U–Pb dating of mineral deposits: from age constraints to ore-forming processes

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1. Introduction

The knowledge of the timing and duration of ore-forming processes are perhaps one of the most desirable pieces of information that geologists require to draw a complete picture of the deposit and to put its genesis into a coherent regional or even global geological framework. In many cases, it represents an essential parameter for establishing detailed genetic models, and can critically impact on exploration strategies. This necessarily requires a reliable, precise and accurate geochronometer.

In the past two decades, U–Pb dating has seen a remarkable success across the Earth Sciences to become the most commonly used absolute isotopic geochronometer. This great success results from considerable improvements in the analytical techniques and in advances of our understanding of the U–Pb system in the geological environment. The paramount advantage of U–Pb dating relies on the coexistence of two chemically identical but isotopically distinct radioisotopes of U (^{238}U and ^{235}U), both of which have their very own decay chain and decay rates. Furthermore, their half-lives are particularly suitable for geologically relevant ages. This allows the determination of two independent dates of which equivalence (concordance) can usually be taken as a sign of the meaningfulness of the date, while discordant dates can be either geologically irrelevant or may be extrapolated to a meaningful date if the cause(s) of this discordance can be identified.

The recent success of U–Pb geochronology is the result of numerous stepwise improvements over the last decades (see detailed history in Davis et al. 2003; Corfu 2013; Mattinson 2013), but has experienced a boost due to coordinated community efforts (EARTHTIME for isotope dilution analysis: http://www.earth-time.org; PLASMAGE for laser ablation analysis: http://www.plasmage.org).

Geochronology was born out of the U–Pb system. Radioactivity was discovered at the dawn of the nineteenth century by H. Becquerel, M. and P. Curie in their work with various uranium compounds (U-salts, U-metal, pitchblende) (Becquerel 1896a; Becquerel 1896b; Curie et al. 1898; Curie and Skolodowska Curie 1898; Skolodowska Curie 1898). Soon after, E. Rutherford first suggested that the Pb/U ratio of geological materials could be used to date them (Rutherford 1906). The next year, B. Boltwood applied this method to 43 uranium ore samples and obtained the first absolute total-U and total-Pb ages ranging from 410 Ma to 2200 Ma (Boltwood 1907). This revolution conclusively supported the suggestion made by Charles Darwin half a century prior, that the earth was several hundred million years old, and was about to provide absolute age calibrations for the geological timescale of A. Holmes (1911; 1913). However, it was not until the turn of 1930 that the existence of two radioactive U isotopes and their respective Pb daughter isotopes was recognized in U ores (Rutherford 1929; Aston 1929; von Grosse 1932), paving the way for modern U–Pb geochronology. Ever since, improvements in mass spectrometry, laboratory procedures and advances in nuclear physics have permitted the analysis of increasingly smaller quantities of U and Pb with improved precision and accuracy. This in turn, enabled a switch from the analysis of U ore minerals, to low-U bearing minerals such as zircon, titanite and apatite in the second half of the last century (Larsen et al. 1952; Tilton et al. 1955; Webber et al. 1956; Tilton et al. 1957). However, dating still involved multigrain mineral fractions which typically show discordance between ^{206}Pb/^{238}U and ^{207}Pb/^{235}U dates, and render their interpretation subjected to debate, assumption and uncertainty. The 1970s to 1980s period arguably marks the turning point of U–Pb geochronology. At that time, the development of low blank single grain zircon dating (Mattinson 1972; Krogh 1973; Krogh and Davis 1975; Lancelot et al. 1976; Michard-Vitrac et al. 1977; Parrish 1987), air-abrasion techniques (Krogh 1982) and in-situ ion probe dating (Hinthorne et al. 1979; Hinton and Long 1979; Froude et al. 1983) concurred to routinely produce concordant U–Pb ages and triggered an expansion in the range of application of U–Pb dating across various minerals, geological terrains and planetary materials. The 1990s saw the advent of the chemical abrasion technique (Mattinson 1994) and of laser-ablation inductively coupled plasma mass spectrometry (Fryer et al. 1993; Horn et al. 2000) that are now common practices in many laboratories around the world. This is the time when U–Pb dating was embraced by the Earth Sciences community, and became an essential tool of geological mapping and mineral exploration. Perhaps as a sign of a mature discipline, the last decade has seen U–Pb practitioners around the world collaborating in a community driven effort to push precision, accuracy and inter-laboratory reproducibility of dates toward unprecedented limits, the EARTHTIME initiative (http://www.earth-time.org).

This century of development of U–Pb dating has left us with a powerful tool for ore deposit studies. While zircon is arguably the most commonly used and understood mineral due to its robustness and minimal amount of Pb it can incorporate in its lattice during crystallization (so-called "common" Pb), a number of other U-bearing minerals are amenable to U–Pb dating (e.g., titanite, apatite, monazite, xenotime, rutile, baddeleyite, perovskite, columbo-tantalite, cassiterite, allanite, calcite, etc). While most minerals can date their crystallization, a handful of them (e.g., apatite, rutile, titanite) actually date their arrival below their respective closure temperature for the U–Pb system. This diversity of minerals allows a variety of ore deposit types and related geological processes (magmatic, hydrothermal, metamorphic, sedimentary and supergene) to be dated. As we write, U–Pb dates have been published on almost the full spectrum of deposit types and an increasing number of minerals are being tested and improved for U–Pb geochronology. However, the systematics of the U–Pb system is only really well-known in zircon and possibly monazite, followed by titanite, apatite, rutile, baddeleyite, and xenotime.

Geochronology can illuminate the apparent geological chaos at some deposits or districts, as well as support, refute or generate hypotheses for ore-forming processes. Nevertheless, only in rare cases does the dated mineral directly date the ore itself (e.g., columbo-tantalite, cassiterite, uraninite). As examples, zircon from a porphyry stock dates magma intrusion and not the cross-cutting copper mineralization, titanite in a skarn dates the high temperature metasomatism and not the deposition of the polymetallic ore at lower temperature. Some minerals may date magmatic crystallization (e.g., zircon, baddeleyite), or metamorphic reactions (e.g., monazite, titanite) and some may date their precipitation from hydrothermal fluids (e.g., monazite, xenotime, calcite, uraninite). In fact, the meaning of any date remains deeply anchored into proper field observations and sample characterization. Some minerals and dating methods (e.g., fission tracks in apatite and zircon, ^{40}Ar/^{39}Ar in micas and K-feldspar, etc) can also record low-temperature events that that post-date ore formation, allowing a fuller understanding of the coupled temperature-time evolution of mineral systems.

While U–Pb geochronology has been extensively used to determine the age of geological events, it remains to current and future generations of scientists to give increasingly more added value to increasingly more precise and accurate dates, feeding quantitative and numerical models or ore-forming processes. For example, when combined with numerical models, the duration of magmatic-hydrothermal events or the probability density distribution of a population of dates may be interpreted in terms magmatic-hydrothermal flux and volume (Caricchi et al. 2014, Chelle-Michou et al. 2017). This will be a critical step if we want to uncover the processes at play during ore formation, and provide mineral exploration professionals with innovative and efficient tools that may help locating a distant or deeply buried deposit, or that could provide early information on the potential size of the explored deposit (e.g., Chelle-Michou et al. 2017).

This chapter reviews the basics of the U–Pb geochronology and the most commonly used dating techniques and minerals while pointing out their respective advantages, weaknesses and potential pitfalls. Through a series of case studies, we illustrate the various usages of U–Pb dating for the study of mineral deposits. Admittedly, U–Pb geochronology is a field that is strongly biased toward the use of zircon and this chapter is not an exception. Nevertheless, we will also shed light on U–Pb dating applied to less commonly encountered and dated minerals.

2. Basics of U–Pb geochronology

2.1. The U–Pb system

On first approximation, both naturally occurring long-lived parent uranium isotopes (^{238}U and ^{235}U) decay to stable lead isotopes (^{206}Pb and ^{207}Pb, respectively) at distinct rates, and thus have different half-lives and decay constants (λ_{238} and λ_{235}). Details of the U decay to Pb are actually more complex and involve a long chain of alpha or beta decays with the production of a number of intermediate daughter isotopes (Fig. 1a). This allows the formulation of two generalized age equations:

$$\left(\frac{^{206}Pb}{^{204}Pb}\right) = \left(\frac{^{206}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{238}U}{^{204}Pb}\right)\left(e^{\lambda_{238}t} - 1\right) \quad (1)$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right) = \left(\frac{^{207}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{235}U}{^{204}Pb}\right)\left(e^{\lambda_{235}t} - 1\right) \quad (2)$$

where ^{204}Pb is the only non-radiogenic isotope of Pb and the subscript 0 indicate the initial isotopic composition of lead at the time (t) when the system closed. In cases where the proportion of initial to radiogenic Pb is negligible, which is common for zircon, monazite, and xenotime, equations (1) and (2) can be simplified:

$$\left(\frac{^{206}Pb^*}{^{238}U}\right) = e^{\lambda_{238}t} - 1 \quad (3)$$

$$\left(\frac{^{207}Pb^*}{^{235}U}\right) = e^{\lambda_{235}t} - 1 \quad (4)$$

where the superscript * indicate the amount of radiogenic Pb that has formed since the system closed. If the system has remained closed since the mineral crystallized, the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ dates should be identical. Dividing equations (1) and (2) yield a third age equation:

$$\frac{\left(\frac{^{207}Pb}{^{204}Pb}\right)-\left(\frac{^{207}Pb}{^{204}Pb}\right)_0}{\left(\frac{^{206}Pb}{^{204}Pb}\right)-\left(\frac{^{206}Pb}{^{204}Pb}\right)_0} = \left(\frac{^{207}Pb}{^{206}Pb}\right)^* = \left(\frac{^{235}U}{^{238}U}\right)\frac{(e^{\lambda_{235}t}-1)}{(e^{\lambda_{238}t}-1)} \tag{5}$$

This equation has the advantage that the determination of the age does not require measurement of the U isotopes because the present-day $^{238}U/^{235}U$ ratio is mostly constant in U-bearing accessory minerals and equal to 137.818 ± 0.045 (2σ; Hiess et al. 2012). However, in practice, $^{207}Pb/^{206}Pb$ dates are relevant only for ages older than ca. 1 Ga (see below). The constancy of this ratio and the low abundance of ^{235}U further allow the measurement of the ^{235}U to be neglected, which is common practice in many laboratories.

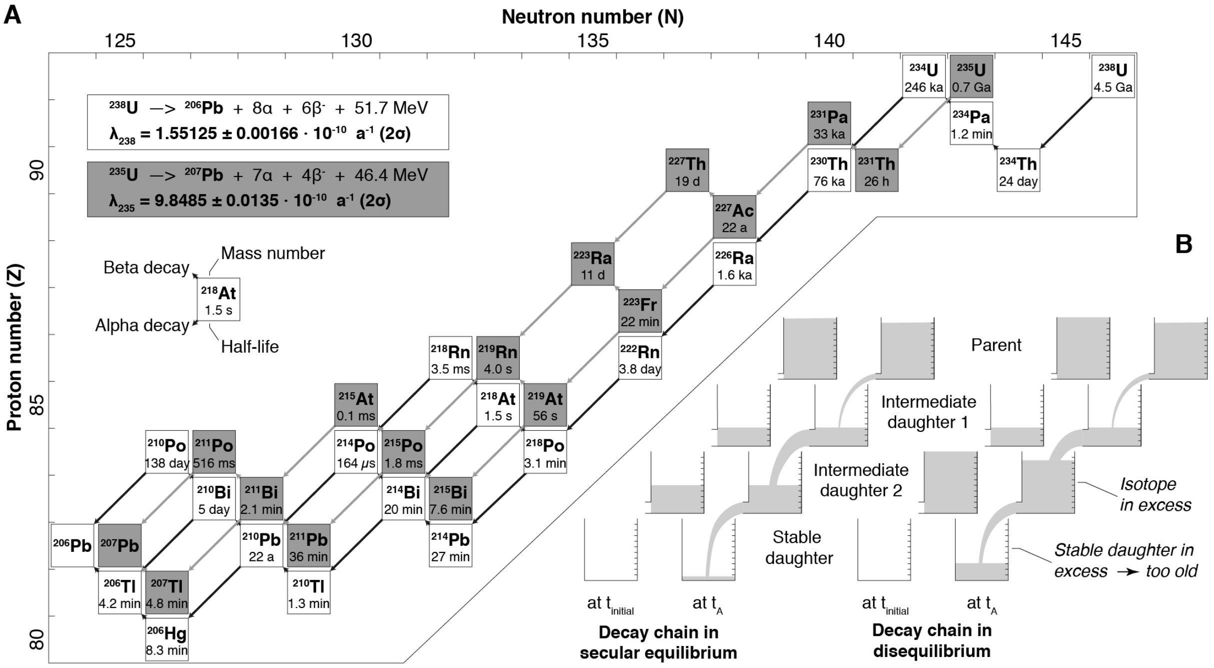

Figure 1. (A) Decay chains of ^{238}U and ^{235}U with the approximate half-live indicated for each radionuclide. **(B)** Cartoon illustrating the difference between a decay chain in secular equilibrium and one in disequilibrium. $t_{initial}$ and t_A refer to the time immediately after and some time after mineral crystallization, respectively.

Decay constants for ^{238}U and ^{235}U are by far the most precisely determined ones among those used in geochronology. Recommended values are those determined by Jaffey et al. (1971) and are $\lambda_{238} = 1.55125 \pm 0.00166 \cdot 10^{-10}\ a^{-1}$ and $\lambda_{235} = 9.8485 \pm 0.0135 \cdot 10^{-10}\ a^{-1}$ (2σ) (Schoene 2014). However, these constants have been suggested to be slightly inaccurate (Schoene et al. 2006;

Hiess et al. 2012), but always within their reported 2σ uncertainties. More accurate values may be available in the future providing further counting experiments are done.

2.2. Data presentation

The trinity of age equations presented above (eqs. 3–5) has promoted the emergence of U–Pb specific plots, the concordia diagrams, that provide a convenient and elegant representation of the data. By far, the most common visual representations of U–Pb data use either the Wetherill concordia plot (Fig. 2a; Wetherill 1956) or the Tera-Wasserburg concordia plot (Fig. 2b; Tera and Wasserburg 1972a; Tera and Wasserburg 1972b). These concordia diagrams are bivariate plots where each axis corresponds to one of the three isotopic ratios used in eqs. 3–5 or their inverse (i.e., $^{206}Pb/^{238}U$, $^{238}U/^{206}Pb$, $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$). On each diagram, the curve represents the line where both isotopic ratios (in abscissa and ordinate) correspond to the same dates, it is the so-called concordia curve. The curvature of the concordia simply reflects the contrasted decay rates of ^{238}U and ^{235}U. If the U–Pb system has remained closed since the crystallization of the mineral and no common Pb is present, the three dates will be the same and plot on the Concordia line, meaning they are be concordant.

For both diagrams (Fig. 2a-b), each analysis is represented by an ellipse where the center is the measured isotopic ratios and the size of the ellipse depicts the analytical uncertainties at a given level of confidence (usually 2σ). Additionally, uncertainties of isotopic ratios plotted on both axis of the concordia diagram are not fully independent from each other and often correlated (e.g., York 1968; Ludwig 1980). This is either due to the use of the ^{206}Pb measurement on both ratios of the Tera-Wasserburg plot or to the use of ^{238}U to calculate ^{235}U for the Wetherill diagram. Thus, the orientation of the uncertainty ellipse reflects the correlation (or covariance) of the errors.

