

Apatite U-Pb Thermochronology: A Review

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Abstract: The temperature sensitivity of the U-Pb apatite system (350–570 °C) makes it a powerful tool to study thermal histories in the deeper crust. Recent studies have exploited diffusive Pb loss from apatite crystals to generate t-T paths between ~350–570 °C, by comparing apatite U-Pb ID-TIMS (isotope dilution-thermal ionisation mass spectrometry) dates with grain size or by LA-MC-ICP-MS (laser ablation-multicollector-inductively coupled plasma-mass spectrometry) age depth profiling/traverses of apatite crystals, and assuming the effective diffusion domain is the entire crystal. The key assumptions of apatite U-Pb thermochronology are discussed including (i) that Pb has been lost by Fickian diffusion, (ii) can experimental apatite Pb diffusion parameters be extrapolated down temperature to geological settings and (iii) are apatite grain boundaries open (i.e., is Pb lost to an infinite reservoir). Particular emphasis is placed on detecting fluid-mediated remobilisation of Pb, which invalidates assumption (i). The highly diverse and rock-type specific nature of apatite trace-element chemistry is very useful in this regard—metasomatic and low-grade metamorphic apatite can be easily distinguished from sub-categories of igneous rocks and high-grade metamorphic apatite. This enables reprecipitated domains to be identified geochemically and linked with petrographic observations. Other challenges in apatite U-Pb thermochronology are also discussed. An appropriate choice of initial Pb composition is critical, while U zoning remains an issue for inverse modelling of single crystal ID-TIMS dates, and LA-ICP-MS age traverses need to be integrated with U zoning information. A recommended apatite U-Pb thermochronology protocol for LA-MC-ICP-MS age depth profiling/traverses of apatite crystals and linked to petrographic and trace element information is presented.

Keywords: apatite; U-Th-Pb; thermochronology; Pb; diffusion; LA-ICP-MS; TIMS; thermal history modelling; inverse modelling



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1. Introduction

Apatite [Ca₅(PO₄)₃(F,Cl,OH)] is a very common accessory mineral in igneous, metamorphic and clastic sedimentary rocks. Due to the low solubility of P₂O₅ in silicate melts and the limited amount of phosphorus typically incorporated into the crystal lattices of the major rock-forming minerals [1], it is a nearly ubiquitous accessory phase in igneous rocks. It is also a very common accessory mineral in metamorphic rocks with varying protolith compositions (e.g., pelitic, carbonate, basaltic and ultramafic rocks), spanning metamorphic grades from transitional diagenetic environments to the granulite and eclogite facies [2]. Apatite in felsic igneous rocks and high-grade felsic gneisses typically yields U concentrations in the range of 1–100 ppm [3]. The incorporation of U (and Th) into the apatite lattice enables the routine dating of individual apatite crystals by the fission track and (U-Th)/He methods. These low-temperature thermochronometers are popular tools for studying upper-crustal and near-surface processes, with temperature sensitivities of c. 60–110 °C and 40–80 °C, respectively [4,5].

The apatite U-Pb system is also becoming increasingly popular as a higher temperature thermochronology tool, with the partial retention zone for Pb (APbPRZ of Cochrane et al., 2014 [6]) determined at c. 350–570 °C based on laboratory diffusion experiments [7]

(Section 3.1). Thermochronological methods assume that daughter isotopes (e.g., ^{206}Pb , ^{207}Pb and ^{208}Pb which are the ultimate decay product of the ^{238}U , ^{235}U and ^{232}Th decay series) are lost from a lattice to an infinite reservoir by thermally activated diffusion. If volume diffusion dominates daughter isotope loss, then a mathematical description can be derived from Fick's Law that relates intrinsic properties of the host lattice (activation energy of diffusion, diffusivity), diffusion geometry, cooling rate and the length scale of diffusion with closure temperature [8]. The variation in closure temperature between the core and boundary of the crystal can be used to define a partial retention zone (such as the APbPRZ) for a given grain size and cooling rate, whose temperature limits indicate where any particular daughter isotope is either completely retained (with respect to diffusion) or can diffuse to the infinite reservoir from any region of the crystal lattice. Extracting thermal history information from a particular mineral—decay scheme is dependent on several key assumptions that are difficult to validate. These include (i) the daughter isotope(s) have been lost by diffusion (e.g., there is an appropriate relationship between diffusion length scale, and age), (ii) the intrinsic diffusion properties of the mineral phase derived from laboratory experiments can be extrapolated down temperature to geological settings, and (iii) the nature of the grain boundaries are known, i.e., is the daughter isotope lost to an infinite reservoir, or not [9]?

Apatite also presents its own unique challenges as a U-Pb thermochronometer. The first U-Pb apatite dating study was undertaken in the 1970s by Oosthuyzen and Burger (1973) [10] using thermal ionization mass spectrometry (TIMS), with their Archean samples from the Barberton Greenstone Belts yielding near-concordant apatite U-Pb age data. However, numerous subsequent apatite U-Pb dating studies have shown that apatite often yields strongly discordant U-Pb dates. While such discordance is expected in thermochronology which exploits daughter Pb loss, it became increasingly apparent that apatite also usually incorporates significant initial Pb (also known as common Pb or Pb_c). This is particularly problematic for young samples which have little time to accumulate substantial radiogenic Pb (Pb^*), or for apatites with low U concentrations. While the presence of common Pb can be corrected for [11] (Section 3.2), the substantial common-Pb correction required for samples with high Pb_c/Pb^* ratios results in large date uncertainties, and also potentially inaccurate dates (and resultant thermal history models) if the initial Pb composition employed is inappropriate (Section 3.2). The ubiquitous presence of common Pb in apatite (including in age reference materials) also hindered the development of U-Pb apatite dating by in situ methods, such as secondary ion mass spectrometry (SIMS) or laser ablation—inductively coupled plasma mass spectrometry (LA-ICP-MS). The development of apatite U-Pb age standards and data reduction schemes employing ^{207}Pb - or ^{204}Pb -based Pb_c corrections to age standards and unknowns [12–14] means that U-Pb dating of apatite by LA-ICP-MS (including the generation of apatite intra-grain U-Pb date transects) is now routinely possible.

1.1. History of U-Pb Thermochronology

Not all of the accessory mineral phases commonly employed in U-Pb dating studies make practical U-Pb thermochronometers. The closure temperatures for Pb diffusion in zircon [15] and monazite [16] are both in excess of 900 °C, significantly higher than the wet granite solidus. Hence, they have had very limited application in U-Pb thermochronology studies of crustal rocks, although potentially regions of the crust that have experienced temperatures above $\gtrsim 900$ °C can be explored by U-Pb monazite or zircon thermochronology by generating U-Pb date profiles at sub-micron resolution from crystal rims [17,18].

Fluid-mediated loss of Pb along fractures or temporal modifications in the crystal volume (dissolution, recrystallisation, new rim overgrowths) invalidate the assumption that Pb has been solely redistributed by volume diffusion (Section 2). For example, there is mounting evidence that titanite frequently dissolves and reprecipitates during metamorphic events [19]. Metamorphic titanite can either preserve U-Pb dates characteristic of high-temperature volume diffusion [20], dates younger than the magmatic crystallisation

ages of the host rocks and thus indicative of growth or reprecipitation [21], or dates that indicate a complex combination of diffusion, recrystallisation and growth [19]. In common with other mineral thermochronometers, detailed petrographic characterization is therefore key to interpreting titanite U-Pb dates [22], and its complex recrystallisation behaviour during tectonothermal events means its application as a U-Pb thermochronometer is presently limited.

The majority of U-Pb thermochronology studies have therefore employed apatite and rutile as thermochronometers. Both U-Pb mineral systems are characterised by temperature windows for the partial retention of Pb that correspond to the middle to lower crustal levels [6,23–25]. Rutile exhibits the unusual combination of chemical and physical stability at both surface and medium to high-grade metamorphic conditions, but is unstable in the sub-greenschist to lower greenschist facies [26,27]. It thus can record thermal history information from middle to lower crustal levels if not affected by sub-greenschist or lower greenschist facies retrogression or deformation on the exhumation path. While apatite is more prone to dissolution-reprecipitation during metamorphism [28], this is not as significant a disadvantage as it may first appear, as the petrographic (primarily chemical but also textural) evidence for apatite recrystallisation is often unequivocal (Section 2.3). Our knowledge of Pb diffusion in apatite is summarized in Section 3.1.

