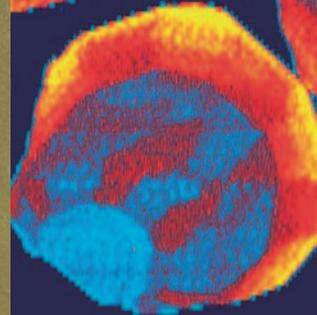


Geochronology and Thermochronology Using Apatite: Time and Temperature, Lower Crust to Surface

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LA-ICPMS map of uranium zoning in the Durango apatite

Apatite can provide geologists with an exceptionally wide range of ages and temperatures to investigate processes that operate from Earth's surface right down to the lower crust. Apatite is a widespread accessory mineral in igneous, metamorphic, and clastic sedimentary rocks and can be dated using four radioactive decay schemes, each with a different temperature window for isotopic closure: Lu–Hf (675–750 °C); U–Pb (350–550 °C); apatite fission track (60–110 °C); (U–Th)/He (40–80 °C). The fission-track and (U–Th)/He methods are popular for studying upper-crustal and near-surface processes, whereas the U–Pb and Lu–Hf systems are used to investigate the thermal, tectonic, and magmatic histories of the deeper crust.

KEYWORDS: apatite, thermochronology, fission track, (U–Th)/He, U–Pb, Lu–Hf

INTRODUCTION: APATITE IS A VERY DATEABLE MINERAL

Apatite (used herein to mean calcium phosphate apatite with the general formula $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$) is a very common accessory mineral in magmatic rocks, as P_2O_5 has a low solubility in silicate melts and phosphorus is not easily incorporated in the crystal lattices of the major rock-forming minerals. Unlike the U-bearing accessory mineral zircon, which is generally restricted to felsic igneous rocks, apatite is found as a minor phase in most igneous rock types. Apatite also occurs in metamorphic rocks of pelitic, carbonate, basaltic, and ultramafic composition at all metamorphic grades and is virtually ubiquitous in clastic sedimentary rocks. Its abundance in the majority of common rock types allied to its ability to incorporate elements that can be used for age dating makes apatite a very useful tool in geochronology. In particular, apatite is useful in thermochronology, which is the branch of geochronology that aims to establish the time–temperature (t – T) histories of rocks.

The thermal histories of minerals within the Earth and in meteorites can provide key information on processes ranging from planetary accretion to plate tectonics. Thermochronological methods such as $^{238,235}\text{U}$ – $^{206,207}\text{Pb}$ (e.g. applicable to apatite, titanite, rutile), fission track, and (U–Th)/He dating (both techniques applicable to apatite and zircon) are tools that constrain the thermal histories of minerals. These methods rely on the fundamental assumption that radiogenic daughter isotopes (e.g. $^{206,207}\text{Pb}$ and ^4He) are redistributed within minerals and are

ultimately lost to an infinite reservoir (the rock matrix) by thermally activated volume diffusion. This assumption is supported by experimental studies over laboratory and natural timescales on apatite Pb and He diffusion and fission-track annealing (e.g. Gleadow et al. 1986; Farley 2000; Cochrane et al. 2014).

The ability to model the behaviour of a thermochronological system, such as diffusion of Pb and He or fission-track annealing in the laboratory and extrapolate it to geological timescales, makes

it possible to construct a *forward model* of the system and so predict how that system will evolve for a given t – T history. Once a forward model has been generated, it then becomes possible to apply an *inverse model*, using the measured present-day condition of a thermochronometric system (e.g. apatite U–Pb or (U–Th)/He isotopic data or an apatite fission-track date and track-length distribution) to generate a computed t – T history (Ketcham 2005; Gallagher 2012). What makes apatite thermochronology so powerful is the ability of forward and inverse modelling to produce continuous t – T histories from three independent (the U–Pb, fission track, and (U–Th)/He) thermochronological systems.

