# Past, Present, and Future of Thermochronology

# Peter W. Reiners

Dept. of Geology and Geophysics Yale University New Haven, Connecticut, 06520, U.S.A. peter.reiners@yale.edu

# Todd A. Ehlers

Dept. of Geological Sciences University of Michigan Ann Arbor, Michigan, 48109, U.S.A. tehlers@umich.edu

# Peter K. Zeitler

Dept. of Earth and Environmental Science Lehigh University Bethlehem, Pennsylvania, 18015, U.S.A. peter.zeitler@lehigh.edu

# INTRODUCTION

In one form or another, geochronologists have been practicing thermochronology<sup>1</sup>, the use of radioisotopic dating to constrain thermal histories of rocks and minerals, for over 40 years. Building from lessons learned over these four decades, thermochronology continues to evolve due to technical developments, increasingly sophisticated theoretical models, and an expanding range of applications in geologic and planetary science. Most recently, interest in earth-surface processes and interactions between tectonics, erosion, and climate has drawn attention to techniques that can address the timing and rates of processes operating at temperatures below about 300 °C.

The purpose of this RiMG volume is to assess the current state of thermochronology, as of *circa* 2005, which is, coincidentally, the 100<sup>th</sup> anniversary of the first radioisotopic date (Rutherford 1905; 1906). Excellent review papers and books on specific topics within this field have been published, but no single volume has yet provided a comprehensive review of current practices, basic theory, and illustrative examples. The motivation for this volume stems from these considerations. Knowing that in a fast-developing field a book like this can

<sup>&</sup>lt;sup>1</sup> Several nomenclative conventions have evolved around variations of the term "thermochronology." We consider the following most appropriate: 1) *Thermochronometer*: a radioisotopic system consisting of radioactive parent, radiogenic daughter or crystallographic feature, and the mineral in which they are found. 2) *Thermochronometry*: the analysis, practice, or application of a thermochronometer to understand thermal histories of rocks or minerals. 3) *Thermochronology*: The thermal history of a rock, mineral, or geologic terrane. In practice, however, *thermochronology* is often also used to denote the study of *thermochronology* in which case it is synomymous with *thermochronometry*. The use of the term *thermochronology* in the latter sense is too common and deeply ingrained in the community (and parallel with conventional usage of geochronology), to attempt any corrective usage recommendation (e.g., the title of this book is *Thermochronology*, referring to the study of, not specific, *thermochronologies*).

quickly become dated, we tried to include sufficient review of fundamentals and the literature to offer students and new users a useful introduction to thermochronology that may have some staying power.

In this chapter, we first review the salient points of thermochronology's history before assessing our current capabilities and challenges and then taking the risk of suggesting where the field is headed. We do not provide a comprehensive history of the method that does full justice to the work of the large and growing cohort of thermochronologists. In this short space, we instead opted to give our perspectives on where the intellectual and technological roots of the discipline lie, which run deeper and go back farther than is sometimes appreciated.

# Geochronology vs. thermochronology

Given that all radioisotopic systems are subject to disturbance and resetting at sufficiently high temperatures, it might be surmised that all radioisotopic dating is essentially thermochronology. Distinctions between geo- and thermochronology are indeed often fuzzy, but thermochronology is largely different in several ways. Some phases form or are stable only at temperatures much lower than the closure temperature for the isotopic system of interest (see Harrison and Zeitler 2005), effectively disqualifying them as thermochronometers. Zircon can form or dissolve in felsic magmas at temperatures where Pb diffusion rates are negligibly slow, for example, and in such cases it provides no useful thermal history information. Authigenic phosphates in supergene deposits provide an analogous example at low temperatures.

The nature of thermochronologic and geochronologic questions are also often fundamentally different. The formation age of minerals is typically irrelevant in thermochronology, whereas rates of processes are often of paramount interest. The numerical values of thermochronologic ages across an orogen, for example, may have little to no geologic significance aside from their inverted value in estimating steady-state cooling (and inferred exhumation) rates and their spatial variations. Geochronologic applications, on the other hand, aim exclusively to determine a singular absolute stratigraphic or magmatic formation age, with little direct concern for durations or rates of processes. There are exceptions to these generalizations. Thermochronology can estimate the absolute timing of events, such as bolide impacts or magmatic processes that may only reset low-temperature systems, and geochronology may estimate rates of processes such as evolutionary change or landscape fluvial incision by bracketing formation ages around paleontologic or geomorphic features. Despite this overlap, the bottom line is that thermochronology is distinguished from geochronology by its ability to resolve both temporal and thermal aspects of geologic processes, and thus both timing and rates of processes.

