CHAPTER 5: QUATERNARY GEOCHRONOLOGY BY SIMS

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INTRODUCTION

The timing of geologic events throughout the Quaternary period covering the past 2.6 Ma is of utmost importance for assessing the current state of the Earth, and to predict future changes. Quaternary geochronology represents a cornerstone in studying the geologic records of climate and landscape changes, biota evolution, and human origins. Quaternary geochronology covers an extremely wide range with regard to scope and methods (e.g., Noller et al. 2000) which even warranted the recent inauguration of a dedicated journal by the same name (Gruen 2006). Secondary ionization mass spectrometry (SIMS) has only recently become a player in this field, and earlier reviews of methods in Quaternary geochronology omitted SIMS (e.g., Noller et al. 2000). The high sensitivity and micrometre-scale spatial resolution of SIMS, however, is in the course of enhancing conventional uranium decay series (U-series) Quaternary geochronology in much the same way as it revolutionized U–Pb and 232Th–208Pb geochronology (e.g., Ireland & Williams 2003).

Because of the extremely low abundances of short lived intermediate U-series isotopes, complex mass spectra, and the low radiogenic yield of Pb in Quaternary minerals, U-series and U–Pb Quaternary geochronology by SIMS is the domain of high transmission, high sensitivity ion microprobes such as the CAMECA ims 1270 and 1280, SHRIMP, and SHRIMP–RG instruments. Many laboratories operating large radius magnetic sector SIMS instruments have published on various aspects of Quaternary geochronology (here citing the first relevant publication of each lab; ANU: Baldwin & Ireland 1995; UCLA: Reid et al. 1997; Curtin: Brown & Fletcher 1999; Stanford-USGS: Dalrymple et al. 1999; Woods Hole: Layne & Sims 2000; Hiroshima: Sano et al. 2002), but it may not be coincidental that the two labs historically engaged in this field (UCLA and Stanford-USGS) are located in volcanically and seismically active regions where interest in the most recent geologic past is high. Research applying SIMS has thus significantly contributed to elucidating important issues such as volcanic unrest, geothermal reservoirs, paleoclimate reconstruction, and land surface changes.

Over the past decade, SIMS Quaternary geochronology publications have steadily increased in number, and it is timely to review SIMS-specific techniques and applications with the aim of (1) providing a theoretical background of U-series dating by SIMS; (2) guiding through the analytical steps involved; and (3) showcasing case studies with emphasis on those where the SIMS approach significantly improved the understanding of the timing of geologic processes compared to conventional methods. Different aspects of U-series dating have been comprehensively reviewed elsewhere (e.g., Ivanovich & Harmon 1992, Bourdon et al. 2003, Condomines et al. 2003, Ludwig 2003, Cooper & Reid 2008), and novices are also referred to introductory chapters in textbooks on radiogenic isotope geochemistry. The treatment of SIMS U–Pb and Th–Pb geochronology (e.g., Ireland & Williams 2003) is limited here to issues pertaining to SIMS dating of young samples (e.g., alternative common Pb corrections, disequilibrium corrections). Chemical dating methods are beyond the scope of this review, and the interested reader is referred to literature on enhanced obsidian hydration dating by SIMS (e.g., Anovitz et al. 2008 and references therein).

THEORY OF U-SERIES DATING

Principles and assumptions

Uranium decays to stable Pb via two separate decay chains, one initiating with parental $^{238}$U (half-life $t_{1/2} = 4.468$ Ga) decaying to its stable daughter $^{206}$Pb, and the second with the respective parent and stable daughter pair $^{235}$U ($t_{1/2} = 0.7038$ Ga) and $^{207}$Pb (Fig. 5-1). The $^{238}$U and $^{235}$U chains involve eight and seven α-decays, respectively (Fig. 5-1). In both decay chains, the half-lives of intermediate daughter isotopes are significantly shorter than those of the
parent isotopes (Fig. 5-1). Bateman (1910) demonstrated that such a decay chain will over time mature to a condition where the activity ratio (number of decays per unit time or \(N \times \lambda\), with \(N = \) number of atoms and \(\lambda = \) decay constant) between shorter lived intermediate daughters (indices 2 to \(n\)) and longer lived parent (index 1) will become unity. This state is known as "secular equilibrium", which for a general decay chain with \(n\) members is expressed by the relation:

\[
N_1 \lambda_1 = N_2 \lambda_2 = N_3 \lambda_3 = \ldots = N_n \lambda_n
\]

Note that activities are conventionally expressed by round parentheses around the elemental symbol. Disequilibrium between parent and daughter isotopes in the U decay chain permits the time elapsed to be measured between an event that generated radioactive disequilibrium at \(t = 0\) and some later time \(t\), whereby the activity ratio of the short lived daughter (index 2) relates to the activity of the long lived parent (index 1) and time as:

\[
N_2 \lambda_2 = N_1 \lambda_1 \left(1 - e^{-\lambda_2 t}\right) + N^0_2 \lambda_2 e^{-\lambda_2 t}
\]

\(N^0\) is the number of atoms initially present (at \(t = 0\)). Equation (2) can be solved for \(t\) under the fundamental assumption that all changes in isotopic abundances result from radioactive decay and ingrowth only (closed system). If \(\lambda_2 >> \lambda_1\), equation (2) simplifies to:

\[
N_2 \lambda_2 = N_1 \lambda_1 \left(1 - e^{-\lambda_2 t}\right) + N^0_2 \lambda_2 e^{-\lambda_2 t}
\]

In certain cases, such as for \(^{230}\text{Th}\) in hydrogenic minerals (e.g., calcite, opal), absence of initial daughter isotope can be reasonably assumed so that equation (3) can be further simplified to:

\[
N_2 \lambda_2 = N_1 \lambda_1 \left(1 - e^{-\lambda_2 t}\right)
\]

Disequilibrium can be generated instantaneously relative to the half-lives of the U-series isotopes involved, or over protracted time periods. Chemical fractionation between U-series parents and daughters occurs due to differential mineral–melt or mineral–fluid partitioning, in particular if ionic charge differences exacerbate fractionation. U and Th are both tetravalent under reducing conditions, but only U can achieve higher oxidation states (U\(^{5+}\), U\(^{6+}\)), which can lead to strong fractionation between U and Th under oxidizing conditions. Other processes that are capable of generating disequilibrium involve isotopic fractionation through preferential leaching or recoil affecting \(^{234}\text{U}\). Recoil results in complete loss of \(^{234}\text{U}\) or dislocation to a radiation-damaged site from which it is readily mobilized. The latter is prevalent only at low temperatures because of rapid annealing of lattice damage at high temperatures associated with igneous processes.

Once a parent–daughter system approaches secular equilibrium, no information on the amount of time passed can be obtained (Fig. 5-2). In this case, either U-series pairs with longer \(t_{1/2}\), or accumulation of the stable daughter isotopes (\(^{206}\text{Pb}\) and \(^{207}\text{Pb}\)), need to be used to determine the age. For completeness, it should be pointed out that \(^{232}\text{Th}\) decay to stable \(^{208}\text{Pb}\) (+6 \(^4\text{He}\)) lacks long lived (>1 ka) intermediate daughters in the \(^{232}\text{Th}\) decay chain, and is thus not further considered here.

Initial disequilibrium in U-series decay chains will also either accelerate or delay the accumulation of stable daughter isotopes relative to equilibrium conditions. These effects are negligible for very short lived intermediate isotopes, but in the case of \(^{230}\text{Th}\), disequilibrium can result in significant excesses or deficits in \(^{206}\text{Pb}\) that require corrections in order to determine U–Pb ages accurately (Fig. 5-3, Schaerer 1984). For \(^{206}\text{Pb}/^{238}\text{U}\), the measured excess/deficit relative to...
the equilibrium ratio at time $t$ equals:

$$\frac{\left(\frac{^{206}\text{Pb}}{^{238}\text{U}}\right)_{\text{equilibrium}}}{\left(\frac{^{206}\text{Pb}}{^{238}\text{U}}\right)_{\text{disequilibrium}}} = \frac{\lambda_{238}}{\lambda_{230}} (f-1) + 1$$  \hspace{1cm} (5)

with $f$ defined as the ratio between mineral (xtal)–melt partitioning coefficients $D$ for Th and U:

$$f = \frac{D_{\text{Th/melt}}}{D_{\text{U/melt}}}$$  \hspace{1cm} (6)

Equivalent relations can be defined for the $^{235}$U decay system with $^{207}$Pb substituting for $^{206}$Pb, and Pa ($\lambda_{231}$) for Th ($\lambda_{230}$) in equations (5) and (6), respectively. Not only accumulation of stable Pb is affected by initial disequilibrium, but also production of $^4$He will be accelerated or delayed by U-series disequilibrium, and corrections are required if young crystals are to be dated accurately (Farley et al. 2002). For completeness, fission track dating is briefly mentioned here as another technique that is based on the radioactivity of U. Here, spontaneous fission of $^{238}$U (at a fission probability of $~5 \times 10^{-7}$ per decay, Dumitru 2000) occurs independently of disequilibrium in the subsequent intermediate daughters.