The low-temperature sensitivities (FIG. 1) of the apatite fission-track (60–110 °C) and (U–Th)/He (40–80 °C) methods make them popular tools for studying upper crustal and near-surface processes. Applications include

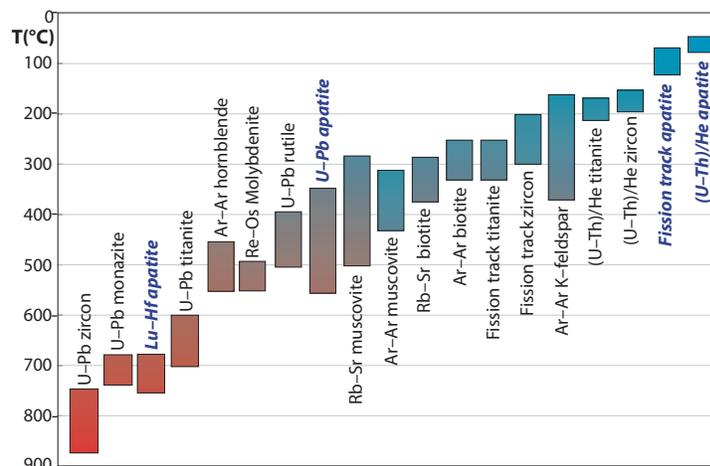


FIGURE 1 Effective closure temperatures for various commonly used thermochronometers. The four relating to apatite and the subject of this paper are in blue.

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quantifying the timing of exhumation during compression and extension along active tectonic margins, investigating the thermal histories of sedimentary basins and their source regions, and examining cratonic stability over timescales of hundreds of millions of years. In addition, apatite low-temperature thermochronology has also been used to quantify vertical fault displacement, to constrain the timing of ore-mineralization events, and to decipher landscape evolution. The higher temperature sensitivity of the U–Pb apatite system (350–550 °C; Figs. 1 and 4) makes it a useful tool to study the thermal and tectonic histories of the deeper crust. The even higher temperature sensitivity of the Lu–Hf apatite system (675–750 °C) makes it particularly well suited for dating zircon-free magmatic rocks. However, the limitations of isochron-based dating make this system unsuitable for generating continuous *t–T* histories.

(U–Th)/He THERMOCHRONOLOGY OF APATITE: YOUNG AND COOL

Helium accumulates in host minerals by the radioactive decay of ^{238}U , ^{235}U , and ^{232}Th , forming the basis of (U–Th)/He dating. In some cases, ^{147}Sm may also produce a significant fraction of ^4He in a sample. These nuclear transformations and their potential for geochronology were recognised during the early 20th century; however, the method was abandoned in the 1950s because of mounting evidence that He was being lost from the host minerals. Zeitler et al. (1987) revived interest in the (U–Th)/He method as a thermochronometer by suggesting that He loss by volume diffusion from apatite can be exploited to recover *t–T* information at temperatures of ~100 °C.

Thermal history information can be obtained from single crystal apatite (U–Th)/He dates if we can determine the diffusion behaviour of He in apatite and correct for He implantation, or “loss by ejection”, during radioactive decay (Fig. 2). Since Zeitler et al. (1987), several independent measurements of the He diffusion properties in apatite (e.g. Farley 2000) have defined a bulk closure temperature of ~70 °C and a helium partial-retention zone (HePRZ) and a temperature range ~40–80 °C (Fig. 1).

Subsequently, several studies (e.g. Schuster et al. 2006) revealed a significant correlation between radiogenic ^4He concentration and He diffusivity in natural apatite, suggesting that He diffusion is slowed down by radiation-induced damage. Flowers et al. (2009) derived the radiation damage accumulation and annealing model (RDAAM), which quantifies the relationship between radiation-damage accumulation, the elimination of that radiation damage by thermal annealing, and the kinetics of He diffusion in apatite. The RDAAM model can resolve thermal histories for apatite grains that exhibit (U–Th)/He dates older than the corresponding fission-track dates, which are thought to occur when the samples have resided for a sufficient duration at temperatures that permit radiation damage to accumulate. Thus, the specifics of the RDAAM model, such as what defines “sufficient duration”, are entirely dependent on the thermal history of the rock in question.

Effects of Alpha Recoil in Apatite (U–Th)/He Dating

Further complications in apatite (U–Th)/He dating arise from the high kinetic energies with which alpha particles (He nuclei) – formed by the decay of ^{238}U , ^{235}U , ^{232}Th , and ^{147}Sm – are emitted, causing displacements of He nuclei in apatite by up to 30 microns relative to the parent nuclide (Farley et al. 1996). These long stopping (recoil) distances result in three complications: (i) ambiguous intracrystal (U–Th)/He dates when the parent isotope is heterogeneously

distributed (i.e. zoned as in Fig. 2A); (ii) implantation of He into the apatite crystal if it shares a boundary with a high-U–Th mineral, such as zircon (Fig. 2A,C), which results in older (U–Th)/He dates; (iii) net loss of He and a reduction in the (U–Th)/He date for small apatite crystals (Fig. 2C). The correction of apatite (U–Th)/He dates for He loss (termed an alpha-ejection correction) is dependent on the size and morphology of the crystals and on the distribution of the parent isotopes. Farley et al. (1996) show that the magnitude of this correction can be up to 50% in small (70 micron diameter) subhedral crystals.