#### HISTORY

#### 1950s and 1960s – development of fundamentals

The field of radioisotopic geochronology is now a century old (e.g., Rutherford 1905, 1906), and the understanding that diffusion is a means of resetting or perturbing ages is not a new idea either (e.g., Hurley 1954 and references therein). In the scientific boom years following the second world war, many ages were measured by an expanding range of techniques. One immediate observation was that many of the ages obtained by different techniques on the same samples did not agree and many were too young to represent formation ages. In general, geochronologists and petrologists were acutely aware that the measurements they were making might be dating processes other than rock formation, with diffusion and thermal resetting being major suspects, although radiation damage was also considered a potential culprit. This can be seen in the work of Patrick Hurley and his interpretations of

previous studies of He retention in a wide variety of minerals (Hurley 1954), in the work of Paul Damon and colleagues on He retentivity in zircon (Damon and Kulp 1957), in examinations of Ar diffusion in various rock-forming minerals (Evernden et al. 1960; Fechtig and Kalbitzer 1966; Musset 1969), and in Richard Armstrong's notion of a "metamorphic veil" (Armstrong 1966). Thermal resetting was also directly or indirectly invoked in a number of early field studies including Mason (1961) and Hurley et al. (1965) on mineral ages near the Alpine Fault, Hart (1964) and Hanson and Gast (1967) in examining suites of mineral ages near contact aureoles, and Westcott (1966), Harper (1967), Jäger et al. (1967), and Dewey and Pankhurst (1970) in interpreting regional suites of mineral ages from orogens.

Although thermal effects on radioisotopic ages were generally recognized, they received little quantitative attention in the early part of the 20th century and throughout the 1950s, as technological developments allowed both the U-Pb and K-Ar method to develop through advances in chemical methods and static gas mass spectrometry. In hindsight, given geochronologists' focus at that time in determining reliable formation ages rather than thermal histories, and given what we now know to be the greater retentivity of minerals for Pb and Ar compared to He, it is clear why these methods became dominant at a time when U-He workers were struggling with ages that were often too young. In any event, this period saw the rapid development of U-Pb and K-Ar dating and the abandonment of the U-He method. Other important technical developments towards the end of this period include the development of fission-track dating of geological materials by Chuck Naeser and Gunther Wagner (e.g., Naeser 1967; Wagner 1968; Naeser and Faul 1969), development of the Ar-Ar method [see McDougall and Harrison (1999) for a full account], and the impetus given to geochemistry by the lunar program.

By the late 1960s, all of the basic techniques that we use today were in fact in existence and most were under active development, with the exception of (U-Th)/He dating, which was seeing only sporadic use. Geochronologists were aware that high temperatures and diffusion could reset ages, they were conducting laboratory and field studies to study this phenomenon, and they were beginning to use mineral ages to constrain orogenic processes. The stage was clearly set for the development of modern thermochronology.

## 1970s - a decade of closure

Three developments in the 1970s were to prove essential to the birth of modern thermochronology. First, E. Jager and colleagues including Gunther Wagner, having accumulated considerable numbers of mineral ages from the Alps, concluded that they were recording the thermal history of the region, and published papers in support of this conclusion (e.g., Purdy and Jäger 1976; Wagner et al. 1977). Further, they used petrological data and petrogenetic grids to assign temperature values to specific isotopic systems. This directly leads to the notion of dating suites of minerals to establish thermal histories. Over the same interval, Chuck Naeser and colleagues were applying the fission-track method to a variety of geological settings of known thermal history such as boreholes and contact aureoles and relating their results to laboratory annealing experiments (Calk and Naeser 1973; Naser and Forbes 1976), and Berger (1975) and Hanson et al. (1975) revisited the studies of Hart (1964) and Hanson and Gast (1965) for K-Ar and Ar-Ar data. Finally and most significantly, in 1973, Martin Dodson published his landmark paper introducing the concept of closure temperature (defined as the temperature of a system at the time given by its apparent age), thereby providing a clear theoretical basis for understanding many mineral ages as cooling ages owing to the interplay between the kinetics of diffusion (or annealing) and accumulation rates in cooling radioisotopic systems (Dodson 1973, 1979; see discussion in Harrison and Zeitler 2005).

#### 1980s - modern thermochronology is born

The first literature use of the word "thermochronology" appears in a paper by Berger and York (1981). By modern thermochronology, we mean the explicit use of kinetic data to interpret suites of isotopic ages in terms of thermal histories. During this period, Andy Gleadow and the Melbourne group pursued improvements in the interpretation of fission-track data, incorporating the use of confined track length data into their kinetic models for apatite data, and developing the notion of the partial annealing zone (PAZ) (Gleadow et al. 1993), which has been adapted to the diffusive context with the notion of the partial retention zone (PRZ) (Baldwin and Lister 1998; Wolf et al. 1998). Concurrently Mark Harrison put Ar-Ar thermochronology on a firm theoretical footing in a series of papers starting with a precocious undergraduate thesis devoted to the cooling history of the Quottoon pluton and extending through a series of contributions spanning his PhD work with Ian McDougall at the Australian National University (e.g., Harrison and Clarke 1979; Harrison et al. 1979, 1985; Harrison and McDougall 1980a,b, 1981, 1982). Martin Dodson extended his ideas about closure to include the notion of closure profiles (Dodson 1986). The end of the decade saw publication of papers which set the stage for the development of the multidomain model for K-feldspar age spectra (Gillespie et al. 1982; Zeitler 1987; Lovera et al. 1989, 1991; Richter et al. 1991), and also a paper on He diffusion in, and (U-Th)/He dating of, apatite (Zeitler et al. 1987) that engendered an appreciation for the potential utility of the method in many geologic applications. Finally, the interval spanning the 1980's some of the first applications of "detrital thermochronology" were attempted (Wagner et al. 1979; Zeitler et al. 1986, Cerveny et al. 1988).