The validity of the closed system assumption is largely uncontested for zircon U-series dating because U-series elements are immobile in zircon even at magmatic temperatures (e.g., Cherniak & Watson 2003). For other accessory minerals, actinide diffusion is largely experimentally unconstrained, but geologic case studies indicate closure at high temperatures, for example in the case of allanite (Vazquez & Reid 2004). In contrast to U and Th, He diffuses quickly in zircon, and will accumulate only following eruptive quenching (Reiners et al. 2004). Excess He is thus essentially unknown in volcanic zircon which offers great potential for reliable (U–Th)/He dating of volcanic eruptions. For U-series dating of low temperature materials such as calcite or opal, the closed system assumption is frequently verified by solving for initial ($^{234}$U/$^{238}$U) and comparing the initial ratio to that of a reservoir value (e.g., modern sea water); deviation from the expected ratio is interpreted as open system behavior such as diageneric alteration (Edwards et al. 2003).
Detection limits and datable materials

Secular equilibrium and detection limits. Secular equilibrium imposes an upper limit for U-series chronology. In the case of complete initial absence of a short lived intermediate daughter, radioactive ingrowth of the daughter over approximately five half-lives leads to daughter/parent activity ratios ~3% below unity, i.e., within typical SIMS analytical uncertainties and thus indistinguishable from secular equilibrium (Fig. 5-2). In the case of strong initial daughter excesses, achieving the same relative deviation from equilibrium requires longer time periods: for an initial daughter/parent activity ratio of 10, the daughter/parent activity will be ~3% above the secular equilibrium ratio after ~8 half-lives (Fig. 5-2). Strong enrichments of U-series intermediate daughters, however, are rare, because D values for actinides mostly differ by a factor of <10 (Blundy & Wood 2003)

SIMS U-series dating is generally performed near analytical detection limits due to the very low abundances of short lived U-series intermediate daughter atoms in sample or standard materials. As a guide for assessing the practicality of SIMS analysis of uraniferous materials for U-series dating, expected count rates for $^{226}$Ra, $^{230}$Th, $^{231}$Pa, and $^{234}$U positive ion species are calculated in Fig. 5-4. Useful ion yields (ions detected/atoms sputtered) for species of interest ($^{230}$ThO$^+$, $^{231}$PaO$^+$, and $^{234}$UO$^+$; note: O is used here as shorthand for the abundant isotope $^{16}$O) are from the literature or estimated from chemically similar species. For $^{230}$ThO$^+$, $^{231}$PaO$^+$, $^{234}$UO$^+$, and $^{226}$Ra$^{138}$Ba as a proxy for $^{226}$Ra; Hervig et al. 2006) useful ion yields are approximately 1%. Assuming a sputter rate of 0.05 $\mu$m/sec/nA/sec (typical for zircon) and a total counting time of 1 hour, the detection limits are ~0.5 ppm for $^{234}$U, ~2 ppm for $^{230}$Th, and ~70 ppm for $^{231}$Pa and $^{226}$Rd (Fig. 5-4). Higher sputter rates (e.g., for opal) result in lower detection limits, whereas elevated backgrounds increase detection limits, whereby the detection limit scales with the square root of the background intensity. Interferences such as $^{233}$U$^{12}$C on $^{234}$UO$^+$ may require analysis of $^{234}$U$^+$ instead of $^{234}$UO$^+$, which is less abundant than $^{234}$UO$^+$ by a factor of ~2 (Paces et al. 2004). Note that these calculations assume secular equilibrium, and while U-series isotopes of interest can be enriched in some minerals, analysis of equilibrium reference materials is required for calibrating or monitoring instrumental fractionation.

Based on these considerations, the principal targets for SIMS U-series analysis are the long lived (~$10^4$ a) intermediate daughter isotopes in minerals enriched in actinide elements, with abundances exceeding few 10s to 100s of ppm U. In the subsequent paragraphs, occurrences and U-series element-partitioning behavior of some uraniferous minerals are summarized, and their potential for U-series geochronology is discussed.

Zircon. Zircon (ZrSiO$_4$) is an accessory mineral common in evolved silicic and carbonatitic rocks. It crystallizes both from melts and hydrothermal fluids (Watson & Harrison 1983, Hoskin & Schaltegger 2003). Nominally, zircon incorporates U with a mineral–melt partitioning coefficient $D_U$ of ~100 (Blundy & Wood 2003), but U and Th abundances frequently vary significantly, even within individual zircon crystals (Fig. 5-5). Because of this variability, it is difficult to provide a range of typical U abundances in zircon, but U abundances between 10 and 1000 ppm are common, whereby high U zircon with of up to several wt.% UO$_2$ exists in some rhyolitic rocks (e.g., Buff Peak zircon with ~3 wt.% UO$_2$; Schmitt 2007). Trace element variations in zircon also control its cathodoluminescence (CL) activity, and CL images are frequently

![Fig. 5-4. SIMS U-series analysis detection limits as a function of U abundance. Calculations assume secular equilibrium, a zircon density of 4.65 g/cm$^3$, and a sputter rate of 0.05 $\mu$m/sec/nA, typical for zircon bombardment with a 50 nA $^{16}$O$^+$ beam. Thin horizontal lines are drawn for relative uncertainties of 1.3, and 10% based on counting statistics for a 60 min analysis. The detection limit (thick solid line) is calculated for the average background at mass/charge 246.3 = 0.04 cps, as measured in 40 sequential analyses of Puy de Dome and AS-3 zircon grains, using the approximation for the detection limit D.L.(at 99% confidence) = 2.3 $\times$ (2 $c_{bck}$)$^{0.5}$ ($c_{bck}$ = total background counts).](image-url)
used to target actinide-rich domains in zircon following the empirical rule that CL-dark regions are higher in U and Th (Fig. 5-5). Despite the apparent complexity of zircon CL patterns, these may or may not reflect significant differences in crystallization age. Average $D_{Th}/D_{U}$ is approximately 0.2 for a wide variety of magmatic rock types (Bindeman et al. 2006), but two to three-fold variations in Th/U exist in igneous zircon even within single crystals (Lowenstern et al. 2000).

Zircon is extremely resistant to hydrothermal alteration or weathering. Moreover, U and Th diffusion occurs over vanishingly small length scales so that zircon U-series ages can be reliably interpreted as crystallization ages (Cherniak & Watson 2001, Cherniak & Watson 2003). Intricate age zonation at a few micrometres spatial resolution has been documented through depth profiling of zircon (Reid 2008, Fig. 5-6). Bulk analysis of age-zoned zircon such as the grain depicted in Figure 5-6 would produce mixed ages with little geologic significance. Even at the lateral dimensions of the ion microprobe primary beam of few 10's of μm, averaging different age domains is possible. SIMS depth profiling which greatly enhances spatial resolution relative to the lateral dimensions of the analysis crater is thus an important tool to extract reliable crystallization ages from zoned crystals (Reid 2008).

**Allanite** Allanite is an epidote-group mineral which incorporates significant amounts of Th and U into its structure and which occurs in silicic igneous rocks and regional metamorphic rocks. Its general mineral formula is $[\text{A}_2\text{M}_3\text{Si}_3\text{O}_{12}(\text{OH})]$, where the A sites contain Ca, Sr, or REE, and the M sites octahedrally coordinated cations such as Al, Fe, Mn, or Mg (Gieré & Sorensen 2004). Allanite U-series dating of young volcanic rocks harnesses the preferential incorporation of Th into its structure relative to U ($D_{Th}/D_{U} \sim 50$), and the high abundances of Th (typically 1–2 wt.% ThO$_2$, Catlos et al. 2000, Vazquez & Reid 2004) that facilitates analysis of $^{230}$Th. What fuels interest in allanite U-series dating most, however, are systematic compositional variations that provide a record of magmatic differentiation. For example, changes in La/Nd or Mn/Mg due to cation substitution in A and M sites, respectively, can be related to compositional

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**Fig. 5-5.** Cathodoluminescence images of Laacher See carbonate zircon 129 "mask" (A, B) compared to $^{232}\text{ThO}_2$:90ZrO$_4^-$ ion intensity map generated in multi-collection mode under bombardment with a ~1 μm diameter Cs$^+$ primary beam (C). Bright area in C is higher in Th by about ~20-fold compared to dark area.

