Revival of U, Th–^{4}He geochronometer

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U, Th–^{4}He is an useful geochronometer that records low temperature geological events that may otherwise go unrecorded in minerals like apatite, zircon and titanite. However, it is important to separate pure, coarse grains for dating to minimize errors on He concentration determination due to pressure of contaminants and ejection effects. This article discusses the potential of this dating technique in natural settings and the important factors like suitable grain selection and appropriate corrections that should be employed to obtain meaningful ages using this technique.

THE production of ^{4}He from decay of isotopes in the U and Th series in rocks and minerals was first suggested as a geochronometer by Rutherford[1] in 1905. However, the technique was generally considered to be unreliable due to diffusive loss of He possibly associated with radiation damage or due to the ejection of high energy α-particles from the phase being dated[2]. In most cases, the He ages were younger than expected. However, recently, it has been proposed that the low He ages reflect their sensitivity to temperatures lower than other thermometers and are actually geologically significant. Thus they can provide useful information on the time–temperature evolution of rocks and their exhumation history, generating a renewed interest in the U, Th–^{4}He dating systematics for U, Th-rich minerals like apatite ($Ca_5(PO_4)_3$ (F, Cl)), zircon ($ZrSiO_4$) and titanite (sphene, $CaTiSiO_5$).

From the measured U, Th and ^{4}He concentrations in the samples, the age can be obtained from the following simple equation assuming a closed system behaviour:

$$\alpha = U[7.942(e^{\lambda_{238}t}-1) + 0.0504(e^{\lambda_{235}t}-1) + 6\{(Th/U) \times (e^{\lambda_{232}t}-1)\}],$$

where α and U, Th are the amounts of He, U and Th present at time t and λs are the decay constants of ^{238}U, ^{235}U and ^{232}Th. There are no fundamental limitations to the range of accessible ages – He ages as young as a few hundred kyr as well as 4.56 Ga (on a meteorite) have been reported[3,4]. However, with samples having $< \sim 1$ Ma of crystallization ages, secular disequilibrium in the ^{238}U series may affect the age obtained[3].

U, Th/^{4}He dating of apatite

So far, apatite has been commonly investigated to check the applicability of this dating tool. The most widely accepted procedure for apatite He dating involves *in vacuo* extraction of He by heating the sample in a furnace or with laser heating followed by purification and analysis of emitted gases by mass spectrometry. In order to avoid heterogeneity between splits analysed for the parent and daughter, the same apatites are analysed for U and Th after removal from the vacuum system and dissolution, generally by inductively-coupled-plasma-mass-spectrometry. It has been seen experimentally that He is totally outgassed from the apatites when heated at 1050°C for 20 min. Also, several experiments on apatites from the Pacoima Canyon Pegmatite, Southern California have demonstrated that heating up to this temperature does not alter the U and Th abundances of the samples beyond 2σ analytical uncertainty[5].

For U, Th/He dating of apatites, precaution should be taken to ensure 100% pure apatite separates. Apatites are commonly separated from their host using a combination of heavy liquid and magnetic separations followed by handpicking. Care should be taken to ensure that no zircons/sphenes contaminate the separates. As these contaminants can have orders of magnitude more U and Th than the apatite, their presence even in trace quantities can compromise He concentration determination. Screening for inclusions in the mineral separates can be done under a microscope. A scanning electron microscopy scan on a polished grain mount prior to working with the sample can provide a direct way to identify samples with inclusions as well as zonation. Besides, it has been seen that thermal release pattern of He is different for minerals with inclusions. For example, for apatites from Otway basin, Australia, inclusion-free grains release He quantitatively after 20 min at 950°C, whereas those with inclusions yield additional He when heated to 950°C for another 20 min, probably releasing the more tightly bound He component from the inclusions[6].

In order to test the reliability of the technique in any mineral, it is important to characterize the rate and mechanism of He diffusion from that mineral and to assess the sensitivity of diffusion to variations in chemical compositions and grain sizes. Another point of consideration is the fact that α-particles from U and Th series decay are emitted with high kinetic energies and require tens of micron to come to rest within the solid matter. In case the parent nuclides are not uniformly distributed in the mineral, the

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long stopping distances can cause substantial spatial fractionation of the parent/daughter ratios. Both these points have been studied in considerable detail – He diffusion and He ages have been studied in apatites to see the effect of diffusion behaviour on thermochronometry[5], and a mathematical framework for quantitative evaluation of stopping effects on U, Th/He ages has been developed[7].