During the 1980s some backlash and confusion developed over the significance of ages from thermally sensitive systems. Dodsonian closure temperatures, which are strictly only relevant for samples that have cooled montonically from high temperature and that have known kinetic properties and diffusion length scales, were often portrayed more like magnetic blocking temperatures; in fact many people at the time (and some still do) used "blocking temperature" to refer to isotopic closure. While the original choice of terms might have been arbitrary, at this point it is important to distinguish between systems with such high activation energies that in effect have a single "off-on" blocking temperature (like remagnetization of single-domain magnetite), and isotopic systems with more modest activation energies which allow both time and temperature to play significant roles in daughter isotope retention or fission-track annealing. The term closure properly serves to remind us that the conceptualization only applies to systems that have closed due to cooling; closure temperature has little to no relevance to interpretations of samples whose ages primarily reflect thermal histories involving reheating or prolonged isothermal stagnation.

Finally, the 1980s saw an increasing number of applied papers using mineral ages to constrain and solve tectonic problems. Most applications focused on quantifying the timing of geologic events such as when faults became active within an orogen, or the timing of exhumation. Many studies also used thermochronometers to estimate rates of tectonic processes (e.g., rates of exhumation) by assuming steady-state 1D thermal gradients and a closure temperatures. The later third of this volume discusses applications of thermochronometers to different settings and summarizes work by many different groups over the last 2 decades.

#### 1990s and 2000s

One of the most important developments in the 1990s was the theoretical maturation of the multidomain model for K-feldspar <sup>40</sup>Ar/<sup>39</sup>Ar age spectra, largely by the group at UCLA, and its application in a large number of regional studies (Harrison et al. 1991, 1993; Fitzgerald and Harrison 1993; Lovera et al. 1993, 1997, 2002). Time-temperature models provided by K-feldspar <sup>40</sup>Ar/<sup>39</sup>Ar methods are in some sense the holy grail of thermochronology in that they provide continuous histories, approximations to which are often the focus of laborious

efforts of multiple thermochronometers providing single ages corresponding (theoretically) to a single temperature. K-feldspar  ${}^{40}$ Ar/ ${}^{39}$ Ar dating continues to attract wide use, as well as occasional theoretical criticism (e.g., Villa 1994; Parsons et al. 1999), the merits of which are debated. Provided certain sample and analytical criteria are met (Lovera et al. 2002), there is as yet no convincing empirical evidence suggesting problems with the theory or application of multidomain K-feldspar  ${}^{40}$ Ar/ ${}^{39}$ Ar thermochronometry (Harrison et al. 2005).

The 1990s also saw the pioneering work of Ken Farley and coworkers in bringing (U-Th)/ He geochronology of apatite and other minerals to become routine measurements capable of exciting new applications (e.g., Farley et al. 1996; Wolf et al. 1996, 1998). Over the same time period, widespread adoption of laser heating for gas extraction (e.g., Kelley et al. 1994; House et al. 2000) and automation in noble-gas laboratories greatly reduced the effort required to obtain data, providing increased throughput, greater quality control, and lower system blanks. From a phenomenological standpoint, it is not clear whether lasers have increased insight into the workings of thermochronometers, as the nature of diffusion boundaries within mineral grains remains cryptic and often smaller and more complex than can be internally sampled using a laser on a routine basis (although there are exceptions in which crystal and domain sizes scale similarly and can be used to model thermal histories; Hess et al. 1993; Hawkins and Bowring 1999; Reiners and Farley 2001). Nevertheless, this area remains a frontier in which there is a great deal of interest and ongoing work.

A potentially promising development in radiogenic He chronometry is reminiscent of the shift from K/Ar to Ar/Ar dating in the 1960s and 70s: the bombardment of samples by high-energy protons to form abundant and homogeneously distributed <sup>3</sup>He provides the opportunity to simultaneously degas <sup>3</sup>He and <sup>4</sup>He and examine, with high precision, the internal distribution of <sup>4</sup>He within crystals (Shuster et al. 2003; Shuster and Farley 2003, 2005). Modeling intradomainal <sup>4</sup>He profiles allows detailed constraints on subtle but critical features of cooling in temperature ranges near and significantly below those of the closure temperature of the system of interest. The method has also been used to date formation of weathering horizons (Shuster et al. 2005).

Another development in this period has been the building of more complex numerical models used for interpretation of thermochronometer data. For example, forward and inverse models of thermochronologic data became available and widely used (e.g., Laslett et al. 1987; Gallagher 1995; Ketcham 1999, 2005; Willett 1997). Furthermore, forward modeling of crustal thermal fields to aid in interpretation of thermochronometer data also became more common. It is worth noting that the influence of topography, erosion, and faulting has long been appreciated in the geothermics community, going back to early publications by Lees (1910), Bullard (1938) and Benfield (1949). Unfortunately, much of the geothermics literature has been under utilized by thermochronologists until work by Parrish (1985) provided a fairly complete analysis of the implications of erosion on geotherms and thermochronometer interpretation.