**Fig. 5-6.** Depth profiling of Toba zircon showing concordance between $^{230}$U-$^{206}$Pb and $^{238}$U-$^{206}$Pb ages (Reid 2008).
variations in the host melt over time (Vazquez & Reid 2004). Vazquez & Reid (2004) estimated Th diffusion in allanite to occur over length scales of a few micrometres at most for crystal storage under magmatic temperatures (~800°C) and durations of hundreds of thousands of years so that post-crystallization re-equilibration in allanite is largely negligible for Th isotopes.

**Opal** In contrast to minerals mentioned above, opal (amorphous, hydrated silica SiO2·nH2O) is a low temperature, hydrogenic mineral. It is used as a geochronometer in paleohydrology (e.g., for the Yucca Mountain nuclear repository site, Paces et al. 2004) and environmental studies (e.g., pedogenic opal, Maher et al. 2007). Common opal typically has much higher U abundances (>1000 ppm, Amelin & Back 2006) than precious opal, and U abundances correlate with ultraviolet (UV) fluorescence. U and Th are characteristically extremely fractionated with Th/U ratios between ~10–3 and 10–4, and 206Pb/238U ratios are also low (10–5–10–7, Amelin & Back 2006). Precious opal, by contrast, tends to display lower U abundances, higher Th/U ratios of ~1, and elevated common Pb abundances so that it is of limited use for geochronology (Amelin & Back 2006).

**Other accessory magmatic minerals** No SIMS U-series data for accessory minerals in igneous rocks other than zircon and allanite have been published to the author's knowledge. There exist, however, many potentially datable accessory minerals, both in mafic and silicic rocks. Based on their propensity for enriching actinide elements, such minerals include baddeleyite (ZrO2), zirconolite (CaZrTi2O7), chevkinite-perrierite (A4BC2D2 nH2O), where A = [La, Ce, Ca, Sr, Th], B = [Nb, Ta, Ti, Al, Fe3+, Zr, Sn, W], X = [O, OH], and Y = [O, OH, F], Lumpkin & Belkin 2002), and pyrochlore (A2B2X6Y nH2O, where A = [Na, Ca, Mn, Fe2+, Sr, Sb, Cs, Ba, REE, Pb, Bi, Th, U], B = [Nb, Ta, Ti, Al, Fe3+, Zr, Sn, W], X = [O, OH], and Y = [O, OH, F], Lumpkin & Ewing 1995), which are characteristic accessory minerals in mafic, alkaline, or carbonatitic rocks, that commonly lack other datable minerals. In addition, apatite (Ca5[PO4]3[OH, F, Cl]), titanite (CaTiSiO3), and monazite (Th, REE)[PO4, SiO4]) are potentially amenable for U-series dating, and they are common accessory minerals in silicic rocks. Apatite and titanite, however, tend to display only comparatively modest enrichments in U and Th, which limits analytical precision.

**Bulk sample 238U-230Th analysis by SIMS**

Although not the main focus of this review, bulk U-series dating by SIMS is briefly mentioned here. Several studies have harnessed the high sensitivity of SIMS for actinides (typically exceeding that of TIMS and ICP–MS techniques by at least one order of magnitude, Goldstein & Stirling 2003) for Quaternary geochronology. In these studies, rocks, minerals or corals were digested in bulk, and ion-exchange column separation techniques were used to enrich U and Th. Layne & Sims (2000) evaporated purified Th-enriched solutions on carbon planchets and analyzed the dried residue using a CAMECA ims 1270. Bischoff et al. (2005) loaded pre-concentrated U and Th on single ion-exchange beads (~100 μm diameter), which were subsequently charred and mounted in epoxy for analysis using SHRIMP–RG. Both studies applied oxygen primary beams, and analyzed positive secondary ions as atomic species. Analytical uncertainties were generally found to be similar or better than those of conventional techniques (Layne & Sims 2000, Bischoff et al. 2005).

**Applicable methods and time ranges**

**U–Pb** Among the individual parent-daughter systems in U-series geochronology, U–Pb dating stands out as it can be applied over the entire geologic time scale. Because extensive reviews of SIMS U–Pb dating are available (e.g., Ireland & Williams 2003), only the lower bounds of applicability of SIMS U–Pb dating are discussed here. Multiple case studies have demonstrated that concordant SIMS 238U–206Pb and 238U–230Th zircon ages can be obtained (Vazquez et al. 2007, Reid 2008, Fig. 5-6), and thus the lower age limit for U–Pb dating can be empirically constrained as the age at which 238U–230Th dates become more precise than 238U–206Pb dates, typically for ages ~200–300 ka. For Quaternary samples, SIMS U–Pb dating focuses on 238U–206Pb because of the low abundance of 235U (present day 238U/235U = 137.88) and concomitantly low radiogenic 207Pb. Moreover, SIMS analytical uncertainties for U–Pb of 1–2% (relative) largely prevent a meaningful check for concordance between young 235U–207Pb and 238U–206Pb ages as a criterion for Pb-loss, but metamictization and Pb mobility can be ruled out for most Quaternary zircon with typical U abundances (Cherniak & Watson 2001). It is, however, advantageous to use 207Pb as a proxy for common Pb (Balchin & Ireland 1995, Schmitt et al. 2003a), instead of 204Pb. This is because 207Pb/206Pb throughout the Cenozoic is...
essentially invariant (e.g., Getty & DePaolo 1995). Conventionally 204Pb-corrected ages for Quaternary zircon analyses are less precise due to a combination of high uncertainties of 204Pb measurements and low radiogenic yields, and can lead to an overcorrection in U–Pb ages, likely due to unidentified interferences on the 204Pb peak (Schmitt et al. 2003a, Fig. 5-7). Because 207Pb intensities are about ~15 times higher than 204Pb, there will be less uncertainty in the common Pb correction. Using a 207Pb-based common Pb correction, 206Pb/238U ages for Quaternary reference zircon are in good agreement with TIMS results (Schmitt et al. 2003a). Another approach is to use 208Pb as a proxy for common Pb (Compston et al. 2003). Using a common Pb correction in U–Pb ages, likely due to unidentified interferences on the 204Pb peak (Schmitt et al. 2003a, Fig. 5-7). Because 207Pb intensities are about ~15 times higher than 204Pb, there will be less uncertainty in the common Pb correction. Using a 207Pb-based common Pb correction, 206Pb/238U ages for Quaternary reference zircon are in good agreement with TIMS results (Schmitt et al. 2003a). Another approach is to use 208Pb as a proxy for common Pb (Compston et al. 2003).

Conventional 204Pb-corrected ages for Quaternary zircon standard 61.308A (France) (Compston et al. 2003), SIMS data published in Schmitt et al. (2003a). Initial 231Pa-excess results in unsupported 207Pb, leading to a +95 ka age excess (assuming melt equilibrium, Fig. 5-3). Such excesses were detected in some high precision TIMS studies of Quaternary and Tertiary zircon (e.g., Schmitz et al. 2001, Crowley et al. 2007). Other accessory minerals such as allanite or monazite will exhibit excess 208Pb due to preferential partitioning of Th relative to U, but by the same token, these minerals will preferentially be dated by 232Th–208Pb, instead of U–Pb methods. This has the advantage that corrections of disequilibrium are obsolete due to the absence of long lived intermediate daughters in the 232Th decay chain.

\[
\frac{238U}{234U} < \frac{234U}{238U} \] (t\(\frac{1}{2}\) = 245,250 a) is the longest lived intermediate U-series isotope. Magmatic processes such as melting and crystallization do not fractionate 234U and 238U, and fresh igneous rocks and minerals are typically in secular equilibrium (Edwards et al. 2003). Natural waters, by contrast, generally display (234U)/(238U) ratios >1, whereas soil (234U)/(238U) ratios are sub-unity (Edwards et al. 2003). Aqueous precipitates such as carbonates and opal inherit elevated (234U)/(238U) from their precipitating waters. Combined SIMS 238U–234U–230Th and 236U–234U–230U–236Pbopal dating is feasible over time ranges of ~50 ka to ~1 Ma (Paces et al. 2004, Nemchin et al. 2006).

The second longest U-series half-life is that of 238Th (t\(\frac{1}{2}\) = 75,690 a), which results in a maximum age for 238U–230Th dating of ~350 ka. 238U–230Th dating of accessory minerals has been advantageous for low Th (and thus low radiogenic 208Pb) minerals such as opal (Nemchin et al. 2006).