For data that are concordant, it is also convenient to use only the most precise of the three isotopic dates (usually the $^{206}Pb/^{238}U$ or $^{207}Pb/^{206}Pb$ date) and plot them as ranked bars of which the center represents the date and the length reflect the associated uncertainty (Fig. 2c). For a population of dates, the same information can also be presented as a probability density function (Fig. 2c) or a kernel density estimate. The latter is particularly suitable for detrital studies (e.g., Vermeesch 2012).

Because the production of these specific diagrams can be quite labor intensive and calculations in geochronology involve advanced statistical methods, it is recommended to use available software packages dedicated to isotopic geochronology. The most popular and versatile package is the Isoplot Microsoft Excel VBA add-in of K. Ludwig (Ludwig 2012) that has served isotope geochronologists for nearly two decades. However, Isoplot is no longer being updated for later versions of Microsoft Excel (last versions working on Excel 2010 on PC and Excel 2004 on Mac). This led the U–Pb community to start developing multiplatform replacement geochronological applications such as Topsoil and IsoplotR. Topsoil is being developed as a Java standalone application by the CIRDLE development team (Cyber Infrastructure Research & Development Lab for the Earth Sciences, College of Charleston, South Carolina). IsoplotR is a package developed for the R statistical computing and graphics software environment by P. Vermeesch (University College London, UK) and can currently be used through the command line in R or as an online RStudio Shiny applet at http://isoplotr.london-geochron.com. Both programs currently offer limited functionalities, but future versions are expected to have similar and probably enhanced capabilities compared to Isoplot. Finally, density plots (probability density function and Kernel density estimates) can be drafted with Densityplotter (Vermeesch 2012), a standalone Java-based application. It is noteworthy that all these programs are freely available online.

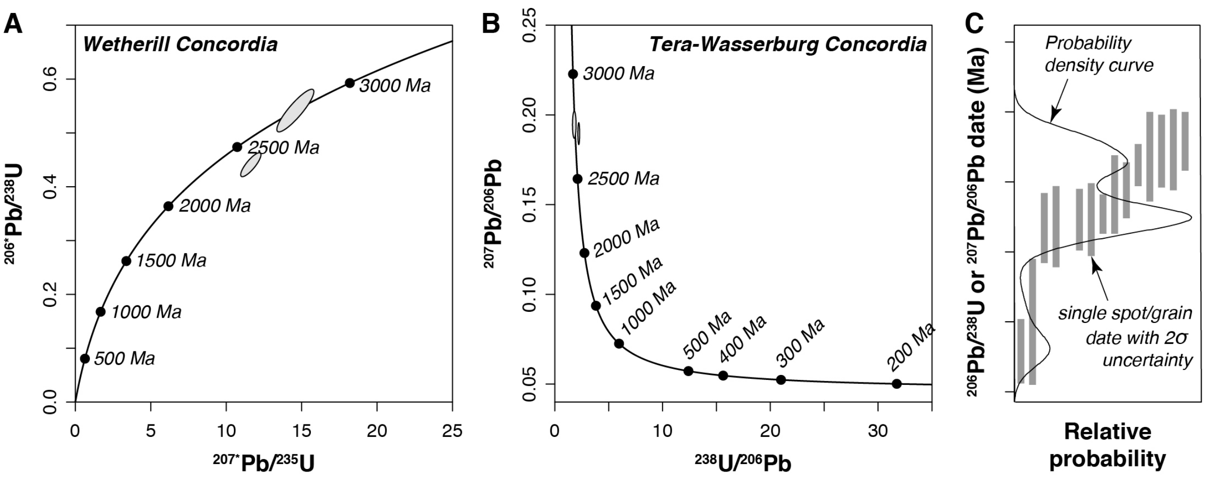

Figure 2. Classical plots used to present U–Pb geochronological data. **(A)** Wetherill concordia plot with one concordant and one discordant analysis shown as example, **(B)** Tera-Wasserburg concordia plot with the same analyses, **(C)** ranked isotopic date plot for synthetic concordant data together with the corresponding probability density curve. Note that the while the y-axis is valid for both the data bars and the density curve, the x-axis labelled "relative probability" is only relevant for the probability density curve. Single spot/grain dates are ranked only to facilitate the reading of the figure.

2.3. Causes of discordance

Since the beginning of isotopic dating, discordance has been the main concern of U–Pb geochronologists. Ultimately, understanding the causes of discordance and trying to eliminate it has been the most powerful driving force to advance U–Pb dating during the second half of the 20th century (Corfu 2013). It is now established that discordance can have a number of origins including: mixing of various age domains, Pb-loss during physical and chemical changes in the crystal lattice (partially opened system), initial intermediate daughter isotopic disequilibrium, incorrect or no correction for non-radiogenic Pb, or a combination of these (Fig. 3). Nevertheless, one should keep in mind that the recognition of some dates as being discordant is intimately tied to the uncertainty of the data. Indeed, low-precision data might appear perfectly concordant, while high-precision ones would actually reveal otherwise (e.g., Moser et al. 2009). This means that any method is blind to discordance at a degree that is inferior to the best age resolution of that method. Below we present the classical causes of discordance and the most appropriate ways to avoid, mitigate or value them.

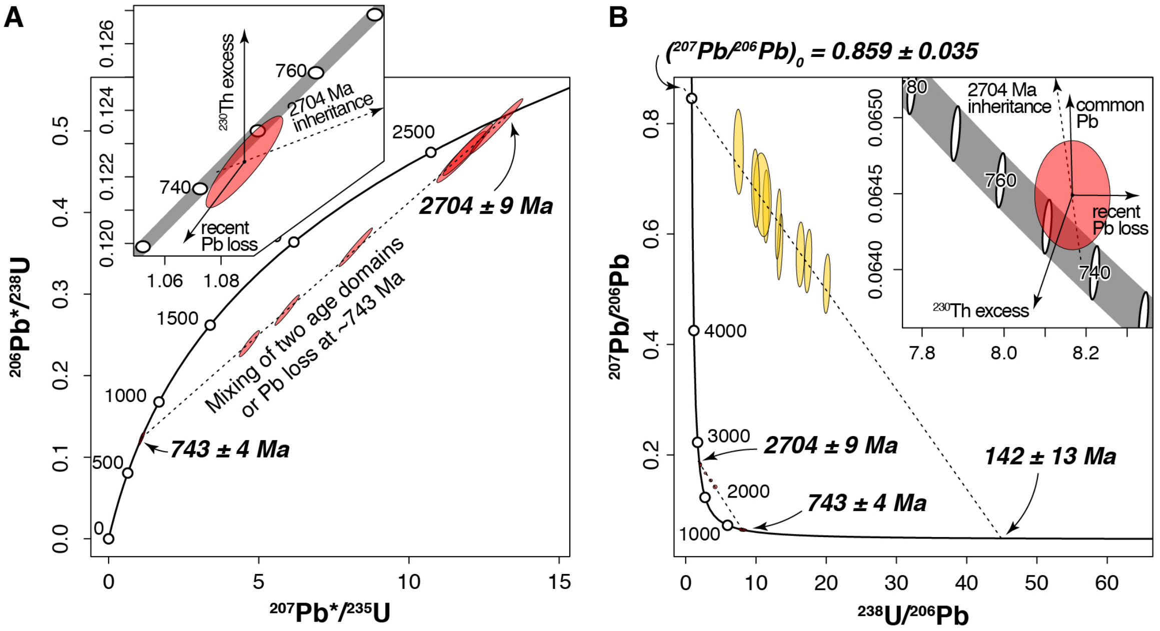

Figure 3. Main causes of discordance plotted on **(A)** Wetherill concordia diagram and **(B)** on a Tera-Wasserburg concordia diagram. Discordance of the red ellipses group is caused by either mixing of two age domains (one at 2704 ± 9 Ma and one at 743 ± 4 Ma) or by Pb-loss of 2704 ± 9 Ma minerals at 743 ± 4 Ma. Discordance of the yellow ellipses group is caused by the presence of common lead in minerals crystallized at 142 ± 13 Ma (Pb$_c$ uncorrected data). Insets shows the possible vectors of discordance.

2.3.1 Mixing multiple age domains

A number of minerals (e.g., zircon, monazite, xenotime) often record multiple growth events. The recognition of different growth zones is crucial for the analysis and interpretation of any dating result. Imagery using transmitted and reflected light together with cathodoluminescence (CL) and back-scattered electron (BSE) microscopy greatly aids in this process but is not always definitive. These images can reveal that a mineral grain can be made up of a sequence of growth zones starting in the center, and mantled by sequential zones towards the rim, all of which can have distinct U–Pb ages. Bulk (whole grain) dating of such multi-domain mineral grains could result in discordant dates, if the age differences are sufficiently large. A similar effect can arise from dating multigrain mineral fractions if they include grains with different isotopic ages. In the case of a simple two component mixture of two different age domains, several analyses could plot along a linear array (a so-called discordia line) in concordia diagrams, of which the lower and upper intercept dates would correspond to the respective ages of the two components (red ellipses on Fig. 3). However, multicomponent mixtures may show more scattered distribution or even plot along artificial, and often poorly correlated discordia arrays of which the upper and lower intercept dates have no geological significance, therefore inhibiting meaningful interpretation of the data.

In order to avoid problems arising from mixing several age domains, imagery of the minerals has become a necessary prerequisite to any dating (either in-situ or whole grain) in order to accurately place the spot of the analysis (for in-situ dating) or to select only those grains (or grain fragment) that have one age domain (for whole grain dating). However, small cores or domains with distinct ages can still go unrecognized if they are present below the imaged surface or have a similar chemistry to the surrounding zones. This effect may be monitored on the time-resolved signal for in-situ measurements (changing isotopic ratio) but would hinder the interpretation of whole grain dates.

2.3.2. Open system behavior

It has long been recognized that the crystallographic lattice of minerals can, under certain conditions, behave as an open system with respect to the U–Pb system (e.g., Holmes 1954; Tilton 1960) through the partial or complete loss of radiogenic Pb. Radiogenic intermediate daughter products of the U decay chains experience a recoil during ejection of the highly energetic alpha particle. The final radiogenic Pb^{2+} is thus situated in a decay-damaged area with enhanced fast pathway diffusion characteristics and could tend to leave this site when appropriate conditions are met. Mechanisms of Pb-loss have been studied extensively, but no simple process can be universally put forward to explain it. Leaching of metamict (radiation-damaged) crystal domains, metamorphic recrystallization, crystal plastic deformation and thermally activated volume diffusion are the most commonly advocated causes of Pb-loss, in decreasing order of importance (see Corfu 2013; Schoene 2014 and references therein). At the sample scale, all these processes will result in discordance of the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U dates if the age difference is large enough. By calculating by a linear regression through a series of discordant analyses, upper and lower intercepts ages can be reconstructed, corresponding to the age of crystallization of the mineral and to the age of the Pb-loss event, respectively (Fig. 3). Multiple Pb-loss events are notoriously difficult to unravel and may present as excess data scatter or even spurious discordia lines. Furthermore, highly metamict crystal domains may also experience U loss or U gain that would result in inversely (i.e., above the Wetherill concordia) or normally discordant data, respectively. In such cases, no age interpretation can be done. Complete recrystallization of a grain may lead to complete loss of all accumulated radiogenic Pb and reset the age to zero. The extremely low diffusion constants for Pb and U in zircon (Cherniak and Watson 2001; Cherniak and Watson 2003; Cherniak et al. 1997) means that volume diffusion is a very inefficient process to remove radiogenic Pb from an undisturbed zircon lattice. It is for this reason that cases of U–Pb system survival have been reported in granulite facies rocks (e.g., Möller et al. 2003; Kelly and Harley 2005; Brandt et al. 2011; Kröner et al. 2015).

Open-system-related discordance is caused by several distinct processes that cause fast diffusion pathways in the zircon lattice, and such discordant data may be difficult to interpret. Features like multiple growth zones, overgrowth rims, dissolution-reprecipitation textures, or metamorphic recrystallization can be recognized in BSE or CL images (Geisler et al. 2007). Furthermore, recrystallized domains have distinct trace element compositions that can be identified by in-situ chemical analysis (Geisler et al. 2007). Pb-loss through fluid leaching of metamict domains can result in the deposition of minute amounts of ‘exotic’ elements that normally would not be able to enter the mineral structure (e.g., Fe or Al in zircon; Geisler et al. 2007). Additionally, the degree of metamictization, crystal ordering and ductile crystal reorientation can be evaluated with Raman spectroscopy, electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM), respectively. Finally, for the specific case of zircon, the chemical abrasion technique (Mattinson 2005) has proven to be a powerful method for removing zircon domains that have suffered Pb-loss due to fission tracks, metamictization or other fast diffusion pathways.

2.3.3. Common Pb

Common Pb is a generic name for the fraction of Pb that is not radiogenic in origin and results from a mixture of initial Pb (i.e., Pb incorporated during mineral crystallization) and/or

Pb contamination (both in nature and in the lab). The measurement of ^{204}Pb (the only non-radiogenic Pb isotope) undoubtedly pinpoints the presence of common Pb. However, ^{204}Pb measurement can be very challenging for low concentrations of common Pb, or may be prone to isobaric interference with ^{204}Hg, inherent to the LA-ICPMS technique (see analytical methods). On a Tera-Wasserburg plot, analyses containing common Pb typically display a linear array of discordant ellipses defining an upper intercept date older than 4.5 Ma which points to the ^{207}Pb/^{206}Pb common Pb composition on the ordinate axis, and a lower intercept providing the age of the mineral (2D isochron; Fig. 3b). If ^{204}Pb/^{206}Pb can be measured, it can be plotted on a third axis and the data regressed to estimate the common Pb composition, the age of the mineral and to evaluate the relative contributions of common Pb and Pb-loss on the cause of discordance (3D isochron; Wendt 1984; Ludwig 1998). This approach has been shown to provide better precision for the common Pb composition than the 2D isochron method (Amelin and Zaitsev 2002; Schoene and Bowring 2006). Another Pb-correction practice in LA-ICPMS and SIMS analysis consists of deducing the common Pb correction from measurement of ^{208}Pb (stable decay product of ^{232}Th) and by assuming concordance of the U and Th systems. However, these correction methods may result in overcorrection of some data that are discordant for reasons other than common Pb only. When possible, it is therefore ideal to apply a more robust correction based on the direct measurement of the sample ^{204}Pb. The Pb isotopic composition from laboratory contamination ("blank") is also an important consideration in high-precision U–Pb geochronology using isotope-dilution TIMS, and is obtained through repeated measurement of blank aliquots.

The isotopic composition of initial Pb incorporated during the crystallization of a mineral is best obtained from measurements of cogenetic low-U minerals such as feldspars, galena or magnetite. Alternatively, initial Pb compositions for a known age may be estimated from bulk Earth evolution models (Stacey and Kramers 1975). However, this last approach is less reliable compared to the measurement of a cogenetic low-U mineral (Schmitz and Bowring 2001; Schoene and Bowring 2006). Finally, for the specific case of zircon where the presence of common Pb is essentially limited to inclusions, fractures and metamict domains (see §6.1), the chemical abrasion technique (Mattinson 2005) has proven to be a powerful method for removing initial Pb from the crystal, leaving only the need for a laboratory blank correction.

