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Geochronology: linking the isotopic record with petrology and textures – an introduction

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Abstract: One of the key aims of geochronology, and the subject of the papers in this Special Publication, is the linkage of isotopic ages to petrological and textural information. A close link between the two types of information greatly improves the constraints available from geochronology on the nature and rates of lithospheric processes such as metamorphism and deformation. There have been several key advances in this area over the past 10–20 years, relating to increased precision and accuracy of isotopic ages but also, and crucially, to the spatial resolution available to geochronologists. This resolution now approaches that on which petrological, chemical and textural information is obtained. We also, in this introduction, identify the barriers that have impeded further progress, which relate both to technical issues as well as to problems of understanding. Finally we set the papers in this volume in the context of the preceding discussion and outline the key ways in which these papers point towards further progress in the future.

Time has always been recognized as a key variable in the Earth sciences, both in its own right and through the constraints that chronological information provides on the rates of, and hence the physical mechanisms for, Earth processes. In the study of the dynamics of the Earth's lithosphere during orogenesis and metamorphism, one of the key requirements of any time datum is that it is relatable in a straightforward manner to other geological information, such as data on temperature, pressure and deformation. It is only through this linkage that chronometric information can achieve its full potential in contributing to progress in understanding the dynamics of mountain belts and other metamorphic settings. This linkage is the focus of the set of papers in this volume, which emanate from a special symposium at the 2002 Goldschmidt Conference, held at Davos, Switzerland. The topic under discussion has been the subject of a review by one of us recently (Müller 2003). Inevitably, there is some overlap between this paper and Müller (2003). However, the emphasis of the two papers is slightly different, with Müller (2003) concentrating largely on new *in-situ* techniques and their resulting prospects, whereas here we give a broader overview of the whole subject, with more emphasis on the dating of high temperature processes and the interrelated achievements of both modelling and experimental work in petrology. We also aim to highlight some general issues that are dealt with in specifics in the subsequent contributions. First, we give a brief account of the progress that has been made over the past two decades in our ability to extract the timing and conditions of deformation and metamorphism from minerals and in the interpretive framework in which these new data are analysed. Next we identify three key barriers that initially impeded further progress and which have been and continue to be the subjects of intensive research effort. Finally, we discuss ways that are being developed to surmount these barriers, with particular reference to the contributions in this volume.

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Progress in quantifying rates of thermal, baric and structural evolution of the lithosphere

The last three decades have seen enormous progress in our understanding of metamorphic belts in general. This progress has its origins in three main fields of activity. Firstly, there has been a dramatic expansion in the number and the quality of experimental constraints on the pressure and temperature conditions of formation of key metamorphic minerals, as evidenced by the increasing variety of mineral end-members incorporated in databases of mineral thermodynamic properties (e.g. Holland & Powell 1998). The acquisition of this new experimental database has gone hand-in-hand with advances in our ability to simulate the phase equilibria of metamorphic rocks using computer models (e.g. Spear 1988; Berman 1991; Powell *et al.* 1998). The pioneering predictive modelling of mineral phase equilibria in the 1970s was restricted to simple chemical systems like KFMASH and was largely semi-quantitative (e.g. Hensen 1971; Thompson *et al.* 1977). In the last 10–15 years, on the other hand, the quantitative analysis of chemical systems that more realistically match real silicate rocks has been made possible by an improved knowledge of basic thermodynamic quantities and activity models for many more phases and mineral chemical end-members (e.g. Holland & Powell 1998). It is also more common to view metamorphic events in terms of P–T–X relations (Berman 1991; Kerrick 1991) in chemically open systems rather than as simple heating of a closed system (Jäger *et al.* 1967).

These advances have greatly improved our ability to model the temperature and depths of burial of exhumed packets of lithosphere presently exposed at the surface of the Earth. Significantly, they have also allowed *segments* of pressure–temperature paths to be extracted from rocks. These latter are key inputs to thermal and mechanical models that seek to clarify the plate tectonic settings of orogenesis (e.g. England & Thompson 1984; Huerta *et al.* 1999; Jamieson *et al.* 2002). A second key input to such models is time, and the constraints that chronometric information provides on the rates at which burial, heating and deformation occur. This is where the second major advance in this field has occurred. The source of information on the chronology of metamorphism is, of course, radiogenic isotope geology and the last three decades have also seen unprecedented advances in our ability to measure the isotope composition of radiogenic elements, both in the precision available and in the quantity of material required for the analyses. This leap forward has largely been driven by technology with the advent, first, of multi-collector mass spectrometers (e.g. Esat 1984; for an early geochronological use see Vance & O'Nions 1990) and techniques for *in-situ* dating of metamorphic mineral phases, such as ion microprobe (e.g. Compston *et al.* 1984; Harrison *et al.* 1995) and laser ablation methods (Horn *et al.* 2000; Ballard *et al.* 2001; Kosler *et al.* 2001; Foster *et al.* 2002).