In addition to non-conventional common Pb correction schemes, initial disequilibrium corrections are a specific requirement for Quaternary zircon U–Pb dating. The effects of disequilibrium on U–Pb (or Th–Pb) ages depend on the partitioning ratio between long lived parent and intermediate daughter, and scales with the half-life of the daughter isotope (see equations 5 and 6). Zircon commonly discriminates against 230Th relative to 238U, because of different zircon–melt partition coefficients. This causes a deficit in 206Pb that for f = 0.2 (equation 6) amounts to approximately ~87 ka (assuming melt equilibrium, Fig. 5-3). Zircon Th/U can be directly analyzed, whereas melt Th/U is inferred from compositions of whole rocks, matrix glass (Reid & Coath 2000), or melt inclusions (Schmitt et al. 2003a). Initial 231Pa-excess results in unsupported 207Pb, leading to a +95 ka age excess (assuming melt equilibrium, Fig. 5-3). Such excesses were detected in some high precision TIMS studies of Quaternary and Tertiary zircon (e.g., Schmitz et al. 2001, Crowley et al. 2007). Other accessory minerals such as allanite or monazite will exhibit excess 208Pb due to preferential partitioning of Th relative to U, but by the same token, these minerals will preferentially be dated by 232Th–208Pb, instead of U–Pb methods. This has the advantage that corrections of disequilibrium are obsolete due to the absence of long lived intermediate daughters in the 232Th decay chain.
applied to volcanic rocks with eruption ages as young as 650 a (Reid et al. 1997), and Holocene zircon $^{238}$U-$^{230}$Th ages have been obtained (Schmitt & Vazquez 2006, Bacon et al. 2007, Fig. 5-8).

In contrast to hydrogenic minerals such as calcite and opal, accessory minerals incorporate some degree of initial $^{230}$Th, so that the second term in equation (3) plays a significant role. An isochron method is thus applied, in which the age is determined based on the slope defined by coeval samples in a $(^{230}$Th$/^{232}$Th) vs. $(^{238}$U$/^{232}$Th) diagram. The age is derived using equation (3), whereby daughter 2 = $^{230}$Th, parent 1 = $^{238}$U, and both sides of equation (3) are divided by the $^{232}$Th activity:

$$N_{230}^{238} X_{232} = N_{232}^{238} X_{232} \left(1 - e^{-\lambda_{230} t}\right) + N_{230}^{232} X_{232} e^{-\lambda_{230} t} \quad (7)$$

This equation is restated in (8) with activities expressed by parentheses:

$$\frac{^{230}{\text{Th}}}{^{232}{\text{Th}}} = \frac{^{238}{\text{U}}}{^{232}{\text{Th}}} \left(1 - e^{-\lambda_{230} t}\right) + \left(\frac{^{230}{\text{Th}}}{^{232}{\text{Th}}}\right)^0 e^{-\lambda_{230} t} \quad (8)$$

This equation represents that of a straight line in a $(^{230}$Th$/^{232}$Th) vs. $(^{238}$U$/^{232}$Th) isochron diagram, whereby age is calculated from slope m by:

$$t = -\frac{\ln(1-m)}{\lambda_{230}} \quad (9)$$

Two approaches are frequently used to determine an age: (1) two-point model isochrons using mineral–melt pairs whereby melt U-series compositions need to be analyzed by bulk techniques due to low U-series isotope abundance in whole rocks or glasses (e.g., Reid et al. 1997), and (2) internal isochrons for multiple spots on single crystals or multicrystal analyses (e.g., Lowenstern et al. 2000). Figure 5-9 presents an example of both isochron approaches: both yielding ages overlapping within uncertainty, with the zircon–melt pair yielding a more precise result compared to zircon data alone. Mineral–melt two point isochron ages are, strictly speaking, model ages because the composition of the melt and mineral crystallized may not be the same as the melt composition inferred from analysis of whole rocks or glass. Fortunately, disequilibrium due to accessory mineral fractionation is much larger than that imparted on melts by magmatic processes such as melting and fractional crystallization of major phases so that uncertainties with regard to melt composition in many cases...
weight little on the overall uncertainty of the two point isochron age (see paragraph on Error assessment). Internal isochrons require that the time scale of crystallization is short relative to the decay rate of $^{230}$Th. Prolonged crystallization, however, is a hallmark of many magmatic systems so that zircon in some cases will not form well defined isochrons but rather fall into a wedge-shaped field (also termed "sphenochron", Chen et al. 1996, Fig. 5-8) for which lower and upper age bounds can be determined applying mixing algorithms such as by Sambridge & Compston (1994).

$^{235}$U–$^{231}$Pa $^{231}$Pa is the third longest lived U-series isotope, and the longest lived intermediate isotope in the $^{235}$U decay chain ($t_{1/2} = 32,760$ ka). While theoretically applicable to an age range of $\sim 150$ ka, and therefore complimentary to $^{230}$Th–$^{238}$U dating, its abundance at equilibrium is $\sim 70$ times lower than $^{230}$Th (Fig. 5-4). Consequently, SIMS $^{231}$Pa analysis has been primarily conducted with the goal of constraining Pa partitioning in zircon to provide an empirical basis for correcting high precision U–Pb ages (e.g., Schmitz & Bowring 2001, Crowley et al. 2007) rather than to employ it as a new chronometer. Experimental constraints on partitioning of $^{231}$Pa are lacking, but lattice strain partitioning models suggest strong compatibility of pentavalent Pa in zircon (Blundy & Wood 2003). If valid, initial $^{231}$Pa excesses could indeed lead to significant unsupported $^{207}$Pb, a possibility that has been raised frequently in the U–Pb TIMS literature (e.g., Anczkievicz et al. 2001). Schmitt (2007), however, detected only minor excesses in $^{(231)}$(Pa)/(235U) in zircon from Holocene Salton Buttes rhyolite. An initial activity ratio of $\sim 2$ measured in Salton Buttes zircon demonstrates that Pa is indeed more compatible in zircon compared to U, but $^{231}$Pa disequilibrium will cause only small excesses in $^{207}$Pb (Schmitt 2007). Additional analyses of $^{(231)}$(Pa)/(235U) in zircon crystals from the China Hat rhyolite support these earlier findings, as demonstrated by the $^{(231)}$(Pa)/(235U) vs. $^{(230)}$Th/(238U) model concordia for initial zircon $^{(231)}$(Pa)/(235U)$_0 = 2$ and $^{(230)}$Th/(238U)$_0 = 0.2$ (Fig. 5-10). The zircon ages are concordant with the eruption age ($57 \pm 8$ ka, 2$\sigma$, Heumann 1999) and the zircon $^{(230)}$Th/(232Th) vs. $^{(238)}$(U)/(232Th) isochron age of $66 \pm 9$ ka (2$\sigma$, MSWD = 0.57), both overlapping within uncertainties (Fig. 5-10). For China Hat rhyolite initial $^{(231)}$(Pa)/(235U)$_0 = 0.6$ (Heumann 2004), this results in a model $D_{Pa}/D_{U}$ ($D = \text{zircon–melt partition coefficient ratio of } 3.4 \pm 0.4$. This is equivalent to the values proposed by Schmitt (2007) for Salton Buttes zircon.

Other short lived chronometers Of the short lived U-series isotopes, only $^{226}$Ra ($t_{1/2} = 1599$ a) is briefly considered here. In situ SIMS analysis of $^{226}$Ra is hampered by its extremely low abundance (see Fig. 5-4), especially as Ra is predictably incompatible in most minerals (using Ba as a proxy, Blundy & Wood 2003). Even in minerals where $^{226}$Ra is compatible (e.g., K-feldspar: Blundy & Wood 2003, leucite: Fabbrizio et al. 2008), enrichment is at best $\sim 10$-fold relative to the melt. Low abundances of parent and daughter nuclei limit the capability of in situ SIMS $^{230}$Th–$^{226}$Ra dating. There is, however, potential for SIMS $^{226}$Ra analysis of doped experimental samples.

METHODS Sample Preparation
The main advantage of SIMS U-series analysis is its capability to measure spatially resolved isotopic compositions. Sample preparation techniques for bulk digestion methods followed by SIMS analysis of chemically separated and/or enriched U-series isotopes are described in Layne & Sims (2000) and Bischoff et al. (2005). Samples for spatially resolved analysis are prepared by embedding crystals either in epoxy resin, or alternatively in a soft metal (e.g., indium In). It is also possible to perform in situ analysis using
petrographic thin sections or polished blocks. Samples are required to be solid and flat, and must not outgas under ultrahigh vacuum. Sample holder dimensions of commercial instruments are typically ~2.54 cm in diameter, but the useful area is restricted to the inner ~2 cm bull’s eye because steering of primary and secondary beams is compromised when targeting areas near the edges of the sample holder. Standard petrographic grinding and polishing techniques are employed, but for euhedral crystals such as zircon, it is also possible to press grains into In metal so that crystal faces are flush with the mount surface, without any further grinding or polishing (Fig. 5-11). Sample processing is followed by several cleaning steps in order to remove surface contaminants (e.g., dilute HCl for zircon). Prior to analysis, samples are plated with a thin (several tens of nm) Au layer to generate a conducting sample surface.