2.3.4. Intermediate daughter disequilibrium (^{230}Th and ^{231}Pa)

The age equations presented above (eqs. 1–5) are valid under the assumption that the decay chains are in secular equilibrium, that is, one atom of Pb is created for every decay of one atom of U (Fig. 1b). However, elemental fractionation during mineral crystallization or partial melting would likely disrupt a previously established secular equilibrium (Fig. 1b). This effect should ideally be accounted for in geochronology. Nevertheless, most intermediate decay products of the U series have half-lives of many orders of magnitude smaller (microseconds to years) than the half-lives of U (Ga; Fig. 1a) and potential disequilibrium would have negligible effect on the U–Pb dates even at the best of current analytical capabilities (i.e., 0.5‰ uncertainty on the date). However, intermediate daughters ^{230}Th (^{238}U decay chain) and ^{231}Pa (^{235}U decay chain) have half-lives that are long enough (75.6 ka and 32.8 ka, respectively; Fig. 1a; Robert et al. 1969; Schärer 1984; Parrish 1990; Cheng et al. 2013) to critically impact on the accuracy of the calculated date if disequilibrium is not accounted for (Schärer 1984; Parrish 1990; Anczkiewicz et al. 2001; Amelin and Zaitsev 2002; Schmitt 2007). For example, during monazite crystallization, Th (of which ^{230}Th) is preferentially incorporated into the crystal lattice compared to U, thus resulting in excess ^{206}Pb (e.g., Fig. 1b) and in erroneously old ^{206}Pb/^{238}U dates if the excess ^{230}Th is not accounted for (Figs. 3, 4a). In turn, the Th-uncorrected ^{207}Pb/^{206}Pb date for the same crystal would be too young (Fig. 4b). Conversely, zircon preferentially incorporates U over Th, rendering ^{230}Th-uncorrected ^{206}Pb/^{238}U dates typically too young (Fig. 4a). Similarly, the ^{207}Pb/^{235}U isotopic system is potentially affected by ^{231}Pa excess as has been reported for zircon (e.g., Anczkiewicz et al. 2001).

The magnitude of the correction that needs to be applied to correct the isotopic dates for initial ^{230}Th and ^{231}Pa disequilibrium depends on the distribution coefficient of Th/U and Pa/U between the dated mineral and the liquid from which it crystallized (a melt or an aqueous fluid), respectively (Schärer 1984). For the ^{207}Pb/^{206}Pb date, it also depends on the age of the mineral (Parrish 1990). Figure 4 shows the effect of initial ^{230}Th and ^{231}Pa disequilibrium has on the ^{206}Pb/^{238}U, ^{207}Pb/^{206}Pb and ^{207}Pb/^{235}U dates. It shows that for low mineral/liquid distribution coefficients ($D_{Th}/D_{U}<1$) date offsets converge to a minimum of -109 ka and -47 ka for the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U dates, respectively. However, if the distribution coefficients are high (>1), excess ^{206}Pb/^{238}U and ^{207}Pb/^{235}U dates up to few Ma can be expected. Conversely, Th/U distribution coefficient <1 causes excess ^{207}Pb/^{206}Pb dates of few ka to ca. 0.5 Ma (depending on the age of the mineral), and distribution coefficient >1 causes ^{207}Pb/^{206}Pb dates deficit up to few Ma for Precambrian samples (Fig. 4b).

In practice, the Th/U ratio of the mineral is measured as ^{232}Th/^{238}U or estimated from the measured amount of its stable daughter isotope ^{208}Pb by assuming concordance of the U–Pb and Th–Pb dates. For minerals crystallized from a melt, available Th/U mineral-melt distribution coefficients (Fig. 4a) can then be used to reconstruct the Th/U of the melt needed for the Th-disequilibrium correction (e.g., adopting the values from Tiepolo et al. 2002; Klemme and Meyer 2003; Prowatke and Klemme 2005; Klemme et al. 2005; Prowatke and Klemme 2006; Rubatto and Hermann 2007; Stepanov et al. 2012; Beyer et al. 2013; Chakhmouradian et al. 2013; Stelten et al. 2015). Alternatively, direct measurement of melt inclusions hosted in the dated mineral, of glass or of whole rock Th/U ratio are also commonly used. Choosing the most appropriate estimate of the melt Th/U ratio at the time of mineral crystallization (using partition coefficient or direct measurement on whole rock or melt inclusions) should be done at the light of all possible information concerning the crystallization conditions of the dated mineral (e.g., temperature, crystallinity, co-crystallizing Th-bearing mineral phases, etc; see examples in Wotzlaw et al. 2014; Wotzlaw et al. 2015).

In essence, ^{230}Th- and ^{231}Pa-corrections are based on the assumption that the dated mineral crystallized from a liquid in secular equilibrium with respect to the U-series. While this might be an acceptable assumption for some magmatic systems (at least for ^{238}U and ^{230}Th) (Condomines et al. 2003), it should not be regarded as a rule, especially for hydrothermal systems in which Th and U have distinct solubilities (Porcelli and Swarzenski 2003; Drake et al. 2009; Ludwig et al. 2011). Indeed, the contrasted partitioning behavior of U and Th into a hydrothermal fluid causes isotopic disequilibrium in the fluid (^{230}Th excess or deficit). In cases where the existence of this fluid is very short (e.g., for magmatic-hydrothermal systems) no time is given for radiogenic ingrowth in the fluid which would remain out of secular equilibrium. Finally, the fractionation of U and Th promoted by the crystallization of U- and Th-bearing hydrothermal minerals may further enhance isotopic disequilibrium. In such cases, the Th-correction (or Pa) should aim at determining the Th/U ratio of the last medium where the decay chain was in secular equilibrium before the crystallization of the mineral. This equates to determining the bulk source (in secular equilibrium) to sink (dated mineral) distribution coefficient of Th/U, regardless of the intermediate process(es), assuming short transport timescales and a unique source of U and Th. For example, Chelle-Michou et al. (2015) used the Th/U ratio of the porphyries (same as for magmatic zircons; Chelle-Michou et al. 2014) to correct the dates obtained on hydrothermal titanite from the Coroccohuayco skarn deposit. In this case, the U-series elements (mainly U and Th) were likely sourced from the magma which was assumed to be in secular equilibrium and transported to the site of deposition by a magmatic fluid in a short period of time.

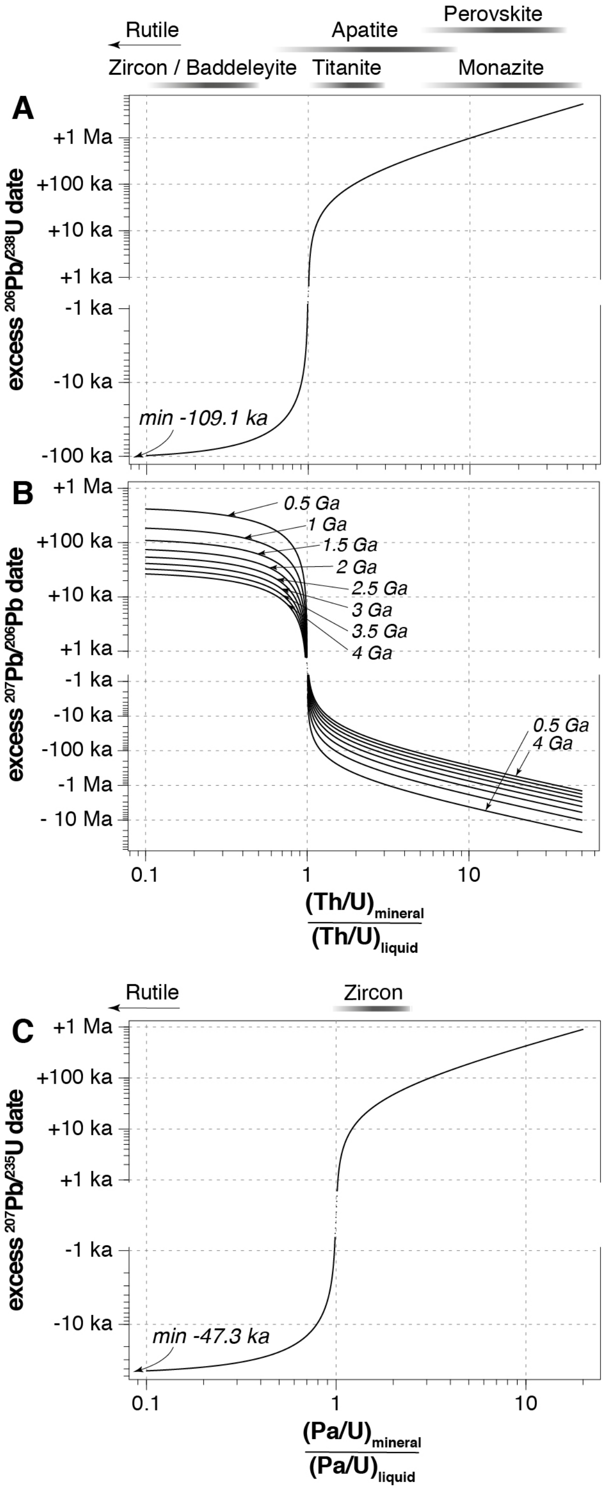

Figure 4. Excess in **(A)** ^{206}Pb/^{238}U and **(B)** ^{207}Pb/^{206}Pb dates due to initial ^{230}Th disequilibrium, and **(C)** excess in ^{207}Pb/^{235}U date due to initial ^{231}Pa disequilibrium as a function of Th/U and Pa/U mineral/liquid distribution coefficients, respectively (after Schärer 1984; Parrish 1990). Typical ranges of mineral/melt distribution coefficients for commonly dated minerals are shown for reference.

3. A note on Th–Pb geochronology

Although less commonly used than U–Pb geochronology, Th–Pb dating may, in some cases, be advantageous and complementary to U–Pb dating. Due to comparable ionic radii of U and Th and similar valence (tetravalent except for oxidized systems where U in mostly hexavalent), most minerals hosting U into their structure will also incorporate Th (if it is available in the system), and vice versa. The single long-lived isotope of Th, ^{232}Th, decays to ^{208}Pb through a chain of alpha and beta decays. The Th–Pb decay offers the possibility of a third independent geochronometer embedded within the mineral allowing for a further assessment of the robustness and meaningfulness of the obtained date. In addition, the nearby masses of ^{235}U, ^{235}U and ^{232}Th on one side, and of ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb on the other side, allows for simultaneous measurement of U–Th–Pb isotopes from the same volume of analyte (ablated volume or dissolved grain). The generalized age equation writes as follow:

$$\left(\frac{^{208}Pb}{^{204}Pb}\right) = \left(\frac{^{208}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{232}Th}{^{204}Pb}\right)\left(e^{\lambda_{232}t} - 1\right) \quad (6)$$

Where λ_{232} is the ^{232}Th decay constant. If common Pb is negligible equation (6) can be simplified to:

$$\left(\frac{^{208}Pb^{*}}{^{232}Th}\right) = e^{\lambda_{232}t} - 1 \quad (7)$$

The ^{232}Th decay constant is much smaller to that of ^{235}U (half-life of 14 Ga) and is commonly considered to be $4.947 \pm 0.042 \cdot 10^{-11}$ a^{-1} (2σ; Holden 1990). Despite a good accuracy of the ^{232}Th decay constant as suggested by the common concordance of Th–Pb and U–Pb dates (e.g., Paquette and Tiepolo 2007; Li et al. 2010; Huston et al. 2016), its precision is an order of magnitude lower than those of ^{238}U and ^{235}U. This can represent the main source of systematic uncertainty on Th–Pb dates and the main limitation of this system when working below the percent precision level. However, unlike uranium, intermediate daughter isotopes of the ^{232}Th decay chain have short half-lives such that any isotopic disequilibrium formed during mineral crystallization will fade within few decades only. Therefore, the ^{232}Th decay chain can be considered to have remained in secular equilibrium on geological timescale. It results that on cases where U–Pb dates require a large initial ^{230}Th-disequilibrium correction and parameters required for this correction are difficult to estimate (e.g., hydrothermal minerals), Th–Pb dates may be much more accurate than U–Pb ones (but often of lower precision).

Due to the very long half-live of ^{232}Th, the optimal use of Th–Pb geochronology (highest analytical precision) is achieved for old sample and/or minerals with high Th concentrations so that large amount of ^{208}Pb have been accumulated. In the case of Th-rich minerals (e.g., monazite and perovskite, and, to a lesser extent, xenotime, apatite, titanite and allanite), thorogenic ^{208}Pb (i.e., ^{208}Pb*) would typically be so abundant than common Pb correction may not introduce significant uncertainties into the computed ^{208}Pb*/^{232}Th ratio or may even be neglected.

^{208}Pb/^{232}Th dates are most commonly presented as bars of which the center represents the date and the length reflect the associated uncertainty. To evaluate the concordance of the Th–Pb and U–Pb systems, concordia diagrams (^{208}Pb*/^{232}Th vs ^{206}Pb*/^{238}U or ^{207}Pb*/^{235}U) offer a convenient graphical representation of the data.

4. Analytical methods (including data reduction, Pb-correction, uncertainty propagation and data presentation)

Currently, three methods are commonly used to measure isotopic ratios necessary for U–Pb geochronology: (1) laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS); (2) secondary ion mass spectrometry (SIMS); and (3) isotope dilution-thermal ionization mass spectrometry (ID-TIMS). Each of these methods have particular strengths and weaknesses (see summary in Table 1). In most cases, U–Pb geochronology involves the separation of the mineral of interest through gravimetric and magnetic techniques (e.g., heavy liquids, Wilfley shaking table, Frantz magnetic separator) and the selection of individual grains (picking) under binocular microscope. However, in-situ dating with LA-ICPMS and SIMS can also be done directly on polished thin section, thus preserving the petrographic context of the dated mineral, which may be key for the interpretation of the data in some cases.

The main difference between these three techniques resides in the way the dated material is prepared, ionized and introduced into the mass spectrometer. Below, we present an overview of the main aspects of the state-of-the-art procedures for these methods, while highlighting their respective advantages and disadvantages and the handling of uncertainties. For more details on the technical aspects of mass spectrometry, the interested reader is referred to a number of good textbooks and papers (e.g., Ireland and Williams 2003; Parrish and Noble 2003; Gehrels et al. 2008; Arevalo et al. 2010; Arevalo 2014; Carlson 2014; Ireland 2014; Schoene 2014; Schaltegger et al. 2015).

4.1. Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS)

LA-ICPMS is an efficient U–Pb dating technique that allows high spatial resolution and high sample throughput. Analysis is done directly from a thin section or from polished grains mounted in epoxy resin that have been imaged by transmitted and reflected light, CL and/or

BSE techniques prior to analysis. Typical analytical uncertainties for zircon dates are on the order of 3-5 % for single spot and of 0.2-2 % for the weighted mean dates (Fig. 5). However, accuracy may not be better than 3% (Klötzli et al. 2009; Košler et al. 2013), which should be considered when comparing LA-ICPMS U–Pb dates from different studies or with dates from other isotopic systems.

Table 1. Comparison of the three analytical techniques used for U–Pb dating.