The two steps forward described above have largely been powered by technology and data. These newly available databases provided the initial impetus for developments in the third main field which has led progress in understanding orogenic belts: the numerical simulation of the mechanical and thermal adjustments that are the consequences of orogenesis and the causes of metamorphism. The application of analytical solutions of heat transport equations to one-dimensional models of metamorphic belts in the 1970s (Bickle *et al.* 1975), was followed by more general one-dimensional models involving numerical solutions (England & Thompson 1984), and has culminated more recently in the development of two-dimensional models that more fully simulate the temperature and deformation fields in orogenic belts (Huerta *et al.* 1999; Jamieson *et al.* 2002). These models were initially designed as an interpretive framework for thermobarometric, chronometric and structural data, but they also make predicitions about the pressure–temperature–deformation–time histories of deeply buried rocks (and the surface development of orogenic belts) that the newly available databases can be used to test.

One of the key requirements that the numerical models make of pressure–temperature–deformation–time data is that the time constraint is not only precise and accurate but that it can be easily related to the other three variables (e.g. Thompson & England 1984). In other words, chronological constraints can add immeasurably more to our understanding of metamorphism if they can be linked unequivocally to P–T–X–d data. Moreover, one of the key outputs of numerical models is P–T–X–d *evolution.* That being the case, a deep understanding of the portion of a P–T–X–d history when different minerals, or parts of them, record time, pressure, temperature and deformation, is clearly essential if these types of data are to test such models. The recent attempts at achieving such an understanding are the subject of many of the contributions in this book. As these articles make abundantly clear, however, the linkage of a time constraint obtained from radiogenic isotopes in minerals to other types of information, such as petrological and structural data, is not always

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straightforward. The reasons why are discussed in the next section. It is important to note that while faster analytical protocols have increased the sample throughput, this does not *per se* guarantee an improved understanding of isotopic ages. We will see below (and throughout the book) that the variables potentially controlling the isotope record of a mineral are numerous. Recognizing the relative importance of these controls requires thorough and time-consuming sample characterizations. While high-precision isotope work can require even more time-consuming preparation and validation/control efforts, in routine analyses the limiting factor is no longer the time required for an isotopic analysis but the process of selecting a geologically and mineralogically meaningful sample before the analysis is begun.

Barriers to progress in linking the isotopic record with petrology and textures

There have been three principal barriers to a closer linkage between chronological data and information on the structural/petrological history of metamorphic rocks.

(a) The requirements for good petrology are that the entropy and volume changes for chemical equilibria between mineral phases are large (e.g. Spear 1993). Thankfully, and serendipitously, this requirement is met by many equilibria between common mineral phases in metamorphic rocks – minerals such as garnet, plagioclase feldspar, the micas, and the aluminosilicates. In general, it is also the deformation of these minerals – mica fish or rotated garnets for example – that tell us about the structural history of a rock and its relationship to phases of burial and heating (e.g. Passchier & Trouw 1996). The requirement made of a mineral to produce a good date, on the other hand, is that the mineral contains a large amount of an element that decays radioactively on a timescale that is appropriate and that the same mineral incorporates small amounts of the radiogenic daughter element when it grows. Serendipity plays its part here too and, again, this requirement is met by many minerals. Key examples of such minerals are zircon and monazite (for the U–Th–Pb isotopic systems) and biotite, muscovite and amphibole (for the Rb–Sr and K–Ar systems). One of the fundamental problems with linking petrological/textural information with geochronology arises because minerals like zircon and monazite have proved difficult to relate to the metamorphic assemblage that define the P–T and, often, the structural evolution. This difficulty arises because the datable minerals are present as accessory phases whose relationship to the main rock texture is often equivocal but, more importantly, because their chemistry, involving silicates or phosphates of trace elements like Zr and the rare earth elements (REE), is only peripherally related to the major chemical equilibria in the rock (involving Fe, Mg, Ca, Al etc.) that are used to establish the P–T history. Simply put, we can generally obtain very precise ages for the crystallization of minerals like zircon and monazite, but it is not often obvious when these minerals crystallize in relation to other more fundamental aspects of the history of the rock, such as the crystallization of the major minerals that records the deformation and P–T history. $^{40}Ar/^{39}Ar$ dating of amphiboles is able to link their thermobarometry (Raase 1974) with the dating of separate amphibole generations (Villa *et al.* 2000) but the thermobarometry of amphiboles is still comparatively poorly developed. Some other K–Ar chronometers have their own problems that are more relevant to point (c) below. For garnets, on the other hand, detailed P–T reconstructions can be made and accurate and precise dating is also possible, though faced with serious analytical challenges. Taken together, each mineral has its strengths for either P–T reconstructions, dating or the establishment of textural relationships, but the 'one does it all' mineral does not exist in nature. For the latter, different strategies have to be employed depending on the context.