SIMS Analytical Conditions

**Primary beam** SIMS U-series analysis is typically conducted with a mass-filtered primary beam of $^{16}\text{O}^2-$ or $^{16}\text{O}^-$ ions generated in a duoplasmatron source. Oxygen primary beams employed have currents mostly between ~10 and 60 nA, and are focused into ~15–40 μm diameter spots (e.g., Schmitt et al. 2006, Schmitt 2007, Maher et al. 2007). With primary beam impact energies of 22.5 kV and oblique incidence, zircon sputter rates are ~0.05 μm$^3$/nA/sec (or 0.2 pg/nA/sec, Schmitt 2007), whereas those for opal are reported to be approximately four to five times higher (e.g., Maher et al. 2007). For a typical U–Th analysis duration of ~20 min, the depth of the analysis crater will thus be a few μm, about one order of magnitude smaller than the lateral resolution of the primary beam spot.

**Secondary ion species** For the analysis of silicate minerals, the abundance of oxide molecular ion species (e.g., ThO$^+$, PaO$^+$, and UO$^+$) is about two to ten times that of the corresponding atomic species at the peak of the energy distribution (typically 10 keV with an energy band-pass of 50 eV). By contrast, Pb isotopes are analyzed as atomic species (Pb$^+$). Mass tables for $^{230}\text{Th}^{\text{–238}}\text{U}$ SIMS analysis of zircon, allanite, or opal thus contain as a minimum the following species: $^{230}\text{ThO}^+$, $^{232}\text{ThO}^+$, and $^{238}\text{UO}^+$. For U–Pb, the key masses of interest are: $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$, $^{208}\text{Pb}^+$, $^{232}\text{Th}^+$ (or $^{232}\text{ThO}^+$), $^{238}\text{U}^+$, and $^{238}\text{UO}^+$. In addition, reference species that relate to stoichiometric components in the target mineral are typically included ($^{7}\text{SiO}_2^+$ for opal, $^{90}\text{ZrO}_4^+$, and/or $^{90}\text{Zr}^{92}\text{ZrO}_4^+$ for zircon). These can be used as a normalizing species to calculate relative sensitivity factors (RSFs) from standards with known concentrations to determine U and Th concentrations in the unknown materials. In addition, these species also serve as reference peaks for magnet-centering for neighboring low intensity U-series peaks. Finally, one or more background mass stations are included which are characteristically 0.04 amu (Maher et al. 2007) to 0.3 amu (Schmitt et al. 2006) to the high mass side of $^{230}\text{ThO}^+$ and $^{231}\text{PaO}^+$ to correct for tailing of the adjacent $^{232}\text{ThO}^+$ peak. For zircon and other accessory minerals with high Th abundances, it is highly advisable also to include a background with mass/charge $= 244.03$ (232-Th$^{12}\text{C}^+$) because of a possible isobaric interference on 246.03 (232-Th$^{12}\text{C}^+$). For opal dating, $^{234}\text{U}^+$ and/or $^{234}\text{UO}^+$ are included in the mass table (Paces et al. 2004, Maher et al. 2007).

**Interferences** Most mass interferences for U-series and Pb-isotope analysis require a mass-resolving power (Δm/m) of ~4000–5000 (Compston et al. 1994). For zircon, interferences result from molecular isobars involving oxides of Si, Zr, heavy rare earth elements and/or Hf (Fig. 5-11). In addition to matrix elements, isobars need to be considered that involve elements present in the conductive coating (e.g., $^{197}\text{AuO}_2\text{H}^+$) or embedding.
material (e.g., $^{232}$Th$^{12}$CO$^2$). The latter interference is particular detrimental to $^{230}$ThO$^+$ analysis, as it is irresolvable at $\Delta m/m < 40,000$. All sources of C (e.g., beam overlap with epoxy, Fig. 5-12) or residual C coating from electron beam imaging thus need to be carefully avoided (Schmitt et al. 2006). Due to low abundances of Th in opal, this interference is likely to be uncritical, but for $^{234}$UO$^+$ analysis, epoxy overlap can cause an interference on mass 250 from production of $^{238}$U$^{12}$C$^+$ (Paces et al. 2004). By contrast, $(^{234}\text{U})/(^{238}\text{U})$ activities for opal calculated from atomic species are not adversely affected from beam overlap onto epoxy (Paces et al. 2004).

**Detection**  Secondary ion intensities for minor isotopes of U, Th, and Pb are measured using electron multipliers that are shielded from scattered charged particles by deflecting the secondary ion beam using electrostatic analyzers. For the CAMECA ims 1270, this results in abundance sensitivities for $^{232}$Th$^{16}$O$^+$ at mass 247 of ~250 ppb (Schmitt 2007). Most studies used peak-switching into a single EM detector, but there is potential for multicollection because it reduces analysis time while maintaining comparable precision to single EM analysis. For high U zircon or high Th minerals such as allanite, secondary ion intensities of major isotopes $^{238}$UO$^+$ and/or $^{232}$ThO$^+$ may require Faraday cup analyses. If multiple detectors are used, correction for differential yields are applied, e.g., by normalizing to an invariant isotopic ratio such as $^{235}$U/$^{238}$U. If this is attempted via measurement of $^{235}$U$^{16}$O$^+$/$^{238}$U$^{16}$O$^+$, interferences such as $^{238}$U$^{12}$CH$^+$ must be absent. EM deadtime corrections are of second order importance due to relative low count rates achieved in U-series isotope analysis.

**Data Analysis**

**Data reduction and representation**  Isotopic fractionation of heavy masses is insignificant in SIMS, and activity ratios such as $(^{230}\text{Th})/(^{232}\text{Th})$ or $(^{234}\text{U})/(^{238}\text{U})$ can be calculated directly from measured intensities after subtraction of backgrounds, and possibly correcting for secondary intensity drift. Inter-element activity ratios require relative sensitivity corrections which are strongly dependent on analytical conditions (e.g., primary beam species, sample charging, energy window analyzed) and composition of the matrix. Consequently, appropriate RSFs need to be determined on compositionally well matched standard materials (see below) for each individual analysis session, preferentially on the same mounts as the unknown materials. RSF calibration for SIMS U–Pb zircon dating that is based on empirical correlations between UO$^+$/U$^+$ or UO$_2^+$/$U^+$ and U–Pb are described in detail elsewhere (e.g., Compston et al. 1984, Stern & Amelin 2003). U–Th fractionation in SIMS is generally much smaller (RSF ~0.9–1.1) compared to U–Pb (zircon RSF ~0.2), and is also largely insensitive to any variations in the production of atomic vs. molecular oxide species. Two approaches of determining the U–Th RSF are used: first, in cases where radiogenic (*) $^{208}\text{Pb}^*$/206$\text{Pb}^*$ can be precisely determined (e.g., for Precambrian zircon such as AS-3, Paces & Miller 1993), true $^{232}\text{Th}^{238}\text{U}$ can be calculated from measured $^{208}\text{Pb}^*$/$^{206}\text{Pb}^*$ and the standard's known age. The RSF is then determined from the ratio of measured Th and U species (e.g., $^{232}\text{ThO}^+$/238UO$^+$) to true $^{232}\text{Th}^{238}\text{U}$ (Reid et al. 1997). The advantage of this method is that it is independent of assumptions for U-series equilibrium in the standard, and the only requirement is that standards are concordant with regard to U–Pb and Th–Pb ages.

A second approach is used when $^{208}\text{Pb}^*$/$^{206}\text{Pb}^*$ cannot be precisely determined (e.g., due to high common Pb of the reference mineral). In this case, RSF is calculated from a measured parent–daughter ratio (e.g., $^{230}\text{ThO}^+$/238UO$^+$) of a secular equilibrium
standard material, multiplying it with the respective decay constants (e.g., Paces et al. 2004, Vazquez & Reid 2004). Schmitt (2007) similarly determined U–Pa RSF by analyzing Miocene Buff Peak high U zircon. By independently calibrating U–Th RSF on AS-3 zircon (see above), it was demonstrated that Buff Peak zircon is in secular equilibrium with regard to \((^{230}\text{Th})/^{238}\text{U})\), and thus equilibrium of the shorter lived \(^{231}\text{Pa}\) daughter could be reasonably assumed (Schmitt 2007).