	LA-ICPMS	**SIMS**	**CA-ID-TIMS**
Spatial resolution	Spot diameter typically of 10–50 µm, depth of 15–40 µm	Spot diameter typically of 10–15 µm, depth of 1-2 µm	Whole mineral grain or grain fragment. Mixing of age domains is hard to avoid.
Standardization	External with a known reference material and accuracy controlled with a secondary standard	External with a known reference material and accuracy controlled with a secondary standard	Internal with tracer solution (preferably double Pb - double U isotope tracer)
Sample preparation	Mineral separate mount or thin section, Imagery (CL, BSE, ...)	Mineral separate mount or thin section, Imagery (CL, BSE, ...)	Mineral separation, imagery, chemical abration (for zircon only) and washing, digestion, column chemistry
Time required for sample preparation	Few days for mineral separation, sample mount preparation and imagery	Few days for mineral separation, sample mount preparation and imagery	Few days for mineral separation and imagery; 1 day for chemical abrasion of zircon; ≥ 3 days for acid digestion; 1 day for chemical separation of Pb and U.
Time required for one analysis (sample or standard)	2–3 minutes	15–30 min	3–4 hours
Analytical precision (reference for typical zircon: see Fig. 5)	2–5 % on single spot date and ~0.2–2 % on weighted mean date	1–5 % on single spot date and ~0.1–1 % on weighted mean date	0.1–0.05 % on single grain $^{206}\mathrm{Pb}/^{238}\mathrm{U}$ date and ~0.02 % on weighted mean date
Accuracy	~1–5%	~1–5%	0.03–0.3 %; fully traceable to SI units
Preferred geologic application	Large scale survey, detrital geochronology, in-situ dating, minerals with inherited cores	In-situ dating, complexely zoned minerals	Used when highest temporal resolution or highest accuracy are necessary
Limitations	Imprecise common Pb correction, matrix matched standard material	Matrix matched standard material required for $^{206}\mathrm{Pb}/^{238}\mathrm{U}$ and $^{207}\mathrm{Pb}/^{235}\mathrm{U}$ dates, but not required for $^{207}\mathrm{Pb}/^{206}\mathrm{Pb}$ dates	Only very limited spatial resolution (microsampling)

The LA-ICPMS setup consists of a laser of short wavelength in the UV range (typically 193 nm), an ablation cell and an ICPMS instrument. The sample is placed into the ablation cell along with several standards. During ablation, repeated laser pulses are focused on the surface of the dated mineral. The resulting ablated aerosol is subsequently transported by a carrier gas (usually He ± Ar ± N_2) toward the Ar-sourced plasma torch at the entry of the mass spectrometer where it is ionized and transferred into the ion optics of the mass spectrometer. LA-ICPMS U–

Pb dating is mostly carried out on single-collector sector-field ICP-MS instruments that offer sequential measurement of individual Pb and U isotopes in a mixed ion-counting – Faraday cup mode.

The spot size used for LA-ICPMS geochronology mainly depends on target size and the U concentration of the dated mineral. As a reference, 25-35 μm spots are commonly used for zircon and can be as low as 5 μm for monazite (Paquette and Tiepolo 2007). Crater depth for a 30-60 s analysis is on the order of 15-40 μm depending on the fluence of the laser and on the ablated material. However, laser-induced U–Pb fractionation increases with crater depth during ablation, which negatively impacts on the analytical uncertainty of the measured Pb/U ratio. Ultimately, this is an important limiting factor for precision and accuracy in LA-ICPMS geochronology (Košler et al. 2005; Allen and Campbell 2012). The technique requires a laser setup that yields reproducible ablation with small particles (subsequently more efficiently ionized in the plasma torch) and that limits crater depth to no more than the spot diameter by minimizing the laser fluence (e.g., Günther et al. 1997; Horn et al. 2000; Guillong et al. 2003).

Another important limitation of LA-ICPMS U–Pb dating is the imprecise common Pb correction due to the difficulty of precisely measuring common ^{204}Pb due to an isobaric interference with ^{204}Hg (traces of Hg are contained in the Ar gas). Common Pb correction protocols using ^{208}Pb may be employed and are preferred over simple rejection of discordant analyses. It results that, age interpretation of minerals with elevated common Pb contents (e.g., titanite, rutile) may be hampered by large age uncertainties due, in part, to the large uncertainties associated with the common Pb-correction.

LA-ICPMS and SIMS (see below) U–Pb dating are comparative techniques that require analysis of a reference material, which is as close as possible to the chemical composition and the structural state of the unknown (sample). It is analyzed under identical ablation conditions to the sample to determine the machine fractionation factor of any measured element concentration; this fractionation factor is then applied to the element ratios and concentrations of the unknowns. A series of analyses unknown (~10) is typically bracketed by analyses of a reference material (~2-4) to correct for elemental fractionation and monitor for machine drift. In addition, at least one secondary standard should be repeatedly analyzed during the same session in order to demonstrate the accuracy of the fractionation correction. This enables an estimate of the long-term excess variance of the laboratory that is required in the uncertainty propagation protocol (see below). A list of commonly used reference materials and their reference values is provided in Horstwood et al. (2016). Standards for LA-ICPMS and SIMS U–Pb dating should be homogenous in age, trace element composition, and have comparable trace element concentration and structural state (matrix match) as the unknowns (Košler et al. 2005). Failure to match the matrix of the unknown results in different ablation behavior (rate, stability, fractionation) and ultimately compromises the accuracy of the date (Klötzli et al. 2009). Therefore, a mineral of unknown age should be standardized using a reference material from the same mineral. Furthermore, different degrees of metamictization also impact on the matrix match between standards and unknowns and can be an important source of inaccuracy for zircon dates (as much as 5 % inaccurate; Allen and Campbell 2012; Marillo-Sialer et al. 2014) and possibly for other minerals as well (e.g., titanite, allanite, columbo-tantalite).

Interlaboratory comparisons for LA-ICPMS and SIMS U–Pb dating have highlighted discrepancies of U–Pb ages for a series of standards measurements which is sometimes outside of the reported 2σ uncertainties (Košler et al. 2013). This is thought to reflect different data reduction strategies in different laboratories (e.g., Fisher et al. 2010) and uncertainty propagation protocols, that are not always thoroughly documented. This has triggered a community driven effort to establish standard data reduction workflow, uncertainty propagation protocols, and data reporting templates (Horstwood et al. 2016) that should be embraced by the LA-ICPMS community. New community-derived standards for LA-ICPMS dating suggest the use of the *x/y/z/w* notation for uncertainty reporting where: *x* refers to the analytical (or random) uncertainty, *y* includes the variability of standards measured in the same lab, *z* includes the systematic uncertainty of the primary standard isotopic composition (and of the common Pb correction if appropriate), and *w* includes the decay constant uncertainty (Horstwood et al. 2016; McLean et al. 2016). Comparing LA-ICPMS U–Pb data with data from other LA-ICPMS, SIMS or ID-TIMS laboratories should be done at the *z* uncertainty level, while comparison with geochronological data from other isotopic systems have to include decay constant uncertainties (Chiaradia et al. 2013). Raw data processing, visualization and uncertainty propagation protocols for LA-ICPMS U–Pb dating have been implemented in the freely available *ET_Redux* software (McLean et al. 2016) and allow more robust interlaboratory data comparison and collaborative science.

4.2. Secondary ion mass spectrometry (SIMS)

Compared to LA-ICPMS, SIMS U–Pb analysis has greater spatial resolution and sensitivity, allowing for the analysis of microscopic rims or domains in zircon, monazite, xenotime or other minerals. SIMS analysis involves the ablation of sample with a high-energy O^- or O_2^- ion beam within a high vacuum chamber. A small fraction of the ablated material forms atomic ions or molecular ionic compounds that are subsequently accelerated into a mass spectrometer.

Typical SIMS craters are 10-15 μm in diameter and 1–2 μm deep, therefore this technique has higher spatial resolution and is by far less destructive than LA-ICPMS and permit subsequent isotopic analysis (e.g., O, Hf–Lu) to be done on the same spot (slight repolishing would be required before SIMS analysis). Analysis is done directly from a thin section, polished grains mounted in epoxy resin, or from entire grains pressed into indium when analyzing U and Pb isotopes along a profile from the surface to the interior of a grain (depth profiling). The accuracy of the obtained result depends on extrinsic factors such as the position of standard and unknowns in the mount and the quality of the polishing. SIMS analysis of zircon typically yields U–Pb dates of 0.1–1% precision and accuracy (Fig. 5); it is the preferred method when analyzing complex minerals (e.g., thin metamorphic rims), very small grains (e.g., xenotime outgrowths on zircon; McNaughton et al., 1999) or valuable material.

Pb isotopic fractionation in SIMS is subordinate when compared to LA-ICPMS techniques. Therefore, ^{207}Pb/^{206}Pb dates can be calculated directly from counting statistics. In contrast, there is a significant difference in the relative sensitivity factors for Pb^{+} and U^{+} ions during SIMS analysis. The fractionation of the ^{206}Pb^{+}/^{238}U^{+} ratios is highly correlated with simultaneous changes in the ^{254}UO^{+}/^{238}U^{+} ratios which forms the basis of a functional relationship that enables the calibration of the ^{206}Pb/^{238}U dates. Although the ^{206}Pb^{+}/^{238}U^{+} versus ^{254}UO^{+}/^{238}U^{+} calibration is the most widely used, other combinations of ^{238}U^{+}, ^{254}UO^{+} and ^{270}UO$_2$ have proved successful. As in the case of LA-ICPMS, the SIMS ^{206}Pb/^{238}U calibration is carried out with reference to a matrix matched reference material (e.g., Black et al. 2004). This is quite straightforward for zircon and baddeleyite (ZrO_2), but more difficult for chemically and structurally more complex minerals (e.g., phosphates, complex silicates, oxides). In the latter cases, matrix correction procedures using a suite of reference materials accounting for the effect of highly variable amount of trace elements have been developed (e.g., Fletcher et al. 2004; Fletcher et al. 2010). Calibration biases are also introduced through different degrees of structural damage from radioactive decay (White and Ireland 2012). It is highly recommended to analyze a reference zircon as unknown again to control the accuracy of the technique (validation or secondary standard; Schaltegger et al. 2015).

The common Pb correction is carried out via measurement of ^{204}Pb, ^{207}Pb or ^{208}Pb masses. The main challenge of SIMS analysis is the resolution of molecular interferences on the masses of interest (Ireland and Williams 2003), which requires careful consideration when analyzing phosphates or oxides.

No standard data treatment protocol exists for SIMS dates. In fact, the two types of equipment (SHRIMP from Australian Scientific Instruments and IMS 1280/90 from

CAMECA) provide very differently structured data that require different data treatment software.

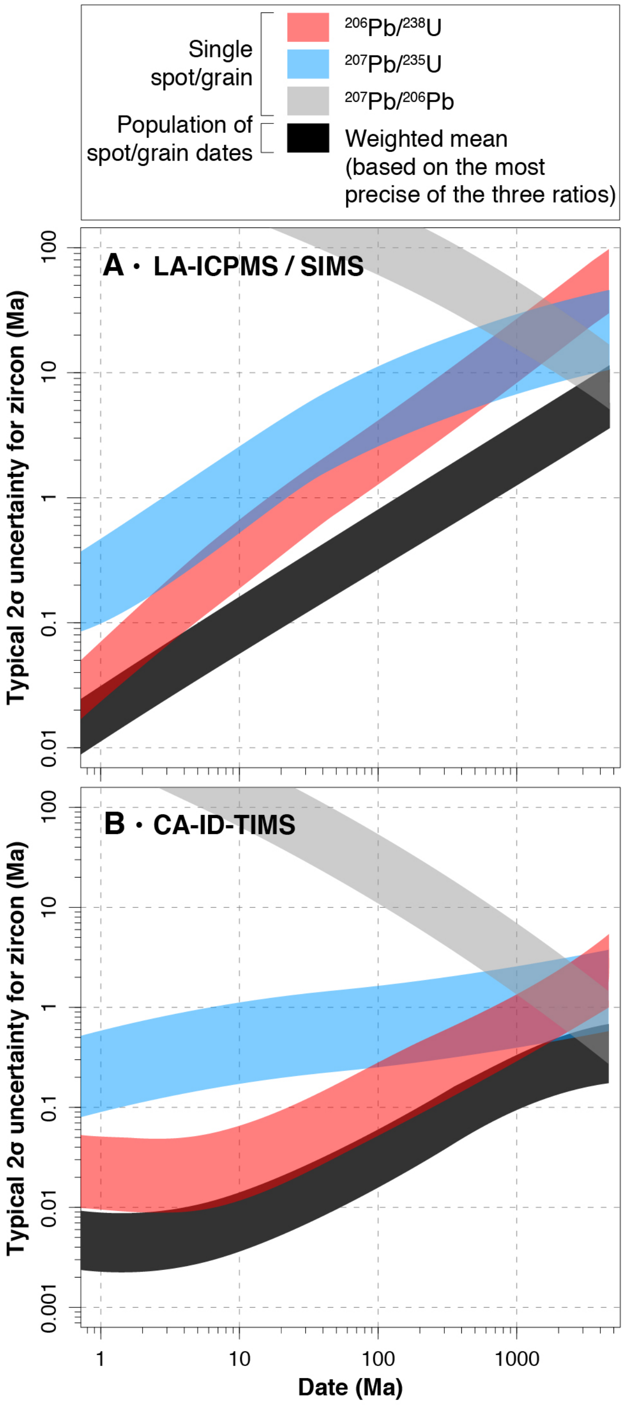

Figure 5. Typical analytical uncertainties for zircon $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$, $^{207}Pb/^{206}Pb$ single spot/grain dates for modern **(A)** LA-ICPMS, SIMS and, **(B)** CA-ID-TIMS dating techniques. Weighted mean dates refers to the weighted mean of a set of statistically equivalent single spot/grain dates based the most precise isotopic ratio (typically $^{206}Pb/^{238}U$ for dates younger than ca. 1 Ga and $^{207}Pb/^{206}Pb$ for dates older than 1 Ga)

4.3. Isotope dilution-thermal ionization mass spectrometry (ID-TIMS)

The U–Pb method that offers the highest precision and accuracy is Chemical Abrasion, Isotope Dilution, Thermal Ionization Mass Spectrometry (CA-ID-TIMS; Table 1, Fig. 5). This method involves the dissolution and analysis of entire zircon grains and other accessory minerals, and, hence, disregards any protracted growth history recorded in this grain. Zircon imaging prior to dating can be taken to increase the chances of analyzing a single-aged grain or grain population. The ID-TIMS community is organized as a part of the EARTHTIME consortium (Bowring et al. 2005), which is working together to improve precision and accuracy of U–Pb dating.

It is now standard to pre-treat zircons with the "chemical abrasion" procedure of Mattinson (2005). This process involves heating the zircon at 900°C for 48 hours, followed by partial dissolution in $HF + HNO_3$ at 180-210°C for 12 to 18 hours. The heating re-establishes the zircon crystalline structure by annealing any radiation-related structural damage in slightly affected domains. The partial dissolution procedure then only removes domains with more severe structural damage and leaves a proportion of the original grain behind. The surviving zircon fragment is then considered to be perfectly crystalline and is used for isotope ratio analysis. Chemically abraded zircon grains are recognized to be more concordant and provide more reproducible U–Pb results. This treatment is not currently applied for SIMS or LA-ICPMS analysis techniques, but initial experiments have yielded positive results (Kryza et al. 2012; Crowley et al. 2014; von Quadt et al. 2014). The procedure has been tested on other accessory phases including baddeleyite (Rioux et al. 2010), but without clear evidence of improving concordance.

The dissolved grains are mixed with a (^{202}Pb–)^{205}Pb–^{233}U–^{235}U tracer solution (e.g., as provided by EARTHTIME; ET535 and ET2535; Condon et al. 2015; McLean et al. 2015), and the Pb and U isotopes isolated from other trace elements through chromatography. Isotopic compositions are most commonly measured as Pb^+ and UO_2^+ on a thermal ionization mass spectrometer from the same filament either by ion counting methods (using a secondary electron multiplier or a Daly-based photomultiplier device), or by a combination of ion counters and high-sensitivity, high-resistance Faraday collectors. Uranium may also be measured separately as U^+ by solution MC-ICP-MS utilizing a mixed ion counting – Faraday measurement setup, or as U^+ on a double or triple filament assembly in a TIMS.

An important part of high-precision, high-accuracy U–Pb geochronology is the correct treatment of all sources of uncertainty and their correct propagation into the final age. The ID-

TIMS community has been adopting the *x/y/z* notation for uncertainty reporting (e.g., 35.639 ± 0.011/0.014/0.041 Ma) where: *x* is the random uncertainty (or analytical; including counting statistics, common Pb and Th-disequilibrium corrections), *y* includes the systematic uncertainty from tracer calibration and, *z* includes the decay constant uncertainty (Schoene et al. 2006; Schoene and Bowring 2006; McLean et al. 2011). Comparison of ID-TIMS U–Pb data with U–Pb data from SIMS or LA-ICPMS techniques should consider the *y* uncertainty level, while comparison with data from other isotopic systems (e.g., Re-Os, ^{40}Ar/^{39}Ar) should include both decay constant and systematic uncertainties (*z* level). Final age precision is mainly defined by the ratio of radiogenic to common Pb (Pb*/Pb$_c$), which is, in the case of zircon, a function mainly of procedural Pb blank. Total blank levels of <0.5 pg of Pb are currently state-of-the-art.