(b) The first problem described above is largely due to the unfairness of nature. The second difficulty is a technical one. Since the early 1960s, electron microprobe analysis has provided all petrologists with a tool to study the chemistry of minerals on a micrometre scale. One of the key barriers to a deeper appreciation of chronometric data is that, until relatively recently, the spatial resolution available to petrologists was not available to isotope geologists. As a result chronological constraints were obtained from samples of rock up to several grams in size while chemical data derived from micrometre-sized spots. Furthermore, the chemical variability on a micrometre scale, and the crucial linkage to textural information that the electron microprobe opened up, was largely lost to geochronologists, who were forced to crush large volumes of rock to obtain a mineral separate sizeable enough to obtain a precise age, thus losing a vast amount of textural information. One of the key advances over the past decade or so, discussed in some of the papers in this volume, has been the development of *in-situ* dating techniques (for reviews see Kelley (1995)

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and Compston (1999) and references therein) that have allowed the retention and exploitation of textural information in the acquisition and interpretation of chronometric data.

(c) The final problem results from neither the perfidy of nature nor our anaemic technological abilities but to an inadequacy in our understanding. The recording of isotopic ages, pressure–temperature data and deformational features relies on the attainment of equilibrium at some point in the rock's history, be it isotopic, chemical or textural. Thereafter, the preservation of that record relies on the dominance of chemical, textural and isotopic *dis*equilibrium. The problem is that the exact time at which the attainment of equilibrium is left behind and is superseded by disequilibrium conditions is not necessarily the same for the chemical, textural and isotopic sub-systems within a rock, or even a mineral, and our understanding of this issue is still far from complete. It is now increasingly realized that disequilibrium textures are common, and can be found if one pays special attention.

The gross attainment of equilibrium in any chemical system is primarily controlled by reaction rates. Reaction rates are, in turn, determined by temperature, the availability of fluids and deformation (Rubie & Thompson 1985; Putnis 2002; see also Baxter 2003). If reaction rates were the only factor, the interpretation of data from petrology and geochronology might be relatively simple with all information recorded as minerals grew. Moreover, growth of a rotated garnet or a mica fish during differential stress would be datable through the time of growth of these minerals. It must be remembered, however, that because chronologically useful minerals like zircon and monazite behave as part of a chemical sub-system whose link to the major element chemistry of the rock is only imperfectly understood (see above), we are still left with the problem that the relative reaction rates for the two different sets of minerals, those used for petrology/structural data and those commonly used for geochronology, are only poorly understood. Indeed, it is well-known that zircon can survive pervasive metamorphic recrystallization of the major metamorphic assemblage and preserve inherited ages (Gulson & Krogh (1973) and many others subsequently).

But life is not even that simple. Even when chemical reaction and recrystallization are pervasive, the attainment of isotopic, chemical and textural equilibrium in a rock may not always be simultaneous. The additional control on the attainment of chemical equilibrium is the rate at which material is transported to the site of reaction or along chemical potential gradients, especially where fluids are absent or are present in quantities that are too small to allow the efficient advection of material. In the absence of such fluids, the rates of diffusive transport of chronologically useful trace elements may not be the same as for those elements that determine the major element chemistry of mineral phases. Instances of isotopic disequilibrium at the time of mineral growth are well-known in (mainly coarse-grained) eclogite-facies rocks (Jagoutz 1988; Thöni & Jagoutz 1992; Luais *et al.* 2001; Thöni 2002), where temperatures may be too low and fluid volumes too small to facilitate the attainment of isotopic equilibrium. In these latter instances, it appears that isotopic equilibrium is less readily attained than textural and chemical equilibrium. The behaviour that has received much more attention is the opposite one, however, i.e. where mineral reaction has stopped but mineral chronometers continue to re-equilibrate (e.g. Dodson 1973). Mineral grains that grow at specific temperature and pressure, and usually at high temperatures, can in principle continue to exchange material by diffusion long after reaction has stopped as chemical potentials continue to change in response to the evolving pressure and temperature conditions (e.g. Spear 1993). They do this by intracrystalline transport down chemical potential gradients to their margins where exchange with other mineral grains occurs. As a result, a smooth profile is developed. If the starting material was chemically homogeneous and was subjected to an external gradient, an observable compositional zoning with a bell-shaped ('error function') profile is observed (e.g. Ganguly *et al.* 1998); if the starting material had sharp growth zoning, the zonation is smoothly flattened. The recording of pressures and temperatures only occurs when this diffusional transport decreases to length scales that are no longer measurable. Decoupling of isotopic age information from thermobarometric constraints can occur if intracrystalline transport of the trace elements on whose isotope systems chronometers are based occurs at higher rates. The recognition of the importance of such processes to the recording of both age and petrological information was recognized in the 1970s by the pioneering work of Dodson (1973), which led to the definition of the concept of 'closure temperature' – a working hypothesis that is still being tested – to describe the temperature/time point at which mineral chronometers and thermobarometers start recording their information.

However, it has also been argued that transport of isotopes through a crystal into the

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intergranular fluid always requires a major distortion of the crystal structure and must, therefore, occur at a rate that is less than or equal to the transport/exchange rate of the structure-forming major cations (Villa 1998). While observations appear to confirm that Ar diffusion is indeed limited by Si–Al exchange (Nyfeler *et al.* 1998), the database is not nearly of a satisfactory size as yet and additional confirmations are necessary. If diffusive re-equilibration has continued down to lower temperature conditions, a characteristic error function profile should be observed. Whatever the transport mechanisms for isotopes in minerals and rocks – diffusion or chemical reaction – recent observations of extremely short diffusion distances for major elements in ultrahigh-temperature garnets (Cooke *et al.* 2000) imply that equilibration rates in natural systems can be slower than is often assumed (see also Baxter 2003).