It has been clearly seen that diffusion from apatites can be well explained by volume diffusion from a sphere[5]. The diffusion behaviour is characterized by a strong linear segment from 80 to 290°C, beyond which the diffusivity tails-off[5,8,9]. The He closure temperature for apatites estimated using the low temperature linear behaviour of He diffusion in an Arrhenius plot (considering that the high temperature behaviour is largely irrelevant)[8,9] is 74 ± 5°C. This is even lower than the closure temperature of ~ 100°C obtained from apatite fission track method. As a consequence, apatite (U–Th)/He ages document the latest stages of cooling in the uppermost crust.

In the simplest case the temperature dependence of diffusivity is characterized by an activation energy (E_α) and diffusivity at infinite temperature (D_0) by the relation:

$$D/a^2 = D_0/a^2 \exp(-E_\alpha/RT),$$

where R is the gas constant, T is the absolute temperature and a is the diffusion domain radius. For each heating step, the volume of radiogenic ^{4}He released in a given time is used to calculate D/a^2. Laboratory measurements of diffusivity over a range of temperatures will yield a line on an Arrenhius plot with a slope proportional to E_α and a y-intercept of $\ln(D_0/a^2)$. From these two quantities the closure temperature may be computed from the equation

$$(E_\alpha/RT_c) = \{(-ART_c^2 D_0)/(a^2 E_\alpha s)\},$$

where T_c is the closure temperature, A a geometric factor and s the cooling rate[10]. More generally, ages can be calculated numerically along time–temperature paths. Wolf *et al.*[5] have shown that the closure temperature so obtained is not affected in any way by grain size or shape, or even chemical composition. The above conclusions have been reached after a study of apatites of size between 60 and 180 μm in diameter and a large range in anion composition that encompasses most of the composition found in igneous rocks. The closure temperature so obtained is lower than that reported from any other dating technique and is bound to have important implications for geochronological purposes.

A key question to be addressed is the applicability of laboratory diffusion data to natural settings. To evaluate this validity, apatites collected from boreholes with well characterized down hole temperatures and thermal histories have been studied. It has been seen from such a study in eastern Otway basin that the shape and position of the He age–temperature profile is in general agreement with the model apatite age profiles generated based on laboratory diffusivity data for several apatites from the Peninsular Ranges of California and the much studied Durango apatite[6,11].

When α-ejections from the minerals are considered, they are important for small grains and advantageous to analyse the largest crystals available from any rock sample. However, implantation from the host rock as well as from nearby grains can be ignored for all practical purposes generally, considering the concentration contrast of parent nuclides between the minerals of interest and the host rock and the spacing between parent-rich accessory grains. Farley *et al.*[7] have shown by careful characterization of dated grains that it is possible to correct for ejection effects to better than a few per cent even in very small grains, provided that the distribution of parent nuclides is either homogeneous or is known. Alpha ejection is roughly proportional to the surface/volume ratio of the grain, and using Monte Carlo modelling, retentivity (number of decays which remain confined in the grain divided by the total number of decays), in cylinders with varying radii and length/radius ratios has been computed for ^{238}U decay series for homogeneous distribution[7] of U. From this study it is obvious that for grains smaller than a few hundred micrometres in minimum dimension, ejection effects will be considerable. For example, a sphere of 100 μm radius retains only 82% of its alphas. Although the computations were only done for ^{238}U series decay, the conclusion are applicable to ^{232}Th and ^{235}U series decays as well. For average apatites having cross-sections between 75 and 170 μm, F_T values have been found to vary between 67 and 85%, that would underestimate the He ages between 15 and 33% without corrections. The work demonstrates that it is important to select coarse crystals for dating; correct morphologies are also important. For example, a cylindrical crystal would be more appropriate for dating than a prismatic one. However, needle-like morphologies, which are so common in apatites, are inappropriate for He dating. Another interesting observation from the study is the insensitivity of retentivity to zonation of parent nuclides in these apatites. For example, an elevenfold increase in concentration from core to rim reduces retention by 3% only, and even a fiftyfold exponential increase from core to rim produces a 12% drop in retentivity, assuming removal of the outer 20 μm of the crystal.