In the last decade modeling approaches have moved beyond 1D applications to consider the influence of 2D and 3D heat transfer on thermochronometer age interpretation. Recognition in the thermochronology community that thermal gradients in the upper 1–5 km are spatially variable within orogens due to topography, faulting, and other processes has sparked interest in using thermochronometer data to quantify the rates of tectonics and erosional processes. As a results of this interest, thermochronometer data are now increasingly used to constrain thermal-kinematic and geodynamic models of tectonic (e.g., Rahn and Grasemann 1999; Batt et al. 2001; Beaumont et al. 2001; Ehlers 2005), topographic, and erosional processes (e.g., Stuwe et al. 1994; Mancktelow and Grasemann 1997; Ehlers and Farley 2003; Braun 2005). A more thorough discussion and overview of modeling procedures for thermochronometer grain scale and crustal processes are presented in this volume.

# **CURRENT PRACTICE**

At present, by far the most commonly used thermochronometers are  ${}^{40}$ Ar/ ${}^{39}$ Ar in micas and amphiboles (e.g., McDougall and Harrison 1999; Kelley 2002), and in K-feldspar (Harrison et al. 2005), fission-tracks in apatite (e.g., Donelick et al. 2005) and zircon (e.g., Tagami et al. 2005), and (U-Th)/He in apatite (e.g., Farley 2002) and zircon (e.g., Reiners 2005). These techniques have typical closure temperatures ranging from as high as 400–600 °C to as low as 60–70 °C (Table 1). Other thermochronometers used less commonly include fission-tracks in titanite (e.g., Coyle and Wagner 1998), (U-Th)/He in titanite (Reiners and Farley 1999; Stockli and Farley 2004), and monazite (Farley and Stockli 2002), and U/Pb or Th/Pb in monazite (Harrison et al. 2005), apatite (Chamberlain and Bowring 2001), titanite (Schmitz and Bowring 2003), and other phases. Thermochronologic constraints from U/Pb and Th/Pb work on accessory phases is seeing increasing use owing to the greater number of ion probes now available for radioisotopic dating, as well as advances in understanding of Pb diffusion (e.g., Cherniak 1993; Cherniak and Watson 2001) and closure profiles within minerals (Harrison et al. 2005).

Although not a focus of this volume, it is worth noting that the Rb/Sr (e.g., Jenkin et al. 2001), Sm/Nd, and Lu/Hf systems have also seen increasing use as thermochronometers, with the latter two finding increasing use in garnet (Scherer et al. 2001; Ducea et al. 2003) and apatite (Barfod et al. 2002). In general, the Sm/Nd, Lu/Hf, and (U-Th)/Pb systems provide relatively high temperature thermochronologic constraints (>450 °C). Their utility as thermochronometers has been facilitated in part by increased temporal resolution of high-temperature portions of time-temperature paths that have come from both increased precision and numbers of phases dated in the same rocks. The recognition that distinct systems provide ages that are consistently resolvable has helped extend the reach of thermochronology to higher temperatures (e.g., Hawkins and Bowring 1999).

In practice, given the sorts of minerals that yield consistent results and their fairly low closure temperatures, almost all thermochronological studies have been directed at the more felsic rocks of the continental crust. Minerals suitable for dating are also found in meteorites (e.g., Min 2005) and, perhaps more commonly than realized, in oceanic crust (e.g., John et al. 2004), and thermochronometry poses potential for understanding a range of processes in these settings as well.

The various papers in this volume discuss the systematics and kinetics of different mineral systems in more detail, but to provide an overview, Table 1 summarizes the approximate temperature ranges and time-temperature responses of thermochronometer systems commonly used today [also see Hodges (2003) for a more complete summary].

It is beyond the scope of this chapter to explore how well various thermochronometers perform when compared. There has been little if any community effort devoted to controlled comparisons of diffusion measurements or in developing standards to facilitate this. Although laboratories tend to use similar technologies, this is not universally the case, and most thermochronologists know of the pitfalls that can afflict, for example, the accuracy of temperature measurements made using thermocouples or pyrometers. Fortunately, the results from the numerous applied studies that have now been done suggest that to at least first order, we know the relative performance of mineral systems fairly well, as expressed by the closure temperatures listed in Table 1. It is extremely important to understand that the closure temperatures listed in this table serve as a useful shorthand for representing the "retentivity" of a system, but that in the actual case of reheating, these temperatures have little to no significance, the response of the system being a function of both the duration and magnitude of the heating event.

Decay System	Mineral	Approximate precision (%, 1σ)	Closure Temperature (°C)	Energy (kJ/mol)	References
(U-Th)/Pb	zircon	1–2	006<	550	Cherniak and Watson (2001); Cherniak (2001)
	titanite	1–2	550-650	330	Cherniak (1993)
	monazite	1–2	${\sim}700$	590	Cherniak et al. (2004)
	apatite	1–2	425–500	230	Chamberlain and Bowring (2001); Cherniak et al. (1991)
$^{40}{\rm Ar}/^{39}{\rm Ar}$	hornblende	-	400–600	270	Harrison (1981); Dahl (1996)
	biotite	1	350-400	210	Grove and Harrison (1996); Harrison et al. (1985)
	muscovite	1	300–350	180	Robbins (1972); Hames and Bowring (1994)
	K-feldspar	1	150-350	170–210	Foland (1994); Lovera et al. (1991; 1997)
Fission-track	titanite	9	(a) 240–300 (b) 380–420	440-480	<ul><li>(a) Coyle and Wagner (1998);</li><li>(b) Watt and Durrani (1985); Naeser and Faul (1969)</li></ul>
	zircon (a) zero-damage (b) "natural"	amage 6 al"	<ul><li>(a) 330–350</li><li>(b) 230</li></ul>	(a) 300–350 (b) 210	<ul> <li>(a) Tagami et al. (1998); Rahn et al. (2004)</li> <li>(b) Brandon and Vance (1992); Brandon et al. (1998)</li> </ul>
	apatite	8	90-120	190	Laslett et al. (1987); Ketcham et al. (1999)
(U-Th)/He	titanite	3-4	160–220	190	Reiners and Farley (1999)
	zircon	3-4	160-200	170	Reiners et al. (2004)
	apatite	3-4	55-80	140	Farley (2000)

Table 1. Summary of commonly used thermochronometers and features.