Studies from experimental and natural systems suggest a lower limit for Pb-diffusion of ca. 490–500 °C for rutile crystals with radii of 50–1000 µm at cooling rates of 0.1–1 °C/Myr [24,29,30]; the upper temperature limit is less well constrained at ca. 640–700 °C [24]. These closure temperature estimates are distinguishably higher than the estimates of 370 °C (90 µm radius) to 500 °C (200 µm radius) of Mezger et al. (1989) [31], based on the cooling history of granulite terranes with cooling rates of 1–2 °C/My. The study of Mezger et al. (1989) [31] was the first to note a correlation between single crystal TIMS dates obtained from a U-Pb thermochronometer and grain size. Schmitz and Bowring (2003) [32] obtained single crystal U-Pb TIMS rutile, titanite and apatite dates from the Archean Kaapvaal craton and adjacent (craton-marginal) Proterozoic belts to constrain the thermal evolution of cratonic lithosphere beneath South Africa. Schoene and Bowring (2007) [33] produced single (and sub-)crystal U-Pb TIMS titanite and apatite dates from the Barberton Greenstone Belt and showed using a finite-difference numerical model that the topology of Pb-Pb date vs. grain size curves were consistent with slow, non-linear cooling and not later thermal resetting. Blackburn et al. (2011, 2012) [25,34] obtained U-Pb TIMS rutile and titanite dates on Archean and Proterozoic crustal xenoliths of the North American craton entrained within Early Cenozoic volcanics. The approach exploited the topologies of the data on Wetherill concordia that resulted from the combined effects of diffusion and the production rate differences between the ^{238}U and ^{235}U decay systems to distinguish between slow cooling and reheating t-T paths, with the U-Pb data implying extremely low exhumation rates (–2.5 to 2.5 m/My) consistent with the long-term stability of cratons.

The advent of in situ (SIMS, LA-ICP-MS) U-Pb dating approaches has enabled intra-grain U-Pb date profiles to be obtained from accessory mineral phases such as apatite or rutile, from which thermal history information can potentially be extracted. Early LA-ICP-MS studies that present intra-grain U-Pb date profiles focused on rutile [30,35]. Such studies show a general trend of increasing spatial resolution commensurate with advances in instrumentation, and increasingly sophisticated attempts [36] to extract thermal history information from the intra-grain U-Pb date profiles.

Two key studies in 2014 extracted continuous thermal history information through inversion of high spatial intra-grain U-Pb date profiles on rutile [29] and apatite [6]. Smye and Stockli (2014) [29] inverted rutile $^{206}\text{Pb}/^{238}\text{U}$ date depth profiles with <1.2 µm depth resolution from lower-crustal rutile from the Ivrea Zone in the Southern Alps. An in-house MATLAB® code was employed to predict the radial distributions of radiogenic ^{206}Pb for a given thermal history, which enabled inversion of $^{206}\text{Pb}/^{238}\text{U}$ date depth profiles to yield thermal history information. This approach was extended to apatite by Seymour et al. (2016) [37]. Cochrane et al. (2014) [6] applied apatite U-Pb thermochronology to Triassic

rocks from the Northern Andes. U-Pb TIMS dates were combined with grain size and diffusion parameters to generate plausible thermal history solutions by inverting U-Pb dates using a controlled random search method for the t-T modelling (HeFTy [38]). The resultant thermal histories are compatible with independent geological constraints and t-T models derived from inversion of high spatial resolution (15 μm), intra-grain apatite LA-MC(multi-collector)-ICP-MS U-Pb date transects, which demonstrate that volume diffusion governed the displacement of Pb.

Paul et al. (2019) [39] used a similar approach to Cochrane et al. (2014) [6] (inversion of apatite U-Pb single crystal TIMS dates and grain size information, and apatite LA-MC-ICP-MS U-Pb date transects) on similar Triassic leucosomes and S-type granites in the Northern Andes. However, they discovered that intra-grain U zonation resulted in considerable scatter when single crystal dates were compared with grain size, and therefore U zonation must be taken into account when inverting U-Pb date and grain size information to seek thermal history solutions. In situ U-Pb dating approaches (which can measure U zonation) thus yield significantly more accurate thermal history solutions than single crystal TIMS U-Pb analyses when investigating rocks which contain compositionally zoned apatites (Section 4.2). Popov and Spikings (2021) [9] explored Pb radiogenic ingrowth and diffusion in apatite inclusions within other minerals using numerical modelling. Their results indicate that the host minerals can hamper diffusive Pb loss from the apatite inclusions by limiting the Pb flux across their boundaries, and the resultant thermal histories that assume a fully open boundary are likely erroneous (Section 4.3). In cases where the apatite boundaries are flux-limited, heterogeneities in U and Th concentration within apatite are less important on modelled single crystal U-Pb dates but can cause intra-grain U-Pb dates to increase towards the crystal boundaries.

1.2. Key Issues in Apatite U-Pb Thermochronology

This review focuses on the assumption that Pb is redistributed and lost from apatite by volume diffusion, and thus that fluid mediated recrystallization played an insignificant role. Particular emphasis is also placed on extracting continuous thermal history information by either inversion of intra-grain U-Pb date transects or inverting U-Pb TIMS single crystal dates combined with grain size and diffusion parameters [6]. However, as apatite is very prone to dissolution-reprecipitation during metasomatism and metamorphism [28], the assumption that U-Pb dates are the result of simple thermally activated Pb diffusion can be erroneous without detailed knowledge of the crystal growth/alteration history [40]. Establishing if U-Pb date information is consistent with volume diffusion is therefore paramount (Section 2) and involves employing petrographic or geochemical evidence for metasomatic or low-grade metamorphic dissolution-reprecipitation reactions, or by interrogating the systematics of the U-Pb data. Other challenges (Section 3) include our knowledge of Pb diffusion in apatite and how to constrain the initial Pb composition. The various approaches to inverse thermal history modelling are discussed in Section 4 along with the issues of U zoning and boundary conditions, while Section 5 details the optimal approaches and workflow for sample preparation and in situ analysis (e.g., depth profiles vs. rastering).

2. Determining If Apatite U-Pb Dates Are Consistent with Volume Diffusion

Thermochronological methods assume that daughter isotopes are lost from a lattice to an infinite reservoir by thermally activated diffusion, leading to a mathematical description that relates intrinsic properties of the host lattice (activation energy of diffusion, diffusivity), diffusion geometry, cooling rate and the length scale of diffusion with closure temperature [8]. However, it is extremely unlikely that temperature will be the rate-controlling parameter for isotope transport if fluid interaction has occurred (due to fluid circulation and/or deformation) [41–45]. Aqueous fluid interaction in the crust is key in modifying the isotope record in nature [46], while deformation plays a role as a conduit for fluid transport on a large-scale (e.g., faults) or by creating short circuit pathways for fluid ingress

within minerals (e.g., micro-fractures and other crystallographic defects) [47]. The debate on whether isotope transport in minerals is dominated by thermally-activated diffusion or if mineral dates are ‘geohygrometers’ that date fluid circulation episodes [46] is contentious in the literature, particularly for the interpretation of Ar isotope distributions in K-feldspar and muscovite [48–52]. Apatite is also highly susceptible to various fluid-induced chemical and textural changes over a wide P-T range [28], and can also exhibit phases of metamorphic growth [40,53]. Recognising episodes of metasomatic and metamorphic apatite dissolution-reprecipitation or neocrystalline growth is therefore key when applying U-Pb thermochronology.

2.1. Petrogenesis and Trace Element Systematics of Metasomatic Apatite

Given that the temperature window for diffusion of Pb in apatite (Section 3.1) corresponds to middle to lower crustal levels, U-Pb thermochronology studies are undertaken on metamorphic and igneous bedrock. Apatite in crystalline bedrock is typically fluorapatite, as F partitions strongly into apatite in metamorphic rocks and most quartz-bearing igneous rocks with the other major anions on the halogen site (e.g., Cl and OH) only present in minor amounts; [28]). Petrographic evidence for metasomatism of fluorapatite by syn- and post-metamorphic aqueous fluids containing H₂O, CO₂ and Cl is common in granulite-facies fluorapatite [54], where transmission electron microscopy imaging shows that voids, presumably once fluid-filled, are seen along the interface of the host apatite with monazite inclusions [55]. The formation and growth of such monazite (or xenotime) inclusions or rim overgrowths are interpreted as the result of coupled dissolution-reprecipitation processes during metasomatic alteration of apatite [45]. Dissolution-reprecipitation is a process whereby a mineral phase in the presence of a reactive fluid is replaced either by the same phase (with a different composition) or by an entirely new phase. Interconnected porosity within the precipitated phase [55] allows fluids to infiltrate through the metasomatized area and thus facilitate mass transfer of elements to and from the micron-scale, fluid-filled reaction front. During metasomatic alteration of the apatite, these micro-pores within the interconnected pore system provide nucleation sites for the formation of monazite and xenotime inclusions, as Na and/or Si are preferentially removed out of the apatite-fluid system compared to the REEs [28].

Apatite formed during metasomatic processes often has trace-element compositions characterised by low REE contents, high Ca, F and Sr contents, and minor Eu-anomalies [3,56]. As such, their trace element systematics are indistinguishable from low to medium-grade metamorphic apatite (Section 2.2). Dissolution-reprecipitation metasomatic reactions can also occur during the cooling of igneous rocks, especially in fluid-rich systems such as pegmatites, where late-stage fluids may catalyse the precipitation of REE + Y-poor apatite, monazite and xenotime from REE + Y-rich primary igneous apatite [57], especially locally along fluid pathways in the rock.