Influence of crystal size on apatite U, Th/He thermochronology has also been studied in apatites from Bighorn Mountains, Wyoming[12]. The size effect on He age depends strongly on the thermal history of the rock, as seen from this study. In case the rock undergoes rapid cooling from temperatures corresponding to nearly complete He diffusive loss to nearly complete He retention, the crystal size influence may not be considerable. However, if the rock has been in the partial retention zone for long periods of time (~30–70°C for >10^7 years) in which radiogenic He is only partially retained due to diffusive loss, the influence of crystal size can be considerable. In fact, a strong correlation between apatite grain size and He age from a single rock may imply slow cooling. For example, He ages from apatites of Bighorn Mountains, Wyoming show a range of 98–348 Ma correlating with grain sizes of 32–99 μm in

one case, and 107–232 Ma correlating with grain sizes of 42–103 μm in another[11]. The crystal size–age correlation of these samples corresponded with thermal histories for rocks in the upper 0.75 km of the Precambrian basement involving subaerial exposure, burial by sedimentary rocks followed by exhumation.

Other important points worth consideration are the amount of He that will be lost at ambient temperatures on the earth's surface as well as the sensitivity of the closure temperature determined to the choice of the cooling rate. The He loss[5] from any sample on the earth's surface is negligible even over periods of 100 m.y. at temperatures of the order of 25°C. But it is not only the mean annual temperature that has to be considered, but also the maximum temperature that the sample has experienced. Previous works have shown that forest/range fires and ambient temperature fluctuations can lead to diffusive loss of cosmogenic ^{3}He from some minerals[13,14]. However, from modelling of the distribution of peak temperatures with depths in a rock exposed to fire, it has been seen that while the loss of He for apatite at the rock surface maybe as high as 30%, the retention rises rapidly with depth[15]. In fact, the rise of retention is so rapid that even for apatites located at 3 cm depth, there is absolutely no loss of He. From the same study it has been seen that the diurnal and annual temperature fluctuations experienced by a rock also get rapidly damped with depth and do not affect He ages significantly. While the closure temperature is ~75°C for a cooling rate of 10°C/Ma, it maybe up to ~90°C for a cooling rate[5] of 100°C/Ma. This clearly indicates that the temperature solution has a weak dependency on cooling rate, and even for an order of magnitude change in this value, there is only a ~10% change in the calculated closure temperature.

In spite of all these uncertainties, this low temperature thermochronometry can be useful. Apatite He ages record the temperature history experienced by rocks in the upper 3 km of the crust that is generally controlled by erosion and/or tectonic processes. For example, normal faulting causes rocks in the footwall to experience enhanced and recent cooling relative to the hanging wall that is recorded as younger He ages in the footwall[16]. For rocks experiencing a constant exhumation rate, the He age pattern reaches a steady state in which ages increase approximately linearly with depth. The slope of the profile approximates the exhumation rate and is often used to determine the rate of geologic processes[17].

U, Th/^{4}He dating of zircon

As mentioned earlier, zircon is another potential mineral for U, Th–^{4}He dating with a closure temperature of ~170–190°C, although this mineral has not been much investigated as yet for the applicability of this dating tool. While the fission track technique in zircon has effective closure temperature in the intermediate to higher temperature portion of K-feldspar cooling models, U, Th/He system overlaps with the lower temperature part of the K-feldspar ^{40}Ar/^{39}Ar cooling curves derived from multi-domain diffusion model[18]. Because of its high abundance in a wide range of rock types, high U and Th concentration as well as its resistance to physical and chemical weathering, zircon is extremely advantageous for geochronometry. However, there are some important differences between apatite and zircon as far as He extraction is concerned. While He can be extracted from apatite at ~1000°C, much higher temperatures are required for He extraction from zircons. Also, while weak nitric acid is capable of dissolving apatite, for zircon traditional dissolution techniques use hydrofluoric acid and high-temperature bombs. Farley *et al.*[3] had suggested an alternative approach for analysing zircons – laser heating followed by flux melting in lithium metaborate. In fact, it has been seen that lasing at 1300°C for ~1 h is sufficient to extract all He from zircons, except in some exceptional cases[19]. However, Tagami *et al.*[19] have cautioned that during lasing there are possibilities of U volatilization as well as fragmentation and partial loss of zircons in case of repeated laser heating and subsequent cooling. This raises an important problem in U, Th–He geochronometry for zircons, since some zircons are extremely retentive of He and require multiple extraction steps for extraction of all He in the samples; but this might lead to fragmentation and loss of zircon prior to U, Th analysis.

