Gaft, M., Andrut, M. and Plötze, M. 2003: Spectroscopic methods applied to zircon; Reviews in Mineralogy and Geochemistry, v. 53, no. 1, p. 427–467.

Nicola, J. and Rutt, H. 2001: A comparative study of zircon ($ZrSiO_4$) and hafnon ($HfSiO_4$) Raman spectra; Journal of Physics C: Solid State Physics, v. 7, no. 7, p. 1381.

Pujols, E.J. 2011: Temporal and thermal evolution of extensional faulting in the central Gulf of Suez and detrital zircon (U-Th)/He constraints on the thermo-tectonic Paleozoic and Mesozoic history of the Sinai, Egypt; M.Sc. thesis, The University of Kansas, Lawrence, Kansas, 246 p.

Reiners, P.W. 2005: Zircon (U-Th)/He thermochronometry; Reviews in Mineralogy and Geochemistry, v. 58, no. 1, p. 151–179.

Reiners, P.W., Farley, K.A. and Hickes, H.J. 2002: He diffusion and (U-Th)/He thermochronometry of zircon: initial results from Fish Canyon Tuff and Gold Butte; Tectonophysics, v. 349, no. 1, p. 297–308.

Reiners, P.W., Spell, T.L., Nicolescu, S. and Zanetti, K.A. 2004: Zircon (U-Th)/He thermochronometry: He diffusion and comparisons with $^{40}Ar/^{39}Ar$ dating; Geochimica et Cosmochimica Acta, v. 68, no. 8, p. 1857–1887.

Shuster, D.L., Flowers, R.M. and Farley, K.A. 2006: The influence of natural radiation damage on helium diffusion kinetics in apatite; Earth and Planetary Science Letters, v. 249, no. 3, p. 148–161.

Zhang, M., Salje, E.K.H., Capitani, G.C., Leroux, H., Clark, A.M., Schlüter, J. and Ewing, R.C. 2000a: Annealing of alpha-decay damage in zircon: a Raman spectroscopic study; Journal of Physics: Condensed Matter, v. 12, no. 13.

Zhang, M., Salje, E.K.H., Farnan, I., Graeme-Barber, A., Daniel, P., Ewing, R.C., Clark, A.M. and Leroux, H. 2000b: Metamictization of zircon: a Raman spectroscopic study; Journal of Physics: Condensed Matter, v. 12, no. 8.