2.2. Petrogenesis and Trace Element Systematics of Metamorphic Apatite

Apatite crystal size in metasedimentary rocks increases with increasing metamorphic grade (<20 µm at chlorite grade to >200 µm in migmatite; [58,59]). Coarse-grained detrital apatite persists into the greenschist facies [53,58,60] with neocrystalline greenschist-facies apatite growth in some cases clearly nucleating on an igneous apatite precursor, likely due to a coupled dissolution-reprecipitation process ([53], Figure 1). The igneous apatite detrital cores yield U-Pb ages and trace element compositions (Section 2.3) characteristic of the igneous source, while the neocrystalline apatite rims are extremely depleted in the REE + Y, U and Th. This lanthanide and actinide depletion (particularly the LREE and Th) is characteristic of apatite in low- to medium-grade metamorphic rocks (both metapelites and metabasic rocks). However, low to medium-grade metamorphic rocks often have very variable and complex chondrite-normalised apatite REE spectra [60]. This is because such rocks rarely preserve equilibrium assemblages, even on a thin-section scale, as reaction rates are slow compared to the rates of change in the physical conditions the

rock has experienced (P, T or changes in fluid composition). Even though the trace element signature of low to medium-grade metamorphic apatite is highly distinct to that of igneous apatite (Section 2.3), discriminating between metamorphic apatite from different protolith types (pelites and basic rocks) remains challenging [53]. This is because both monazite (an accessory phase in metapelites) and epidote/allanite (a rock-forming mineral in both metapelites and metabasic rocks) are capable of incorporating significant proportions of the actinides and REEs in their crystal structures and can control the whole-rock budgets of those elements [61]. Apatite growth at low metamorphic grades may thus have its REE and actinide budgets scavenged by cogenetic epidote/allanite and/or monazite growth [53,60].

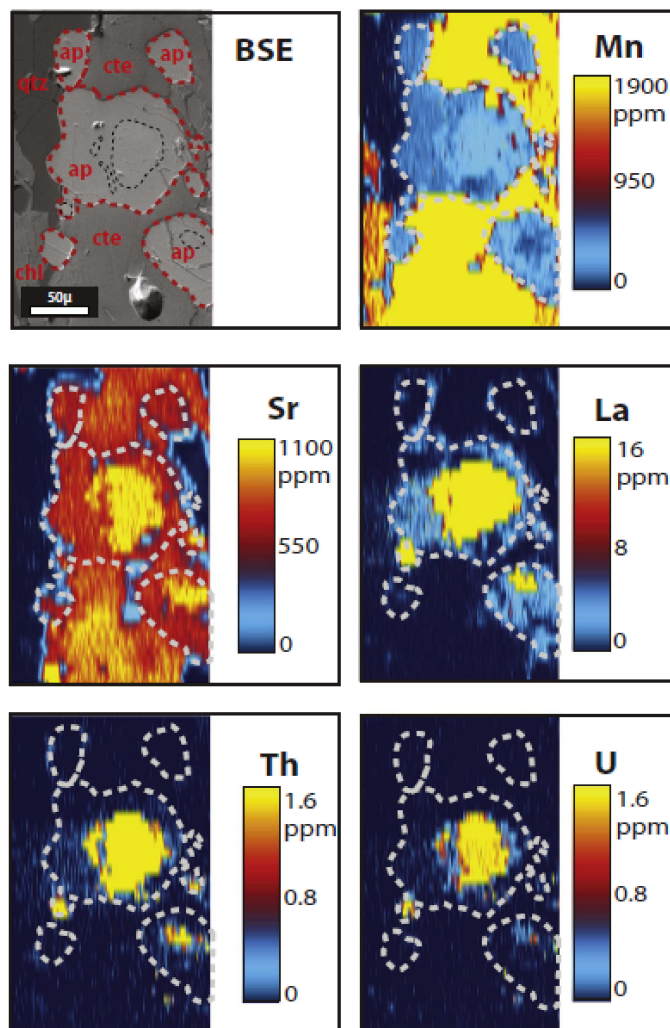


Figure 1. BSE and LA-ICP-MS trace-element mapping of apatite from a low-grade meta-greywacke sample from the New Zealand Alps, modified from Henrichs et al. (2018) [53]. The detrital cores of granitic origin are BSE-bright (inside dashed black line on BSE panel) and exhibit high Th, U, Sr and REE that broadly overlaps with the composition of granitic apatite from the literature [3] and neocrystalline metamorphic apatite with low Th, U and REE contents (ap = apatite, qtz = quartz, cte = carbonate, chl = chlorite).

At high-metamorphic grades, mineral assemblage equilibration rates are much faster, and hence dispersed intra-sample apatite trace-element spectra are typically not encountered (e.g., [53,58,62,63]). This indicates that all low-grade and porphyroclastic (i.e., detrital) apatite has long since been consumed or overprinted [3]. Apatite in higher-grade metamorphic rocks is almost universally fluorapatite [2], and also typically contains higher REE- and actinide-abundances than apatite from lower-grade metamorphic lithologies. Bingen

et al. (1996) [62] studied an amphibolite to upper granulite-facies transect through high-K calc-alkaline gneisses, with the REE, Th and U contents of apatite increasing progressively with increasing grade and related to the breakdown of allanite, hornblende and titanite at the cpx-in isograd and the breakdown of monazite at the opx-in isograd. Apatite from the opx-grade rocks has REE-contents and ratios indistinguishable from granitoid apatite [64]. Leucosome apatite typically presents geochemical signatures similar to that of S-type granitoid apatite (Section 2.3), with low Th/U, low La/Ce and flat chondrite-normalised REE-profiles [3,53,63].

2.3. Identifying Apatite Which Has Not Experienced Dissolution-Reprecipitation

Recognising episodes of metasomatic and metamorphic apatite dissolution-reprecipitation or neocrystalline growth is key to the successful application of apatite U-Pb thermochronology [40]. In addition to conventional petrographic evidence (Figure 1), apatite trace-element geochemistry is an excellent tracer of rock type. Based on an extensive apatite trace-element chemistry database compiled from a diverse suite of rock types, O'Sullivan et al. (2020) [3] showed that sub-classes of igneous rocks, low-grade and high-grade metamorphic apatite are all easily discriminated on a $\log(\sum \text{LREE ppm})$ vs. $\log(\text{Sr/Y})$ diagram, where LREE is defined as La to Nd.

The six fields on the O'Sullivan et al. (2020) [3] biplot are: alkali-rich igneous rocks (ALK); mafic I-type granitoids and mafic igneous rocks (IM); low to medium-grade metamorphic and metasomatic rocks (LM); high-grade metamorphic and partial melts (HM); S-type granitoids and 'felsic' I-types (S); ultramafic rocks including carbonatites, lherzolites and pyroxenites (UM). Discrimination is based on three trends identified from the compiled literature data set: (1) Increasing metamorphic grade; the LREE content is low in low-grade metamorphic apatite and increases with metamorphic grade with a corresponding decrease in the Sr/Y ratio. (2) SiO_2 content of the source melt; the Sr and Y contents of magmatic apatite negatively correlate and positively correlate with the SiO_2 content of the source melt, with the exception being apatite from alkali-rich melts, which is instead discriminated by its extremely high LREE contents. (3) Dissolution and reprecipitation of apatite under low-grade metamorphic or metasomatic conditions will result in a LREE-depleted apatite with a high Sr/Y ratio. The correct classification of this separation using SVM based on the training dataset is on average c. 85% per class; importantly the low to medium-grade metamorphic and metasomatic (LM) apatite class was correctly identified with a 98% success rate.

Exploring the U concentration data (Figure 2) for the six apatite classes is highly relevant for apatite U-Pb thermochronology studies. The peak in the U content distribution in the igneous apatite classes increases from UM (1.75 ppm), through to ALK (10 ppm), IM (12.5 ppm) to S (75 ppm). The high-grade metamorphic (HM) apatite has a peak in U content at 20 ppm, while low to medium-grade metamorphic and metasomatic apatite (LM) has a bimodal U distribution with peaks at 0.5 ppm and 7.5 ppm. The latter peak likely corresponds to lower amphibolite-facies apatite, as REE and U concentrations as in metapelites are at their lowest in the upper greenschist-facies and increase as the metamorphic grade increases while Th/U ratios decrease [60]. The small peak of lower U concentrations observed on the left-hand tail of all four igneous classes likely represents minor low to medium-grade metamorphic or metasomatic reworking in a small proportion of the dataset.