Quaternary U–Pb data are frequently displayed in the \(207\text{Pb}/206\text{Pb}\) vs. \(238\text{U}/206\text{Pb}\) concordia diagram (Schmitt 2007).  An additional advantage of the \(207\text{Pb}/206\text{Pb}\) vs. \(208\text{Pb}/206\text{Pb}\) diagram (Tera & Wasserburg 1972), an approach pioneered for SIMS data by Baldwin & Ireland (1995). Baldwin & Ireland (1995) regressed data for SIMS data by Baldwin & Ireland (1995). (234U)/(238U) probability diagram (Lowenstern et al. 2000, Fig. 5-13). (230Th)/(238U) activity diagrams are in use for displaying opal results (Fig. 5-13). (234U)/(238U) vs. (230Th)/(232Th) diagram (Figs. 5-8, 5-9, 5-13), or as model ages derived from the two point isochron slope defined by crystal and melt compositions in an age probability diagram (Lowenstern et al. 2000, Fig. 5-13). (234U)/(238U) vs. (230Th)/(232Th) activity diagrams are in use for displaying opal results (Fig. 5-14, Paces et al. 2004, Maher et al. 2007).

Only a few direct comparisons exist between U-series ages of "young" zircon determined by different techniques (TIMS and SIMS). In particular for cases where zircon crystallized over significant age ranges, differences in sampling scale of bulk methods (mg-sized samples for bulk analysis,

**Standards** Ireland & Williams (2003) have summarized the characteristics of the main zircon U–Pb standards in use. Comparatively little work has been done on Quaternary reference zircon, but for Quaternary zircon standards 61.308A and 61.308B, bulk TIMS results (Wiedenbeck et al. 1995) agree well with spatially selective analysis by SIMS (Schmitt et al. 2003a, Fig. 5-7) and laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS, Cocherie et al. 2009). Because RSFs are matrix-dependent, standards and unknowns should be carefully matched by composition. For U–Pb zircon dating, matrix effects have been described for high U zircon (Williams & Hergt 2000), but they are negligible for U–Th fractionation for zircon with UF2 of up to 4 wt.% (Schmitt 2007).

U–Pb zircon standards are also analyzed to check for the accuracy of the \(^{208}\text{Pb}*^{206}\text{Pb}^*\) vs. \(^{230}\text{Th}^{238}\text{U}\) RSF calibration. SIMS analysis of AS-3 standard zircon (1099 Ma, Paces & Miller 1993) and as 91,500 zircon (1065 Ma, Wiedenbeck et al. 1995) yielded unity \(^{230}\text{Th}/^{238}\text{U}\) ratios within uncertainty (e.g., Reid et al. 1997, Schmitt et al. 2006, see also caption to Fig. 5-9). For Th–U RSF calibration on allanite, Vazquez & Reid (2004) analyzed equilibrium allanite from the ~760 ka Bishop Tuff and the 500 ka Middle Toba Tuff.

Fig. 5-13. Comparison between SIMS and TIMS zircon results for Deer Mountain rhyolite (Reid et al. 1997, Heumann et al., 2002). SIMS ages show range which is inconsistent with fitting an isochron (A). Zircon–whole rock model ages are shown in (B) with a probability density curve which indicates protracted, and episodic zircon crystallization between near-eruption and equilibrium ages (Reid et al. 1997).
cumulative ~100s of ng for SIMS, Fig. 5-9) and the bias of SIMS analyses in polished grain mounts towards grain interiors can account for discordant bulk TIMS and U-concentration weighted average SIMS ages (Charlier et al. 2005). For zircon with relative simple crystallization history from Puy de Dome (France), bulk TIMS/α-spectrometry results (12.7 ±1.6 ka 2σ error, Condomines 1997) agree with the U-concentration weighted average SIMS age (14.8 ±2.4 ka 2σ error, Fig. 5-9).

For opal U-series dating, M21277 Virgin Valley uraniferous opal is commonly used as a standard. It is ~2.2 Ma old (207Pb/235Pb age) and has U abundances between ~600 and 1100 ppm (Amelin & Back 2006). It is also shown to be in secular equilibrium with regards to (230Th)/(238U) and (234U)/(238U) (Nemchin et al. 2006). Although opal is structurally and compositionally more variable than zircon (e.g., Amelin & Back 2006), matrix-dependent bias in Th–U fractionation is not documented (e.g., Paces et al. 2004).

**Error assessment** Sources of random analytical error in SIMS include counting errors, RSF uncertainties, primary beam instabilities, surface roughness, or changes in surface conductivity with depth. In addition, potential sources of systematic bias are matrix effects, drift in detector gain, and detector non-linearity. These sources of uncertainty can be monitored through analysis of suitable secondary standards that are prepared and mounted together with the unknown samples. Significant depth-dependent Th–U fractionation is absent, both for zircon and opal, whereas significant fractionation of U–Pb with increasing crater depth occurs during sputtering of opal (e.g., Nemchin et al. 2006). For older crystals, RSF uncertainties (1–2 %, Ireland & Williams 2003) typically dominate, whereas for Quaternary crystals counting errors are prevalent due to low signals. However, if signal intensities are strong (e.g., for chemically separated and enriched bulk samples), SIMS uncertainties <0.5 % are achieved for 236Th/232Th ratios (Layne & Sims 2000).

Zircon ages are generally calculated by linear regression in isochron diagrams such as 207Pb/206Pb vs. 238U/206Pb or (230Th)/(232Th) vs. (238U)/(232Th), where ages are determined from the concordia intercept and slope, respectively. The analytical precision of SIMS is such that in many cases, crystal age heterogeneities can be detected which would otherwise be averaged in bulk analysis. This, however, can result in poor linear regression fits.

Instead of an isochron age for a grain population, individual model ages can be calculated. In cases where model ages show significant spread, the resulting age spectra can be deconvoluted into multiple age components by using mixing algorithms that are based on minimization of error residuals for discrete age populations with Gaussian error distribution (Sambridge & Compston 1994, Fig. 5-8).

For 238U–230Th dating, two point isochrons through melt and crystal compositions can yield
model ages (Fig. 5-13). The caveat in this method is that whole rock or glass $^{238}\text{U}/^{230}\text{Th}$ compositions may be inappropriate if these compositions have been modified since the time of zircon crystallization. This could occur via fractional crystallization (in particular of accessory minerals), assimilation, magma mixing, or assimilation. In such a case, zircon–whole rock or zircon–glass isochron ages could be biased. Heumann et al. (2002) argued that allanite fractionation subsequent to zircon crystallization could lead to systematically older zircon model ages (Fig. 5-15). These effects are, however, generally small compared to uncertainties in the zircon analysis, at least within reasonable bounds for variability of melt compositions.

**Comparison with other in situ techniques**

Only a few studies have explored the potential of in situ U-series analyses using multicollector–laser ablation–inductively coupled plasma–mass spectrometry (MC–LA–ICP–MS). Stirling et al. (2000) used a Plasma 54 multiple collector ICP–MS instrument and demonstrated that ablation using a mixed He–Ar carrier gas significantly reduced U–Th fractionation. Their limitations were relatively large sample sizes (~10 μg) at 150 μm spatial resolution, and U-concentration requirements of >100 ppm (Stirling et al. 2000). Bernal et al. (2005) and Eggins et al. (2005) utilized a Neptune Finnigan MAT equipped with a 193 nm excimer laser and ablation in a He atmosphere. Their glass analyses consumed ~0.5 μg in about 30 s (Bernal et al. 2005). Potter et al. (2005) focused on analysis of low-U carbonates using a Nu Plasma MC–ICP–MS coupled to a 193 nm excimer laser, for which a typical analysis consumes ~70 μg of carbonate.

Aside from Stirling et al. (2000), no other LA–ICP–MS study has reported $^{238}\text{U}/^{230}\text{Th}$ compositions for materials with significant amounts of $^{232}\text{Th}$ such as zircon. Overall, the main advantages of SIMS compared to MC–LA–ICP–MS are higher useful yields for U-series species (typically one order of magnitude, Goldstein & Stirling 2003), smaller sample requirements (about 10 times less for materials with >100 ppm U, Bernal et al. 2005), and lower abundance sensitivities (by ~3-fold, Eggins et al. 2005) which provide a cleaner mass spectrum for the minor $^{230}\text{Th}$ isotope. Longer analysis times are a drawback of SIMS compared to MC–LA–ICP–MS.