At the simplest level, thermochronometric data are used to determine the time-temperature history of a sample (e.g., Ketcham et al. 2005). After a thermal history is determined, numerical or analytical thermal models or simply geologic constraints can be used to interpret the processes responsible. Thermal models can be used to simulate the exhumation, and/or burial, history of the thermochronometric record as a function of geologic processes that are free parameters in the model. In practice, the range of geologic processes simulated in this type of model can be large and encompass geomorphic, faulting, magmatic, thermo-physical (e.g., basal heat flow) and basin evolution processes. Model thermal histories can be compared to observed thermal histories to determine the combinations of model parameters that provide a good fit to the data.

Unfortunately, interpretations of thermochronometric data are seldom unique because different combinations of model parameters (e.g., basal heat flow and erosion rate) can produce an equally good fit to the data. Thus, a rigorous interpretation of a data set usually results in the identification of *the range* of solutions that satisfy the observation rather than a single solution. Unfortunately, all too often studies that attempt to quantify, for example, the kinematic history of a fault fail to report the range of solutions that satisfy a thermochronometric data set.

Most recently, attempts have been made to couple crustal scale thermal models with increasingly complex process based models to better understand rates of landscape evolution, or the dynamics of orogenesis. The coupling of thermal and landform evolution and/or geodynamics models with thermochronometry pushes the utility of thermochronometric data to its limit. Coupled models introduce many more free parameters and require a careful evaluation of these parameters as well as large, carefully sampled data sets to ascertain meaningful results. The next decade will undoubtedly reveal the limit of thermochronometric data to quantify processes such as the evolution of drainage basins and/or couplings between climate and tectonics.

## PROSPECTS

# Existing and emerging techniques and approaches

It is likely that the recent trend towards highly automated sample processing and smaller sample sizes will increase sample throughput from laboratories, and this will be aided by lower costs, (e.g., if inexpensive quadrupole mass spectrometers can be shown to serve adequately for Ar-Ar as well as He work), because if the capital cost of new laboratories were lessened more facilities could be established. Should it reach a sufficient threshold, higher throughput opens the possibility of constructing synoptic data sets for critical portions of orogens, or even of whole orogens themselves. In addition, as interest in detrital thermochronology grows, there will be a great need for increased throughput in order to meet demand.

Work on laser microsampling in <sup>40</sup>Ar/<sup>39</sup>Ar dating has revealed the potential of intracrystalline <sup>40</sup>Ar profiles to reveal details of cooling histories and other powerful constraints (e.g., Kelley and Wartho 2000). The prospect of measuring in-situ <sup>4</sup>He diffusion profiles by laser ablation may also be realized (Hodges and Boyce 2003), though several additional complications will need to overcome including complications posed by combined effects of U-Th heterogeneity and long alpha-stopping distances, as well as attaining sufficient resolution relative to the features in minerals that serve as diffusion pathways. If these hurdles can be overcome, continuous time-temperature histories at the low temperatures accessible by closure profiles in the (U-Th)/He system will be a particularly valuable tool for understanding near-surface processes. Laser profiling in single crystals has also found application in characterization of parent distributions, which can be vital for accurate alpha-ejection corrections in zoned crystals (Hourigan et al. 2005).

The application of standard radioisotopic decay schemes to "new" phases has been a standard source of progress in thermochronometry for some time and may continue to be in the future, because of the unique thermal sensitivity and natural occurrence patterns of each mineral. Specific systems that have shown particular promise recently include <sup>40</sup>Ar/<sup>39</sup>Ar and <sup>4</sup>He/<sup>3</sup>He thermochronometry of supergene weathering deposits (Vasconcelos 1999; Shuster et al. 2005). Development of thermochronometers with temperature sensitivities lower than that of apatite (U-Th)/He may prove powerful in some circumstances such as subsurface weathering profiles and submarine samples, but such sensitivities may also make the systems susceptible to diurnal heating or other surficial temperature fluctuations, restricting their application to certain settings. On the other hand, the sensitivity of low-temperature thermochronometers, and especially the contrasting kinetic responses of different systems, to surficial (or very nearly surficial) thermal processes, may prove valuable in understanding such phenomena if strategically applied (Mitchell and Reiners 2003; Shuster et al. 2005).