These data show that the extreme U depletion seen in low to medium-grade metamorphic (both metapelites and metabasites) and metasomatic apatite means that it is nearly always unsuitable for U-Pb thermochronology, especially greenschist-facies apatite ($\text{U} < 1$ ppm). The U contents of high-grade metamorphic and leucosome apatite (20 ppm) and S-type granitoid apatite (75 ppm) are much more amenable to extracting continuous thermal history information from spatially resolved intra-grain U-Pb dates. Importantly, if trace-element information (LREE, Sr, Y) can also be acquired (either during U-Pb analysis or separately and spatially referenced to the U-Pb dates), then domains of low-grade

metamorphic or metasomatic reworking can be identified using the $\log(\sum \text{LREE ppm})$ vs. $\log(\text{Sr/Y})$ biplot of O'Sullivan et al. (2020) [3].

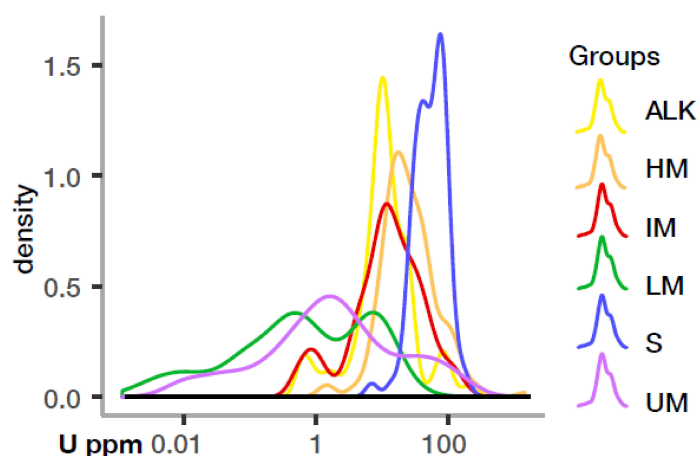


Figure 2. Kernel Density Estimate distributions of apatite trace element data (ppm) for individual elements from the compositional database of O'Sullivan et al. (2020) [3]. Abbreviations for groups: ALK = alkali-rich igneous rocks; IM = mafic I-type granitoids and mafic igneous rocks; LM = low- and medium-grade metamorphic and metasomatic; HM = partial-melts/leucosomes/high-grade metamorphic; S = S-type granitoids and high aluminium saturation index (ASI) 'felsic' I-types; UM = ultramafic rocks including carbonatites, lherzolites and pyroxenites. Modified from O'Sullivan et al. (2020) [3].

3. Pb Diffusion and Correcting for Common Pb

3.1. Pb Diffusion in Apatite

Pb diffusion in apatite was first studied by Watson et al. (1985) [65], who measured Pb by wavelength-dispersive electron microprobe analysis in natural Durango apatite via in-diffusion from a Pb-doped silicate melt that was saturated in apatite. Cherniak et al. (1991) [23] utilised ion (Pb^{2+}) implantation into apatite, combined with isothermal heating experiments to determine the diffusion properties of Pb after performing depth profiling using Rutherford backscattering. Both datasets are consistent [7], and show that (i) the closure temperatures of the analysed apatites range between 536 °C and 457 °C, for cooling rates of 50 °C/My and 1 °C/My, respectively (200 µm diameter, infinite cylinder), and (ii) damage that might have been caused by ion-implantation had little effect on diffusion. However, apatite from rock samples (anhydrous, coarse-grained plutonic lithologies) that have been subsequently heated to much higher temperatures (up to c. 575 °C; grain-size fraction of 50–125 µm) can preserve pre-metamorphic igneous crystallisation ages in some cases [66]. No studies have been performed to test (i) the relationship between Pb diffusion and apatite composition, (ii) the degree of anisotropy of Pb diffusion in apatite and (iii) potential differences in the diffusivity of Pb^* vs. Pb_c in apatite. For example, in apatite fission track dating, it has long been established that chemical composition (especially Cl) and crystal orientation exhibit a strong control on fission track annealing [67]. Frei et al. (1997) [68] hypothesized that Pb^* is typically tetravalent (due to electron stripping during recoil following alpha-decay), in contrast to the assumed divalent behaviour of Pb_c . While Kramers et al. (2009) [69] documented diffusivity of Pb^* in zircon that was three to four orders of magnitude lower than that of Pb_c (presumably because of preferential substitution into the lattice of radiogenic Pb^{4+} for Zr^{4+}), this has yet to be tested for apatite, where preferential substitution into the lattice of common Pb^{2+} for Ca^{2+} is likely and radiogenic Pb^{4+} is presumably hosted interstitially or in defects [70]. Diffusive loss of uranium during cooling is insignificant for the purposes of thermochronology because the diffusion parameters of uranium in Durango apatite (out-diffusion from U doped apatite [71]) yield closure temperatures >1000 °C.

3.2. Correcting for Common Pb—What Approach and What Initial Pb Value to Choose?

There are a wide variety of methods for common Pb correction and determining the isotopic composition of the initial Pb component. In U-Pb thermochronology studies individual intra-grain analyses must be corrected for initial Pb to calculate a U-Pb date. Two key considerations are that (i) the spatially resolved intra-grain dates can no longer be regarded as a suite of co-genetic analyses, and (ii) the initial Pb isotopic composition will evolve with time as Pb is exchanged between the apatite crystal and the rock matrix.

One approach to estimate the initial Pb composition involves analysing a low-U co-genetic phase (e.g., K-feldspar) which exhibits negligible in-growth of radiogenic Pb. However, such an approach may be invalid in rocks which have experienced a prolonged and complex tectonothermal history because the low-U phase may not “lock in” the isotopic composition of the initial Pb at the same time as the mineral phase being analysed for U-Pb thermochronology. For example, assuming that Pb loss followed Fick’s law through geological time (i.e., no fluid interaction), and using the Pb diffusion in orthoclase data of Cherniak (1995) [72], the Pb closure temperature for orthoclase is c. 100 °C higher than an apatite crystal of equivalent diameter, and c. 200 °C higher for a K-feldspar an order of magnitude larger in diameter than an apatite crystal (which is likely given that K-feldspar is a coarse, rock-forming mineral and apatite is typically accessory). However, fluid interaction in K-feldspar is ubiquitous and it also undergoes numerous sub-solidus textural re-equilibration events down to almost surface temperatures, and so diffusion is probably never the dominant processes [73,74].

The initial Pb isotopic composition can also be determined from crustal Pb evolution models [75]. While such an approach yields an initial Pb isotopic composition that evolves with time, a global crustal Pb evolution model constraint may not be appropriate for the rock sample being analysed. If the crystal has only been open to diffusive loss of Pb for a short time duration and there is a significant spread in U/Pb ratios, then the initial ratio can be derived from an isochron plot. The spatially resolved intra-grain dates could be regarded as a suite of effectively co-genetic analyses, and the common Pb isotopic composition determined through either a total-U/Pb isochron (a three-dimensional $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plot [76]) or projecting an intercept through the uncorrected data on Tera–Wasserburg Concordia. A low-U co-genetic phase (e.g., K-feldspar) which exhibits negligible in-growth of radiogenic Pb likely represents the best estimate of the initial Pb isotopic composition [39], but this common Pb constraint should still be critically assessed and compared to those derived from crustal Pb evolution models and isochron-based approaches.

As apatite typically yields low Pb^*/Pb_c ratios, it is thus highly sensitive to the choice of initial Pb composition. Different choices of common Pb correction (e.g., crustal Pb evolution models vs. a low-U co-genetic phase such as K-feldspar) can result in good-fit thermal histories whose uncertainty limits do not overlap, and thus the data must be thoroughly interrogated using the approaches outlined above to constrain the initial Pb composition. Once an appropriate initial Pb isotopic composition is determined, then the two correction strategies that are most relevant to apatite U-Pb thermochronology are the ^{204}Pb - and ^{207}Pb -correction methods [11]. The ^{208}Pb -correction method is less commonly applied to apatite U-Pb dating as it is best suited for samples with low Th/U (e.g., <0.5).

The ^{204}Pb - and ^{207}Pb -correction methods each have their own respective advantages and disadvantages in U-Pb thermochronology studies. U-Pb thermochronology exploits the diffusive loss of Pb, and thus the U/Pb* data (if sufficiently precise) will therefore still not be concordant following common Pb correction. The main advantage of the ^{204}Pb correction method is that it does not assume U/Pb* concordance. However, it does require accurate measurement of ^{204}Pb (and in LA-ICP-MS studies either ^{200}Hg or ^{202}Hg to correct for isobaric interference of ^{204}Hg on ^{204}Pb) and is thus ideally suited to U-Pb dating by high-precision ID-TIMS or LA-MC-ICP-MS analyses. While the ability to accurately correct for common Pb using the ^{204}Pb -correction method may seem advantageous, it must be emphasised that it still requires an appropriate choice of initial Pb. Additionally, in

(MC)-ICP-MS studies, the low abundance of the ^{204}Pb isotope and propagating through the associated uncertainties of the isobaric correction of ^{204}Hg on ^{204}Pb results in inferior precision on ^{204}Pb -corrected dates compared to the ^{207}Pb -correction method. The ^{207}Pb -correction method assumes initial concordance in $^{238}\text{U}/^{206}\text{Pb}$ — $^{207}\text{Pb}/^{206}\text{Pb}$ space (Tera-Wasserburg Concordia) and represents a projection from the $^{207}\text{Pb}/^{206}\text{Pb}$ initial through the analysis onto Tera-Wasserburg Concordia—i.e., it assumes concordance which will frequently not be the case in U-Pb thermochronology studies. It is therefore inherently less accurate than the ^{204}Pb -correction method, which can potentially propagate through to inaccurate thermal history models.