Like for apatite, in this case also the requirement is for euhedral, equant and large grains to minimize errors associated with α-ejection correction as well as for quickly cooled zircons to minimize diffusive loss of He. Although unzoned, inclusion-free grains are preferable, because zircons have high concentration of U and Th, presence of inclusions that are not highly enriched in U is not problematic. However, it is important to have unzoned zircons as seen from the analyses of zircon from Tardee rhyolite with known eruption age of 58.4 ± 0.7 Ma. The mean He ages of these zircon grains are much older, being 78.8 ± 7.0 Ma, attributed to overestimation of α-ejection losses due to high U content in the core and lower density in the rim[19]. Zoning of U content in any grain can be inferred by inspecting the spontaneous and induced fission track densities of the grain. It has been seen that U,Th/^{4}He ages of single Zr grains from rapidly cooled volcanic rocks of Fish Canyon Tuffs, Buluk Tuffs and Utasoa Rhyolites are in good agreement with their reference eruption ages[19].

U, Th/^{4}He dating of titanite

Titanite is another potential mineral for U, Th/^{4}He dating considering its high U, Th content as well as its common occurrence in crustal rocks. In order to actually investigate the potential of U, Th/^{4}He geochronometry in titanite, the diffusivity characteristics of radiogenic He in this mineral from various geological settings and ages have been explored[20]. The study indicates a closure temperature of ~200°C for a cooling rate of 10°C/Ma. However, since the diffusion domain size equals the physical grain size (inferred from

correlation of D/a^2 and $1/r^2$ as well as 1 : 1 correlation between observed and predicted diffusivities assuming diffusion domain a~grain size r), there is a dependence of the closure temperature with crystal size. The difference happens to be ~11 to 15°C for a factor of two size differences. The diffusion results also show non-Arrhenius behaviour in the early low temperatures, attributed to the presence of secondary and very small domain sizes associated with surface irregularities. However, since these sites seem to contain <1% of the total He, it should not affect the closure temperature significantly that is estimated from the linear segments of the Arrhenius plot. The titanite (U–Th)/He ages, like in the case of zircon, are useful for constraining the cooling histories at temperatures near the lower limit of those accessed by feldspar $^{40}Ar/^{39}Ar$ dating. Some erroneous ages may result from inhomogeneous He distribution arising from diffusive He loss resulting in rounded He concentration profiles. In this case, arbitrary fragment of the crystal will yield different and erroneous ages depending on whether it is from the edge or core of the crystal. Reiners and Farley[20] propose He extraction by resistance heating or $LiBO_2$ fusion rather than laser fusion that results in U loss by volatilization. From this work, the reasonable agreement of U, Th/^{4}He ages of titanites from Fish Canyon Tuff and Mt. Dromedary with known K/Ar and $^{40}Ar/^{39}Ar$ ages demonstrates the accuracy of titanite–He dating for quickly cooled samples. But a problem with this dating method is the effect of long alpha-stopping distances since, unlike apatite, where large euhedral crystals are easily obtained and which permit measurements of the dimensions for correction of He loss, titanite grains are irregular fragments of larger crystals after separation processes. In this case it becomes essential to obtain internal fragment of a grain for which no correction is required. Also titanite U, Th/^{4}He age might be compromised by radiation damage that affects He diffusivity. However, in spite of some problems involved in U, Th–^{4}He dating techniques of titanite, it can be extensively used to understand the low temperature histories of various terrains. But, till date, it has been least studied compared to zircon and apatite and further studies are required.

Summary

The renewed interest in (U–Th/He) thermochronometry is driven by an improved understanding of the behaviour of He in minerals and better analytical techniques available. U, Th-rich minerals like apatite, zircon and titanite can be considered suitable for application of this dating technique. Based on diffusion experiments, the low closure temperature of He in all the three minerals determined suggests unique applicability of this dating tool to various geological problems like cooling histories of rocks as they pass through the upper few kilometres of the crust. However, it is important to select suitable grains for dating as well as incorporate appropriate corrections for diffusive loss of He from the samples.