Inaccuracies introduced during the correction for He loss can be minimised by the careful selection of euhedral grains. Further improvements in the He-loss correction can be made by (i) abrading the outermost 20 microns of the grain, which increases the fractional retention of He to unity in unzoned crystals, and (ii) determining the distribution of the parent isotopes using an in situ method, such as an ion-probe or a laser ablation–inductively coupled plasma mass spectrometer (LA–ICPMS). Zoning of the parent isotope can yield a large dispersion in (U–Th)/He apatite dates from a single sample. For example, a preferential enrichment of the parent isotope near the apatite crystal rim would yield a larger quantity of He close to the grain boundary (e.g. Fig. 2A), resulting in a greater amount of He loss by diffusion for any given *t–T*. Farley et al. (2011) formulated a method to quantify the U and Th distribution in polished sections of apatite by quadrupole–LA–ICPMS mapping, and concluded that these effects can significantly alter computed *t–T* models.

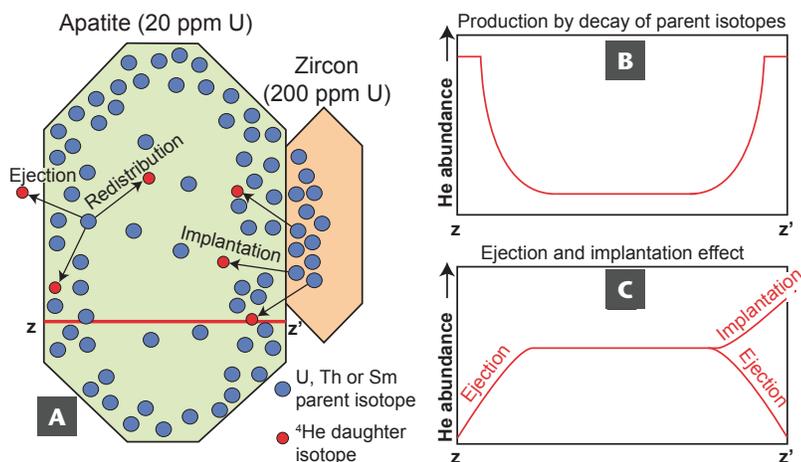


FIGURE 2 (A) Schematic diagram of an apatite crystal sharing a grain boundary with a zircon. The apatite is zoned, with higher parent isotope concentrations in the rim of the grain. Note cross-section transect labelled *z–z'*. (B) Graph across transect *z–z'* showing how He is distributed according only to its production within the apatite. (C) Graph across transect *z–z'* showing how He is redistributed either by long He-stopping (recoil) distances or by the implantation of He derived from the adjacent zircon.

APATITE FISSION-TRACK DATING: YOUNG AND COOL

Fission-track dating is based on the spontaneous fission decay of ^{238}U [decay constant (λ_f) = $8.5 \times 10^{-17} \text{ a}^{-1}$]. The fission products – two highly charged daughter nuclides – fly apart in opposite directions at high velocity, producing a linear damage trail in the host mineral or U-bearing glass known as a fission track. Fission tracks are enlarged using a standardized chemical etching process so they can be observed under an optical microscope (reviews in Gallagher et al. 1998; Donelick et al. 2005).

The concentration of U in apatite is typically 1–100 ppm, which generates a statistically useful quantity of spontaneous fission tracks for samples older than ~1 Ma. By comparing the spontaneous fission-track density with the U content of the host mineral (apatite in our case; FIG. 3A,B), a fission-track date can be calculated which temporally constrains the t - T cooling path through the fission-track partial annealing zone (PAZ), a temperature range across which fission tracks go from being perfectly preserved at low temperatures (where there is insufficient energy to cause significant repair of the fission tracks) to being completely healed (annealed) at high temperatures via thermally activated diffusion in the apatite structure. Fission tracks are partially annealed (shortened) at temperatures within the PAZ (e.g. FIG. 3C). The apatite PAZ is estimated at 60–110°C (FIG. 1), although this varies with apatite composition (e.g. Cl content; Green et al. 1986).

