

Significant Ages—An Introduction to Petrochronology

Martin Engi and Pierre Lanari

*Institute of Geological Sciences
University of Bern
Baltzerstrasse 3
3012 Bern
Switzerland
engi@geo.unibe.ch
pierre.lanari@geo.unibe.ch*

Matthew J. Kohn

*Department of Geosciences
Boise State University
Boise, Idaho, 83725
U.S.A.
mattkohn@boisestate.edu*

INTRODUCTION AND SCOPE

Question: Why “Petrochronology”? Why add another term to an already cluttered scientific lexicon?

Answer: Because petrologists and geochronologists need a term that describes the unique, distinctive way in which they apply geochronology to the study of igneous and metamorphic processes. Other terms just won’t do.

Such evolution of language is natural and well-established. For instance, “Geochronology” was originally coined during the waning stages of the great Age-of-the-Earth debate as a means of distinguishing timescales relevant to Earth processes from timescales relevant to humans (Williams 1893). Eighty-eight years later, Berger and York (1981) coined the term “Thermochronology,” which has evolved as a branch of geochronology aimed at constraining thermal histories of rocks, where (typically) the thermally activated diffusive loss of a radiogenic daughter governs the ages we measure. Thermochronology may now be distinguished from “plain vanilla” geochronology, whose limited purpose, in the words of Reiners et al. (2005), is “...exclusively to determine a singular absolute stratigraphic or magmatic [or metamorphic] formation age, with little concern for durations or rates of processes” that give rise to these rocks.

Neither of these terms describes what petrologists do with chronologic data. A single date is virtually useless in understanding the protracted history of magma crystallization or metamorphic pressure–temperature evolution. And we are not simply interested in thermal histories, but in chemical and baric evolution as well. Rather, we petrologists and geochronologists strive to understand rock-forming processes, and the rates at which they occur, by integrating numerous ages into the petrologic evolution of a rock. It is within this context that a new discipline, termed “Petrochronology”, has emerged¹. In some sense petrochronology may be considered the sister of thermochronology: petrochronology typically focuses on the processes leading up

¹ Several parts of this introduction are taken from a discussion that took place in the forum GEO-METAMORPHISM in June, 2013.

to the formation of igneous and metamorphic rocks—the minerals and textures we observe and the processes that formed them—whereas thermochronology emphasizes cooling processes in the wake of igneous, metamorphic, and tectonic events. Typically petrochronology is “hot”, thermochronology is “cold”. While each field has its unique features, and while their disciplinary boundaries overlap, each complements the other.

Any rock sample we study, whether igneous, sedimentary, or metamorphic, results from the transformation of one or more previous rocks. Petrologists and geochemists have found that such transformation rarely erases a rock’s memory completely, instead most samples contain relics from more than one stage of their evolution. Whether and how these affect an age determination is essentially a question of resolution—both spatial and chronometric—i.e., of isotopic and chemical analysis. Analytical efforts in petrochronology typically find that several stages or generations of mineral formation are evident in any single rock sample, in which case we conclude that such a rock does not have, *sensu stricto*, one age.

In fact, one is led to wonder what the term “age” may signify in everyday geologic usage. It might seem clear what is meant, for example, by the age of a basaltic lava flow: the time of deposition or solidification. But what is the age of a meta-basalt? Does it refer to the point on the prograde path when its mineralogy and texture would define it as “metamorphic”, and no longer igneous? The pressure peak? The maximum temperature? The point on the retrograde path where mineralogy and chemistry no longer change measurably? And by what methods can that singular metamorphic age be measured? Actually, defining “an” age of a volcanic rock presents its own problems. How do we choose among the ages of initial melting, magma movement or rejuvenation, crystallization of antecrysts and duration of residence in a magma chamber, eruption, or solidification? And what does an age mean for a clastic rock, where each grain may have a slightly different parent, and materials may be reworked. The concept of “an age” really makes sense only within a defined petrogenetic context.

This recognition leads us to a practical definition: Petrochronology is the branch of Earth science that is based on the study of rock samples and that links time (i.e., ages or duration) with specific rock-forming processes and their physical conditions. Petrochronology is founded in petrology and geochemistry, which define a petrogenetic context or delimit a specific process, to which chronometric data are then linked.

SIGNIFICANCE OF AGE DATA

Chronometers essentially rely on the behavior of specific elements, more specifically of ions or isotopes, in a mineral (or group of minerals) chosen for dating. To assess chronometric data, two criteria need to be combined: transport properties (diffusivity), and analytical quality. Diffusion of the elements relevant to the chronometric system in the chosen mineral, say Pb in zircon or Ar in feldspar, sets basic limits on how a chronometer can be applied and what meaning the age data have: Where diffusion is relatively fast, the age of a mineral refers to the time when radiogenic daughter material started to accumulate in that mineral. Such systems are used for *thermochronology*, and the resulting *cooling age* specifies the amount of time that mineral has remained below a particular temperature, called the *closure temperature* (T_c). This age will correspond to the time of formation only if that mineral crystallized (and remained) at temperatures below T_c or was somehow shielded from diffusive loss of the daughter isotope. By contrast, in systems where diffusion is extremely slow, commonly for the U–Pb, Th–Pb, Lu–Hf, or Sm–Nd decay systems, minerals remain closed up to high temperature, and radioisotopic dating commonly returns *formation ages*, i.e., the time of crystallization. For igneous rocks, this may reflect a pulse of crystallization, catalyzed by transport or degassing events or possibly related to magma recharge. For metamorphic rocks, it may represent a particular mineral reaction, an event of fluid infiltration, or deformation-induced recrystallization.