The EARTHTIME community has generally accepted and adopted a software package consisting of *Tripoli* raw data statistics and *U-Pb_Redux* data treatment and visualization (Bowring et al. 2011; McLean et al. 2011).

5. Guidelines for interpreting U–Pb dates

5.1. Date and age

Isotopic dating makes a distinction between a *date* and an *age*. The term ‘date’ refers to a number in time unit (usually Ga, Ma or ka) calculated from an age equation (eqs. 1–5). The term ‘apparent age’ is sometimes used as a synonym for ‘date’. A ‘date’ becomes an ‘age’ as soon as in can be interpreted in terms of a geological process (Schoene 2014). Both terms may be appropriate for single grain/spot or weighted mean data and may be accurate or inaccurate. This semantic distinction reflects the clear distinction that should be made between data and their interpretation, which is at the core of scientific rigor and integrity.

As discussed in the preceding sections, the interpretation of U–Pb dates is not straightforward, even for concordant data. It requires a close and quantitative control of the way how an analytical result has been produced, including the knowledge of sources of error and their correct propagation into the final result (metrology), a good characterization of the sample material, and finally a good knowledge of the geological context. The lack of considering these aspects may very well lead to over-interpretations and erroneous conclusions.

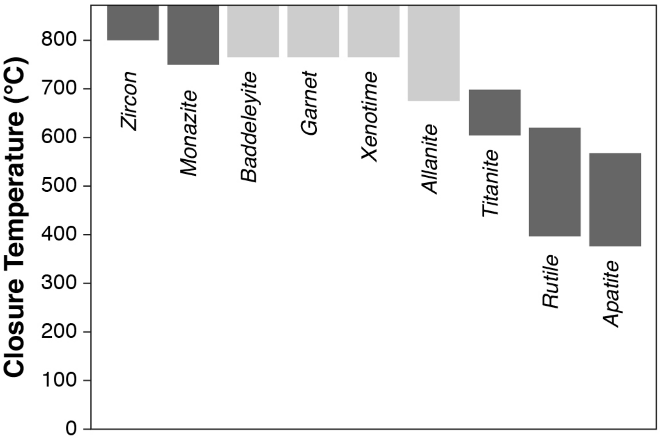

Figure 6. Typical range of closure temperature for minerals used for U–Pb dating. Dark grey bars indicate robust closure estimates while light grey bars indicate approximate estimates. Modified from Chiaradia et al. (2014), with additional data for apatite (Cochrane et al. 2014), rutile (Vry and Baker 2006), baddeleyite (Heaman and LeCheminant 2001), garnet (Mezger et al. 1989), xenotime and allanite (Dahl 1997).

5.2. Geochronology vs thermochronology

All minerals used for U–Pb dating can be theoretically subjected to some degree of thermally activated volume diffusion of U and Pb. The measured date reflects the time elapsed since closure of the isotopic system. While geochronology corresponds to dating of a mineral that has crystallized, rapidly cooled or remained below it closure temperature, thermochronology deals with minerals that have crystallized and/or spent some time above their respective closure temperatures, or in the partial retention temperature window of their daughter nuclide. As discussed above (causes of discordance) partial resetting of the U–Pb system by diffusion is a possible source of discordance. While the effect of post crystallization diffusion can usually be neglected for zircon, monazite and most other minerals due to their high closure temperature for Pb (>700 °C, Cherniak and Watson 2001; Cherniak and Watson 2003; Cherniak et al. 2004); Fig. 6), Pb diffusion in minerals such as titanite, rutile and apatite is more likely to occur and should carefully be evaluated before interpreting U–Pb dates as they might record the age of closure rather the age of crystallization. Ultimately, thermochronological U–Pb data on these minerals may be used to constrain the high-temperature (>350 °C) thermal history of the studied geological object (Schoene and Bowring 2007; Kooijman et al. 2010; Blackburn et al. 2011; Cochrane et al. 2014). Nevertheless, it appears that most minerals used for U–Pb dating can be used as geochronometers, of which partial resetting of the U–Pb system is often controlled by the stability of the mineral phase itself or Pb-loss along fast diffusion pathways (cracks, metamict domains), rather by volume diffusion (Fig. 6).

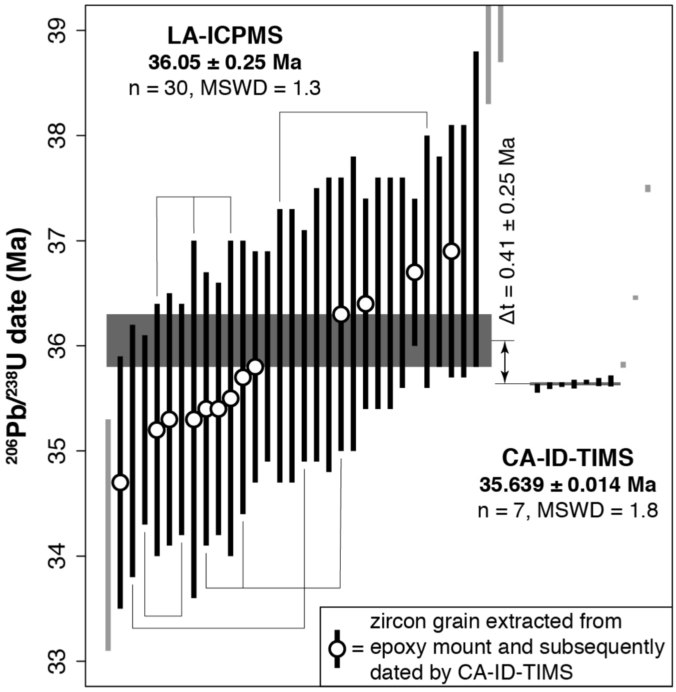

Figure 7. Ranked LA-ICPMS and CA-ID-TIMS ^{206}Pb/^{238}U zircon dates and weighted means for the hornblende-biotite porphyry (sample 10CC51) from the Eocene Coroccohuayco porphyry-skarn deposit, Peru. Data from Chelle-Michou et al. (2014). Single spot/grain analyses are plotted at the level of their analytical uncertainties (2σ) and weighted mean dates include the analytical uncertainties and: (i) an additional excess variance obtained from repeated measurement of the secondary standard (91500) and the systematic uncertainty in the standard mineral isotopic composition, for LA-ICPMS data; (ii) the systematic uncertainty related to the composition of the isotopic tracer, for CA-ID-TIMS data. Data bars in black are included in the calculation of the weighed mean date. Multiple LA-ICPMS dates from the same zircon grain are connected with thin lines.

5.3. Precision and weighted mean

The weighted mean age is the most common representation of the age of a relatively short-lived geological event recorded at the scale of the sample (e.g., magma emplacement, hydrothermal fluid circulation) and is usually interpreted as the best age estimate. Weighted mean calculations are applied to a set of individual analyses in order to reduce the uncertainty of the population. It implicitly assumes that the data correspond to repeated analyses (samples) of the exact same value and that the uncertainties are only due to analytical scatter. In this case, the mean square of the weighted deviates (MSWD or reduced chi-squared) of a data population to the weighted mean should be around to 1. In turn, MSWD >> 1 would suggest excess scatter of the data given their respective uncertainties (i.e., they are unlikely to represent a single population), and values <<1 suggest that the reported uncertainties are larger than what would be expected from a single population. In detail, acceptable MSWD values actually depend on the number of points pooled together (Wendt and Carl 1991; Spencer et al. 2016). For example, values between 0.5 and 1.5 are acceptable for a population of 30 points (at 2σ).

However, the accuracy of weighted mean ages has been repeatedly questioned (Chiaradia et al. 2013; Chiaradia et al. 2014; Schoene 2014). Indeed, the advent of high precision dating techniques (CA-ID-TIMS) has highlighted that data that might look statistically equivalent at the level of their uncertainties, can actually hide a spread of data that can only become apparent with more precise dating methods. An illustration of this is provided in Figure 7 which shows LA-ICPMS and CA-ID-TIMS ^{206}Pb/^{238}U zircon dates from a porphyry intrusion from the Coroccohuayco porphyry-skarn deposit, Peru (Chelle-Michou et al. 2014). It is noteworthy that those grains analyzed by CA-ID-TIMS have previously been analyzed with LA-ICPMS (with 1 to 3 spots each) before being removed from the epoxy mount for further processing. Data points are plotted at the level of their analytical uncertainties and weighted mean dates include additional dispersion and standard/tracer calibration uncertainties (see caption of Fig. 7 for more details) so that they can be compared at their right level of uncertainties (i.e., neglecting only decay constant uncertainties). Both the LA-ICPMS (36.05 ± 0.25 Ma, n = 30, MSWD = 1.3) and CA-ID-TIMS (35.639 ± 0.014 Ma, n = 7, MSWD = 1.8) weighted means yield acceptable MSWDs (in agreement with their respective number of data points), thus suggesting they could correspond to statistically equivalent data populations, respectively. Independently from each other, these weighted dates would be interpreted as the age of the porphyry intrusion at the Coroccohuayco deposit. However, Figure 7 highlights that these ages do not overlap within uncertainties (Δt = 0.41 ± 0.25 Ma), therefore indicating that at least one of them is inaccurate. In this case, the more precise single grain CA-ID-TIMS ages highlight more than 1 Ma of zircon crystallization in deep-seated crystal mushed (or proto-plutons) before their incorporation into felsic melts, ascent and emplacement of the porphyry intrusion at an upper crustal level (Chelle-Michou et al. 2014). These older zircon crystallization events cannot be resolved at the uncertainty level of LA-ICPMS dating for which data points pool together that are actually not part of the same population and therefore include data older than the emplacement age, resulting in a weighted mean age that is too old. While it is common practice in zircon CA-ID-TIMS dating to take the youngest point as best representative of the age of magma emplacement or eruption, this practice is not appropriate for in-situ or CA-free ID-TIMS dating techniques where the weighted mean date of the youngest cluster having an acceptable MSWD remains the best option, although it might sometimes be slightly inaccurate.

This example highlights the limitations of the weighted mean approach to complex and protracted natural processes. The statistical improvement in precision may be done at the cost the accuracy of the dated process. The calculated weighted mean date can be either too old (e.g., if grains crystallized from an earlier pulse of magma are included), too young (e.g., if several grains have suffered similar amounts of unrecognized Pb-loss) or just right by coincidence. In fact, the time resolution of geochronology is ultimately limited by the precision of single data points, rather than by the number of data that are pooled together to statistically reduce the age uncertainty.

5.4. Accuracy of legacy U–Pb data and misinterpretation

Cases where the same rock has been dated several times using the same isotopic system and the same mineral are rare but necessary examples to put some perspective of the accuracy of legacy U–Pb data. Ore-related porphyry intrusions at the Miocene Bajo de la Alumbrera porphyry copper deposit have received much attention over the past decade. These rocks have been repeatedly dated by U–Pb zircon geochronology using different analytical methods (LA-ICPMS and CA-ID-TIMS) at different times (Harris et al. 2004; Harris et al. 2008; von Quadt et al. 2011; Buret et al. 2016). The early LA-ICPMS zircon dating survey of Harris et al. (2004, 2008) concluded that the deposit formed on a million-year time scale. However, subsequent high precision CA-ID-TIMS studies have decreased this duration by almost two orders of magnitude, to a maximum duration of 29 ka (Buret et al. 2016).

Available data for three porphyries are compiled Figure 8 with their respective weighted means. Single LA-ICPMS date broadly range from 8.5 Ma to 6.5 Ma while those obtained by CA-ID-TIMS are significantly less scattered between 8.2 and 7.1 Ma. Weighted mean dates can show as much as ~1 Ma of age difference for the same porphyry between LA-IPCMS and CA-ID-TIMS which is far outside the reported analytical uncertainties (see P2 porphyry on Fig. 8). The same is true for high-precision CA-ID-TIMS data, which show differences up to ~0.1 Ma in excess of the analytical uncertainty. Furthermore, these discrepancies persist even when systematic uncertainties are taken into account (i.e., 3% reproducibility for LA-ICPMS, calibration of the primary standard or of the tracer solution). Similar age discrepancies up to ~0.8 Ma between LA-ICPMS and SIMS U–Pb zircon weighed mean ages have been noted by Ballard et al. (2001) on porphyries from the Eocene Chuquicamata Cu deposit, Chile.

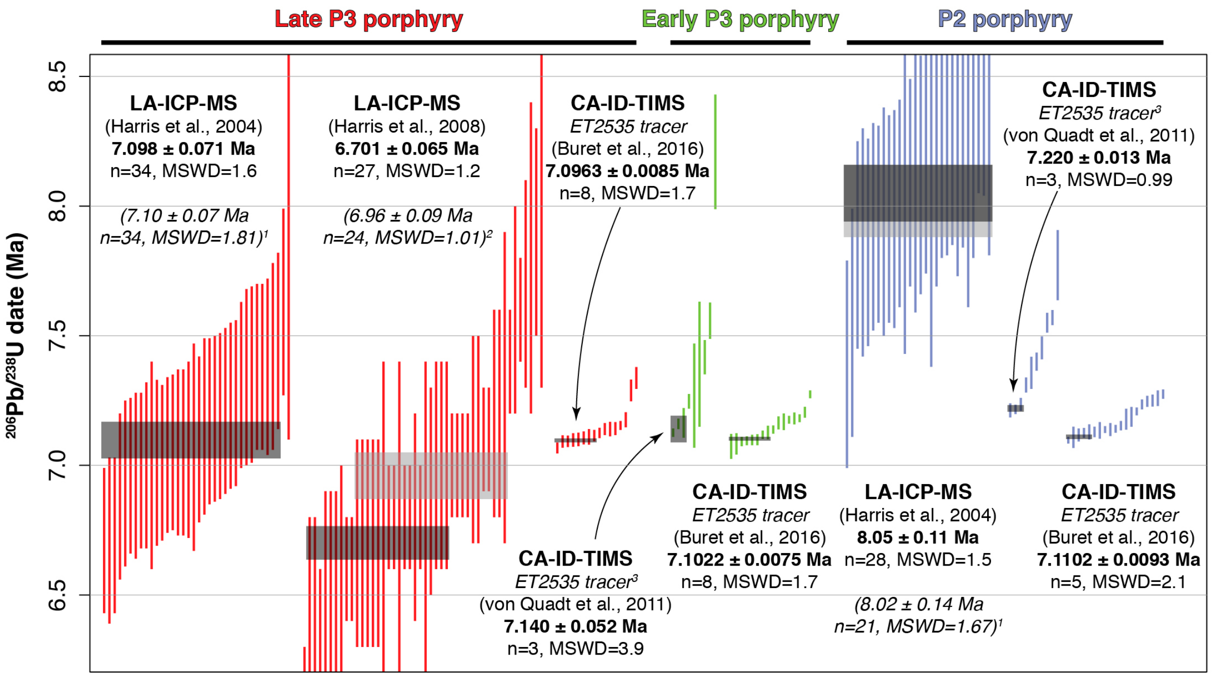

Figure 8. Compilation of ^{206}Pb/^{238}U Th-corrected dates acquired with different methods for three porphyry intrusions at the Bajo de la Alumbrera porphyry copper deposit, Argentina. Data are from Harris et al. (2004), Harris et al. (2008), von Quadt et al. (2011), and Buret et al. (2016). The horizontal grey bands represent the weighted mean dates recalculated by us and include analytical uncertainties based on U–Pb dates from tables provided in the aforementioned publications. ^{1} weighted mean date reported in Harris et al. (2004). ^{2} weighted mean date reported in Harris et al. (Harris et al. 2008). ^{3} tracer used in von Quadt et al. (2011) (written communication to the authors). All uncertainties are given at 2σ (95% confidence).