Improving the link between accessory phase chronometers and petrological information

There are two obvious potential solutions to problem (a) in the previous section – the fact that chronometric information is most precisely recorded by a set of accessory minerals which participate only marginally in the reaction history that determines the identity and chemistry of a different set of minerals which record the pressure–temperature–deformation history of a rock.

- One is to use our newly acquired prowess with isotope ratio measurement to squeeze chronological information out of major minerals. This approach has produced some notable successes and will be addressed in later sections.
- The other obvious avenue is to develop more sophisticated techniques to link the petrogenesis of accessory phase chronometers to that of the main mineral assemblage. This approach is the subject of this section.

This latter process has always been a key step in the interpretation of accessory mineral ages (e.g. Smith & Barreiro 1990; Vavra 1993; Kingsbury *et al.* 1993; Pan 1997; Bingen & van Breemen 1998). The principal technique involves using textural relationships. The crystal habit of zircon grains has long been used to constrain the conditions under which they grew (e.g. Vavra 1993). More recently, the advent of *in-situ* isotopic analysis using high mass resolution ion microprobes has allowed the harnessing of other types of textural information, for example, the simple observation that accessory mineral inclusions in major phases like garnet must mean that the accessory phases are older (Harrison *et al.* 1995; Zhu *et al.* 1997; Foster *et al.* 2000). However, the possibility of inheritance, for zircon in particular (Gulson & Krogh 1973) but also for monazite (Parrish 1990), may render such an observation of dubious value. A second approach has been to use aspects of the chemistry of the accessory phases, such as the Th and U contents of zircon or the nature of its chemical zonation (e.g. Maas *et al.* 1992; Williams *et al.* 1996) which are thought to be controlled by the environment of formation. Two further approaches have come to the fore more recently and are still the subject of intensive research effort. The first is relevant to monazite and has involved attempts to exploit empirical and experimental constraints on the relationship between its temperature of growth and the partitioning of REE between monazite and other accessory minerals (xenotime: Gratz & Heinrich 1997, 1998; Heinrich *et al.* 1997; Foster & Parrish 2003) or between monazite and garnet (Pyle & Spear 2000; Pyle *et al.* 2001). The second is relevant to both monazite (Pyle & Spear 1999; Foster *et al.* 2000; Foster & Parrish 2003) and zircon (Schaltegger *et al.* 1999; Rubatto 2002; Whitehouse & Platt 2003; Whitehouse 2003) and involves the examination of those aspects of the chemistry of major minerals – namely their trace element chemistry – that *do* link to aspects of the chemistry of the accessory minerals.

All these approaches – textural and chemical – are utilized by work reported in this volume. Perhaps the most promising for the quantitative understanding of the petrogenesis of monazite and zircon is that involving links between the chemistry of these accessory phases and that of the rock-forming minerals. All minerals contain trace contents of elements other than those that determine their major chemistry. For example, garnet readily incorporates the heavy rare earth elements (HREE). In general, the concentrations of these trace elements are low enough that their concentrations in the major mineral phases are generally determined by Henry's law partitioning (but see Pyle & Spear (2000) and Pyle *et al.* (2001) for an alternative view for yttrium in garnet). These elements, such as the REE and other trace constituents of the major minerals, are often the major constituents of the accessory minerals used for geochronology. For example, the chemistry of monazite is dominated by the REE. Because the REE are

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major elements in monazite, the specific REE chemistry of that mineral, e.g. the relative concentrations of heavy and light REE, is determined not by Henry's law partitioning but by pressure, temperature, the bulk composition of the reacting reservoir at the time of their growth and the nature of the reacting mineral assemblage (Gratz & Heinrich 1997, 1998; Heinrich *et al.* 1997; Pyle & Spear 2000; Pyle *et al.* 2001). For zircon, the situation is slightly different: the REE are not major elements but their concentrations in this mineral are increasingly being used, in a manner analogous to monazite, to link its growth to that of major minerals like garnet (e.g. Schaltegger *et al.* 1999; Rubatto 2002; Whitehouse & Platt 2003; Whitehouse 2003).

This 'microchemical' approach has been exploited increasingly over the past few years and offers huge potential for the future. Besides offering the obvious reward of a closer link between the geochronology and the petrology, the approach has the second great advantage that, with the increasing sophistication of techniques for the *in-situ* U–Pb dating of monazite, zircon, allanite and other accessory phases, the geochronological data obtained are acquired on almost the same scale as the petrological data. **Foster & Parrish** explore this microchemical approach along with a number of others that can tie monazite growth to other aspects of the history of metamorphic rocks. One such approach is the direct derivation of temperature estimates from the REE chemistry of monazite and an observed or assumed equilibrium with xenotime (Gratz & Heinrich 1997, 1998; Heinrich *et al.* 1997) or with garnet (Pyle & Spear 2000; Pyle *et al.* 2001). While this approach has achieved some success, Foster & Parrish highlight problems in its application related to uncertainties over the presence of xenotime at the time of monazite growth or the degree of equilibration between the two minerals. They suggest, however, that the approach may be relatively robust as a means of determining the temperature at which garnet breaks down as the resultant release of large quantities of yttrium and HREE by this process is especially likely to lead to xenotime growth.