To calculate the apparent fission-track date of a mineral, an estimate of both the amount of ^{238}U decay recorded in the mineral (given by the spontaneous fission-track density) and the amount of ^{238}U (the parent isotope) is required. The spontaneous fission-track density is traditionally calculated by manually counting etched fission tracks using optical microscopy. Uranium concentration measurements in fission-track analysis are usually made by bombarding the apatite grain mount with thermal neutrons in a nuclear fission reactor to induce fission of ^{235}U . The induced fission tracks register in the apatite crystals and in an external detector (low-U [<1 ppm] muscovite) that is placed in intimate contact with the apatite grain mount. The induced fission-track density in the external-detector muscovite is a function of the apatite ^{235}U content and of the integrated thermal-neutron flux within the apatite crystals in the reactor. The latter is determined by measuring the induced fission-track densities of muscovite detectors placed in contact with a silicate glass standard having a known U concentration. Fission-track dates are then calculated using a zeta-calibration approach (Hurford and Green 1983), which involves comparing the fission-track dates of unknowns to those of fission-track age standards.

Alternatively, uranium concentrations in fission-track dating can be undertaken by LA-ICPMS, which increases the speed of analysis and sample throughput because it avoids the need for neutron irradiation. Hasebe et al. (2004) presented an “absolute” calibration approach to LA-ICPMS fission-track dating that adopted a value for the ^{238}U spontaneous fission decay constant (λ_f) and introduced calibration factors for etching and observation of tracks. An alternative approach, adopted by Donelick et al. (2005) and Chew and Donelick (2012), is to include all of these parameters (which are difficult to quantify) into a single term that is calibrated by reference to an age standard, analogous to the zeta calibration approach of Hurford and Green (1983). An LA-ICPMS approach also facilitates multi-element analyses during a single ablation (Chew and Donelick 2012), including U–Pb date and chemical composition data (such as the rare earth elements and other trace elements, including Cl). These data are useful in detrital apatite provenance studies and for characterizing the annealing behaviour of fission tracks in apatite.

Fission-Track Annealing Kinetics and Thermal History Modelling

The annealing behaviour of fission tracks in apatite is not completely understood, but it is highly temperature dependent and moderately dependent upon crystallographic orientation. It is also a function of chemical composition and crystal structure of the host apatite (e.g. Green et al. 1986; Carlson et al. 1999; Barbarand et al. 2003). Fission-

track annealing models attempt to correlate fission-track annealing kinetics with measurable parameters, commonly referred to as kinetic parameters, which take into account variations in chemical composition or etching characteristics of the host apatite (e.g. Carlson et al. 1999; Barbarand et al. 2003). These kinetic parameters include the fission-track etch figure diameter parallel to the crystallographic c axis (D_{par}) (FIG. 3A) and the apatite Cl content (measured either by electron microprobe or by LA-ICPMS).

In addition to the fission-track date, which temporally constrains the t - T path taken through the PAZ, the apatite fission-track method also yields information on the nature of the t - T path taken through the PAZ (FIG. 3C). This information is obtained from the distribution of confined fission-track lengths in a sample (Gleadow et al. 1986), confined fission-tracks being horizontal (or $<10^\circ$ from horizontal) tracks that lie parallel to an apatite’s c -axis prismatic section (FIG. 3A,B). Unannealed, spontaneous fission-track lengths in natural apatites typically range between ~14.5 μm and 15.5 μm , depending on the chemical composition. An apatite grain exhibiting a fission-track population with mean track lengths in this typical range and a narrow variation in track length distribution would be interpreted to have cooled rapidly from temperatures $\geq 110^\circ\text{C}$ to temperatures $\leq 60^\circ\text{C}$ at the time indicated by its apatite fission-track date. A shorter mean track length, with a broad standard distribution, indicates that the sample resided in the PAZ for a significant period