It would be presumptuous to name the causes of these discrepancies without having the entire set of original technical and analytical data at our disposal. Nevertheless, we can make some conjectures. Potential causes may be: (1) that different populations of zircons grains or domains (within a single grain) where hand-picked and dated; (2) the use of inappropriate data reduction, common Pb correction, initial Th-correction and error propagation protocols; (3) a distinct difference in ablation rate between sample and standard zircon resulted in inaccurate correction for fractionation (for LA-ICPMS data); (4) inaccurate isotopic tracer calibration (for ID-TIMS data); and/or (5) unidentified concordia parallel Pb-loss (for the LA-ICPMS data).

In the case of Bajo de la Alumbrera, the most recent data by Buret et al. (2016) are deemed to be the most accurate (in addition of being the most precise) and tightly constrain the age of porphyry emplacement and zircon crystallization. This example illustrates the difficulty of dealing with legacy U–Pb data which might or might not be accurate. Obviously, there are published ages that are inaccurate, but they would remain unnoticed until new dating is done with state-of-the-art techniques. In particular, reporting of *x/y/z* (for ID-TIMS) and *x/y/z/w* (for LA-ICPMS) uncertainties and comparison of disparate U–Pb dates at the level of their *y* uncertainty should be systematic. Again, these potential biases should be carefully accounted for when interpreting short time differences on the order of the analytical uncertainty of single dates. This also highlight the need for thorough reporting of analytical and data handling procedures, or even, using common analytical procedures and data reduction platforms (Košler et al. 2013).

6. What mineral can we date with the U–Pb system and what does it date?

As of today, a great number of minerals have been used for U–Pb dating, many of which in the context of mineral deposits. A non-exhaustive list of these minerals is provided in Table 2 which presents their main characteristics and usefulness for dating ore deposits. It is noteworthy that this table only presents a selection of some useful minerals, but others might also be amenable to U–Pb dating. Furthermore, ongoing and future developments will likely improve our understanding of the U–Pb system in these and new mineral species while allowing better precision, accuracy and interpretation of the dates.

Ideal minerals for U–Pb dating should necessarily contain traces of U, and as little common (initial) Pb as possible. They should also have a low diffusivity for Pb so as to accurately record the radiogenic Pb ingrowth. Many minerals used for U–Pb dating are accessory minerals (zircon, baddeleyite, titanite, monazite, xenotime) but a handful of them are major rock forming minerals (calcite, garnet) or even ore minerals (cassiterite, columbo-tantalite, uraninite, wolframite) (see Table 2). This exceptional mineralogical diversity allows most types of ore deposit and ore forming processes to be dated directly or indirectly with the U–Pb method. However, in detail, all minerals do not provide equally precise, accurate and/or meaningful dates. In Table 2, we have classified the minerals in three categories depending on the average quality of the date that they can provide. Nevertheless, we stress that this classification should only be taken as a 'rule of thumb' and that each case would be different. For example, zircon might give very imprecise and discordant dates while xenotime from the same sample would return more precise and concordant dates (e.g., Cabral and Zeh 2015).

Table 2. Minerals suitable for U–Pb dating in the context of mineral deposits.

Mineral	**Formula**	**Main types of mineral deposit where U-Pb dating can be done (non-exhaustive list)**	**Event dated**	**Principal limitations**	**Additional comments**	**Average quality of U–Pb dating**[†]	**Some references with application to mineral deposits**
Allanite	$(Ca,Ce,La,Y)_2(Fe^{2+},Fe^{3+},Al)_3O(SiO_7)(SiO_4)(OH)$	Skarn; IOCG: Fault-related U(±REE)	Hydrothermal activity, metasomatism; magmatism	Low to moderate amount of common Pb; No matrix-matched standard available; High amount of excess ^{206}Pb (initial ^{230}Th excess)[§];	Possibility of Th–Pb dating	XX	Pal et al. (2011); Chen and Zhou (2014); Deng et al. (2014)
Apatite	$Ca_5(PO_4)_3(F,OH,Cl)$	IOCG; REE(±U,P) vein; Magmatic Ni-Cu-PGE(±Co) sulphide;	Cooling; hydrothermal activity	Low to high amount of common Pb; low U concentration; No matrix-matched international standard available (zircon or in-house standard; see Chew et al., 2011); Can be sensitive to initial ^{230}Th excess[§].	No metamictization; Possibility of Th–Pb dating	X	Romer (1996); Amelin et al. (1999); Gelcich et al. (2005); Stosch et al. (2010); Seo et al. (2015); Huston et al. (2016)
Baddeleyite	ZrO_2	Magmatic Ni-Cu-PGE(±Co) sulphide; Banded iron formation; Orogenic Au; Diamond-bearing kimberlite; Rare-metal carbonatite	Alkaline and mafic to ultramafic magmatism, hydrothermal activity	Crystal orientation affects ^{206}Pb/^{238}U ratios and dates measured with SIMS (Wingate and Compston, 2000);	Limited common Pb, no metamictization	XXX	Corfu and Lightfoot (1996); Schärer et al. (1997); Amelin et al. (1999); Wingate and Compston (2000); Müller et al. (2005); Li et al. (2005); Wu et al. (2011); Zhang et al. (2013); Bjärnborg et al. (2015); Wall and Scoates (2016)
Brannerite	$(U,Ca,Ce)(Ti,Fe)_2O_6$	Fault-related U(±REE-F-Ba-Th); Magmatic-hydrothermal/epithermal U(± Ni-Co-As-Mo-Pb-PGE-Au); Archean Au paleoplacer	Hydrothermal activity	Moderate to high amount of common Pb; easy resetting of the U–Pb system (Pb loss) with hydrothermal fluids; no matrix-matched standard available		X	Frei (1996); Zartman and Smith (2009); Oberthür et al. (2009); Bergen and Fayek (2012)
Calcite	$CaCO_3$	MVT Pb-Zn±F	Hydrothermal activity, diagenesis	Moderate to high amount of common Pb; easy resetting of the U–Pb system (Pb and U mobility) with hydrothermal fluids; difficulty to interpret the event being dated; No international matrix-matched standard available (in-house standard)	Date sometimes determined with the isochron method; Inverse discordance is not uncommon (U loss). Mostly Pb_c uncorrected ^{238}U/^{206}Pb dates	X	DeWolf and Halliday (1991); Brannon et al. (1996); Coveney et al. (2000); Grandia et al. (2000); Rasbury and Cole (2009); Burisch et al. (2017)
Cassiterite	SnO_2	Granite-related Sn(±Mo-W-Cu-Pb-Zn-Sb-Ag) greisen, skarn and lode; Supergene Sn	Hydrothermal activity, supergene alteration (?)	High amount of common Pb; No international matrix-matched standard available (in-house standard)	Date often determined with the isochron method	X	Gulson and Jones (1992); Yuan et al. (2011); Chen et al. (2014); Zhang et al. (2014); Li et al. (2016)
Colombo-tantalite	$(Mn,Fe^{2+})(Nb,Ta)_2O_6$	Rare-metal (±Sn-W) pegmatite, greisen and granite	Late magmatic stage, hydrothermal resetting	Low to moderate amount of common Pb; in-situ dating often standardized to zircon mineral, the use of Coltan-139 standard is suggested by Che et al. (2015); can be highly metamict	Inverse discordance is not uncommon (maybe related to inclusions); possible inclusions of uraninite; chemical abrasion is possible	XXX	Romer and Wright (1992); Romer and Smeds (1994); Romer and Smeds (1996); Romer et al. (1996); Romer and Smeds (1997); Glodny et al. (1998); Smith et al. (2004); Baumgartner et al. (2006); Dewaele et al. (2011); Melleton et al. (2012); Melcher et al. (2015); Che et al. (2015); Van Lichtervelde et al. (2016)
Garnet	$(Ca,Ce,La,Y)_2(Fe^{2+},Fe^{3+},Al)_3O(SiO_7)(SiO_4)(OH)$	Skarn; Metamorphosed deposit	Metasomatim, metamorphism	Moderate to high amount of common Pb; low U content; no matrix-matched standard available	Andradite garnet tend to have higher U content. Date sometimes determined with the isochron method	X	Mezger et al. (1989); Mueller et al. (1996); Glodny et al. (1998); Jung and Mezger (2003); Seman et al. (2017)
Perovskite	$CaTiO_3$	Diamond-bearing kimberlite; Rare-metal carbonatite	Alkaline and ultramafic magmatism	Moderate to high amount of common Pb; prone to Pb loss; in-situ dating often standardized to zircon mineral, perovskite standard described in Heaman (2009)	Possibility of Th–Pb dating	X	Smith et al. (1989); Heaman (2003); Lehmann et al. (2010); Donnelly et al. (2012); Zhang et al. (2013); Rao et al. (2013); Wu et al. (2013a); Wu et al. (2013b); Griffin et al. (2014); Heaman et al. (2015); Castillo-Oliver et al. (2016)
REE-Phosphate (Monazite and Xenotime)	$(Ce,La,Th)PO_4$	Rare-metal (±Sn-W) pegmatite, greisen and granite; Orogenic Au; Banded iron formation; Archean Au paleoplacer; Stratabound polymetallic (Co,Cu,Pb,Zn,Fe,Au,Ag,Bi,W,REE); Unconformity-related U; MVT Pb-Zn; IOCG; granite-related U-Mo; Cordilleran polymetallic	Hydrothermal activity, metamorphim, magmatism	High amount of excess ^{206}Pb (initial ^{230}Th excess)[§]; strong matrix effect due to trace elements needs to be taken in consideration for SIMS dating (e.g., Fletcher et al. 2010)	Limited common Pb. No metamictization. Possibility of Th–Pb dating	XXX	Glodny et al. (1998); Torrealday et al. (2000); Petersson et al. (2001); Pigois et al. (2003); Tallarico et al. (2004); Salier et al. (2004); Fletcher et al. (2004); Schaltegger et al. (2005); Salier et al. (2005); Vallini et al. (2006); Michael Meyer et al. (2006); Rasmussen et al. (2007b); Rasmussen et al. (2007a); Lobato et al. (2007); Mueller et al. (2007); Kempe et al. (2008); Rasmussen et al. (2008); Vielreicher et al. (2010); Fletcher et al. (2010); Sarma et al. (2011); Muhling et al. (2012); Aleinikoff et al. (2012a); Aleinikoff et al. (2012b); Mosoh Bambi et al. (2013); Moreto et al. (2014); Cabral and Zeh (2015); Zi et al. (2015); Vielreicher et al. (2015); McKinney et al. (2015); Taylor et al. (2015); Catchpole et al. (2015); Huston et al. (2016); Van Lichtervelde et al. (2016)
	YPO_4			Moderate excess ^{206}Pb (intial ^{230}Th excess)[§]; strong matrix effect due to trace elements needs to be taken in consideration for SIMS dating (e.g., Fletcher et al. 2010)			
Rutile	TiO_2	Metamorphic and magmatic Ti; Porphyry Cu-Au; Orogenic Au	Cooling; hydrothermal activity	Low U concentration in most cases, but rutiles from high-grade metamorphic rocks tend to have higher U contents (Meinhold 2010); moderate amount of common Pb		XX	de Ronde et al. (1992); Norcross et al. (2000); von Quadt et al. (2005); Kouzmanov et al. (2009); Morisset et al. (2009); Shi et al. (2012)
Titanite (Sphene)	$CaTiOSiO_4$	Skarn; IOCG; Orogenic Au; VMS	Late magmatic stage, hydrothermal activity; metasomatism; metamorphism; (cooling)	Low to moderate amount of common Pb; Titanites BLR-1 and MKED-1 proposed as matrix-matched standards (Aleinikoff et al., 2007; Spandler et al., 2016), common use of zircon or in-house standards.	Possibility of Th–Pb dating	XX	Corfu and Muir (1989); Romer and Öhlander (1994); Romer et al. (1994); Eichhorn et al. (1995); Mueller et al. (1996); Norcross et al. (2000); Salier et al. (2004); Bucci et al. (2004); Wanhainen et al. (2005); De Haller et al. (2006); Skirrow et al. (2007); Mueller et al. (2007); Chiaradia et al. (2008); Smith et al. (2009); Li et al. (2010); Dziggel et al. (2010); Chelle-Michou et al. (2015); Deng et al. (2015b); Deng et al. (2015a); Seo et al. (2015); Fu et al. (2016); Poletti et al. (2016)
Uraninite	UO_2	U(±Au,REE,…) deposits; Stratiform polymetallic (Co,As,Pb,Zn,Cu,Mo,…) epithermal	Hydrothermal activity; Metamorphism	Prone to U and Pb mobility (loss and gain) and recrystallization; low to high amount of common Pb; no international matrix-matched standard available (in-house standard)	Chemical dating (EMP) is common	X	Hofmann and Eikenberg (1991); Hofmann and Knill (1996); Fayek et al. (2000); Polito et al. (2005); Alexandre et al. (2007); Ono and Fayek (2011); Carl et al. (2011); Philippe et al. (2011); Dieng et al. (2013); Decree et al. (2014); Luo et al. (2015); Skirrow et al. (2016)
Zircon	$ZrSiO_4$	All type of intermediate to acidic magmatism, differentiate products of mafic to ultramafic magmatism, Porphyry-systems (incl. Epithermal, Skarn), VMS, …	Magmatic, hydrothermal, detrital provenance and deposition, metamorphic	Can present very complex zoning patterns with several age domains	Limited common Pb. Chemical abrasion is possible	XXX	Most of the references provided for the other minerals also present zircon U-Pb dating.
Wolframite	$(Fe^{2+},Mn)WO_4$	Granite-related W±Sn±Mo deposits, greisen, skarn, lodes and pegmatite	Hydrothermal activity	Low to moderate amount of common Pb; no matrix-matched standard available; Possible alteration of the mineral; Prone to host fluid and mineral inclusions		X	Romer and Lüders (2005); Pfaff et al. (2009); Lecumberri-Sanchez et al. (2014); Harlaux et al. (2017)
Other minerals: (urano)thorite, vesuvianite, bastnaesite, polycrase, coffinite, …		U deposits; REE deposits; …	Hydrothermal activity; Metamorphism; Supergene alteration	–	–	–	Romer (1992); Romer (1996); Rasmussen et al. (2008); Dill et al. (2010); Wu et al. (2011); Bergen and Fayek (2012); Dill et al. (2013); Cottle (2014); Downes et al. (2016)

[†] XXX: Low common Pb, high U and structurally robust minerals; XX: Moderate common Pb, low U and structurally robust minerals; X: Common Pb-rich, low U, structurally and/or chemically weak minerals. This classification should only be taken as a 'rule of thumb' as each case would be different.

[§] Refer to Figures 4 to assess the magnitude of initial ^{230}Th-disequilibrium of the expected age of the mineral.

6.1. Low common Pb, high U and structurally robust minerals

The most dated mineral is arguably zircon. This is mainly due to its virtual ubiquity in the geological environment, its chemical and mechanical resistance in a range of extreme geological processes from the surface to the deep Earth crust and to the low diffusivity of U and Pb in its crystal lattice (Cherniak and Watson 2001; Cherniak and Watson 2003; Cherniak et al. 1997; Harley and Kelly 2007). Importantly, zircon may contain tens to thousands of ppm of U (Hoskin and Schaltegger 2003) while essentially excluding initial Pb upon crystallization (Watson et al. 1997). This is mainly due to the large charge and ionic radius differences between Pb^{2+} (1.26 Å) and Zr^{4+} (0.84 Å) in eight-fold coordination in zircon. In fact, common Pb in zircon is often limited to small inclusions and to structurally damaged parts of the crystal which are readily removed with a chemical abrasion procedure while preserving the crystalline portion of the mineral (Mattinson 2005). The quality and ubiquity of this mineral has triggered most of the technical development of U–Pb geochronology including a wealth of international reference materials used for in-situ dating methods in all laboratories around the world.