Combining multiple thermochronometers in the same samples to increase the temperature range of thermal histories is fairly common, but few examples exist of combinations of thermochronometers with electron-spin-resonance, thermoluminescence, or cosmogenic nuclide analyses that constrain rates and timing of exposure. Comparisons of erosion rates from steady-state interpretations of bedrock thermochronometric ages and both in situ and basin-scale (stream sediment sample) cosmogenic nuclide abundances have been made in several cases, often with intriguingly different erosion rate estimates over the contrasting timescales of each system (e.g., Kirchner et al. 2001; Vance et al. 2003; Stock et al. 2004). But another approach that may hold potential for understanding surface processes is measuring cosmogenic and radiogenic (and in some cases nucleogenic) abundances in the same crystals. Possible examples include <sup>4</sup>He, <sup>3</sup>He, and Ne isotopes in detrital zircons or supergene weathering deposits, to determine relationships between formation, thermochronologic, and exposure ages.

Thermochronology of detrital minerals has been used since the mid-late 1980s to constrain provenance and thermal histories of source terrains (e.g., Cerveny et al. 1988; Brandon and Vance 1992; Garver and Brandon 1994). Several new approaches have emerged recently that hold promise. One is modeling of observed probability density functions of many detrital <sup>40</sup>Ar/<sup>39</sup>Ar grains ages from alluvium from a drainage basin, using predictions of various tectonic models combined with the basin's hypsometry (Hodges et al. 2005). While this or similar approaches have been used with zircon fission-track dating for some time, its application in detrital <sup>40</sup>Ar/<sup>39</sup>Ar methods has been one of the fruits of vast improvements in automation and sample throughput, and once again demonstrates that in as is often the case in thermochronology, quantity has a quality all its own. Another advance in detrital thermochronology is measurement of both formation (U/Pb) and cooling ages [(U-Th)/He and/or FT] in single zircons, providing improved resolution of provenance, depositional ages, and long-term orogenic histories of source terrains (e.g., Rahl et al. 2003; Reiners et al. 2005).

# Kinetics, partitioning, and other fundamentals

There are still many important unresolved issues associated with the fundamental kinetics and systematics of diffusion and annealing that to some degree limit the robustness of interpretations from thermochronology. Fission-track annealing models remain vigorously debated, especially how realistically various models capture the dynamics of long-time, low-temperature annealing that is characteristic of many slowly-cooled terrains (e.g., Ketcham et al. 1999). The precise causes of annealing kinetic variations caused by composition, radiation damage, and other effects is still somewhat primitive. The potential effects of pressure on track stability have also been recently debated (Wendt et al. 2001; Kohn et al. 2002; Vidal et al. 2002). With some exceptions, fission-track annealing is generally regarded as sufficiently complex that calibrations are largely empirical and do not seek quantitative modeling of the

mechanistic atomic scale processes that lead to annealing. Better understanding of the atomicscale processes controlling annealing may be an area of fruitful progress.

Helium diffusion in commonly dated phases also bears several poorly understood and enigmatic phenomenon such as the >280 °C "rollover" in apatite diffusion experiments (Farley 2000, 2002), and the anomalously high (compared with later stages) rates of He diffusion observed in early stages of step heating experiments in zircon (Reiners et al. 2004), titanite (Reiners and Farley 1999), and possibly other minerals (Stockli and Farley 2002). Changes in He diffusion properties at high temperature are generally considered irrelevant to retention during cooling through lower temperatures where ages actually evolve (Farley 2000), and the anomalously high He diffusivity observed at small gas fractions during experiments can be modeled as minor amounts of gas residing in low-retentivity domains which do not significantly affect the bulk crystal's thermochronometric properties (e.g., Reiners et al. 2004). Nevertheless, it is possible that these and other poorly understood non-Arrhenius phenomena may turn out to be more important than currently realized.

Other potentially important but as yet poorly understood aspects of He diffusion that may have broader implications are crystallographic anisotropy in diffusion characteristics (Farley 2000), and the fact that <sup>3</sup>He and <sup>4</sup>He appear to diffuse from apatite at essentially the same rate (Shuster et al. 2003), rather than with the inverse-root-mass dependence expected from kinetic theory. Shuster et al. (2003) suggested that a possible reason may be that movement of He is actually limited by diffusion of crystallographic defects, not the intrinsic diffusion properties of He atoms. If this is true, it raises questions about what other features of noble gas diffusion phenomena may actually be proxies for migration of crystallographic or impurity defects in minerals and how this may affect thermochronologic interpretations.

Radiation damage has long been recognized as affecting diffusion and annealing properties that control thermochronometric systems. The effects of radiation damage on annealing and diffusion are generally most evident in zircon (e.g., Hurley 1954; Nasdala et al. 2004; Rahn et al. 2004; Reiners et al. 2004; Garver et al. 2005), partly because of the high activation barrier to annealing and high U-Th concentrations. Although quantitative understanding of these effects is relatively primitive, there is potential that in certain cases, the effects of radiation damage could be used to an advantage, by essentially providing a range of thermal sensitivities similar to multi-domain behavior in a single sample (Garver et al. 2005).

Finally, there is growing recognition of the potential importance of equilibrium partitioning of noble gases into minerals, and the relationship between this and assumptions of zero-concentration boundaries and infinite reservoirs surrounding minerals of thermochronologic interest. Baxter (2003) has reformulated some of the basic theoretical constructs of noble gas chronometers to effectively explore the relationships between "excess" Ar or He, and the efficiency with which these gases can be transported away from minerals in which they were produced during cooling and closure. Examples in recent literature of  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  ages that make little to no sense in terms of closure temperatures and classic Dodsonian theory (Kelley and Wartho 2000; Baxter et al. 2002), show that "excess" Ar can be quantitatively interpreted to provide important insights into Ar mobility, partitioning, and geologic processes. A firmer understanding of the significance and potential utility of "excess" Ar or He awaits clever experimentation, theoretical investigations, and natural examples consistent with predictions.