![Diagram](image-url)
SELECTED APPLICATIONS

Time scales of magmatic processes

Large volume silicic systems High spatial resolution dating of single zircon crystals opened a fresh perspective on the longstanding problem of how long magmas reside in the crust prior to eruption. Among volcanoes studied, Long Valley caldera has long been recognized as an outstanding type example of an intracontinental magma system that is capable of erupting large volumes of silicic magma in a single caldera-forming event (eruption age ~760 ka, see references in Reid 2008). Long Valley also encompasses end members in the style of crustal volcanism, ranging from small volume pre-caldera and post-caldera rhyolite domes (many <1 km$^3$ in volume) to a cataclysmic explosive event that erupted the voluminous (600 km$^3$) Bishop Tuff. Early studies, which used whole rock and mineral Rb–Sr isochrons and Ar–Ar and Rb–Sr ages from melt inclusion-bearing quartz crystals, inferred long (0.3–1.1 Ma) pre-eruptive magma residence times (e.g., Davies et al. 1994, Van den Bogard & Schirnick 1995, Christensen & Halliday 1996). Reid & Coath (2000) and Simon & Reid (2005) analyzed zircon from Bishop Tuff and demonstrated that on average it formed ~90 ka prior to eruption, with little to no evidence that crystals were carried over from residual magma or plutons pertaining to the pre-caldera episode of rhyolitic volcanism. Short magma residence times of zircon were later corroborated by bulk TIMS analysis of Bishop Tuff.

Early studies, which used whole rock and mineral Rb–Sr isochrons and Ar–Ar and Rb–Sr ages from melt inclusion-bearing quartz crystals, inferred long (0.3–1.1 Ma) pre-eruptive magma residence times (e.g., Davies et al. 1994, Van den Bogard & Schirnick 1995, Christensen & Halliday 1996). Reid & Coath (2000) and Simon & Reid (2005) analyzed zircon from Bishop Tuff and demonstrated that on average it formed ~90 ka prior to eruption, with little to no evidence that crystals were carried over from residual magma or plutons pertaining to the pre-caldera episode of rhyolitic volcanism. Short magma residence times of zircon were later corroborated by bulk TIMS analysis of Bishop Tuff.

Regardless of the possibility of some bias in zircon model ages, SIMS analyses unequivocally reveal protracted zircon crystallization in Deer Mountain rhyolite that otherwise would have gone undetected by bulk analysis techniques.

Basalt-dominated systems To a first order, zircon is an indicator mineral for differentiated melts (Watson & Harrison 1983). Zircon U-series ages thus provide important constraints on the time-scales of magma differentiation. Several case studies have now harnessed the advantages of in situ SIMS to avoid natural or laboratory contaminants for rocks that are intrinsically zircon-poor, and to obtain ages from limited amounts of rock sample such as xenoliths that would potentially yield too few crystals for bulk U-series analysis.

In a study of plutonic xenoliths from Hawaiian volcanoes, Vazquez et al. (2007) determined $^{238}U$–$^{208}Th$ and $^{238}U$–$^{206}Pb$ zircon ages that revealed episodes of differentiated magmatism for the eruptive stratigraphy lack any record. Mafic to intermediate zircon-bearing xenoliths have been investigated from Mount Veniaminof (Aleutian Arc), a volcano surficially dominated by eruption of basalt and basaltic andesite (Bacon et al. 2007). Zircon in miarolitic cavities in diorite xenoliths from Mount Veniaminof are as young as ~5±10 ka and suggest coeval presence of evolved melts capable of explosive eruptions at shallow level and periodic effusive or weakly explosive leakage of fresh basaltic magma recharged from underneath (Bacon et al. 2007). Zircon magma chronology has also been applied to mafic monogenetic volcanoes such as the 12.9 ka Laacher See (Watson & Harrison 1983). Zircon U-series ages from Taupo (New Zealand) presented by Charlier et al. (2005).

For small volume post-caldera rhyolite NW of Long Valley, Reid et al. (1997) documented significant (100s of ka) pre-eruptive zircon crystallization ages. One of these dome lavas, Deer Mountain (Ar–Ar eruption age 101 ±8 ka), yielded zircon model ages that range from as young as ~120 ka with a dominant peak at ~230 ka (Fig. 5-13).

Heumann et al. (2002) presented bulk TIMS data for whole rocks, glass, sanidine, biotite, amphibole, and zircon. While they found that their zircon–whole rock or zircon–glass isochron age was indistinguishable from the SIMS results by Reid et al. (1997), they also noticed that major minerals and glass data did not fall on an isochron. Their interpretation was that the melt composition had been changed due to allanite fractionation (see above, Fig. 5-15), although allanite has not been directly dated, and was only inferred as inclusions in major mineral separates (Heumann et al. 2002). Regardless of the possibility of some bias in zircon model ages, SIMS analyses unequivocally reveal protracted zircon crystallization in Deer Mountain rhyolite that otherwise would have gone undetected by bulk analysis techniques.
isochrons between ~13 ka (eruption age) and ~30 ka (Bourdon et al. 1994). Schmitt (2006) studied zircon from the earliest erupted and most differentiated Laacher See phonolite and documented that (1) most zircon crystals are xenocrystic contaminants in secular equilibrium with Paleozoic to Precambrian U–Pb ages, and (2) a minor population of young (~17 ka) zircon crystals was derived from an isotopically different syenitic magma and scavenged by the phonolite during or shortly before the eruption. These results were interpreted to support rapid (~10 ka) formation of the Laacher See magma chamber, and also to revise protracted basanite–phonolite differentiation timescales of ~100 ka (Bourdon et al. 1994) that were based on closed system $^{230}\text{Th}$-decay despite oxygen isotopic evidence for crustal contamination (Schmitt 2006). New evidence from carbonatitic ejecta (Fig. 5-5) shows that carbonatitic intrusions solidified beneath Laacher See by up to ~20 ka prior to eruption, with no evidence for these shallow magmatic events in the eruptive record of the East Eifel volcanic field.

**Active geothermal reservoirs** U-series dating plays an important role of constraining ages of volcanic or plutonic rocks in magma-driven geothermal reservoirs. Zircon in particular has outstanding chemical and physical stability so that it can yield reliable crystallization ages under conditions of elevated temperatures and intense fluid flow prevailing in active geothermal systems. One of the early case studies was on the Geysers geothermal field (California). Over 400 U–Pb zircon ages from a composite granitic pluton underlying the geothermal reservoir revealed piece-meal emplacement of a sizeable (~300 km$^3$) shallow pluton that intruded between 1.6-1.2 Ma, in part approximately 1 Ma older as previously thought based on Ar–Ar feldspar dating (Schmitt et al. 2003b).

Geothermal wells in the Salton Sea (Imperial County, California) geothermal field penetrated highly altered rhyolitic volcanic rocks at 2–3 km depth and ambient temperatures between ~200–300°C that yielded U–Pb zircon ages of ~400 ka (Schmitt & Hulen 2008). These ages constrain subsidence and sedimentation in the central part of the geothermal field at average rates of 4 mm/a (Schmitt & Hulen 2008). Oxygen isotopic analysis of dated zircon by SIMS revealed that Salton Sea rhyolite and granophyre intrusive rocks have low δ$^{18}$O values between ~3–5‰, suggesting an origin by re-melting of hydrothermally altered basalt (Schmitt & Vazquez 2006, Schmitt & Hulen 2008).

Wilson et al. (2008) used zircon U–Pb age spectra to correlate eruptive units in the subsurface of the Mangakino geothermal field (New Zealand). Comparison between zircon age spectra from surface volcanic rocks with those of hydrothermally altered volcanic rocks from drillholes is a novel tool to determine the host rocks stratigraphy of the geothermal reservoir (Wilson et al. 2008).

**Tephrochronology** Accessory mineral U-series chronology has been successfully applied in Quaternary tephrochronology. For the ~600 ka Rockland tephra, an important stratigraphic marker in western North America, Lanphere et al. (2004) determined near-concordant Ar–Ar plagioclase and U–Pb zircon ion microprobe ages. In many other cases, however, zircon $^{238}\text{U}$–$^{206}\text{Pb}$ or $^{238}\text{U}$–$^{230}\text{Th}$ crystallization ages significantly predate the eruption ages, on average by ~90 ka (Simon et al. 2008).