Typically, spatially resolved age data are combined with compositional data of accessory and/or major phases to recover specific P - T - t or T - t points and paths. In many cases, data for individual growth zones of minerals are required and/or several chronometers are combined to secure the interpretation. Although we commonly focus on collecting ages with high spatial and chronologic resolution, it is not actually the age that matters most to geologic investigations but rather the process itself and our ability to characterize rates.

Chronologic quality is a delicate subject in petrochronology because analytical accuracy and the behavior of elements involved in the system used are both important, and element behavior is difficult to quantify. Traditionally the quality of an age determination, say for garnet using the Sm-Nd system, focused on the MSWD or statistical likelihood that all data conform to a single crystallization event. Today, in part through vastly improved analytical capabilities, we recognize that protracted growth of garnet should *rarely* produce a good MSWD (Kohn 2009). Our ability to measure age differences among different growth zones means that data scatter *should* nearly always exceed analytical uncertainties. While this failure of traditional tests of chronologic significance might undermine some past investigations (there is no single age that we can assign to such a garnet), it opens a vast new spectrum of scientific inquiry related to the growth dynamics of minerals, and consequently the processes that drive mineral growth. So, instead of asking what the age of a pluton is, we might instead ask how rapid is magma transport, what catalyzes degassing and consequent melt crystallization, and how these are related to magma recharge. Similarly, in metamorphic petrology and tectonics, we can now ask how rapid was heating/cooling or burial/exhumation, how are these related to thrusting or extensional processes, and what does this history imply about large-scale deformation of the crust? Addressing these types of questions means that a mineral age must be linked to some other petrogenetic indicator, whether it be other associated minerals of petrogenetic or textural significance, major element chemistry, trace element patterns, or independently estimated temperature or pressure.

PETRO-CHRONO-LOGICAL APPROACH AND AMBITION

A basic and generic petrochronological approach may be formulated in five steps:

1. Identify one or more specific stage(s) of the metamorphic, magmatic and/or structural evolution in a given sample based on textural criteria such as overgrowths, inclusions, fabric alignments, etc. In deformed rocks, it is helpful and often necessary to work with oriented samples and sections, such that fabric characteristics of local assemblages can be related to observed fabrics in hand specimens and to meso- to megascopic observations.
2. Document the phase relations among minerals based on images and compositions as determined using electron beam methods (scanning electron microscopy: SEM; electron probe micro-analysis: EPMA), laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and/or secondary ion mass spectrometry (SIMS) analysis.
3. Attempt to relate one or more specific growth zones of a suitable robust chronometer (e.g., U-Pb, Th-Pb, Lu-Hf, Sm-Nd) to each stage. This step often requires support from trace element data to verify coexistence.
4. Use thermobarometric techniques such as multi-equilibrium, isochemical phase diagrams², Thermoba-Raman-try, and empirical thermobarometry to constrain the Pressure-temperature (P - T) conditions of local equilibria.
5. If steps 1-4 were successful, use a microdating technique to analyze the isotopic ratios in each suitably large growth zone. This can be done by *in situ* analysis or microdrilling for ID-TIMS.

² Also known as "pseudosections", but this term may be misunderstood. Spear FS, Pattison DRM, Cheney JT (2016) The metamorphism of metamorphic petrology. Geological Society of America Special Papers 523 doi:10.1130/2016.2523(02)

Several research groups have applied this type of approach. Ambitious applications have attempted to reconstruct pressure–temperature–deformation–time (P – T – D – t) paths in units that experienced a complex tectono-metamorphic evolution. As an example of the potential of petrochronology, it is instructive to summarize results obtained for a specific area, the Dora Maira terrane in the Western Italian Alps. A variety of techniques have helped elucidate its evolution, with implications for other fields, from tectonic modeling to experimental petrology.

An example: P – T – t path for geodynamic and tectonic modeling

Prescient researchers realized long ago that P – T – t paths of rocks from different structural positions in an orogenic belt can constrain models of large-scale tectonic processes (Thompson and England 1984; Shi and Wang 1987). Theoretical P – T – t paths from numerical models started appearing before they could be reconstructed from rock samples. Numerical models were first restricted to one-dimension problems (Oxburgh and Turcotte 1974; England and Thompson 1984), but they rapidly evolved to complex geometry in two-dimensions (Peacock 1990; Ruppel and Hodges 1994). At the dawn of the 21st century, dynamic thermo-mechanical models were developed and intensively used to predict theoretical P – T – D – t trajectories of rock units involved in various scenarios of subduction and collision zones (e.g., Beaumont et al. 2001; Gerya et al. 2002; van Keken et al. 2002, and many others inspired by these). While much progress has been made since then in investigating geodynamic processes by means of numerical models (Gerya 2011 and references therein), stark differences occur between many model P – T – t trajectories and the natural record, especially for continental collisions (Kohn 2008) and for prograde subduction paths at pressures below 2 GPa (Penniston-Dorland et al. 2015).