# Quantitative interpretations of data with numerical models

In the last decade significant advances have been made in coupling thermochronometric data with numerical models to interpret topographic, erosional, and tectonic histories of orogens. The future will likely follow this trend as computing power continues to be faster, better, and cheaper and the source code for simulating different geologic processes matures.

The development and dissemination of more powerful computer models will most likely require larger data sets and carefully planned sampling strategies to optimize the signal of interest.

A variety of computer programs are currently available for quantifying different aspects of the thermochronometric record of exhumation processes. For example, forward and inverse programs for predicting apatite fission track ages and track lengths and (U-Th)/He ages a function of temperature histories are freely available (e.g., Ehlers et al. 2003; Ketcham 2005; Dunai 2005). 2D and 3D thermal-kinematic, and 2D dynamic models of orogenesis have been successfully used to interpret thermochronometer data (e.g., Batt and Braun 1997; Batt et al. 2001; Beaumont et al. 2001; Ehlers et al. 2003; Braun 2005; Braun and Robert 2005). Several different landform evolution models are also in use to study long-term landscape evolution as a function of hillslope and fluvial processes (e.g., Braun and Sambridge 1997; Ellis et al. 1999). However, with the exception of recent work by Braun (2005), few attempts have been made so far to couple all of the previous types of models into one comprehensive tool for thermochronometric analysis. Future prospects for model intensive interpretations of thermochronometric data clearly include the development and dissemination of refined coupled landform evolution and thermal models, as well as creative applications of these models to multiple thermochronometric systems. The development of more complex numerical models will also allow additional rigor in data analysis because non-uniqueness in interpretations and more complete propagation of uncertainties can be more easily explored.

Inevitably, the increased complexity of numerical and geodynamic models for predicting and interpreting thermochronometric datasets make their routine application somewhat difficult. Historically, thermal and geodynamic modeling have often been fields of study to themselves because of the extensive time and training required to learn and practice modeling that is both geologically useful and sufficiently sophisticated to advance the field. Similarly, collection of thermochronometric data requires unique skills and time investments as well. Much of the future in creative applications of thermochronology will likely rely on either the training of students with interdisciplinary skills (e.g., data collection and programming and modeling) and/or expansion of symbiotic collaborations between modelers and analysts.

#### General comments on the future of thermochronology

There are challenges facing thermochronology, some of which will undoubtedly lead in surprising directions. But we suggest that many if not most of these apparent unresolved issues or outstanding problems will eventually bear fruits that expand and strengthen the field. In some ways, thermochronology is the inevitable outgrowth of the empirical and theoretical maturation of geochronology in general, as it also dealt with challenging issues. As datasets from various radioisotopic systems grew in quality and quantity, complications that once confounded explanation (such as intra- and inter-method age discrepancies or inconsistent experimental diffusion results) have, through hard-won quantitative understanding of kinetic properties, been transformed into powerful tools for piecing together detailed thermal histories. It is in this lemons-to-lemonade context that we mention several challenges we see facing thermochronology today, which could be important in the next forty years of the fields' evolution.

In general one of the greatest needs in thermochronology is better quantitative understanding of the kinetics of diffusion (and annealing), especially from experimental approaches. There are many important limitations to our understanding of Ar and He diffusion in many phases, and not nearly as many attempts to resolve these issues by direct experiments as there are applications with heuristic assumptions and attempted empirical "calibrations". Particularly important in this regard would be development of routine ways of measuring kinetic data directly on unknowns, rather than assuming all samples are the same, as is done for many types of minerals. Kinetic variations among specimens of the same mineral and strategic exploitation of these properties in sampling and analyses may in fact lead to great

advances in understanding kinetic mechanisms and controls in general, not to mention more detailed and accurate thermal histories. A related challenge that is more specific to (U-Th)/He dating is the need for agreed-upon, cost-effective, and reliable protocols for treating alpha-ejection and U-Th zonation on grain-by-grain bases.

Much thermochronologic interpretation assumes that daughter nuclides diffuse simply across zero-concentration grain boundaries into an infinite-sink reservoir. Whereas this idealized model has allowed a great deal of progress in interpreting noble gas thermochronometry, there are some natural examples that could be interpreted as evidence for violations of this behavior. Better theoretical and experimental understanding of the phenomena of excess Ar and He like those of Baxter (2003) may improve the robustness of thermochronologic interpretations in some cases. A better quantitative understanding of these issues may in fact provide important thermochronologic interpretations in unexpected areas (e.g., Kelley and Wartho 2001).