Nevertheless, other minerals such as baddeleyite, columbite group minerals (columbo-tantalite), and REE-phosphates (monazite and xenotime) present U enrichment and common Pb exclusion properties comparable to zircon. Despite their occurrence in the geological environment being more restricted than that of zircon, published data often show the same level of precision as for zircon, according to the analytical method used. Chemical abrasion techniques have been tested on these minerals but show contrasting behavior. In the case of monazite and baddeleyite, chemical abrasion has not shown any significant improvement in term of precision, reproducibility and concordance (Rioux et al. 2010; Peterman et al. 2012). This might be due to the fact that monazite and baddeleyite do not suffer metamictization (Seydoux-Guillaume et al. 2002, 2004; Trachenko, 2004). However, baddeleyite is suggested to become tetragonal at high ion radiation doses, a phase change that may facilitate radiogenic Pb mobility (Schaltegger and Davies 2017). Additionally, chemical abrasion has been successfully applied to columbo-tantalite minerals and improved the concordance of the data (Romer and Wright 1992). It is thought to remove small inclusions of Pb bearing minerals such as uraninite or secondary Nb- and Ta-bearing minerals (Romer et al. 1996).

6.2. Moderate common Pb, low U and structurally robust minerals

Titanite, rutile and allanite represent very interesting properties for U–Pb dating. These accessory mineral species usually have low to moderate amounts of common Pb while being sufficiently enriched in U to allow precise dating in most cases. Analytical protocols and matrix-matched standards for in-situ dating have been developed and allow some labs to routinely date these mineral (Storey et al. 2006; Aleinikoff et al. 2007; Storey et al. 2007; Gregory et al. 2007; Luvizotto et al. 2009; Zack et al. 2011; Darling et al. 2012; Schmitt and Zack 2012; Smye et al. 2014). The use of titanite and especially rutile as geochronometers might be limited by their relatively lower closure temperature of the U–Pb system compared to zircon. Hydrothermal titanite (e.g., in skarn deposits) would crystallize near or just below its closure temperature allowing its use as a geochronometer (Chiaradia et al. 2008; Chelle-Michou et al. 2015), and helping to pinpoint antecrystic zircon growth (i.e., crystallized in earlier magma pulses and incorporated in a later pulse; Miller et al. 2007) in the skarn-forming magmatic intrusion. Rutile is involved in high temperature metamorphic reactions and can produce new zircon upon recrystallization at lower temperature and expulsion of Zr (e.g., Pape et al. 2016). Allanite may have exceedingly high Th/U ratios requiring a very careful approach for accurately correcting and interpreting initial ^{230}Th disequilibrium (Oberli et al. 2004).

6.3. Common Pb-rich, low U, structurally and/or chemically weak minerals

A wealth of other minerals can be used for U–Pb geochronology but tend (most of the time) to produce lower quality data than the minerals described above. This is mainly due to the high ratio of common to radiogenic lead in these mineral ($\gg$1 ppm) together with low U concentrations (< 10 ppm). This results in the chosen common Pb correction having a critical impact on the accuracy and precision of the dates. The best dates are usually obtained with the 3D isochron method (Schoene and Bowring 2006) and potential accompanied with the measurement of a cogenetic common Pb-rich phase (such as the magnetite-apatite geochronometer; Gelcich et al. 2005).

Furthermore, some species such as brannerite, calcite, uraninite, and, to a lesser extent, perovskite and wolframite are prone to resetting of the U–Pb system (Pb-loss), or even U mobility in the presence of hydrothermal fluids that may also promote dissolution/recrystallization of the mineral (e.g., Zartman and Smith 2009; Rasbury and Cole 2009; Ono and Fayek 2011; Bergen and Fayek 2012; Donnelly et al. 2012; Decree et al. 2014, Harlaux et al. 2017). This often results in markedly normally or inversely discordant common Pb-corrected data. Recent, advances in calcite U–Pb dating by LA-ICPMS and ID-TIMS make it possible to routinely achieve uncertainties on the order of 2-5% despite the high amount of common Pb (Li et al. 2014; Coogan et al. 2016; Roberts and Walker 2016; Burisch et al. 2017).

Due to the ubiquity of calcite in vein, cement or replacement phase in mineral deposits, calcite U–Pb dating is expected to open to new opportunities for ore deposit research and to address the timing of crustal fluid flow through direct dating. Yet, the main difficulty of calcite dating is to correctly interpret the event being dated, or if unsure, allow for all reasonable possibilities (e.g., see the case of the Hamersley spherule beds, Australia; Woodhead et al. 1998; Rasmussen et al. 2005).

6.4. Choosing the best mineral for U–Pb dating

The choice of the mineral targeted for U(–Th)–Pb dating should be dictated by the particular event or process of interest, cross-cutting and paragenetic information, and geochemical and/or structural data. Dating without consideration of the geological/petrographic context of the mineral will very likely lead to erroneous interpretation. One such example is the case of post-mineralization rhyodacite porphyry at the Corrocohuayco deposit, Peru. There, most zircon grains (11/13) from this post-mineralization porphyry were dated ~0.5 Ma older that the syn-mineralization porphyries it crosscuts (Chelle-Michou et al. 2014). This unambiguous field relationship shows that it could only be interpreted in the context of proto-pluton remelting, rather than as the age of magma emplacement.

Magmatism is arguably the most easily dated geological process. In the vast majority of cases zircon would be the mineral of choice. Even relatively mafic rocks can host zircon in the most differentiated 'melt pockets' (e.g. the Bushveld complex, South Africa; Zeh et al. 2015). In the cases where zircon is absent from the magmatic rock, usually in ultramafic, mafic or alkaline rocks, baddeleyite or perovskite present good alternatives. Finally, crust-derived granitoids often host zircon grains that are dominantly inherited from their source and minimally reflect new growth from the granitic liquid (e.g., Clemens 2003). In such cases, dating of monazite may be preferred. The main goal of dating these magmatic minerals is to constrain the age of magma emplacement in the crust or of volcanic eruption.

The increasing precision of zircon dates achievable with the CA-ID-TIMS method sheds new light on the long-lived history of magmatic systems. At the sample scale, more than 0.1 Ma of protracted zircon crystallization has been documented at a number of silicic systems, some of which are associated with porphyry copper mineralization (Schütte et al. 2010; Wotzlaw et al. 2013; Chelle-Michou et al. 2014; Barboni et al. 2015; Buret et al. 2017). When combined with complimentary geochemical data, zircon crystallization ages can provide valuable insights into the specific petrological processes responsible the transition from barren to ore-producing intrusions (Chelle-Michou et al. 2014; Tapster et al. 2016; Buret et al. 2016).

Despite its common usage in ore deposit research, the dating of magma intrusion only rarely dates the mineralization itself. In fact, this is only restricted to places where the ore minerals have crystallized under magmatic conditions such as the magmatic Ni-Cu-Cr(±Au±PGE) deposits and possibly some magmatic REE deposits as well. If appropriate crosscutting relationship with the mineralization can be observed, dating magmatic intrusions can elegantly bracket the timing of ore deposition (e.g., von Quadt et al. 2011). In the case of porphyry, greisen, or VMS deposits the age of the ore-related intrusion or of the associated volcanics may often provide a good, if not excellent, approximation for age of the mineralization. Yet, this approach requires much caution as even in classical magmatic-hydrothermal deposits such as W-Sn granite deposits or porphyry Cu deposits, the mineralization can have been sourced by a hidden intrusion at depth while being hosted in a previously emplaced one (e.g., Schaltegger et al. 2005). However, for deposits where the relationship between ore formation and a particular magma intrusion is ambiguous (e.g., IOCGs, orogenic Au deposit, epithermal deposits, distal skarns) or even totally absent (e.g., MVT deposits) it is much more advantageous to determine directly the timing of hydrothermal fluid circulation and/or of ore deposition. The list of ore minerals suitable for U–Pb dating include cassiterite (for Sn deposits), wolframite (for W deposits) columbo-tantalite (in some rare-metal granite, greisen and pegmatite deposits), rutile (for Ti deposits), and minerals associated with U deposits (e.g., uraninite, brannerite). This restricts the types of ore that can dated with the U–Pb method. Alternatively, several gangue mineral species can be used to date hydrothermal fluid circulation, metasomatism and metamorphism. Their relevance for the genesis or reworking of the studied ore deposit is fundamentally linked to their position in the paragenetic sequence with respect to the ore minerals. REE-phosphates such as monazite and xenotime are common in a wide variety of hydrothermal systems ranging from granite-related rare metal deposits to MVT deposits (Table 2) and, if available, would be the ideal minerals to date hydrothermal processes. In few cases, hydrothermal zircons at skarn (Niiranen et al. 2007; Wan et al. 2012; Deng et al. 2015c), IOCG (Valley et al. 2009), orogenic Au (Kerrich and Kyser 1994; Pelleter et al. 2007), and alkaline/carbonatite magmatism related rare-metal deposits (Yang et al. 2013; Campbell et al. 2014) have been reported and can date hydrothermal activity and metasomatism. However, in the absence of these hydrothermal minerals (which is not uncommon), other minerals listed in Table 2 with non-negligible amounts of common Pb can be called on. Titanite or allanite can provide excellent dates for skarn (Chiaradia et al. 2008; Deng et al. 2014; Chelle-Michou et al. 2015; Deng et al. 2015b) and IOCG deposits (Skirrow et al. 2007; Smith et al. 2009; Haller et al. 2011). Ore-stage calcite or apatite may sometimes represent the only minerals suitable for

U–Pb dating at MVT deposits (Grandia et al. 2000) or some REE-P deposits (Huston et al. 2016). The ability of apatite to keep record of Cl, F, OH and SO_4^{2-} of the hydrothermal fluid (or magma) from which it crystallizes (Webster and Piccoli 2015; Harlov 2015) coupled with the possibility to date it with the U–Pb method (Chew and Spikings 2015) opens interesting opportunities to refine ore forming models. Finally, U–Pb minerals such as rutile, apatite and/or titanite can provide invaluable thermochronological information on the thermal evolution of the studied ore deposit during and after its genesis.

7. Case studies of applications of U–Pb dating to mineral deposits

In the following section, we present two case studies that make very distinct use of U–Pb geochronology. The first one focuses on the Witwatersrand gold deposits, South Africa, and illustrates how geochronology based on several mineral species can be used to bracket the age of multiple geological events over long timescales (>10 Ma). The second one discusses how rather than the absolute age, the duration of the mineralizing event at porphyry copper deposits can help understand the ore-forming processes and the main controls on the size (metal content) of the deposits. These two examples embody different timescales of reasoning, different precision, accuracy and spatial resolution requirements, and different uses of the geochronological data.

7.1. Input of multi-mineral U–Pb dating for understanding gold deposition and remobilization in the Witwatersrand basin, South Africa

About 32 % of all gold ever mined and about the same proportion of known gold resources comes from deposits hosted in the Witwatersrand Basin, South Africa (Frimmel and Hennigh 2015), a Mesoarchean detrital sedimentary basin deposited on the Kaapvaal Craton (Fig. 9). The genesis of this enormous accumulation of gold in the crust has triggered one of the "*greatest debate in the history of economic geology*" (see summary in Muntean et al. 2005). Proposed models for the deposition of gold range from a modified paleoplacer to a purely hydrothermal origin. These disparate views arises from contradicting observations that are selectively put forward to favor either model (Frimmel et al. 2005; Law and Phillips 2005; Muntean et al. 2005). In fact, probably none of these end-member models can account for all the geological, chemical and isotopic observations. The most recent models rather consider the very peculiar conditions that prevailed in the Mesoarchean atmosphere, hydrosphere and biosphere (Frimmel and Hennigh 2015; Heinrich 2015). At this time, redox exchanges mediated by microbial life could have triggered the synsedimentary precipitation of the large quantities of gold dissolved in acidic and reduced meteoric and shallow sea waters.

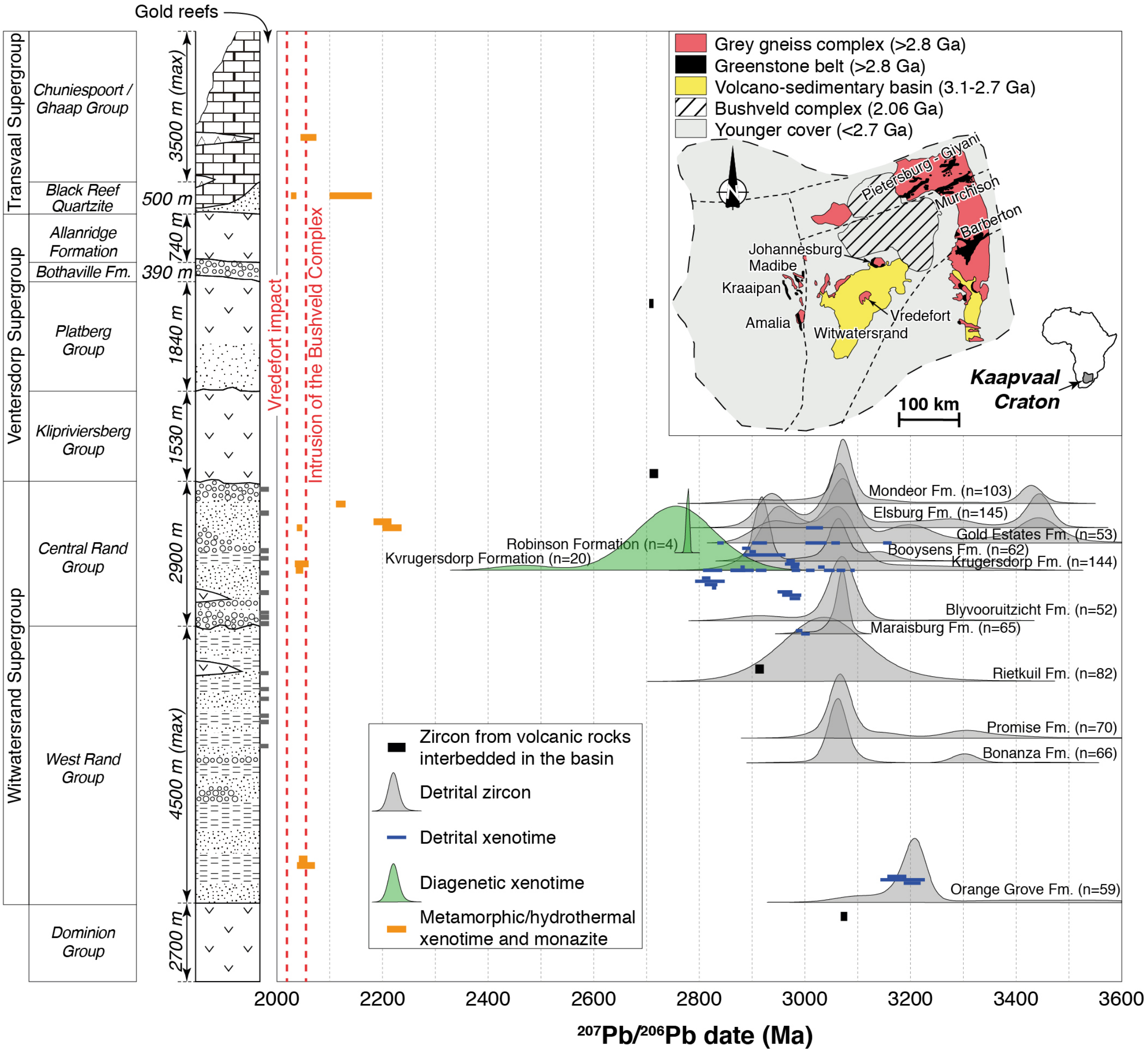

Figure 9. Compilation of available U–Pb data from the Witwatersrand basin plotted against the stratigraphic position of the sample. Stratigraphic column of the Archean to early Proterozoic succession in South Africa from Muntean et al. (2005). Data from the Witwatersrand basin are from Armstrong et al. (1991), England et al. (2001), Kositcin et al. (2003) Kositcin and Krapež (2004), Rasmussen et al. (2007a) and Koglin et al. (2010). Ages of the intrusion of the Bushveld Complex and of the Vredefort impact are from Zeh et al. (2015) and Moser (1997), respectively. Kernel density estimates (KDE) where obtained using DensityPlotter (Vermeesch 2012). Selected data are 95-105 % concordant and data points are plotted at the 2σ uncertainty level. Inset map of the Kaapvaal craton is modified from Poujol (2007).