An excellent example of how P – T – D – t paths may be determined from the study of specific samples comes for the ultra-high pressure (UHP) slice of Dora-Maira located in the Western Alps of Italy. This massif is renowned as one of two localities where coesite inclusions were first discovered in continental rocks, specifically in garnet porphyroblasts (Chopin 1984). As shown in Figure 1, this terrain now sports one of the best constrained P – T – D – t paths for a UHP continental fragment in the world. Detailed field studies of the Dora-Maira UHP slice document it as a coherent piece of continental crust (1 km thick, exposed over 10 by 5 km), composed of granitic gneiss with intercalated (K- or Na-bearing) whiteschists, metabasites (calcsilicate eclogites and eclogite boudins), and marbles (Vialon 1966; Chopin et al. 1991). Several studies have demonstrated that this tectonic slice was subducted to depths greater than ~100 km during the early stages of Alpine collision (e.g., Chopin et al. 1991; Chopin and Schertl 1999; Rubatto and Hermann 2001; Hermann 2003). P – T conditions based on several prograde and retrograde reactions and local assemblages were derived using thermodynamic modeling of phase equilibria for various rock types (Fig. 1). In addition, Hermann (2003) compared the observed phase assemblages and compositions in K-bearing whiteschists with experimentally determined petrogenetic grids and calibrated fluid-absent equilibria, which reduced uncertainties in P – T conditions. Dating of accessory minerals included zircon, monazite, and rutile, with results delimiting a restricted time span of 3.2 Ma for the UHP event (e.g., Gebauer et al. 1997; Rubatto and Hermann 2001; Gauthiez-Putallaz et al. 2016). The vertical burial and exhumation rates for Dora Maira are >3.5 to 4 cm/yr, much faster than the subduction rate expected from the horizontal velocity of 1.5 cm/yr inferred by plate motion paths (Handy et al. 2010). The tightly constrained petrochronologic datasets for this terrane have triggered the curiosity and imagination of modelers who are keen on understanding geodynamic processes. So far, most of the available thermo-mechanical models predict both lower peak temperatures and much lower burial and exhumation rates (e.g., Fig. 7 in Yamato et al. 2008). The lower temperatures may reflect the neglect of frictional heating or heat advection from fluids in the numerical experiments (Yamato et al. 2008; Penniston-Dorland et al. 2015).

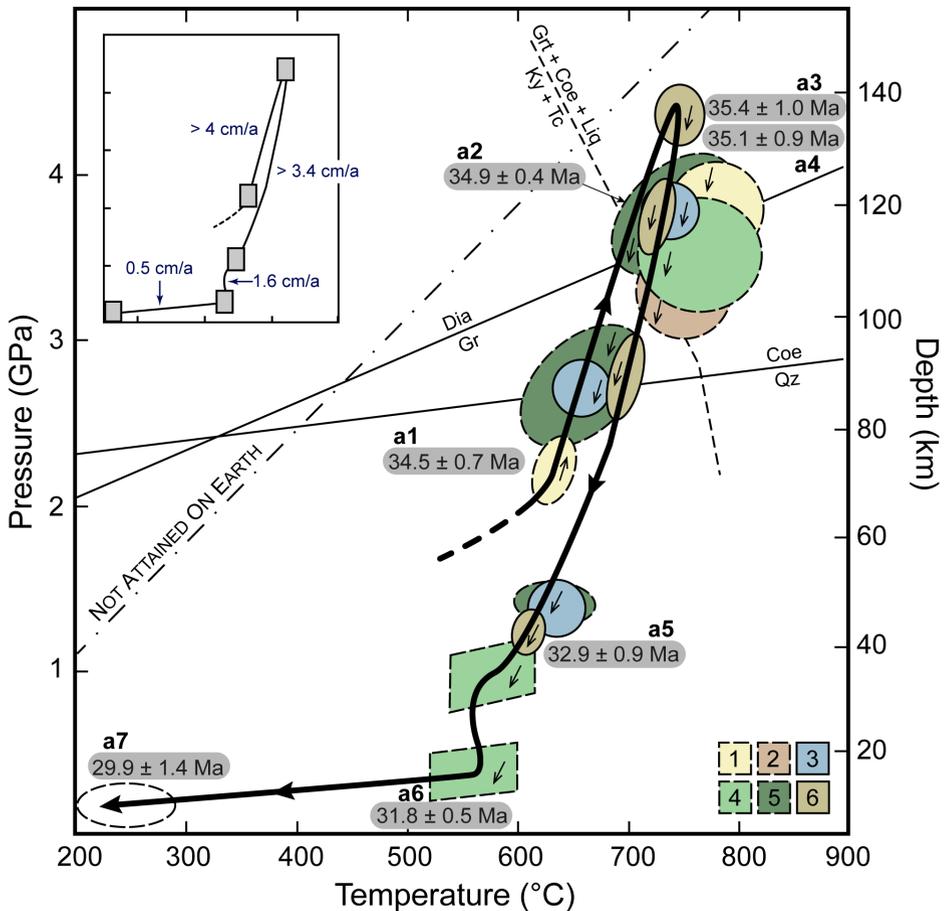


Figure 1. Synthetic P - T - t path for the UHP unit of Dora Maira. Mineral reactions among quartz, coesite, graphite and diamond were calculated using the thermodynamic database of Berman (1988). The reaction $Ky + Tc \rightarrow Grt + Coe + Liq$ is from Gauthiez-Putallaz et al. (2016). P - T estimates for natural mineral assemblages refer to the following lithologies: [1] K-bearing whiteschist (Schertl et al. 1991; Gauthiez-Putallaz et al. 2016); [2] Na-bearing whiteschist (Compagnoni et al. 1995); [3] marbles (Castelli et al. 2007); [4] calcisilicate eclogites (Rubatto and Hermann 2001); [5] eclogite boudins (Groppo et al. 2007). Experimental data [6] are from samples of K-bearing whiteschist (Hermann 2003). Select ages **a1** and **a2** are from Gauthiez-Putallaz et al. (2016), **a3** from Gebauer et al. (1997) and **a4**, **a5**, **a6**, **a7** from Rubatto and Hermann (2001). Note that prograde ages (**a1**, **a2**), while nominally younger than the pressure peak (**a3**, **a4**), are not distinguishable within their 2σ -uncertainties. These ages delimit a maximal time span of 0.7 Ma for burial of the Dora Maira UHP massif from 2.2–2.5 GPa to 3.5 GPa. **Inset:** burial and exhumation rates from Rubatto and Hermann (2001) and Gauthiez-Putallaz et al. (2016). Abbreviations: Coe: coesite; Dia: diamond; Gr: graphite; Grt: garnet; Ky: kyanite; Liq: silicate melt; Qz: quartz; Tc: talc.