More success is achieved through the coupling of textural and chemical information on monazite. Building on earlier regional work (e.g. Smith & Barreiro 1990), and using examples from the Himalaya, Foster & Parrish show how detailed textural observations of the locations of monazite and its possible precursors (e.g. allanite, xenotime) within a single rock can be used to link monazite growth to that of staurolite and garnet. In their example, the monazite grew after allanite and xenotime, before garnet and towards the end of staurolite growth. They then use improvements in petrological modelling of metamorphic rocks, namely a pseudosection approach (Mahar *et al.* 1997; Vance & Mahar 1998), to model the pressures and temperatures over which staurolite and garnet grow to constrain the pressure and temperature of monazite growth. These textural observations are an extension of earlier approaches that have variously put the 'monazite isograd' at the staurolite isograd (Smith & Barreiro 1990) or the kyanite/andalusite isograd (Ferry 2000) in pelitic rocks and the clinopyroxene isograd in metagranitoid rocks (Bingen *et al.* 1996). Foster & Parrish go on to show that these apparent discrepancies may, as might reasonably have been expected, be related to the bulk composition of the rock and give a simple expression for the relationship between monazite growth temperature and the bulk composition of the host rock.

The availability of yttrium (and the HREE, see below) to a growing mineral in a metamorphic rock is probably largely controlled by the presence or absence of garnet (e.g. Pyle & Spear 1999; Foster *et al.* 2000; Pyle *et al.* 2001; Rubatto 2002). In that case, the yttrium content of monazite can also be used for the determination of the growth conditions of monazite by linking it with the growth history of garnet. Foster & Parrish show that monazite grains occluded by garnet (grown before garnet, perhaps at the expense of xenotime) have high Y contents, but that cores of grains in the matrix outside garnet (grown after garnet has sequestered the rock's Y) have low Y contents. Further, the rims of these matrix grains, probably grown during decompressive garnet breakdown, again have high Y concentrations. All these chemical data can be obtained on a micrometre scale using electron microprobe mapping and with full textural control. Furthermore, the ability to perform *in-situ* geochronology of these texturally and chemically characterized grains allows the authors to show that the different types of monazite grains preserve the expected sequence of ages. While uncertainties remain over the extent to which ages of matrix monazite not armoured by occluding garnet reflect growth of new monazite (e.g. Cocherie *et al.* 1998; Vavra & Schaltegger 1999; Foster *et al.* 2000) or diffusive lead loss (e.g. Catlos *et al.* 2002), this general approach has huge potential for the future. Data acquisition is relatively simple and rapid while the constraints on the P–T evolution (e.g. decompression and garnet breakdown) are often unavailable by other means.

Monazite is not the only accessory mineral whose chemistry and textural relationships can be

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used to link its growth with the main metamorphic assemblage. Zircon has long been used in the geochronology of metamorphic and igneous rocks (see Compston (1999) and references therein). As with monazite, however, the main limitation of zircon has now become the uncertainty over the geological and petrological significance of the ages produced. Zircon can apparently grow over a wide range of metamorphic conditions: on the prograde path, at peak conditions or during the retrograde path (e.g. Fraser *et al.* 1997; Liati & Gabauer 1999; Rubatto *et al.* 2001; Rubatto 2002; Hoskin & Black 2000). Moreover, it can grow under sub-solidus conditions, from an anatectic melt or from fluids (e.g. Williams *et al.* 1996). Unlike monazite, inheritance of zircon from protolith magmas, or even of detrital grains from a previous metamorphic cycle, is common (e.g. Gulson & Krogh 1973) and is an extra complexity that must be addressed.

In common with monazite, the ability to date portions of individual zircon grains or to date grains *in-situ* in thin sections vastly increases the potential to link zircon chronology to textural information, though it is only quite recently that ion microprobes have been used in this way. On the other hand, unequivocal textural relationships between zircon and other minerals (e.g. mineral inclusions within zircon, texturally equilibrated grain boundaries between zircon and other minerals) have only rarely been described (e.g. Gebauer *et al.* 1997; Hermann *et al.* 2001; Möller *et al.* 2003). Though Th/U ratios of zircon grains and portions of them have been used for some time to distinguish between possible petrogenetic environments for zircon (e.g. Maas *et al.* 1992; Williams *et al.* 1996), the trace element chemistry of zircon – particularly the REE and Y – is an avenue that has only recently begun to be seriously exploited (e.g. Schaltegger *et al.* 1999; Rubatto 2002; Whitehouse 2003). The REE (and Y) are probably incorporated into zircon as a result of a xenotime coupled solid solution, with the trivalent REE replacing Zr^{4+} and pentavalent phosphorus subsituting for Si^{4+} (Speer 1982). This substitution has recently been shown to have lattice strain-related limits (Hanchar *et al.* 2000). In terms of chondrite-normalized plots, the ubiquitous first-order feature for zircons grown from a melt is a pattern with a steeply positive slope (e.g. Hinton & Upton 1991; Maas *et al.* 1992; Hoskin & Ireland 2000), reflecting the greater ease with which the heavier REE, with smaller cation radii, are accommodated in the zircon structure (Hanchar *et al.* 2000; Whitehouse & Kamber in press). This pattern is accompanied by second-order anomalies in the redox-sensitive REE, positive for Ce, negative for Eu (e.g. Hinton & Upton 1991; Maas *et al.* 1992; Hoskin & Ireland 2000). This pattern is so ubiquitous that, though earlier attempts had been made to use the chemistry of zircon as a provenance indicator (e.g. Heaman *et al.* 1990), Hoskin & Ireland (2000) recently concluded that the REE chemistry of zircon grains from a wide variety of petrologic and tectonic settings was too homogeneous for such a purpose.