(U–Th)/He zircon dating is a potentially useful chronometer that records the time of eruptive quenching, in particular for volcanic rocks that lack datable high-K phases such as sandine, or where excess $^{40}$Ar causes problems (Farley et al. 2002). The accuracy of (U–Th)/He ages for young zircon critically depends on the corrections for initial disequilibrium: in the case of zircon, deficits in $^{230}\text{Th}$ can lead to significant underestimation of the eruption age if the crystals were in disequilibrium at the time of eruption (Farley et al. 2002). Under-estimation of the eruption age occurs because six out of eight $^4\text{He}$ nuclei in the $^{238}\text{U}$ decay chain are produced subsequent to the decay of $^{230}\text{Th}$. By measuring the crystallization age, the disequilibrium at the time of eruption can be directly constrained in order to correct (U–Th)/He ages. The first study to apply combined $^{238}\text{U}$–$^{230}\text{Th}$ and (U–Th)/He zircon tephrochronology was on La Virgen tephra, a ~1 km$^3$ deposit which erupted from Tres Virgenes volcano (Baja California, Schmitt et al. 2006). Combined $^{238}\text{U}$–$^{230}\text{Th}$ and (U–Th)/He zircon dating results average 36 ±3 ka. This is significantly older than published $^{14}$C charcoal ages from a distal tephra deposit of ~6.5 ka. The (U–Th)/He zircon age is, however, stratigraphically consistent with a cosmogenic $^3\text{He}$ age for a basalt lava flow that overlies La Virgen tephra. It is suspected that previously dated charcoal is associated with a reworked deposit and thus not reliable for determining the eruption age of La Virgen tephra (Schmitt et al. 2006).
Environmental studies

**Climate change** Hydrogenic minerals that precipitate in rock fractures or cavities from percolating fluids have the potential of recording the duration, source, temperature, and amount of past fluid flow regimes. Pluvial climate conditions result in increased soil moisture, infiltration, and percolation flux that is recorded by pedogenic minerals. SIMS U-series and U-Pb dating places constraints on growth rates of opal in Miocene tuff deposits in western USA at the Yucca Mountain (Nevada) prospective nuclear repository site (Paces et al. 2004, Nemchin et al. 2006). Opal from Yucca Mountain is finely laminated at the micrometre scale, and earlier bulk dissolution TIMS analyses of individual, 0.1–1 mm thick opal hemispheres were limited by the inability to distinguish between a continuous deposition model, or the alternative scenario of episodic precipitation followed by prolonged intervals of non-deposition (Neymark et al. 2004, Paces et al. 2004). U-series dating by SIMS yielded a microstratigraphically consistent age progression that implied comparatively slow average deposition rates of ~0.68 ±0.22 μm/ka over the past ~1 Ma (Paces et al. 2004). These results were further corroborated by sequential microdigestion of opal followed by TIMS U-series dating and results from $^{238}$U–$^{234}$U–$^{206}$Pb SIMS analysis. $^{238}$U–$^{234}$U–$^{206}$Pb SIMS geochronology extended the datable range for Yucca Mountain opal beyond 1 Ma, while at the same time taking advantage of the higher precision of $^{238}$U–$^{234}$U–$^{206}$Pb dating compared to $^{238}$U–$^{230}$Th dating of near-equilibrium opal (Nemchin et al. 2006). The $^{238}$U–$^{206}$Pb ages, once corrected for the effects of ($^{234}$U)/($^{238}$U) disequilibrium, yielded growth rates of ~0.99 ±0.08 μm/ka that agree with the previously determined growth rates from SIMS U-series dating of the same opal hemisphere. In contrast, Late Miocene–Pliocene opal coatings show more rapid growth rates (1 and 5 μm/ka), based on TIMS $^{207}$Pb/$^{235}$U ages (Paces et al. 2004). These results indicate that opal precipitation was quasi-continuous at least during the Late Pleistocene, and that growth rates may have varied throughout Late Miocene to recent times, potentially as a result of climate-driven changes in groundwater percolation.

**Landscape evolution** The environmental and structural history of land surfaces commonly produces a record in authigenic minerals that formed under near-surface conditions in soils or as pebble coatings in alluvium (Maher et al. 2007). In arid and semiarid environments, growth of these authigenic minerals can be slow and episodic, and their composition strongly depends on water flux and compositions (Maher et al. 2007). Moreover, reworking may lead to multiple growth episodes interrupted by protracted periods of non-growth during erosion and transport (Maher et al. 2007). Fine scale (10–100 μm) layering commonly exists in authigenic minerals, and despite advances in microsampling techniques (e.g., by microdrilling or microdigestion methods) for TIMS analysis, the possibility of averaging over growth layers widely disparate in age remains a serious concern during bulk sampling. In contrast, SIMS *in situ* analysis is capable of targeting individual layers at lateral spatial resolution of ~20–30 μm (Fig. 5-14, Maher et al. 2007). By using shortwave UV fluorescence, Maher et al. (2007) were also able to target U-rich layers of opaline silica intergrown with bands of U-poor calcite. Maher et al. (2007) applied this technique to well characterized silica-rich pebble coatings from pedogenic carbonate horizons and opaline silica from spring deposits from western USA, and determined SIMS ages in concordance with previous TIMS results, albeit much faster and requiring less laborious sample preparation. Another advantage of SIMS, besides its *in situ* analysis capability and comparatively rapid analysis, is that the near non-destructive nature of SIMS allows samples to be preserved for further geochronological, geochemical or mineralogical characterization (Maher et al. 2007).

**FUTURE DEVELOPMENTS**

The strength of SIMS in Quaternary geochronology lies in its capability of performing isotopic analysis at high spatial selectivity, coupled with high sensitivity and minimal sample consumption. U-series ultra-trace element analysis at ppb to ppt levels is hampered by detection limitations that result from the small number of U-series atoms present in the analyte volume. The ability to sample ~ng amounts of material in SIMS spot analyses compared to μg–mg amounts consumed by other techniques (TIMS, ICP MS) has its trade-off in low secondary ion signals and concomitant large counting errors. Moreover, SIMS analysis of U-series isotopes in mineral matrices without prior chemical separation imposes requirements of monitoring inter-elemental fractionation by using suitable standards. RSF calibrations for U–Pb are typically reproducible to within ~1–2%, independent of the SIMS instrumentation used.
It remains unresolved how much of this is due to heterogeneity of the reference materials used to monitor elemental fractionation at the sampling scale of the SIMS crater (Ireland & Williams 2003). For Quaternary applications, however, in-run errors resulting from low count rates for short lived U-series isotopes or radiogenic Pb generally out-weigh uncertainties resulting from RSF calibrations.

Multi-collection increases the duty cycle for secondary ion detection because it reduces the waiting time resulting from magnetic field switching and stabilization, and enhances precision due to minimizing the effects of secondary beam variations during analysis. Initial experiments using the UCLA CAMECA ims 1270 in dual EM collection mode yielded \(^{238}\text{U} - ^{230}\text{Th}\) data for equilibrium standards that are equivalent in accuracy and precision to the results from single EM collection, while reducing the analysis duration by \(-30\%\). Increasing sputter rates while maintaining high lateral spatial resolution could also enhance SIMS analytical precision for U-series ages, for example by employing bright ion sources. Alternative primary beam species such as \(\text{O}_2^+\) have been proposed which produce higher sputtering yields, with the caveat that these analyses require careful charge compensation via electron bombardment (Hervig et al. 2006).

Harnessing the unrivalled sub-\(\mu\text{m}\) spatial resolution of SIMS in depth profiling analysis for U-series and U–Pb geochronology is another avenue of great promise (e.g., Fig. 5-6). It has been empirically determined that positive secondary ion intensities remain nearly constant for depths smaller than the lateral diameter of the crater (Hervig et al. 2006). Fortunately, U–Th fractionation is negligible even for sputter crater depths approaching crater diameters, both for opal and zircon. U–Pb fractionation, by contrast, changes significantly with depth and requires an appropriate correction scheme, or frequent regrinding and repolishing of the sample to re-level the bottom of the crater with the surface, if a continuous depth profile is desired.

Sample requirements for SIMS are minimal which results in negligible losses of material so that other types of analysis can be performed on the same crystals or nearby domains in the same materials. This includes analysis of trace elements or stable isotopes for further sample characterization. For Quaternary magmachronology, the recent calibration of the Ti-in-zircon thermometer (Ferry & Watson 2007) allows a combination of age and temperature information to reconstruct the history of magmas. On the other hand, trace element partitioning in accessory minerals remains poorly understood, in particular for the critical elements U and Th. Experimental calibration of trace element partitioning over the entire pressure, temperature, and compositional (including oxygen fugacity) parameter space applicable to magmas is thus required in order to fully utilize the potential of combined geochronology and trace element analysis of accessory minerals. This also holds for the calibration of saturation and diffusion properties of many accessory minerals other than zircon.

A recent study by Maher et al. (2007) has showed that SIMS can date authigenic minerals reliably from a variety of environments. While it remains to be fully explored how widespread U-rich authigenic minerals are outside the arid and semi-arid landscapes of western USA, the value in \textit{in situ} SIMS geochronology for environmental studies is indubitable. As is the case for magmachronologic applications, there is further potential of mating SIMS geochronology with high spatial resolution analysis of other geochemical tracers such as stable isotopes and trace elements.

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