Some models can reproduce the Alpine subduction P - T trajectories (Gerya et al. 2008; Butler et al. 2014), but only for such slow subduction (which induces higher temperatures) that the duration of the HP–UHP stages is overestimated by a factor of up to 2.5 (Fig. 2). This large discrepancy has promoted alternative proposals that the pressure recorded by the assemblages may exceed lithostatic pressure, and the observed (U)HP parageneses may have formed at shallower depths (Gerya et al. 2008; Reuber et al. 2016). Such proposals might reconcile durations of metamorphism, but would imply that slab-top geotherms in

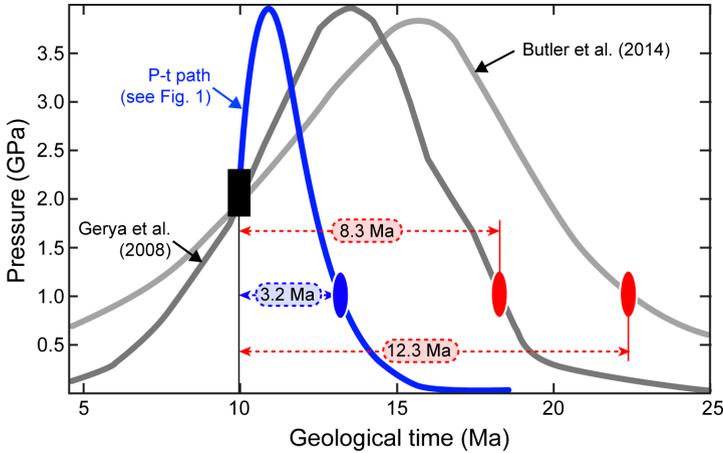


Figure 2. Comparison between the synthetic pressure–time path of Figure 1 (dark) and the representative P – T paths (light) from model V1.5 (Butler et al. 2014) and model 1 (Gerya et al. 2008) for the Dora Maira UHP massif. These two thermal–mechanical models were selected because they show the highest burial and exhumation rates. The duration of the HP–UHP stages suggested by the petrochronological data is shown between the first recorded prograde stage ($P \geq 2$ GPa) to the exhumation to crustal levels ($P < 1$ GPa). The mismatch between durations as recorded by rocks (brief, ~ 3 Ma) vs. models (long, > 8 Ma) implies that natural subduction occurred faster than models are capable of explaining, i.e., rocks can be faster than models.

subduction zones are even hotter than rocks indicate, because the metamorphic temperature recorded by a rock would occur at a shallower depth than the apparent pressure implies. If tectonic overpressures were high, this would exacerbate the already stark discrepancy in P – T conditions between samples (thermobarometry) and models: rocks record generally hotter conditions, models predict generally colder conditions (Penniston-Dorland et al. 2015). So far, the models that favor overpressure by introducing a mechanically heterogeneous crust have not succeeded in reproducing the P – T – t path of the Dora Maira unit. Nor has thermobarometry in this terrane discovered significant pressure-discrepancies, such as one would expect from rock types with such different rheologies as those investigated. Indeed, the range of pressures documented from weak and strong lithologies indicates no significant over- and underpressures, thus thermobarometry does not appear to have registered appreciable deviations from lithostatic pressure. Clearly, alternative geodynamic processes are needed to understand continental subduction (see Guillot et al. 2009 for a review).

Methods of choice, choice of methods

The three sections of this volume present the state of the art and progress regarding

- BASICS: conceptual approaches used in petrochronology (3 chapters);
- METHODS: developments of analytical techniques (4 chapters);
- MINERALS: specific potential and use of mineral groups (8 chapters).

Numerous approaches may be used, so there is no best and certainly no unique approach one could recommend for any specific research ambition or focus. Consequently, current and future studies must make choices. Ideally, petrochronologists will be able to select tools in combination, and in practice much will depend on the specific expertise of the investigators and the available hardware in analytical labs, etc.

However, we must emphasize that the likelihood of obtaining convincing results depends on nothing so much as finding the “right” samples. All of the approaches presented in this

book are time-intensive, and they promise success only when applied to suitable samples. It is seldom evident in the field whether a sample will have the right combination of promising compositions and textures. Experience shows that while many samples may interview for the job of petrochronologic investigation, few are worth hiring, so extensive sampling is recommended. The best machines in the world cannot replace sample selection and detailed documentation. Critical requirements include good structural control in the field, careful microscopy and then accurate chemical / isotopic analysis.

A brief walk through the present volume will expose some of the developments in petrochronology and the main principles and purposes behind them.

Thermodynamic modeling of mineral assemblages and compositions (Chapters 2–3). Quantifying conditions of rock formation is an essential requirement of petrochronology. This task has become quite manageable in metamorphic rocks because thermodynamic models and software based on these are readily available. It is now standard procedure to compute phase diagrams for the approximate bulk composition of a sample under investigation, which allows multi-equilibrium thermobarometry, supports the interpretation of microscopically visible phase relations and reaction textures, all useful to design strategies for *in situ* age dating (Yakymchuk et al. 2017). This approach has proven very helpful, but phase diagrams depict equilibrium relations, and many rock samples contain disequilibrium features (e.g., zoned minerals). Lanari and Engi (2017) emphasize the importance of choosing the appropriate bulk composition if the approach used is based on equilibrium phase relations. That chapter presents successful methods, based on X-ray maps, to accommodate compositional heterogeneity, such as arise where porphyroblasts grow or partial melting occurs. However, the interpretation of ages measured on minerals that grew out of equilibrium, e.g., due to reaction overstepping (Spear et al. 2014), remains a concern.