However, several studies (Schaltegger *et al.* 1999; Rubatto 2002; Whitehouse & Platt 2003; Whitehouse 2003) have recently shown that metamorphic zircons, grown under sub-solidus conditions or from anatectic melts, have variable REE patterns and that these can be used to link zircon growth to that of other petrologically important mineral phases. The most important phase controlling the REE chemistry of metamorphic zircon, as with monazite, is garnet – a fortunate circumstance given the importance of garnet to geothermobarometers. Rubatto (2002) showed that zircon in granulite-facies rocks, that demonstrably grew from anatectic melts, had the characteristic REE pattern of magmatic zircon, regardless of whether or not garnet was present as a restitic phase. Furthermore, she was able to calculate garnet–zircon partition coefficients on the basis that both minerals had equilibrated with the melt phase. Zircons in eclogite-facies rocks from the European Alps, on the other hand, had distinctly flatter HREE patterns that must reflect their equilibrium with garnet. Another possibility is that the zircons grew after the garnet has sequestered most of the HREE budget of the rock to itself. However, the garnets in the eclogite facies rocks were zoned from core to rim so that, using the distribution coefficients calculated from the granulite-facies samples, Rubatto was able to further show that the zircon trace element patterns were in equilibrium only with the rim of the garnets. Such information is an invaluable addition to the tools available to link zircon growth with the main metamorphic assemblage. Second-order features, such as low yttrium levels (cf. monazite above) and less pronounced Eu anomalies in the eclogitic zircons (presumably reflecting the absence of feldspar in these high pressure rocks), provide further vital clues to zircon origin (Rubatto 2002; Whitehouse & Platt 2003). Furthermore, the presence of normal HREE patterns, distinct Eu anomalies and high yttrium contents in slightly older zircons from veins containing an eclogitic-facies assemblage (omphacite–quartz–phengite) but no garnet presumably reflect zircon growth during the prograde path in the presence of albitic feldspar (Rubatto 2002).

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Whitehouse presents a further example of the application of this approach in this volume, using case studies from the granulite facies rocks of the Lewisian Composite Terrane in NW Scotland. The presently exposed Lewisian has a complex crustal history beginning with extraction from the mantle and (perhaps several) granulite-facies metamorphisms in the Late Archean leading to the formation of a complex of tonalite–trondhjemite–granodiorite gneisses (see references in Whitehouse (2003) for reviews). These gneisses were then reworked, certainly more than once, in the early Proterozoic. Such a history is not unusually complex for exhumed Precambrian lower crustal terrains but imposes extreme requirements on any geochronological study. Zircon, along with whole-rock isotopic techniques, has been used extensively in these polymetamorphic terranes because its refractory nature and high closure temperature (e.g. Cherniak *et al.* 1997; Dahl 1997; Mezger & Krogstadt 1997) give it the ability to preserve a memory of early phases of such complex histories. However, the usual issue of which particular phase of the rock's history a zircon age dates, in terms of the petrological and structural information preserved by the major mineralogy and its texture, is as problematic as ever.

Whitehouse presents REE data for zircons from Lewisian exposures in the Outer Hebrides on which U–Pb isotopic data are also presented or have recently been published (Whitehouse & Bridgewater 2001). On the Isle of Lewis, a suite of metasedimentary rocks and basic intrusions contains zircons that display complex structures in cathodoluminescence images. Prismatic rim overgrowths give early Proterozoic ages (1860 Ma) while both cores and core overgrowths inside the early Proterozoic prismatic rims record complex age patterns involving components of Pb loss at 1.86 Ga and 2.4–2.5 Ga and a poorly defined protolith age of 2.7–2.8 Ga. The oldest core has an age of 2.83 Ga and was previously interpreted as having been inherited. However, the new REE data presented in the paper call for a reassessment of some of these conclusions and serve to clarify these age relationships generally. In particular, the new REE data discriminate between the pre-Proterozoic cores and core overgrowths. The cores have typically magmatic REE profiles while the core overgrowths show flat HREE patterns (Gd–Lu) that imply equilibration with garnet (cf. Rubatto 2002). Moreover, the 2.83 Ga core shares the flat REE pattern of the core overgrowths. This shared chemistry with younger, clearly metamorphic, grains suggests that this oldest grain is not inherited. The 1.86 Ga rim overgrowths have REE patterns that are similar to magmatic zircons but with highly variable Eu anomalies that vary from slightly negative to slightly positive – features that imply metamorphic growth in the absence of garnet. In a second case study, involving rocks from South Uist, Whitehouse presents data for zircons from Laxfordian (1.7–1.8 Ga) pegmatites and for their 2.85 Ga host gneisses. The debate here centres around the source of the melts for the pegmatites, which may be local via partial melting of the host gneisses or could be more exotic. Chronological data for the zircons in the pegmatites are ambiguous with cores preserving ages only slightly younger (at 2.76 Ga) than the 2.85 Ga age of the host gneisses. REE analyses of the zircons from the host gneisses and for the cores of zircons from the intrusive phase confirm that the latter are not related to the zircons in the host gneisses.