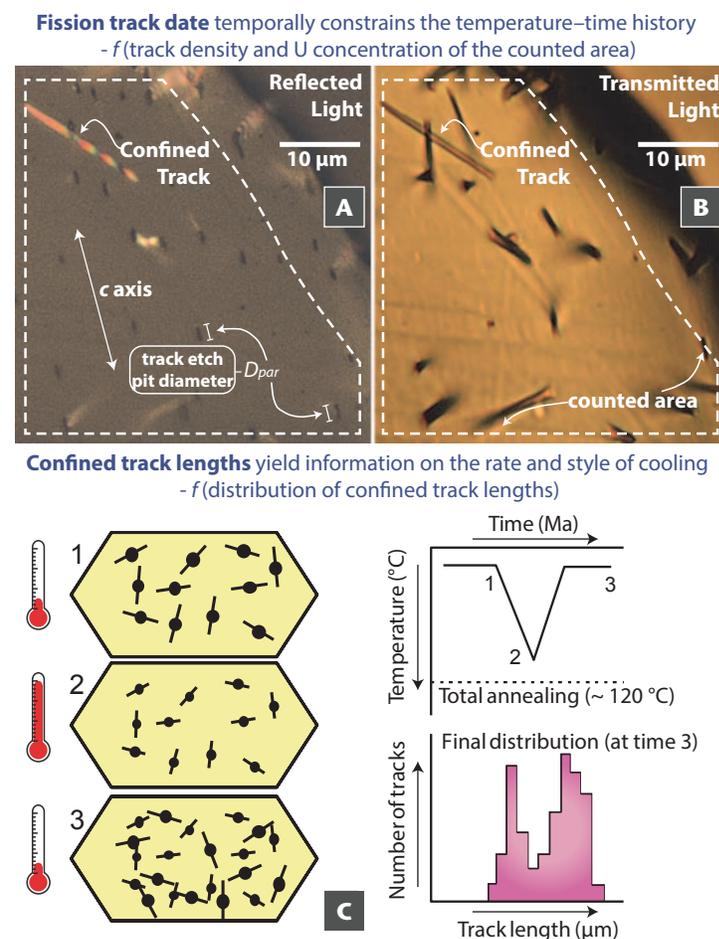


FIGURE 3 (A) Reflected light image of an area of an apatite crystal counted for fission tracks. (B) Transmitted light image of the same area of the apatite crystal counted for fission tracks. (C) Schematic time–temperature history of an apatite starting at the surface (1), followed by reheating (2), and subsequent cooling to near-surface temperatures (3). The resulting track distribution is bimodal (RIGHT).

(dependent on the host rock's specific thermal history) since the formation of the oldest fission tracks. FIGURE 3C illustrates a schematic t - T path characterised by a bimodal track-length distribution. The oldest tracks ($t = 1$, FIG. 3C) formed at temperatures below the PAZ ($\leq 60^\circ\text{C}$). The sample was then heated to temperatures ($\sim 100^\circ\text{C}$) close to the base of the PAZ ($t = 2$, FIG. 3C) generating a series of short, annealed confined tracks. Any tracks that subsequently formed during cooling through the PAZ to near-surface temperatures ($t = 3$, FIG. 3C) are not annealed, resulting in a bimodal track-length distribution. The apatite fission-track date and track-length distribution can be combined to construct t - T paths by inverse and/or forward modelling (e.g. Ketcham 2005; Gallagher 2012).

U-Pb THERMOCHRONOLOGY OF APATITE: OLD AND MODERATELY HOT

Uranium-lead apatite thermochronology exploits the loss of Pb from apatite crystals to generate t - T paths at temperatures between ~ 350 – 550°C (FIGS. 1 and 4). Thermal-history information is obtained by comparing apatite U-Pb dates with grain size, grain geometry, and the intrinsic diffusion properties of Pb in apatite. Volume-diffusion theory predicts a positive correlation between the amount of Pb lost (and therefore, the U-Pb date) during monotonic cooling (i.e. continuous cooling with no reheating) and the average distance that Pb has to diffuse within a crystal to reach an infinite reservoir where its effective concentration is zero. Several studies (e.g. Chamberlain and Bowring 2000; Cochrane et al. 2014), which dated apatites of different grain sizes extracted from the same igneous or metamorphic rock, have obtained this relationship, confirming the hypothesis that Pb was lost by volume diffusion.

The temperatures and rates at which Pb is lost from apatite by volume diffusion are largely a function of its diffusivity at infinite temperature and its activation energy for diffusion (both related to apatite's crystal lattice). These properties are, in turn, determined by the composition and geometry of the unit cell. Thus, the temperature range of partial Pb loss is a function of apatite composition. Lead diffusion in apatite was first studied by Watson et al. (1985), who performed Pb depth-profiling in natural Durango apatite using an electron microprobe. Cherniak et al. (1991) used ion implantation of Pb^{2+} into apatite, combined with isothermal heating experiments, to determine the diffusion properties of Pb in apatite after performing depth profiling with Rutherford backscattering spectrometry. Both data sets are consistent, and the results have been used in several studies (e.g. Schoene and Bowring 2007; Cochrane et al. 2014) to obtain t - T histories from U-Pb apatite dates and grain sizes by computed forward (FIG. 4B) and inverse modelling (FIG. 4A).