1. Rutherford, E., Present problems in radioactivity. *Pop. Sci. Mon.*, 1905, 1–34.
2. Hurley, P. M., The helium age method and distribution and migration of helium in rocks. In *Nuclear Geology* (ed. Faul, H.), 1954, pp. 301–329.
3. Farley, K. A., Kohn, B. P. and Pillans, B., The effects of secular disequilibrium on (U–Th)/He systematics and dating of quarternary volcanic zircon and apatite. *Earth Planet. Sci. Lett.*, 2002, **201**, 117–125.
4. Min, K., Farley, K. A., Renne, P. R. and Marti, K., Single grain (U–Th)/He ages from phosphates in Acupulco meteorite and implications for thermal history. *Earth Planet. Sci. Lett.*, 2002, **209**, 323–336.
5. Wolf, R. A., Farley, K. A. and Silver, L. T., Helium diffusion and low-temperature thermochronometry of apatite. *Geochim. Cosmochim. Acta*, 1996, **60**, 4231–4240.
6. House, M. A., Farley, K. A. and Kohn, B. P., An empirical test of helium diffusion in apatite: borehole data from the Otway basin, Australia. *Earth Planet. Sci. Lett.*, 1999, **170**, 463–474.
7. Farley, K. A., Wolf, R. A. and Silver, L. T., The effects of long alpha-stopping distances on U–Th/He ages. *Geochim. Cosmochim. Acta*, 1996, **60**, 4223–4229.
8. Zeitler, P. K., Herczig, A. L., Mcdougall, I. and Honda, M., Zircon U–Th–He dating of apatite: a potential thermochronometer. *Geochim. Cosmochim. Acta*, 1987, **51**, 2865–2868.
9. Lippolt, H. J., Leitz, M., Wernicke, R. S. and Hagedorn, B., (U–Th)/He dating of apatite: experience with samples from different geochemical environments. *Chem. Geol.*, 1994, **112**, 179–191.
10. Dodson, M. H., *Contrib. Mineral. Petrol.*, 1973, **40**, 250–274.
11. Farley, K. A., Helium diffusion from apatite: General behaviour as illustrated by Durango fluorapatite. *J. Geophys. Res.*, 2000, **105**, 2903–2914.
12. Reiners, P. W. and Farley, K. A., Influence of crystal size on apatite (U–Th)/He thermochronology: an example from the Bighorn Mountains, Wyoming. *Earth Planet. Sci. Lett.*, 2001, **188**, 413–420.
13. Bierman, P. and Gillespie, A., Range fires: a significant factor in exposure age determination and geomorphic surface evolution. *Geology*, 1991, **19**, 641–644.
14. Trull, T. W., Brown, E. T., Marty, B., Raisbeck, G. M. and Yiou, F., Cosmogenic ^{10}Be and ^3He accumulation in pleistocene beach terraces in death valley, California, USA-implications for cosmic-ray exposure dating of young surfaces in hot climates. *Chem. Geol.*, 1995, **119**, 191–207.
15. Wolf, R. A., Farley, K. A. and Kass, D. M., Modeling of the temperature sensitivity of the apatite (U–Th)/He thermochronometer. *Chem. Geol.*, 1998, **148**, 105–114.
16. Ehlers, T. A. and Farley, K. A., Apatite (U–Th)/He thermochronometry: methods and applications to problems in tectonic and surface processes. *Earth Planet. Sci. Lett.*, 2003, **206**, 1–14.
17. Mancktelow, N. S. and Grasemann, B., Time dependent effects of heat advection and topography on cooling histories during erosion. *Tectonophysics*, 1997, **270**, 167–195.
18. Reiners, P. W., Spell, T. L., Nicolescu, S. and Zanetti, K. A., Zircon (U–Th)/He thermochronometry: He diffusion and comparisons with $^{40}Ar/^{39}Ar$ dating. *Geochim. Cosmochim. Acta*, 2004, **68**, 1857–1887.
19. Tagami, T., Farley, K. A. and Stockli, D. F., (U–Th)/He geochronology of single zircon grains of known tertiary eruption age. *Earth Planet. Sci. Lett.*, 2003, **207**, 57–67.
20. Reiners, P. W. and Farley, K. A., He diffusion and (U–Th)/He thermochronometry of titanite. *Geochim. Cosmochim. Acta*, 1999, **63**, 3845–3859.

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