Another issue is the inherent uncertainty involved in inferring exhumational histories from thermal histories. One of the reasons for increasing interest in thermochronology in the last decade is the prospect of bringing radioisotopic dating techniques to bear on nearsurface crustal processes, especially those constraining erosional exhumation. Even if the thermal histories themselves bore no uncertainty, inferring exhumation histories from them requires assumptions about geothermal gradients and their variations in space and time. These assumptions and their uncertainty range widely in complexity depending on the problem being addressed, but often involve spatial and temporal transients in exhumation rates, topography, fluid circulation, and deep-derived (basal) heat flow. Some of the currently most exciting issues such as evolution of paleotopography and erosion rates on  $10^{5}$ - $10^{6}$  yr scales may rely on assumptions that are difficult to test or require extensive integration of other data sets such as heat flow or hydrologic data to constrain models. In many cases, convincing arguments can be made that the essential aspects of interpretations are insensitive to some of these assumptions. But in others, uncertainties such as how groundwater circulation patterns affect the thermal field at depths less than 2–3 km (especially in regions of high topographic relief, e.g., Ehlers 2005), or how magmatic events that may produce little surface expression affect thermal fields to greater depths, are difficult to constrain. At least some of these issues may be addressed by focused high-density sampling of currently active orogens, structures, or topographic features. If groundwater flow significantly deflects isotherms in the uppermost 2–3 km of high relief areas, for example, a careful heat-flow, hydrologic, and thermochronologic study could illuminate the details. Non-uniqueness in interpretations is not new to the Earth sciences, and thermochronologists and modelers can address uncertainties in interpretations by reporting the range of processes and solutions that satisfy a set of observations rather than looking for a single solution.

A general issue facing thermochronology is the problem of nonmonotonic thermal histories. It is generally acknowledged that while most datasets do not uniquely constrain model thermal histories, when data from enough different systems or high-quality multi-domain or closure profile data are available, a range of thermal histories emerges that is commonly sufficiently small to be geologically useful. It may be generally underappreciated, however, that many models often focus on solutions assuming monotonic cooling. When nonmonotonic cooling histories are allowed, it is often more difficult to find a family of thermal histories with a restricted enough range to be useful (e.g., Quidelleur et al. 1997; McDougall and Harrison 1999; Lovera et al. 2002). This is explicitly recognized in most formal inversions of fission-track age and length data, as well as multi-domain <sup>40</sup>Ar/<sup>39</sup>Ar K-feldspar cooling models, but many casual users fail to recognize the importance or limitations of this assumption. Thermal histories from multiple thermochronometers with certain shapes (e.g., concave down, followed by concave up) may be consistent with simplified expectations of reheating, but they are not diagnostic (e.g., Harrison et al. 1979). In this respect, fission-track dating bears a distinct advantage

over noble gas methods, because track-length analysis allows resolution of distinct thermal histories for tracks for different ages. Nonetheless, realistic modeling of age and track-length data for thermal histories involving reheating is often subject to considerable uncertainty (e.g., Ketcham 2003, 2005). Ultimately, geologic considerations may provide critically important information in considering non-monotonic thermal histories, but development of techniques for diagnosing reheating from thermochronologic data alone may be an important goal for future studies. One potential tack may be to use contrasting responses of thermochronometers with strongly varying activation energies. Extremely short duration (1–100 yr) and relatively high temperature reheating events, for example, can produce diagnostic age inversions in fission-track and (U-Th)/He ages in the same minerals, because of their distinct kinetics.

Finally, compared with some disciplines in geophysics and geodesy (e.g., IRIS or UNAVCO), the thermochronological community is not particularly cohesive at the moment and there has been little formal effort to improve shared resources or improve the access to thermochronological data. There are considerable historical reasons for the current culture of each thermochronologist having their own facility and their own protocols. However, we suggest that the time may have come to consider development of a community-wide vision for sharing facilities to help support and encourage comprehensive regional studies. As we outlined earlier and as is discussed elsewhere in this volume (e.g., Ehlers 2005), the demand for large datasets will increase, given intellectual developments driven by modeling, the growing focus on low-temperature systems much affected by complex high-frequency boundary conditions (Braun 2005), intense interest in detrital thermochronology, and analytical demands stemming from community initiatives like Earthscope's USArrray and the Plate Boundary Observatory. These sorts of demands may completely overwhelm the capabilities of a single laboratory, and both cooperative work among laboratories and development of new high-throughput facilities will be required. We suggest that thermochronologists might benefit from pursuing a grander vision. There are important problems in geodynamics that could be solvable given high-enough sampling densities that, while a far stretch for current analytical capacity, are not economically out of reach, even today-investigators are often successful in procuring funds for seismic lines costing millions of dollars, a sum that could support tens of thousands of mineral ages, even using current systems not optimized for analytical throughput.

The future of thermochronology is bright. Intense interest in understanding near-surface processes and links between tectonics, erosion, and climate will continue to motivate advances in a number of areas that should increase the resolution and accuracy of thermochronologic models. New thermochronometeric systems are being developed that will expand accessible temperature ranges, better models of crystal-scale kinetic processes are clarifying age and thermal history interpretations, and analytical innovations will likely soon permit generation of large datasets that can invert for thermal histories of entire drainage basins or orogens, or provide routine closure profiles in single crystals. Improved geodynamic and surface process models will also undoubtedly allow increasingly sophisticated interpretations of tectonogeomorphic evolution. Motivated by exciting problems linking geologic processes such as tectonics, erosion, and climate, the next few decades will undoubtedly witness ingenious innovations and development of powerful analytical, interpretational, and modeling approaches that rival the progress and changes in radioisotopic dating in the last hundred years.

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