Should U-Pb thermochronology studies use the less precise but more accurate ^{204}Pb correction method, or the more precise but less accurate ^{207}Pb -correction method? The age bias in the ^{207}Pb -correction method (due to the projection onto Tera-Wasserburg Concordia) is heavily dependent on when (and how long for) a crystal is open to diffusive loss of Pb due to the topology of the Concordia. Figure 3 shows four discordia intercepts (3000–2000 Ma; 2000–1000 Ma; 1000–100 Ma; 500–100 Ma) that are fully corrected for common Pb by the ^{204}Pb -correction method. The age offset between ^{204}Pb - and ^{207}Pb -correction methods is as expected at a maximum at the middle of the discordia intercept but becomes a relatively minor effect (<0.5%) for samples younger than 500 Ma where the slope of Tera-Wasserburg Concordia shallows significantly. The superior precision of the ^{207}Pb -correction method means this approach is therefore recommended for Phanerozoic samples.

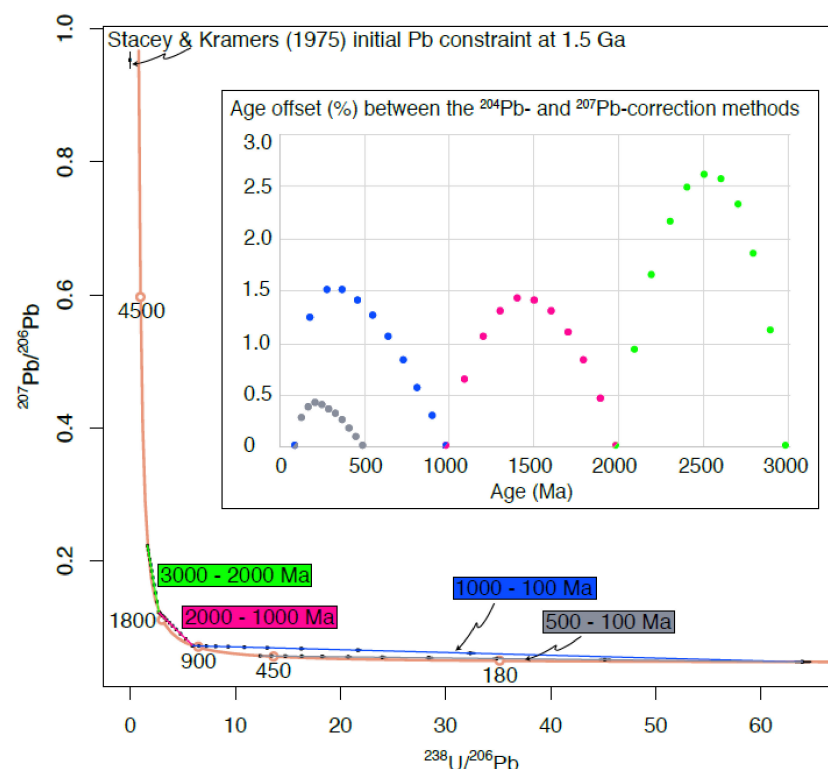


Figure 3. Four discordia intercepts between two age components (3000–2000 Ma; 2000–1000 Ma; 1000–100 Ma; 500–100 Ma) on Tera-Wasserburg Concordia. These discordia intercepts are corrected for common Pb using the ^{204}Pb method—i.e., the discordia intercepts are concordant. The ‘true’ date of any point on the discordia intercepts is given by the ^{206}Pb – ^{238}U date (or if common Pb was present, a ^{204}Pb -corrected ^{206}Pb – ^{238}U date). The relative age difference (in percent) between the ‘true’ date and the ^{207}Pb -corrected date is illustrated in the inset panel and is at a maximum for a 50:50 mixture between the two age components. The difference between the ‘true’ date and the ^{207}Pb -corrected date is minimal (<0.5%) for Phanerozoic samples.

4. Inverse Thermal History Modelling

4.1. Different Approaches to Thermal History Modelling

Numerous variables contribute to bulk and in situ U-Pb dates (e.g., t-T history, grain size, boundary condition, fluid interaction history), and thus mathematical inversion is the optimal approach to seek solutions from potentially hundreds of thousands of iterations, depending on CPU power and code efficiency. Input parameters usually include (i) U-Pb dates, either as bulk dates obtained by ID-TIMS [6,77,78], or in situ dates obtained using LA-(MC)-ICPMS from traverses across polished mineral interior surfaces [39,77] or depth-profiles [18,29], (ii) a length parameter, which may be the cylindrical radius perpendicular to the c-axis (appropriate for bulk dates), or traverse distance or depth (for in situ dates), and iii) an appropriate set of Pb-in-apatite diffusion parameters (which are usually taken from Cherniak et al., 1991 [23]) and diffusion geometry. Additional input should include information about the intra-grain distribution of parent isotopes [39], which is relevant for both bulk and in situ dates, and potentially a kinetic parameter(s) that describes how diffusivities vary with other characteristics such as crystal composition (although these currently remain unconstrained). The latter will become particularly relevant in cases where the data displays complexity beyond what is predicted by volume diffusion.

Cochrane et al. (2014) [6] and Paul et al. (2018) [77] used the computer program HeFTy [38] to invert bulk (ID-TIMS) U-Pb dates, which seeks t-T solutions using a basic Monte Carlo approach that evaluates independent t-T paths. The optimal t-T solutions are represented by discrete t-T points, and are sought by determining the proportion of random samples from the normally distributed uncertainty on the model date that are further from the measured date than the normal date. The user can specify the degree of complexity in the models by increasing the quantity of t-T nodes. HeFTy permits the user to input U-zonation profiles, and was used by Paul et al. (2019) [39] to assess the impact of U-zonation on bulk U-Pb dates. Perhaps one limitation with HeFTy is the lack of an option to model in situ dates, which presumably arises because it was originally designed to model fission track and (U-Th)/He data. Alternatively, a different inversion technique uses a Bayesian Markov chain Monte Carlo (MCMC) approach, which is a probabilistic sampling process. The MCMC approach is an iterative sampling procedure where better fitting models are sought by perturbing the existing best-fit model. Examples of this approach are the stand-alone computer program QTQt [79], and the code “Upbeat” [18] that is implemented in MATLAB. QTQt and Upbeat permit the input of in situ U-Pb dates, and thus they are amenable to modelling LA-(MC)-ICPMS dates. The inversion of in situ dates from apatites with heterogeneous distributions of uranium using QTQt was used to reveal the importance of accounting for uranium distribution, particularly when the rocks spent a considerable amount of time within the APbPRZ ([39]; Figure 4). The Bayesian approach used by Gallagher (2012) [79] does not require the user to specify the degree of complexity that is permitted by the t-T solutions. Instead, the degree of complexity is determined from the data, and this approach prefers simpler models. A potential pitfall of using the MCMC approach is inefficiency when searching large ranges of thermal histories [80], although Upbeat evaluates a series of so-called “walker” t-T paths that broaden the search within possible solution space [18].

Given the inferior precision of in situ date profiles relative to single (bulk) crystal ID-TIMS dates, how does this propagate through to uncertainties on the resultant t-T paths? Cochrane et al. (2014) [6] obtained a reheating pulse in their t-T solutions (obtained using HeFTy) derived from modelling single (bulk) crystal ID-TIMS dates, although a low proportion (<1%) of solutions permitted isothermal paths within the APbPRZ, without re-heating. Importantly, inversion of in situ dates from the same rocks only permitted t-T paths with re-heating topologies. The re-heating topology arises due to the large dispersion in dates compared to diffusion length (grain size for ID-TIMS dates, or core-rim distance for in situ dates). This comparison of bulk vs. in situ dates shows that the in situ dates were sufficiently precise to discriminate between different thermal histories, and were apparently able to improve the overall modelling outcome. In general, more precise

thermal histories will be obtained if several in situ intra-grain date transects/profiles with significant dispersion in variables (including U-Pb dates, diffusion length (e.g., crystal size), diffusivity information, U zonation information) are modelled simultaneously. The precision of in situ spot dates will depend on the volume ablated, and the appropriate volume to ablate will depend on the extent of U and Th zonation [39].