The fundamentals of modeling igneous rocks are not specifically covered in this volume, but the most prevalent models of melting and solidification are MELTS (Ghiorso and Sack 1995), PETROLOG3 (Danyushevsky and Plechov 2011), and MELTS derivatives (Ghiorso et al. 2002; Gualda et al. 2012). While these models appear to work reasonably well for mafic and some rhyolitic compositions, thermodynamic models for compositionally intermediate rocks are lacking, in part because adequate mixing models for amphibole have not yet been assembled. Peraluminous rocks also pose modeling challenges. Still, MELTS and PETROLOG3 provide good starting points, at least for mafic rocks. When combined with accessory mineral solubilities (e.g., Watson and Harrison 1983; Montel 1993; Stepanov et al. 2012; Boehnke et al. 2013), the growth of monazite and zircon can also be modeled.

Diffusion can set limits and open new doors (Chapter 4) As discussed in Kohn and Penniston-Dorland (2017), diffusion can homogenize pre-existing chemical heterogeneities, biasing certain types of petrologic calculations, but can also induce chemical zoning that may be useful for determining rates of geologic processes. One aspect is that diffusivity limits the temperature range in which specific thermometers and chronometers can be trusted, a major worry in some types of chronology (e.g., $^{40}\text{Ar}/^{39}\text{Ar}$ dating). However, quite a different aspect is the door that diffusion opens for delimiting the duration of thermal events by modeling the time-dependent flux of components in response to composition gradients. Diffusion chronometry also is a central topic in Chapter 16 (Dohmen et al. 2017).

Analytical methods for mineral chronometry (Chapter 5–8). Petrochronological work has continually stretched and exploited the range of analytical techniques available. Spatial resolution is a concern to itself, but linking chronometric data with geochemical analyses remains a key challenge. Consequently, much effort has focused on obtaining both types of data using a single instrument, and many chapters emphasize not only the advantages but also the disadvantages of each technique. Nearly all petrologic studies rely on the electron probe

microanalyzer (EPMA) to characterize major and minor element chemistry of minerals, which is required for modeling (Chapters 1–2; Yakymchuk et al. 2017; Lanari and Engi 2017).

From the perspective of combined chronologic and compositional analysis:

- *EPMA* (Chapter 5, Williams and Jercinovic 2017) offers unparalleled spatial resolution for polished sections and grain mounts (ca. 1 μm), but has relatively poor compositional resolution (typically a few tens of ppm) and age resolution, in part because it cannot distinguish isotopes.

- *Laser-ablation inductively-coupled plasma mass spectrometry* (LA-ICP-MS; Chapter 6, Kylander-Clark 2017) and *secondary ion mass spectrometry* (SIMS or ion microprobe; Chapter 7, Schmitt and Vazquez 2017) offer superior compositional resolution (sub-ppm), but with only moderate resolution of ages (a few percent, absolute) and position (typically >10 μm). However, depth profiling into crystal faces can permit sub- μm spatial resolution (e.g., Grove and Harrison 1999; Carson et al. 2002; Cottle et al. 2009; Kohn and Corrie 2011; Smye and Stöckli 2014).

- *Thermal ionization mass spectrometry* (TIMS; Chapter 8, Schoene and Baxter 2017) offers the highest chronologic precision and accuracy, but the poorest spatial resolution (whole grains or partial grains). Nonetheless, zoning in large crystals, such as garnet, can provide direct estimates of mineral growth rates that can be linked directly to tectonic processes.

Preferred clocks and their role in petrochronology (Chapters 9–16). Accessory minerals have dominated much of classical chronometry, whereas major rock-forming minerals (and reactions among these) have played key roles in determining petrogenetic conditions. Over the past decade, the boundaries between these two camps have gradually crumbled, and combined thermometry, trace element fingerprinting, and chronometry are based increasingly on one and the same mineral grain (or subgrain). From the perspective of published chronologic utility:

- *Zircon* (Chapter 9, Rubatto 2017; Chapter 10, Schaltegger and Davies 2017; Chapter 11, Harrison et al. 2017) remains the most popular chronometer because of its high Pb retentivity (Cherniak and Watson 2001), preservation of multiple growth zones (Corfu et al. 2003), resistance to abrasion during transport as a clastic grain, and use of trace elements for thermometry (Watson et al. 2006) as well as chemical fingerprinting (Rubatto 2002; Whitehouse and Platt 2003). Zircon petrochronology from all three basic rock types is discussed in this volume. Metamorphic zircon requires *in situ* analysis by LA-ICP-MS or SIMS because of its complex zoning but sub-wt% U contents. It provides a key monitor of P – T – t paths and fluid processes (Rubatto 2017), even if it remains difficult to pinpoint precisely the conditions, especially of pressure, at which zircon formed. Igneous zircon records magmatic processes (Schaltegger and Davies 2017), where short timescales commonly necessitate high-precision TIMS analysis (Schoene and Baxter 2017). Detrital zircon preserves chemical, isotopic, mineralogical (inclusion) and chronologic records of past Earth processes; Harrison et al. (2017) illustrate the power and impact of this information most comprehensively through their review of Hadean zircons, which are commonly analyzed using SIMS or LA-ICP-MS.

- *REE minerals* (Chapter 12, Engi 2017), especially *monazite* and *allanite*, are increasingly popular targets of petrochronology, owing to their high Th and U contents, low cation diffusion rates (high Pb retentivity; e.g., Cherniak et al. 2004), and, for monazite, low initial Pb (Parrish 1990). Multiple chemically distinct domains in each grain require *in situ* analysis, and can in favorable cases be tied to specific mineral reactions and hence to P – T conditions. While monazite can be dated using EPMA, LA-ICP-MS, and SIMS, allanite's high common Pb content requires isotopic methods of analysis, typically LA-ICP-MS and SIMS because of intra-crystalline zoning. *Xenotime* and *apatite* have received less scrutiny, and Engi (2017) discusses how more research could explore better their petrochronologic value.