One of the main limitations in U-Pb apatite thermochronology is that apatite typically incorporates substantial amounts of initial (non-radiogenic, or common) Pb compared to U (i.e. low $^{238}\text{U}/^{204}\text{Pb}$) when it crystallizes. This results in a slow increase with time in the ratio of radiogenic Pb to non-radiogenic Pb (e.g. $^{206}\text{Pb}_{\text{radiogenic}}/^{206}\text{Pb}_{\text{initial}}$), which means that the majority of U-Pb apatite thermochronology studies have, perforce, concentrated on the t - T histories of old (Archaean and Palaeoproterozoic) cratons (e.g. Schoene and Bowring 2007). The initial Pb isotopic composition can be constrained by high-precision analyses of cogenetic phases, such as K-feldspar, that contain non-radiogenic Pb and no U.

Most previous U-Pb apatite thermochronological studies have employed isotope dilution-thermal ionization mass spectrometry (ID-TIMS) because it yields the best precision and accuracy. On the negative side, this destructive technique provides only an "average" date at the scale of any single apatite crystal. However, volume diffusion creates a heterogeneous distribution of Pb, and, thus, core-to-rim variations in U-Pb dates. Recovery of in situ crystal core-rim date profiles is useful because they can be compared with computed t - T paths generated by modelling of dates obtained by ID-TIMS (FIG. 4B). A close match between the measured in situ dates and modelled dates implies that Pb was lost from the samples by thermally activated volume diffusion, and corroborates the modelled t - T paths.

Cochrane et al. (2014) recently showed that in situ dates obtained by LA-MC(multi-collector)-ICPMS can be used to distinguish between reheating into the Pb partial retention zone (FIG. 4A) and isothermal t - T paths within this same temperature window. Importantly, these different t - T paths can be resolved using a single chronometer ($^{238}\text{U}/^{206}\text{Pb}$) when the dates are as young as ~ 100 Ma. An alternative approach that uses the pattern of U-Pb ID-TIMS apatite dates on concordia has been applied to lower crustal xenoliths to distinguish between reheating events and continuous cooling paths (e.g. Blackburn et al. 2012). This approach is limited to old U-Pb dates (>500 Ma) that span a large age range in order to determine the topology of the Pb-loss curves with sufficient precision. In young samples (<500 Ma), the large age uncertainties in relatively non-radiogenic isotopic compositions often result in concordant dates, precluding the use of Pb-loss curves in Phanerozoic samples.

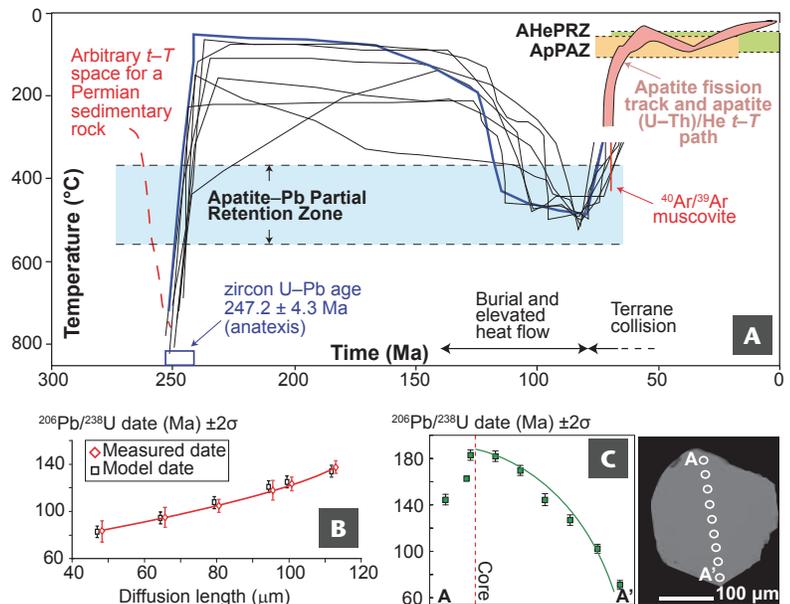


FIGURE 4 (A) Time-temperature (t - T) paths (black lines) of an ~ 247 Ma Early Triassic migmatite formed by anatexis of a Permian sedimentary rock. The t - T path is constrained using $^{238}\text{U}/^{206}\text{Pb}$ apatite dates, grain size information, and independent thermochronometers (Cochrane et al. 2014). The path was inverse modelled using the HeFTy software of Ketcham (2005). (B) Comparison of apatite grain radii versus $^{238}\text{U}/^{206}\text{Pb}$ dates (measured by ID-TIMS) with the predicted $^{206}\text{Pb}/^{238}\text{U}$ dates obtained from the best-fit t - T path from (A). (C) $^{206}\text{Pb}/^{238}\text{U}$ date transect (A-A'; LEFT), with analysis spots superimposed over an apatite back-scattered electron image (RIGHT), showing a convex date profile attributable to Pb volume diffusion in a subhedral grain. APAZ (apatite partial annealing zone); AHePRZ (apatite-He partial retention zone)