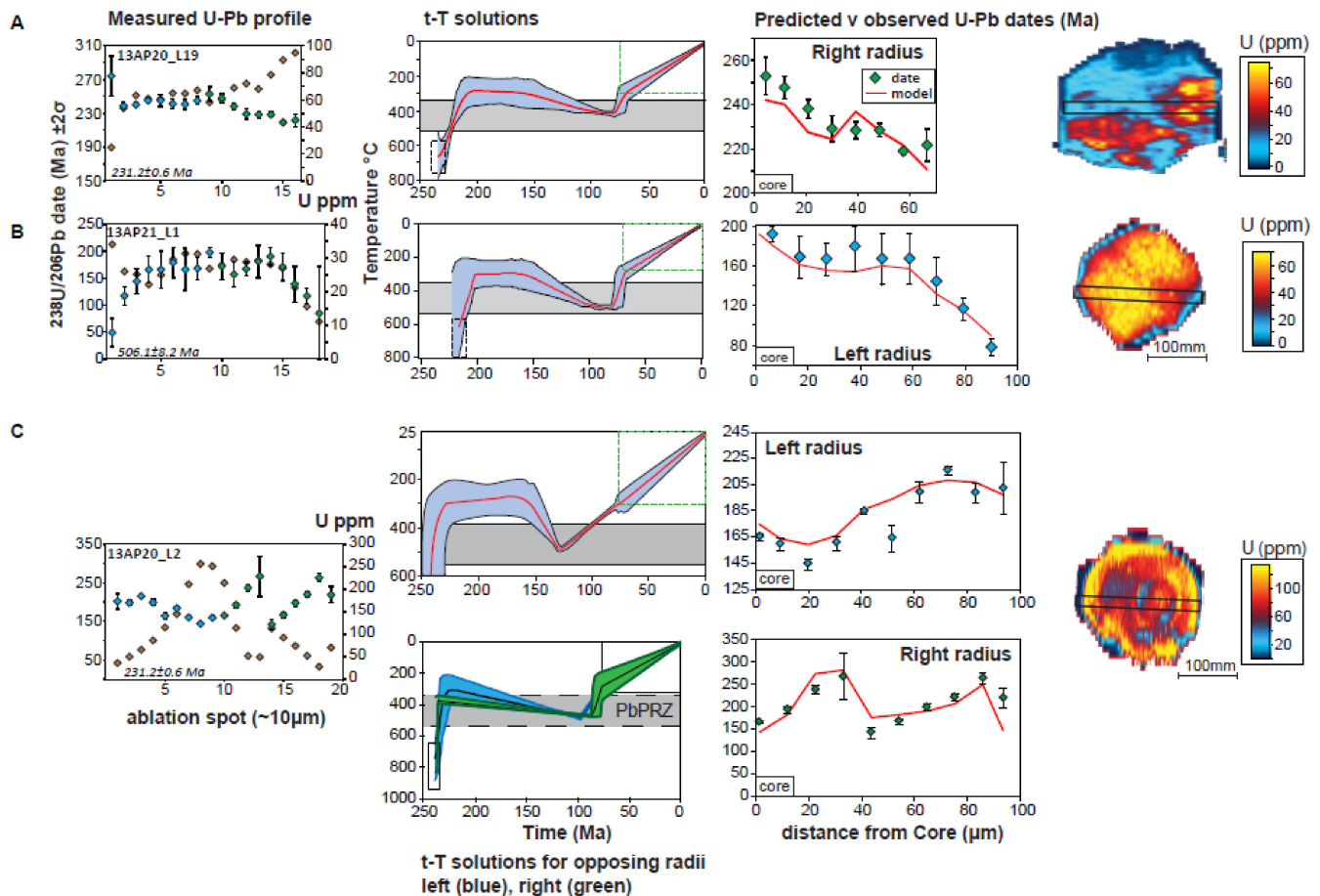


Figure 4. U-Pb date profiles and U concentrations (left-hand panels), thermal history solutions, predicted vs. observed dates and LA-ICP-MS U maps (right-hand panels) modified for three LA-MC-ICP-MS U-Pb date transects across three apatite crystals (panels A–C) modified from Paul et al. (2019) [39]. Blue colours = information (U-Pb date and T-t solution) derived from the left radius of the grain; green colours = information from the right radius. Brown diamonds in the left-hand panels are U concentration measurements; ages quoted in the left-hand panels are U-Pb zircon crystallisation ages from the same sample.

4.2. Parent U Zoning

Uranium diffusion in apatite [71] is significantly slower than that of Pb [23], and hence the diffusion of Pb from U-rich regions should lead to older apparent dates in adjacent U-depleted domains. Paul et al. (2019) [39] obtained in situ U-Pb date profiles from apatite crystals extracted from peraluminous, monzogranitic to granodioritic leucosomes and plutons from the Ecuadorian Andes (the same rock suite that was investigated by Cochrane et al., 2014 [6]). The grains were mounted perpendicular to their c-axes, have a large range in crystal diameter and exhibit marked U zoning as demonstrated by 2D LA-ICP-MS maps (Figure 4, right-hand panels). While some apatite crystals are enriched in U in the core, U-enriched rims, oscillatory U zoning and non-uniform variations including the presence of highly localised small ‘hot-spots’ of elevated U concentrations can be found in any individual rock sample (Figure 4A, right-hand panel). Similarly, while many

apatite crystals yield bell-shaped rim-core-rim date profiles with the oldest dates in the core (Figure 4B), some show inverted profiles with young U-Pb dates in the core and old U-Pb dates at the rim (Figure 4C, 'left radius') and other crystals show an irregular distribution of U-Pb dates which can be crudely described as oscillatory (Figure 4C, 'right radius'), or alternatively yield flat profiles. Again, these different topologies can occur in apatite crystals extracted from the same rock specimen.

The core dates, which in some cases are significantly older than the independently constrained (zircon U-Pb) Triassic crystallisation age, can be convincingly attributed to the diffusion of Pb* from high U (rim) zones into low U zones (core). Forward modelling (using the best-fit thermal history solution from Cochrane et al., 2014 [6]) applied to synthetic crystals with different topologies of rim-core-rim U concentrations yields predicted in situ $^{238}\text{U}/^{206}\text{Pb}$ apatite dates that are older than the crystallisation age of the rock and thus it is reasonable to state that these old core dates are a direct consequence of thermally activated volume diffusion. Both the inverse modelling of Paul et al. (2019) [39] on apatite and Smye et al. (2018) [18] on rutile show that accurate thermal history solutions can be obtained from crystals which are zoned with respect to U when these in situ variations in U concentration and U-Pb dates are modelled. Thermal history solutions derived from in situ analytical techniques are also significantly more accurate than those derived from comparing single (bulk) crystal ID-TIMS dates with their grain size, when parent U zonation is present [39].

4.3. Boundary Conditions

Popov and Spikings (2021) [9] explored Pb radiogenic ingrowth and diffusion in apatite inclusions within other minerals using numerical modelling, with particular emphasis placed on testing the significance of the assumptions that crystals (1) lose radiogenic Pb to an infinite reservoir, (2) have a simple geometry, and (3) are chemically homogeneous. The modelling results indicate that the host minerals can hamper diffusive Pb loss from the apatite inclusions by limiting the Pb flux across their boundaries. Plagioclase and K-feldspar are the most probable rock-forming host minerals for apatite that likely lie inside the field of flux-limited boundary behaviour (based on a reasonable upper limit of $K_{\text{d, feldspar-apatite}} = 5$ for the partition coefficient as there are no studies of Pb partitioning of between feldspars and apatite that would provide direct constraints for Kd). Popov and Spikings (2021) [9] obtained bulk crystal $^{206}\text{Pb}/^{238}\text{U}$ dates of synthetic, chemically homogeneous spherical apatite inclusions in K-feldspar that experienced two different thermal histories (simple monotonic cooling; a complex history with reheating) via forward modelling with flux limited boundaries. Inversion modelling of the resultant $^{206}\text{Pb}/^{238}\text{U}$ dates assumed that the apatite boundaries are open to complete Pb loss. The modelled monotonic cooling history was close to that used to construct the forward model, although inversion modelling failed to detect the simulated reheating event within the more complex thermal history. Popov and Spikings (2021) [9] also showed that when apatite boundaries are flux-limited, heterogeneities in U and Th concentration within apatite have a subordinate effect on bulk-crystal U-Th-Pb dates and can cause intra-grain U-Th-Pb dates to increase towards the boundaries. Clearly, flux-limited boundaries can have significant implications for apatite U-Pb thermochronology, although significant challenges remain. There are presently limited constraints on most of the parameters required to characterise Pb diffusion through mineral matrices that can potentially surround apatite crystals. Additionally, in situ analysis is challenging given the difficulty in ensuring that spatially resolved dates are obtained (i) through the grain centre, and (ii) perpendicular to the c-axis (Section 5). One such in situ U-Pb apatite inclusion study is that of Popov et al. (2020) [52], who undertook U-Pb LA-MC-ICP-MS dating of apatite inclusions in K-feldspars in the Itrongay pegmatite (Madagascar). The U-Pb dates of these inclusions exceed the $^{40}\text{Ar}/^{39}\text{Ar}$ dates of their host feldspar by >50–100 Ma and are interpreted to be apatite xenocrysts derived from the country rocks. However, current analytical protocols for apatite U-Pb thermochronology (Section 5) typically involve the extraction of crystals from the bulk

rock, thus leaving no record of the textural context of the apatite (i.e., inclusion-hosted and potentially flux-limited, or connected to the grain-boundary network and open).