The high closure temperature of zircon is also exploited by **Möller *et al.*** to study polymetamorphic rocks in the contact aureole of a large anorthosite–norite intrusive complex in Rogaland, Norway. The intrusion age of the Rogaland complex is well established at 931–915 Ma but controversy surrounds the relationship between the magmatic event and the development of isograds in the surrounding gneisses. Previous zircon, monazite and titanite ages from the surrounding gneisses range between 1 and 1.05 Ga, a range that is distinctly older than the age of the intrusion and more consistent with an earlier regional metamorphism associated with the Sveconorwegian orogeny. Möller *et al.* combine *in-situ* ion microprobe U–Th–Pb dating with detailed and meticulous textural work, using backscatter and cathodoluminescence imaging, and trace element analysis. The aim, central to the theme of this volume, is to determine the relative timing of zircon growth with respect to petrologically significant phases such as garnet, orthopyroxene, magnetite and spinel. In particular, the authors show that some dated zircon grains exhibit unequivocal textural equilibrium with phases such as magnetite and orthopyroxene, whose isograd pattern is clearly related to the mafic intrusion. Others can be shown to have grown before garnet coronas that develop between orthopyroxene and magnetite during cooling just after intrusion of the Rogaland anorthosite. Furthermore, the ages of these zircons are 927–908 Ma, clearly the same as the Rogaland intrusive and distinctly younger than metamorphic zircon ages from the literature.

It should be noted that Möller *et al.* find evidence for that older population as well – in mineral separates obtained from rocks collected at all distances from the margins of the intrusion.

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However, their excellent textural control for the *in-situ* study demonstrates the close association of the younger population of zircon with magnetite, which both ties zircon growth to the intrusion of the Rogaland mafic igneous body and suggests a reason why previous studies that apply conventional mineral separation techniques – involving the collection of the non-magnetic fraction to obtain the zircon – did not turn up any 910–930 Ma zircon! The preservation of the older regional metamorphic ages in zircons from rocks close to the intrusion confirms that the 927–908 Ma population is not simply due to resetting of older zircons at the high temperatures (>1000 °C) experienced in the inner aureole but that these represent new growth. Besides textural data, these authors also present trace element data for the zircons dated. In particular, they demonstrate that the high Th/U ratios of many of their clearly metamorphic zircons do not support the common assumption of low Th/U ratios for such grains (e.g. Maas *et al.* 1992; Williams *et al.* 1996). They do suggest, however, in common with previous studies (e.g. Rubatto 2002), that the yttrium content of zircon may be an indicator of when zircon grew with respect to P–T sensitive equilibria involving garnet. For example, they suggest that the generally high yttrium contents of zircons in the Rogaland metamorphic aureole may be the result of the breakdown of garnet at the low pressures represented by the contact metamorphism (cf. Foster & Parrish 2003).

Advances in the chronometry of major metamorphic minerals – prograde histories

The isotope systematics of major minerals have long been used to study metamorphic processes (e.g. Steiger 1964; Jäger 1973), in particular the $^{40}Ar/^{39}Ar$ and Rb–Sr systems (see next section). These latter systems were used because key minerals, such as the micas, have high parent/daughter ratios that are amenable to isotopic dating. However, one major drawback of these early approaches was that the minerals used for dating were subject to low temperature re-equilibration, be it by mineral reaction or diffusion of the trace elements relevant to the isotopic systems. As such, information on high temperature metamorphic processes and, crucially, on the prograde metamorphic history was lacking. Progress on this issue will be dealt with in this section.