•*Titanite* (Chapter 13, Kohn 2017) has long been analyzed for U–Pb ages, but until recently its high closure temperature for Pb and other cations was underappreciated, and ages were assumed to reflect cooling (see Frost et al. 2000). That is, geochronologists linked titanite’s utility to thermochronology rather than petrochronology. Like allanite, multiple domains with relatively high common Pb require *in situ* isotopic analysis via LA-ICP-MS or SIMS, and, like zircon, a direct thermometer—the Zr-in-titanite thermometer (Hayden et al. 2008)—links temperature to age. Examples of applications commonly focus on P – T – t paths, but new research is developing its use in understanding igneous petrogenesis.

•*Rutile* (Chapter 14, Zack and Kooijman 2017) is not so commonly analyzed as other accessory minerals because it contains virtually no Th, and U contents are typically <10 ppm. These disadvantages are offset by extremely low common Pb contents, such that high-U rutile can be analyzed *in situ* using LA-ICP-MS or SIMS. Zack and Kooijman (2017) emphasize rutile’s utility in understanding crystallization conditions for low-temperature metamorphic rocks, early stage cooling for high-temperature metamorphic rocks, and rutile’s ability to recover temperatures directly through Zr-in-rutile thermometry. Textural context can be of paramount importance, as it is for most petrochronology involving accessory minerals.

•*Garnet* (Chapter 15, Baxter et al. 2017) is, of course, a major mineral in many rocks, and it is presented in all its glory for its ability to constrain petrogenetic processes through combined major and minor element zoning plus Lu–Hf and Nd–Sm isotopic dating. Generally low parent-daughter ratios and extremely low decay rates require TIMS analysis for accurate dating. While inclusions in garnet commonly can be very helpful in relating garnet growth to specific P – T stages or deformation fabrics, certain inclusions jeopardize garnet dating. These challenges are reviewed by Baxter et al (2017), as are the techniques used to minimize the effects on ages.

•*Major igneous minerals, including olivine, plagioclase and pyroxenes* (Chapter 16, Dohmen et al. 2017), round out this volume and provide useful petrochronologic constraints. Although U-series dating can be applied (with care) to igneous systems, much emphasis is placed on diffusion profiles. These allow the duration and rates of various processes to be estimated, e.g., cooling rates for volcanic bodies and magma chamber time scales, such as crystal growth rates and magma residence time.

EVOLUTION OR REVOLUTION?

The concept of petrochronology was originally proposed (Fraser et al. 1997) to unify the fields of metamorphic petrology and geochronology. These authors demonstrated that the breakdown of a major phase such as garnet or amphibole can trigger zircon growth, and thus geochronological data can be linked to petrologically derived pressure–temperature conditions, helping piece together a P – T –time path.

Previously, we outlined linkages among different branches of science that contribute to the field of petrochronology. As a snapshot of the evolution thus far, we compare how the evolution in each field or technique is reflected in citations over the past years (Fig. 3). For the fields of “Petrology” and “Geochronology + Petrology” the citation frequencies increased linearly from 1970 to ~2002, then growth rates doubled; “Petrochronology” was a term barely cited ten years ago, taking off only after 2010—but look at the rate! Citations of “Thermobarometry” seem to have been growing linearly since the early 80s, as have references to petrological software, i.e., Thermocalc (since the late 80s), “PerpleX”, and “Theriak-Domino” (both since ~2005). However, exponential growth is evident for the chronometric techniques. Citations of SIMS (including SHRIMP) lead the pack, but LA-ICP-MS is catching up.

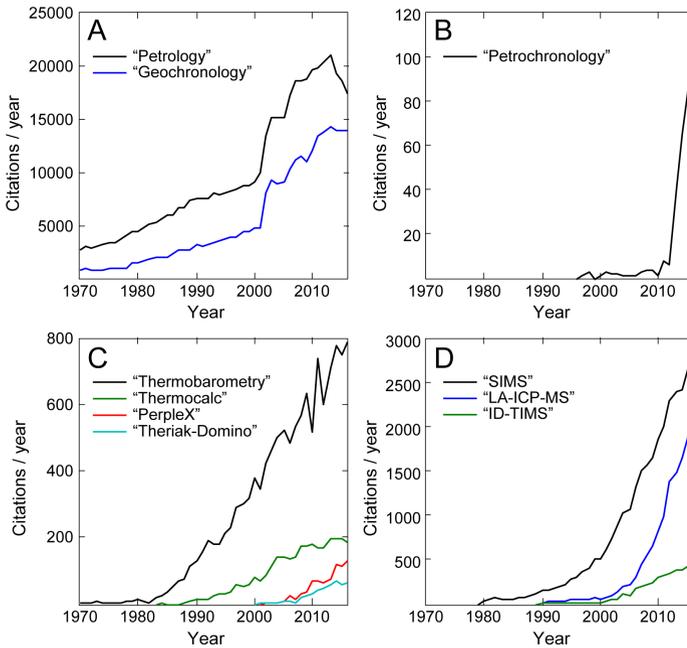


Figure 3. Citations per year, found in Google Scholar (February 2017), using the following criteria, **A:** “Petrology”, “Geochronology + Geochemistry”; **B:** “Petrochronology”; **C:** “Thermobarometry”, “Thermocalc”, “Perple_X”, “Theriak-Domino”; **D:** “SIMS or SHRIMP + Geochronology + Petrology”, “LA-ICPMS or LA-ICP-MS + Geochronology + Petrology”, “ID-TIMS + Geochronology + Petrology”.

The field of petrochronology is evidently young, yet spectacular progress has been made already (Kohn 2016), as evident in the literature and reviewed in this volume. Depending on the scope of applications, studies cover a wide range of scales, from microns to mountain belts. Our understanding has thus deepened, from small-scale processes in the evolution of magmas and rocks, their duration and tempo, all the way to the scale of orogeny, lithospheric tectonics, the nature of Early Earth, and the dynamics of continental recycling.