U–Pb geochronology has been instrumental in the understanding of the formation Witwatersrand goldfields. It first played an essential role in calibrating the depositional age of the sediments (Fig. 9). One of the most significant contribution comes from Armstrong et al. (1991) who dated zircons from volcanic rocks distributed along the sedimentary pile of the basin. They constrained the deposition of the Witwatersrand Supergroup to within a timeframe of ca. 360 Ma from 3074 to 2714 Ma. Subsequent studies have focused on detrital zircon and xenotime from the main formations present along the stratigraphic column and intimately associated with the gold-bearing reefs (England et al. 2001; Kositcin and Krapež 2004; Koglin et al. 2010). These have confirmed the previous depositional ages but provide additional insight in the source of the detritus that filled the basin, as well as secular changes in the catchment area of the basin over time. Results show that the source area of detritus has an increasing age-range of rocks undergoing erosion over time. Apart from the lowermost part of the Witwatersrand Supergroup (Orange Formation, West Rand Group) which has dates clustering around 3.21 Ga, zircon dates from the West Rand Group cluster around 3.06 Ga, with only few older and younger dates (Fig. 9). Furthermore, zircon dates from the Central Rand Group shows additional peaks at 2.96-2.92 Ga and 3.44-3.43 Ga with several intervening dates in between these main peaks. Dates of detrital xenotime are mostly within the 3.1-2.9 Ga range but also extend as low as 2.8 Ga (Fig. 9). Koglin et al. (2010) and Ruiz et al. (2006) further link the gold-rich sediments to the presence of the 3.06 Ga zircon age peak. When compared with outcropping Archean terrains of the Kaapvaal Craton, these zircons could have originated from the greenstone belts west of the Witwatersrand basin (Madibe and Kraaipan), rocks in the immediate proximity of the basin (e.g., Johannesburg and Vrefefort Dome) or from equivalent units located northwest of the basin that might be present below the post-Witwatersrand cover (Koglin et al. 2010). More distal candidates such as the Murchison and the Barberton greenstone belts have also been proposed (Ruiz et al. 2006; Koglin et al. 2010). This interpretation is also compatible with paleocurrent directions and isotopic data (Koglin et al. 2010).

A paleoplacer model requires that all of the gold deposited in the basin originated from the same eroding massifs that sourced the sediments. However, such gigantic quantities of gold are two orders of magnitude in excess of all the gold ever mined and discovered in the potential outcropping massifs that sourced the zircons. This observation has been a major argument against any sort of paleoplacer model (e.g., Phillips and Law 2000; Law and Phillips 2005; Frimmel and Hennigh 2015). The existence of a now vanished or buried, hypothetical massif as a source of this huge amount of gold would pose an equally important question about how this massif would have been exceptionally well endowed with gold.

An epigenetic (hydrothermal) origin of the gold is supported by several petrographic observations. Yet, cross-cutting relationship suggest that hydrothermal activity took place before deposition of the Platberg Group, that is, before ca. 2.7 Ga (e.g., Law and Phillips 2005; Meier et al. 2009). U–Pb dating of diagenetic xenotime have yielded a major peak between 2.78-2.72 Ga which could be related to a heating event and flood-basalt volcanism during the deposition of the Klipriviersberg Group, immediately following the deposition of the Witwatersrand Supergroup (Fig. 9; England et al. 2001; Kositcin et al. 2003). Although this timing for gold introduction would be consistent with temporal constrains, the association of gold with this 2.78-2.72 Ga xenotime has not been reported. Additionally, U–Pb dating of metamorphic-hydrothermal REE-phosphates (monazite and xenotime) paragenetically associated with some gold or unrelated to gold mostly records ages between 2.06-2.03 Ga throughout the stratigraphic succession from the Witwatersrand to the Transvaal Supergroups (Fig. 9; England et al. 2001; Kositcin et al. 2003; Rasmussen et al. 2007a). This age is consistent with the emplacement age 1of the Bushveld complex on the northern flank of the Witwatersrand Basin (Zeh et al. 2015) which most likely triggered fluid circulation, gold remobilization and peak greenschist metamorphic conditions in the basin (Rasmussen et al. 2007a).

While none of the available U–Pb data for the Witwatersrand basin (Fig. 9) can firmly date gold deposition, or conclusively explain how gold was deposited, they have provided the necessary temporal framework on which to challenge relative chronological data. They have brought significant arguments against each of the classical models invoked for the formation of this district (syngenetic vs epigenetic) while confirming that gold remobilization occurred long after the formation of the deposit and contributed to the emergence of new ore forming models (Frimmel and Hennigh 2015; Heinrich 2015). This example highlights the necessity to properly constrain each U–Pb date against paragenetic, cross-cutting and stratigraphic observations in order to draw meaningful conclusions. The Witwatersrand gold deposits result from a long-lived and multi-episodic geological history where U–Pb geochronology provided constraints on basin formation, sediment provenance, diagenesis and metamorphism. It is noteworthy that the different minerals that were dated (zircon, monazite, xenotime), individually record a limited portion of the multiple processes that shaped the Witwatersrand basin and proved to be highly complementary to each other. Unveiling this protracted history did not require particularly high-precision dating methods, as LA-ICPMS and SIMS instruments with high sample throughput (Table 1) proved very affective. Additionally, the very high spatial resolution achievable with a SIMS instrument was crucial in unlocking the U–Pb information in tiny xenotime and monazite crystals identified from thin sections.

7.2. *Zircon U–Pb insights into the genesis on porphyry copper deposits*

Porphyry copper deposits (PCDs) typically form at convergent margins in association with subduction or post-subduction magmatism (e.g., Richards 2009). Metals and sulfur fixed in these deposits are thought to have been sourced from a cooling and degassing fluid-saturated magma body emplaced at shallow depths within the upper crust and transported to the site of deposition by magmatic-hydrothermal fluids (Hedenquist and Lowenstern 1994; Sillitoe 2010; Pettke et al. 2010; Simon and Ripley 2011; Richards 2011). Ultimately, very efficient fluid focusing and sulfide precipitation together with post-mineralization ore deposit preservation will favor the presence of economic porphyry deposits at erosion levels.

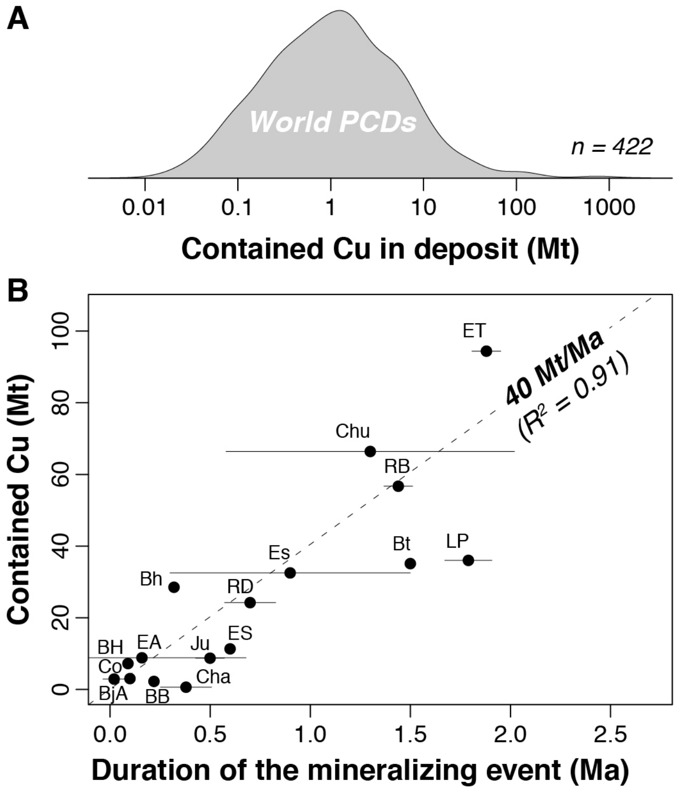

Figure 10. (**A**) probability density distribution of Cu endowment in global porphyry copper deposits (PCDs). Data from Singer et al. (2008). (**B**) Correlation between the duration of the mineralizing event and the total amount of Cu deposited (adapted from Chiaradia and Caricchi, 2017). BH: Batu Hijau (Indonesia), BjA: Bajo de la Alumbrera (Argentina), Co: Coroccohuayco (Peru), EA: El Abra (Chile), BB: Boyongan-Bayugo (Philippines)), Bh: Bingham (US), Cha: Chaucha (Ecuador), Ju: Junin (Ecuador), ES: El Salvador (Chile), Es: Escondida (Chile), LP: Los Pelambres (Chile), Chu: Chuquicamata (Chile), RB: Rio Blanco (Chile), Bt: Butte (US), ET: El Teniente (Chile), RD: Reko Diq (Pakistan).

The USGS global database of PCDs shows that these deposits span more than four orders of magnitude in copper endowment (Singer et al. 2008; Fig. 10a). Yet, the specific factors that control the size of these deposits have remained speculative. Comparing 'standard' and 'giant' PCDs, Richards (2013) speculated that the formation of the largest deposits result from a combination of copper enrichment in the magma, the focusing of fluids in structural corridors and, long-lived hydrothermal activity may favor the formation of the largest deposits. Among these possible factors, the timescale of PCD formation may play a significant role in their size. Compiling geochronological data (U–Pb on zircon and Re-Os on molybdenite) from PCDs around the world, Chelle-Michou et al. (2017) and Chiaradia and Caricchi (2017) have highlighted a correlation between the duration of the mineralizing event and the total mass of copper deposited, suggesting an average copper deposition rate of about 40 Mt/Ma (Fig. 10b). This relationship probably reflects the mass balance requirement for a giant deposit to be sourced by a large body of magma, which is incrementally injected into the upper crust over long timescales (see Chelle-Michou et al. 2017).

Similar conclusions where reached by Caricchi et al. (2014) who suggested that magmatism associated with economic PCDs is distinguishable from background pluton-forming magmatism and large-eruption-forming magmatism by large magma volumes emplaced at average rate of magma injection (~0.001 km^3/yr). This conclusion was drawn through inverse thermal modelling of high-precision CA-ID-TIMS U–Pb zircon age distributions.

While geochronology on PCDs has been mostly used to determine the formation age of these deposits, high-precision geochronological data can now be used to elucidate the duration of the ore-forming process. Figure 10b shows that the duration of ore-formation may be a significant control on their size (i.e., metal endowment) and, by inference, on the specific processes responsible for their formation. In addition, high-precision geochronological data may be able to help test the validity of numerical models of PCD formation (e.g., Weiss et al., 2012), or directly as input data into numerical models aiming at quantifying the time-volume-flux-geochemistry relationships of the magmatism associated with PCD genesis (e.g., Caricchi et al. 2014; Chelle-Michou et al. 2017; Chiaradia and Caricchi 2017). These studies only start to unearth the great potential of high-precision CA-ID-TIMS U–Pb dating for PCD exploration, and can also significantly contribute to a better understanding of PCD magmatic ore-forming processes.

Concluding remarks

Over the past two decades U–Pb geochronology has become an essential tool for the study of ore deposits. After a century of development, more than 16 minerals can now be dated with the U–Pb technique allowing its use for most types of ore deposits. U–Pb dating is most commonly used to provide the age of a particular geological event related to a studied deposit (e.g., magmatism, hydrothermal activity, sedimentation, metamorphism, ore deposition and remobilization), depending on the mineral(s) available for dating. The choice of the mineral(s) and of the analytical technique (LA-ICPMS, SIMS or ID-TIMS) used for dating mainly depends on the scientific questions that need to be answered and on the opportunities offered by the studied deposit. This point is perhaps one of the main limitations of the U–Pb dating of ore deposits. For example, MVT deposits rarely contain minerals suitable for U–Pb dating (potentially calcite, provided it has low initial Pb), in which case the use of other isotopic systems will be necessary (e.g., Rb-Sr on sphalerite, Re-Os on sulfides). In addition, as we have seen in the case of the Witwatersrand basin, the spatial resolution required for the analysis may sometimes critical guide the choice of the analytical method.

Recent advances that combine numerical modelling with U–Pb geochronology for porphyry copper deposits suggest that high-precision zircon U–Pb data may also be used as a window to better understand the magmatic aspect of the ore-forming process (Caricchi et al. 2014) and to unravel the fundamental controls on the size of the deposit (Chelle-Michou et al. 2017; Chiaradia and Caricchi, 2017). Comparable studies on other deposit types could potentially advance our understanding of ore-forming processes and may generate innovative tools for mineral exploration.

A further important development of U–Pb geochronology concerns its coupling with textural and geochemical data (e.g., trace elements, Lu–Hf isotopes, O isotopes) obtained on the same grain or on the same spot as the U–Pb data. This is commonly referred to as ‘petrochronology’ and allows temporal information relative to the evolution and/or the source of the liquid (a magma or an aqueous fluid) from which the mineral precipitated and potentially the rate of its evolution (e.g., Ballard et al. 2002; Smith et al. 2009; Valley et al. 2010; Pal et al. 2011; Rao et al. 2013; Yang et al. 2013; Griffin et al. 2014; Rezeau et al. 2016; Poletti et al. 2016; Gardiner et al. 2017). In particular, high-precision petrochronology on zircon and baddeleyite can provide unprecedented insight into the processes at play during magma evolution, the potential turning point leading to mineralization, or, the link between small intrusive bodies (dykes or stocks) or volcanic products and their larger deep-seated plutonic source (e.g., Wotzlaw et al. 2013; Chelle-Michou et al. 2014; Wotzlaw et al. 2015; Tapster et al. 2016; Buret et al. 2016; 2017; Schaltegger and Davies, 2017).

The field of U–Pb geochronology is working towards a level of maturity whereby inter-laboratory reproducibility will be guaranteed in most labs around the world and where each date and its uncertainty can be fully traceable to SI units. This however, should not mask the high-level of competency and training required to certify the quality of the analysis, to maintain the lab at the best level (picogram levels of common Pb contaminations can be dramatic in a CA-ID-TIMS lab) and, very importantly, the interpretation of the dates into geologically relevant ages. As we have shown, there are numerous potential pitfalls that, if not carefully accounted for, can result in unsupported or even wrong conclusions.

The improving precision, accuracy and spatial resolution of analyses now achievable, challenges paradigms of ore-forming processes and will continue to contribute significant breakthroughs in ore deposit research and potentially also contribute to the development of new mineral exploration tools. The full added value of U–Pb geochronology will however only be assured through its coupling with geochemical data, high-quality field and petrographic observations and numerical modelling.

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