Lu–Hf DATING OF APATITE: MOSTLY OLD AND HOT

Typically, both igneous and metamorphic apatites have REE concentrations of several thousand parts per million. Apatite is, therefore, amenable to dating by the Lu–Hf isochron method, which exploits the β -decay of radioactive ^{176}Lu to a stable daughter isotope (^{176}Hf) as a result of apatite strongly fractionating Lu over Hf. Isochron geochronology requires that all samples defining the isochron begin with identical ratios of the daughter isotope to a non-radiogenic reference isotope of the daughter element (in this case, identical initial $^{176}\text{Hf}/^{177}\text{Hf}$) and that all samples have subsequently remained closed systems with respect to the parent and daughter elements (e.g. Barfod et al. 2003). An example Lu–Hf apatite isochron from the Smålands Taberg mafic cumulate in Sweden (Larsson and Söderlund 2005) is presented in FIGURE 5. This isochron has had additional constraint by using a phase with a low Lu/Hf ratio (plagioclase), and the whole-rock sample, and demonstrates the precision that can be achieved using the Lu–Hf apatite system; the isochron date of 1204.3 ± 1.8 Ma yields an uncertainty of $\pm 0.15\%$. The Lu–Hf apatite system is particularly well suited for dating igneous rocks that may be difficult to date with traditional techniques (i.e. when baddeleyite and zircon are absent).

Difficulties in ionizing Hf by ID–TIMS are at first hampered the application of the Lu–Hf system as a geochronometer, but high-precision Hf data are now routine with the advent of the LA–MC–ICPMS technique. Examples include Lu–Hf dating of apatite within Skaergaard intrusion mafic cumulates (Barfod et al. 2003), the Smålands Taberg Fe–Ti ore deposit (Larsson and Söderlund 2005), and apatite from medium- to high-grade metamorphic terranes (e.g. Barfod et al. 2003, 2005). Diffusion data for the REEs in apatite imply a closure temperature of at least 700°C for the Lu–Hf system (Cherniak 2000). This is consistent with the study by Barfod et al. (2005) from the Adirondack lowlands in New York (USA) where Lu–Hf systematics were investigated for centimetre-sized apatite crystals that had remained undisturbed during upper amphibolite-facies metamorphism at $675\text{--}700^\circ\text{C}$. A conservative estimate of the partial retention zone of Hf in apatite is $675\text{--}750^\circ\text{C}$ (FIG. 1).

Near-depositional Lu–Hf dates have been reported for a shark tooth from the Lower Eocene London Clay, England (Barfod et al. 2003). This intriguing result suggests that the Lu–Hf system is a promising tool for dating biogenic apatite (fossil bones and teeth) and for the direct dating of sedimentary formations. However, the same study also demonstrated that biogenic apatite in porous matrices was highly susceptible to post-depositional resetting of the Lu–Hf isotopic system. Subsequent work has confirmed that most Lu–Hf dates on biogenic apatite are substantially younger than their depositional ages (Herwartz et al. 2013). The nanometre-scale crystal sizes of biogenic apatite in fossil bones, dentine, and enamel result in intensive Lu–Hf exchange during burial for most fossil sites; Lu–Hf depositional ages are only preserved when there has been limited REE and Hf diffusion between the sediment and the fossil. Fine-grained argillaceous sediments with low permeability, or carbonate matrices with low REE abundances, appear to be the optimal lithologies encasing biogenic apatite to inhibit diffusion (Herwartz et al. 2013), making such sediments potentially good candidates for Lu–Hf dating.