For these reasons, the time to dedicate a RiMG volume to petrochronology is ripe, for the field is burgeoning, combining many diverse directions, aiming to elucidate time and tempo of processes that have shaped the Earth (and sister planetary bodies) at all scales. We trust that this RiMG volume, compiling current petrochronological methods and reviewing applications, will stimulate and nourish future work in this field. It is with this intent that the authors of each chapter have outlined current limits and identify potentially useful directions for study.

ACKNOWLEDGMENTS

It is a pleasure to thank Ian Swainson, the Editor of the RiMG Series. He has provided expedient and unflinching support in producing this volume. We also thank Frank Spear for his perceptive comments that helped us improve this Introduction. This work was funded by US-NSF grants EAR-1321897, -1419865, and -1545903 to MJK and by the Swiss Nationalfonds grants 200021-117996/1, 200020-126946, and -146175 to ME.

REFERENCES

- Baxter EF, Caddick MJ, Dragovic B (2017) Garnet: A rock-forming mineral petrochronometer. *Rev Mineral Geochem* 83:469–533
- Beaumont C, Jamieson RA, Nguyen M, Lee B (2001) Himalayan tectonics explained by extrusion of a low-viscosity crustal channel coupled to focused surface denudation. *Nature* 414:738–742
- Berger GW, York D (1981) $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Thanet gabbro, Ontario: looking through the Grenvillian metamorphic veil and implications for paleomagnetism. *Can J Earth Sci* 18:266–273
- Berman RG (1988) Internally consistent thermodynamic data for minerals in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$. *J Petrol* 29:445–522
- Butler JP, Beaumont C, Jamieson RA (2014) The Alps 2: Controls on crustal subduction and (ultra)high-pressure rock exhumation in Alpine-type orogens. *J Geophys Res: Solid Earth* 119:5987–6022 doi:10.1002/2013JB010799
- Castelli D, Rolfo F, Groppo C, Compagnoni R (2007) Impure marbles from the UHP Brossasco–Isasca Unit (Dora–Maira Massif, western Alps): evidence for Alpine equilibration in the diamond stability field and evaluation of the $\text{X}(\text{CO}_2)$ fluid evolution. *J Metamorph Geol* 25:587–603
- Chopin C (1984) Coesite and pure pyrope in high-grade blueschists of the Western Alps: a first record and some consequences. *Contrib Mineral Petrol* 86:107–118 doi:10.1007/bf00381838
- Chopin C, Schertl H-P (1999) The UHP unit in the Dora-Maira massif, Western Alps. *Int Geol Rev* 41:765–780
- Chopin C, Henry C, Michard A (1991) Geology and petrology of the coesite-bearing terrain, Dora-Maira massif, Western Alps. *Eur J Mineral* 3:263–291
- Compagnoni R, Hirajima T, Chopin C (1995) Ultra-high-pressure metamorphic rocks in the Western Alps. *In: Ultrahigh Pressure Metamorphism*. Coleman RG, Wang X (eds) Cambridge University Press, Cambridge, p 206–243
- Dohmen R, Faak K, Blundy JD (2017) Chronometry and speedometry of magmatic processes using chemical diffusion in olivine, plagioclase and pyroxenes. *Rev Mineral Geochem* 83:535–576
- Engi M (2017) Petrochronology based on REE-minerals: monazite, allanite, xenotime, apatite. *Rev Mineral Geochem* 83: 365–418
- England PC, Thompson AB (1984) Pressure–temperature–time paths of regional metamorphism I. Heat transfer during the evolution of regions of thickened continental crust. *J Petrol* 25:894–928
- Fraser G, Ellis DJ, Eggins S (1997) Zirconium abundance in granulite-facies minerals, with implications for zircon geochronology in high-grade rocks. *Geology* 25:607–610 doi:10.1130/0091-7613(1997)025<0607:ZAIGFM>2.3.CO;2
- Gauthiez-Putallaz L, Rubatto D, Hermann J (2016) Dating prograde fluid pulses during subduction by in situ U–Pb and oxygen isotope analysis. *Contrib Mineral Petrol* 171:15 doi:10.1007/s00410-015-1226-4
- Gebauer D, Schertl HP, Brix M, Schreyer W (1997) 35 Ma old ultrahigh-pressure metamorphism and evidence for very rapid exhumation in the Dora Maira Massif, Western Alps. *Lithos* 41:5–24
- Gerya T (2011) Future directions in subduction modeling. *J Geodynam* 52:344–378 doi:10.1016/j.jog.2011.06.005
- Gerya TV, Stöckhert B, Perchuk AL (2002) Exhumation of high-pressure metamorphic rocks in a subduction channel: A numerical simulation. *Tectonics* 21:1056, doi:10.1029/2002TC001406
- Gerya TV, Perchuk LL, Burg J-P (2008) Transient hot channels: perpetrating and regurgitating ultrahigh-pressure, high temperature crust–mantle associations in collision belts. *Lithos* 103:236–256
- Groppo C, Lombardo B, Castelli D, Compagnoni R (2007) Exhumation history of the UHPM Brossasco–Isasca Unit, Dora-Maira Massif, as inferred from a phengite–amphibole eclogite. *Int Geol Rev* 49:142–168 doi:10.2747/0020-6814.49.2.142
- Guillot S, Hattori K, Agard P, Schwartz S, Vidal O (2009) Exhumation processes in oceanic and continental subduction contexts: A review. *In: Subduction Zone Geodynamics*. Lallemand S, Funicello F (eds) Springer Berlin Heidelberg, Berlin, Heidelberg, p 175–205
- Handy MR, Schmid SM, Bousquet R, Kissling E, Bernoulli D (2010) Reconciling plate-tectonic reconstructions of Alpine Tethys with the geological–geophysical record of spreading and subduction in the Alps. *Earth-Sci Rev* 102:121–158 doi:10.1016/j.earscirev.2010.06.002
- Harrison TM, Bell EA, Boehnke P (2017) Hadean zircon petrochronology. *Rev Mineral Geochem* 83:329–363
- Hermann J (2003) Experimental evidence for diamond-facies metamorphism in the Dora–Maira massif. *Lithos* 70:163–182 doi:10.1016/S0024-4937(03)00097-5
- Kohn MJ (2016) Metamorphic chronology—a tool for all ages: Past achievements and future prospects. *Am Mineral* 101:25–42
- Kohn MJ (2017) Titanite petrochronology. *Rev Mineral Geochem* 83:419–441
- Kohn MJ, Penniston-Dorland SC (2017) Diffusion: Obstacles and opportunities in petrochronology. *Rev Mineral Geochem* 83:103–152
- Kylander-Clark ARC (2017) Petrochronology by laser-ablation inductively coupled plasma mass spectrometry. *Rev Mineral Geochem* 83:183–198
- Lanari P, Engi M (2017) Local bulk composition effects on metamorphic mineral assemblages. *Rev Mineral Geochem* 83:55–102