5. A Recommended Apatite U-Pb Thermochronology Protocol

Based on the U-Pb LA-ICP-MS analysis of apatite from several hundred crystalline bedrock samples from a diverse suite of tectonic settings in the Trinity College Dublin laboratory, the significant majority of samples yield Tera-Wasserburg systematics that are not compatible with volume diffusion (i.e., the U-Pb analyses lie along a Tera-Wasserburg discordia intercept). The analytical protocol for U-Pb LA-ICP-MS thermochronology described below is significantly more involved than for conventional U-Pb geochronology. Therefore, unless there is independent evidence that significant volume diffusion took place as the apatite passed through the temperature window for partial retention of Pb (APbPRZ), then a conventional and more rapid U-Pb LA-ICP-MS dating procedure is recommended, as it can also screen for potential volume diffusion which can then be explored further. Such independent evidence might include independently constrained mid-crustal temperature-time histories, or a tectonic setting consistent with apatite U-Pb volume diffusion (e.g., slowly exhumed cratonic rocks, prolonged heat flow in the roots of a volcanic arc complex).

A conventional U-Pb dating procedure can identify apatite U-Pb volume diffusion as it yields a suite of analyses that all fall within a characteristic ‘pie-shaped’ wedge geometry on Tera-Wasserburg concordia ([18]; Figure 5A). The apex of the wedge is defined by the initial Pb constraint on the $^{207}\text{Pb}/^{206}\text{Pb}$ axis, and the other two vertices are defined by two lower intercepts on the Tera-Wasserburg concordia curve. The older lower concordia intercept represents the core of crystals and may record the crystallisation age or an older cooling event which passed through the APbPRZ, while the younger concordia intercept represents outer regions of the crystal(s) which record the time the system last cooled to temperatures lower than the APbPRZ.

Samples with such a wedge-shape geometry on Tera-Wasserburg concordia are worth investigating further for extracting continuous thermal histories from apatite U-Pb thermochronology. Other possibilities for generating such a wedge-shape geometry include secondary rim overgrowths (Figure 5B) or variable grain recrystallisation (Figure 5C). Such processes may be particularly hard to distinguish from volume diffusion on Tera-Wasserburg concordia on a grain mount where conventional U-Pb LA-ICP-MS dating has been undertaken, as there may be preferential sampling of core vs. rim regions depending on the laser spot placement and the exposure level of the crystal after polishing. In addition, CL and BSE imaging may not detect apatite regions characterised by secondary overgrowths or recrystallisation [40]. However, it is still likely that the majority of wedge-shape geometries of apatite U-Pb data on Tera-Wasserburg concordia are associated with volume diffusion, as low- to medium-grade metamorphic secondary overgrowths (e.g., Figure 1) or recrystallised regions would typically have very low U concentrations [3,53] and thus effectively represent a common Pb component (cf Section 2.3).

In addition to being suggestive of whether volume diffusion has taken place, the systematics of apatite U-Pb data on Tera-Wasserburg concordia also reveal whether the apatite crystals have a high enough Pb^*/Pb_c ratio so as to avoid employing a substantial common-Pb correction. Unless the samples are very old (likely >1 Ga), the low U contents of ultramafic and low-to medium-grade metamorphic apatite are unlikely to be suitable candidates for apatite U-Pb thermochronology, and the higher U contents of S-type [6] and high-grade metamorphic apatite are preferred (cf. Section 2.3). Once an appropriate sample has been chosen, only euhedral crystals should be picked and analysed, as the surface of the euhedral crystal can then be assumed to represent the boundary of the diffusion domain. Apatite thermochronology can be done via U and Pb isotopic analyses using ID-TIMS. However, while this approach usually yields the most precise dates, it utilises single or several crystals and provides no intra-grain date information that can be related to petrographic features, or parent isotope zonation. Arguably a far better approach is to

use an in situ isotopic method such as LA-(MC)-ICP-MS, which provides spatially resolved dates that are usually obtained through the crystal centre perpendicular to the c-axis. These spatially resolved dates should be coupled with petrography (e.g., CL, SEM-BSE) and LA-ICP-MS trace element maps. The two main approaches are depth profiling through crystals mounted parallel to the c-axis on double-sided tape ([29,37]; Figure 6A) or undertaking a date transect across crystals mounted with their c-axes oriented parallel to the incident laser beam on epoxy mounts polished to reveal the crystal interiors ([6,39]; Figure 6B).

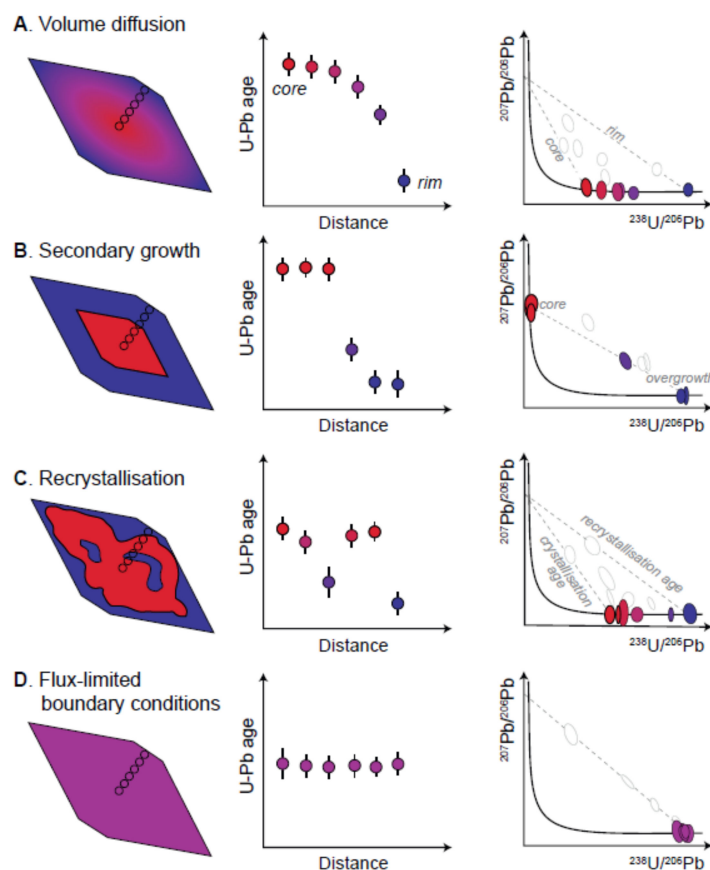


Figure 5. U-Pb date profile collected by LA-ICP-MS across a half-width of an accessory mineral grain and the resultant U-Pb date profile topology on Tera-Wasserburg Concordia, modified from Smye et al. (2018) [18]. The filled ellipses on Tera-Wasserburg Concordia are analyses corrected for common Pb; the unfilled ellipses are the same analyses uncorrected for common Pb. (A) Volume diffusion from grain cores into the grain boundary. (B) Following a phase of secondary growth. (C) Partial recrystallisation of an accessory mineral grain. (D) The case where the grain boundary cannot host radiogenic Pb (flux-limited boundary condition).

These approaches have their own respective advantages and disadvantages and have significant implications for the analytical protocol. The mounting protocol for depth profiling is substantially simpler, and this approach can yield dates with micron-level depth resolution perpendicular to the c-axis [29,37]. This resolution is substantially better than the diameter of the laser spot, although because a minimum sample volume is required the laser beam diameter must be large (typically c. 50 μm). However, it is then challenging to obtain CL, BSE and LA-ICP-MS trace element maps on the crystal that was depth profiled. If ablation is allowed continue deep into the crystal, it can aid subsequent splitting of the crystal into two halves with tweezers, which can then be mounted and polished for petrographical investigation. Split-streaming [81], whereby the aerosol is split between an MC-ICPMS or SF(sector field)-ICP-MS to measure U-Pb isotopic ratios and

a Q(quadrupole)-ICPMS to measure petrogenetically diagnostic trace elements, is also another alternative.