CONCLUSIONS AND FUTURE DEVELOPMENTS

The presence of apatite in the majority of common rock types (mafic and felsic igneous rocks, metamorphic rocks, and clastic sedimentary rocks) makes it a very useful tool in geochronology and thermochronology. It is a particu-

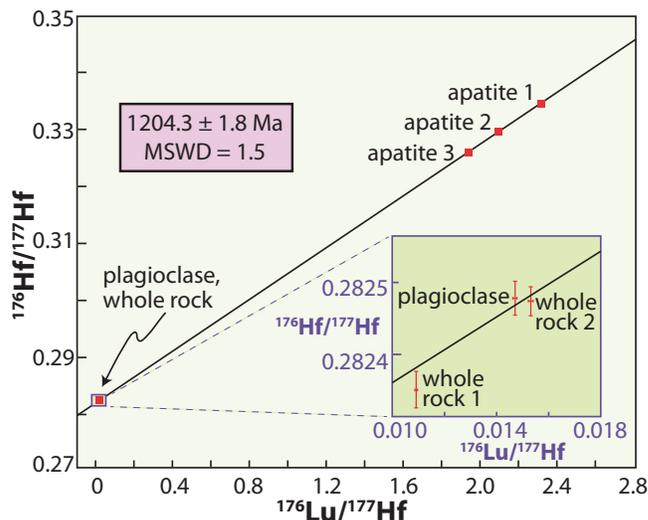


FIGURE 5 Lu–Hf apatite/whole rock/plagioclase isochron of a mafic cumulate from Smålands Taberg (Sweden) illustrating the applicability of the Lu–Hf apatite system to dating zircon-free magmatic rocks. SOURCE: LARSSON AND SÖDERLUND (2005)

larly powerful thermochronometer because it can yield continuous t – T histories as a result of combining three independent thermochronological systems (remembering that the Lu–Hf system cannot generate continuous histories): (U–Th)/He, spontaneous U fission, and U–Pb. These three systems can be used to investigate the thermal and tectonic histories of the upper to middle crust.

Although there have been many recent advances in our understanding of the kinetics of diffusion (and annealing), there are still many important unresolved issues in thermochronology. For example, the physical basis of fission-track annealing at the atomic scale remains incompletely understood, and annealing models are constrained by empirical laboratory experiments and geological cases studies. There is, therefore, a significant gap in our understanding of the relationship between the underlying diffusion processes responsible for the gradual repair of radiation damage in unetched (latent) fission tracks and the thermal annealing behaviour of fission tracks as revealed by chemical etching. It may become possible to develop diffusion-based models of track annealing to explain the observed differences in annealing properties between different minerals (e.g. titanite and zircon) and also within a mineral group with known compositional variation (such as apatite). The advent of automated image analysis for automated fission-track dating (e.g. Gleadow et al. 2009) opens up the possibility of acquiring far larger datasets than are currently possible with manual methods. Such datasets could include different modes of track length (confined and semi-tracks) and etch-pit diameter measurements that can be related to annealing properties.

Many (U–Th)/He thermochronology studies have shown that the range of single-grain ages obtained from a single rock sample are more dispersed than expected when considering only the analytical uncertainties (Brown et al. 2013). Many of the complicating factors in (U–Th)/He thermochronometry (α -ejection, He implantation, radiation damage, parent isotope zonation) could be more successfully constrained if a measure of the spatial distribution of the parent and daughter isotope concentrations could be obtained from within a grain. One approach to constrain the daughter product (^4He) diffusion profile is to introduce a uniform reference concentration of ^3He by proton irradiation of the sample. Thermal history information encoded in the sample's ^4He distribution could

then be obtained by step-heating measurements of the $^4\text{He}/^3\text{He}$ ratio (Shuster and Farley 2004). Another approach to extract thermal history information from (U–Th)/He apatite data is to analyse 20 to 30 apatite grains – with varying grain sizes, morphologies, and numbers of crystal terminations – from each sample (Brown et al. 2013).

Recent advances in U–Pb apatite geochronology include the ability to undertake routine U–Pb LA–ICPMS apatite analyses that can account for the variable amounts of initial Pb in both apatite standards and unknowns (Chew et al. 2014). Example applications include in situ apatite U–Pb age profiles (Cochrane et al. 2014) and detrital U–Pb apatite geochronology. The latter approach may prove useful in provenance studies where the source regions are either not zircon-bearing (e.g. mafic sources) or there has been substantial sedimentary recycling of detrital zircon. No studies have systematically tested the relationship between Pb diffusion and apatite composition; the intrinsic Pb diffusion properties of apatite may also vary with halogen, REE, and cation composition. Cochrane et al.

(2014) reported anomalously outlying ages when $^{238}\text{U}/^{206}\text{Pb}$ dates from a leucosome were compared against apatite grain size. Xenocrystic apatite crystals (i.e. those sourced from the country rock) with high Th/U ratios (>0.5), yielded $^{238}\text{U}/^{206}\text{Pb}$ dates that were younger than magmatic apatites with low Th/U ratios (<0.2) with the same grain size. We speculate that compositional variations can enhance Pb volume diffusion rates in apatite.

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