- Oxburgh ER, Turcotte DL (1974) Thermal gradients and regional metamorphism in overthrust terrains with special reference to the Eastern Alps. *Schweiz Mineral Petrogr Mitt* 54:642–662
- Peacock SM (1990) Numerical simulation of metamorphic pressure–temperature–time paths and fluid production in subducting slabs. *Tectonics* 9:1197–1211
- Penniston-Dorland SC, Kohn MJ, Manning CE (2015) The global range of subduction zone thermal structures from exhumed blueschists and eclogites: Rocks are hotter than models. *Earth Planet Sci Lett* 428:243–254 doi:10.1016/j.epsl.2015.07.031
- Reiners PW, Ehlers TA, Zeitler PK (2005) Past, present, and future of thermochronology. *Rev Mineral Geochem* 58:1–18
- Reuber G, Kaus BJP, Schmalholz SM, White RW (2016) Nonlithostatic pressure during subduction and collision and the formation of (ultra)high-pressure rocks. *Geology* 44:343–346 doi:10.1130/g37595.1
- Rubatto D, Hermann J (2001) Exhumation as fast as subduction? *Geology* 29:3–6
- Rubatto D (2017) Zircon: The metamorphic mineral. *Rev Mineral Geochem* 83:261–295
- Ruppel C, Hodges KV (1994) Pressure–temperature–time paths from two-dimensional thermal models: Prograde, retrograde, and inverted metamorphism. *Tectonics* 13:17–44 doi:10.1029/93TC01824
- Schaltegger U, Davies JHFL (2017) Petrochronology of zircon and baddeleyite in igneous rocks: Reconstructing magmatic processes at high temporal resolution. *Rev Mineral Geochem* 83:297–328
- Schertl H-P, Schreyer W, Chopin C (1991) The pyrope–coesite rocks and their country rocks at Parigi, Dora Maira Massif, Western Alps: detailed petrography, mineral chemistry and P – T path. *Contrib Mineral Petrol* 108:1–21
- Schmitt AK, Vazquez JA (2017) Secondary ionization mass spectrometry analysis in petrochronology. *Rev Mineral Geochem* 83:199–230
- Schoene B, Baxter EF (2017) Petrochronology and TIMS. *Rev Mineral Geochem* 83:231–260
- Shi Y, Wang C-Y (1987) Two-dimensional modeling of the P – T – t paths of regional metamorphism in simple overthrust terrains. *Geology* 15:1048–1051 doi:10.1130/0091-7613(1987)15<1048:tmotpp>2.0.co;2
- Spear FS, Thomas JB, Hallett BW (2014) Overstepping the garnet isograd: a comparison of QuiG barometry and thermodynamic modeling. *Contrib Mineral Petrol* 168:1–15
- Spear FS, Pattison DRM, Cheney JT (2016) The metamorphism of metamorphic petrology. *Geol Soc Am Spec Papers* 523 doi:10.1130/2016.2523(02)
- Thompson AB, England PC (1984) Pressure–temperature–time paths of regional metamorphism II. Their inference and interpretation using mineral assemblages in metamorphic rocks. *J Petrol* 25:929–955
- van Keken PE, Kiefer B, Peacock SM (2002) High-resolution models of subduction zones: Implications for mineral dehydration reactions and the transport of water into the deep mantle. *Geochem Geophys Geosystem* 3:1–20 doi:10.1029/2001GC000256
- Vialon P (1966) Etude géologique du massif cristallin Dora–Maira, Alpes cottiennes internes, Italie. Thèse d'état, Université de Grenoble
- Williams HS (1893) The making of the geological time-scale. *J Geol* 1:180–197
- Williams ML, Jercinovic MJ, Mahan KH, Dumond G (2017) Electron microprobe petrochronology. *Rev Mineral Geochem* 83:153–182
- Yamato P, Burov E, Agard P, Le Pourhiet L, Jolivet L (2008) HP–UHP exhumation during slow continental subduction: Self-consistent thermodynamically and thermomechanically coupled model with application to the Western Alps. *Earth Planet Sci Lett* 271:63–74 doi:10.1016/j.epsl.2008.03.049
- Yakymchuk C, Clark C, White RW (2017) Phase relations, reaction sequences and petrochronology. *Rev Mineral Geochem* 83:13–53
- Zack T, Kooijman E (2017) Petrology and geochronology of rutile. *Rev Mineral Geochem* 83:443–468