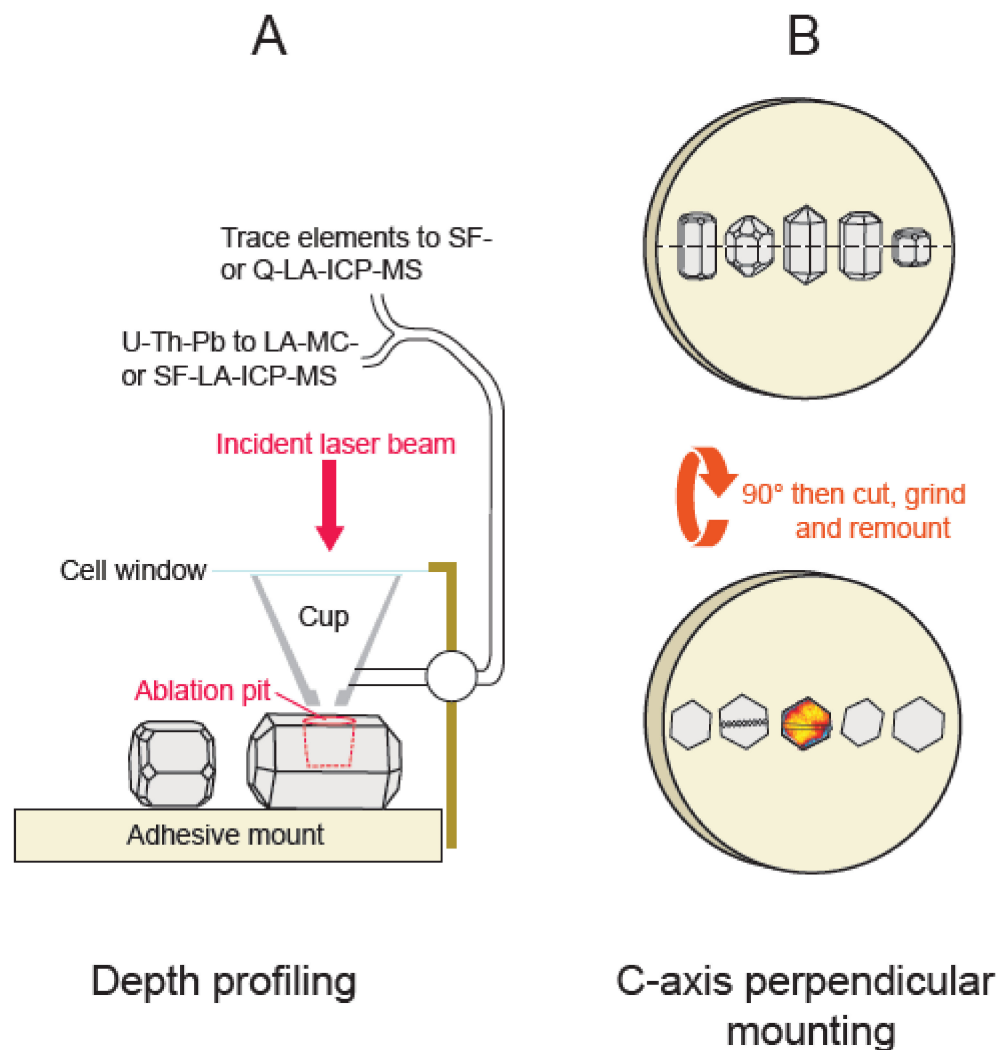


Figure 6. The two main crystal mounting approaches for generating in situ intra-grain date profiles. **(A)** Depth profiling through crystals mounted parallel to the c-axis on double-sided tape [29,37]. **(B)** Undertaking a date transect across crystals mounted with their c-axes oriented parallel to the incident laser beam on epoxy mounts polished to reveal their crystals interiors [6,39]. The apatite crystals are first mounted parallel to their c-axes and centred on a common ‘centre’ line to assure that all crystals are ultimately ground to the same depth. This apatite block is then cut out of the epoxy, rotated 90°, ground to close to the centre line and remounted and polished.

If the crystal is to be mounted in epoxy, ensuring the crystals are mounted with their c-axis perpendicular to the mount surface and all crystals are polished to half-thickness is challenging. The approach of Paul et al. (2019) [39] is illustrated in Figure 6b. It involves first mounting apatite crystals of variable size parallel to their c-axes and centred on a common ‘centre’ line to assure that all crystals are ultimately ground to the same depth. This apatite block is then cut out of the epoxy, rotated 90°, ground to close to the centre line and remounted and polished, exposing a surface across the apatite core in an orientation orthogonal to the c-axis. This approach makes it easy to obtain CL, BSE and LA-ICP-MS trace element maps prior to acquiring spatially resolved U-Pb dates. However, the spatial resolution of the U-Pb date transects is now limited to the laser beam diameter, typically around 15 microns for a LA-MC-ICP-MS system employing spots [6] or rasters [39].

Inverse modelling approaches are covered in Section 4.1, while determining linking spatially resolved U-Pb dates with petrography (e.g., CL, SEM-BSE and LA-ICP-MS trace element maps) is discussed in Section 2. It is emphasised that CL and BSE imaging may not detect apatite domains characterised by secondary rim overgrowths or dissolution-reprecipitation [40]. Therefore, spatially resolved LA-ICP-MS trace element data (in particular the LREE, Sr and Y [3]) are key to identifying regions of fluid- or deformation-enhanced recrystallisation in the apatite. In this respect, mounting crystals perpendicular to their c-axes and ensuring the crystal centre is exposed on the mount surface makes it easy to link the spatially-resolved dates with potential recrystallised domains identified by trace element analysis. Another advantage of this mounting approach is that it facilitates a key test on the accuracy of the inverse modelling, by enabling thermal histories from opposing core-rim radii from the same crystal to be directly compared [39]. A comparison should then be made of all the t-T solutions obtained from single apatite crystals from the same rock.

6. Conclusions

Recent studies have exploited diffusive Pb loss from apatite crystals to generate t-T paths between ~350–570 °C, by comparing apatite U-Pb ID-TIMS dates with grain size or by LA-MC-ICP-MS age depth profiling/traverses of apatite crystals, and assuming the effective diffusion domain is the entire crystal. Such studies have shown the broad applicability of the apatite U-Pb system to resolve middle to lower crustal thermal histories, but several key challenges remain.

Recognising episodes of metasomatic and metamorphic apatite dissolution-reprecipitation or neocrystalline growth is key to the successful application of the apatite U-Pb thermochronometer, as such processes invalidate a key assumption of thermochronology, namely that Pb has been lost by Fickian diffusion. In addition to conventional petrographic evidence, apatite trace-element geochemistry is an excellent tracer of rock type and the trace element systematics of metasomatic and low-grade metamorphic apatite are highly distinct. However, no systematic studies have been performed to test the relationship between Pb diffusion and apatite composition, the degree of anisotropy of Pb diffusion in apatite and potential differences in the diffusivity of Pb* vs. Pb_c in apatite. Flux-limited boundaries can have significant implications for apatite U-Pb thermochronology, and there are presently limited constraints on most of the parameters required to characterise Pb diffusion through mineral matrices that can potentially surround apatite crystals.

Apatite usually incorporates significant Pb_c. This is particularly problematic for young samples which have little time to accumulate substantial Pb* or for apatites with low U concentrations such as greenschist-facies apatite (U << 1 ppm). The U contents of high-grade metamorphic and leucosome apatite (mean c. 20 ppm) and S-type granitoid apatite (mean c. 75 ppm) are much more amenable to U-Pb thermochronology. The substantial common-Pb correction required for samples with high Pb_c/Pb* ratios results in large date uncertainties, and also potentially inaccurate dates (and resultant thermal history models) if the initial Pb composition employed is inappropriate. A low-U co-genetic phase (e.g., K-feldspar) which exhibits negligible in-growth of radiogenic Pb likely represents the best estimate of the initial Pb isotopic composition, but this common Pb constraint should still be critically assessed and compared to those derived from crustal Pb evolution models and isochron-based approaches. The superior precision of the ²⁰⁷Pb-correction method means this approach is therefore recommended for Phanerozoic samples. For older samples, particularly those that have spent an extended time in the APbPRZ, the ²⁰⁴Pb-correction method is recommended.

For in situ intra-grain date traverses, mounting crystals perpendicular to their c-axes and ensuring the crystal centre is exposed on the mount surface makes it easy to link the spatially-resolved dates with potential recrystallised domains as identified by trace element analysis. Another advantage of this mounting approach is that it facilitates a key test of the accuracy of the inverse modelling, by enabling thermal histories from opposing

core-rim radii from the same crystal to be directly compared. A comparison should then be made of all of the t-T solutions obtained from single apatite crystals from the same rock. Such a mounting protocol also facilitates assessment of whether apatite crystals are zoned with respect to U. When significant parent U zonation is present, thermal history solutions derived from intra-grain date traverses are significantly more accurate than those derived from comparing single (bulk) crystal ID-TIMS dates with their grain size. When parent U zonation can be shown to be minor to absent from LA-ICP-MS mapping, the superior precision of thermal history solutions derived from comparing single (bulk) crystal ID-TIMS dates with their grain size is preferred.

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