In this respect, the big step forward came in the late 1980s with pioneering work applying the new generation of multicollector thermal ionization mass spectrometers to the Rb–Sr, Sm–Nd and U–Pb isotopic dating of garnet (e.g. Mezger *et al.* 1989; Christensen *et al.* 1989; Vance & O'Nions 1990; Burton & O'Nions 1991). Later, multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) opened up other possibilities involving the Lu–Hf system (e.g. Duchêne *et al.* 1997; Scherer *et al.* 2000). Like the micas that were traditionally used for Rb–Sr and $^{40}Ar/^{39}Ar$ isotopic dating, garnet is ubiquitous in metamorphic rocks. However, it has several key advantages over these traditionally used minerals for the isotopic dating of metamorphic processes: it is a much more critical participant in many key geothermobarometrically sensitive mineral equilibria (e.g. Spear 1993) and it is much more robust to resetting by both diffusion (Ganguly *et al.* 1998) and mineral reaction. As such, it could potentially provide key information on the prograde history of metamorphic belts that was not accessible with the above-mentioned geochronometers based on major metamorphic minerals and which was directly relatable to the petrology of the rock. Moreover, garnet has high Sm/Nd and U/Pb ratios (though see below for a discussion of the possible influence of inclusions) and low Rb/Sr ratios – at the opposite end of the spectrum from metamorphic whole rocks and many metamorphic minerals. The latter allows good analytical precision to be obtained on ages provided that isotope ratios can be measured with the precision that first became available through multicollector mass spectrometers in the 1980s. Attempts have been made to date other major metamorphic minerals, e.g. the aluminosilicates and staurolite, with the U–Pb system (e.g. Lanzirotti & Hanson 1995) but considerable debate continues over the extent to which the U–Pb system in these minerals and garnet are dominated by accessory phases (Vance *et al.* 1998*a*).

While the precision of garnet dating by the Sm–Nd system is not in doubt, accuracy has been a much more difficult question to assess. The problem here is that the Sm and Nd contents of garnet are low (usually at least as low as 1 ppm and often down to 10 ppb; e.g. Hickmott *et al.* 1987; Schwandt *et al.* 1996; Bea *et al.* 1997; Prince *et al.* 2000). As such, the Sm–Nd isotope systematics of garnet are open to domination by REE-rich accessory phases. The mass balance is such that only a few millionths of the mass of a separated garnet sample need be monazite for the garnet systematics to be dominated by it – a fraction that is impossible to spot using traditional hand-picking methods. This has two potential manifestations (Prince *et al.* 2000; Thöni 2002):

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(a) the Sm/Nd ratio of the measured separate can be lowered to such an extent that all chronological precision is lost; (b) contamination by non-cogenetic inclusions that is not catastrophic enough to eradicate the age precision can bias the 'garnet' age to that of the inclusions.

Nevertheless, garnet chronometry using traditional mineral separation techniques has achieved notable success (e.g. Mezger *et al.* 1989; Christensen *et al.* 1989, 1994; Vance & O'Nions 1990, 1992; Burton & O'Nions 1991, 1992; Vance *et al.* 1998*b*; Vance & Harris 1999; Stowell *et al.* 2001; Thöni 2002; Stowell & Tinkham 2003) but it is not robust. It is the experience of the lead author on this paper that the success rate, as measured by the ability to obtain age precisions of 1–3 Ma, is less than 50%. What is required is an easy means to separate the inclusions from the garnet. Note that this is not just a question of achieving greater precision. The process of doing isotopic analyses on a set of four garnets, for example, takes perhaps five weeks; four of those weeks are hand-picking the initial separate. If a process were developed that would allow us to obtain clean garnet separates more quickly then the rate at which one could obtain a lot of data – a key aspect of any chronological study of structurally and thermally complex metamorphic belts – would be greatly improved.

One way to separate the garnet signal from that of the inclusions is to use a chemical leaching protocol that dissolves inclusions while leaving garnet behind to be attacked later in a separate analysis. An important requirement of such a technique is that the parent/daughter ratio of the garnet that is left behind is not affected by the leaching process, otherwise an erroneous age will be produced. Such leaching protocols have been successfully developed over the past few years, some developed specifically to improve precision and accuracy (e.g. Frei & Kamber 1995; Frei *et al.* 1997; Amato *et al.* 1999; Baxter *et al.* 2002), others to explore the systematics of isotope behaviour in garnet and its inclusions (e.g. Zhou & Hensen 1995; Schaller *et al.* 1997; Vance *et al.* 1998*a*). Here, **Anczkiewicz & Thirlwall** detail a new approach, involving sulphuric acid, to leaching garnet to improve Sm–Nd isochron precision. The paper is primarily concerned with REE phosphates such as monazite and xenotime because sulphuric acid does not dissolve silicates. The other major problem inclusion is allanite, which is a silicate and is not amenable to separation from garnet using sulphuric acid but which has been successfully removed using dilute HF (Amato *et al.* 1999). The advantage of the newly proposed approach is that, besides the fact that significant improvement in age precision results from the removal of inclusions of mineral phases that are near-ubiquitous in metapelitic garnets with a consequent doubling of the Sm/Nd ratio in some cases, it involves a low-blank single-step leach. Crucially, the authors suggest that little picking is required before the leaching and isotopic analysis is performed, thus vastly increasing the rate at which these analyses can be done. The authors also show that little or no improvement in Sm/Nd ratio is obtained for garnets from garnet granulites and mafic granulites from lower crustal settings. In both cases the rocks are pseudomagmatic, one of them in an arc setting with mantle-like initial Nd and Sr isotopic compositions (Anczkiewicz & Vance 2000). In this case they are unlikely to contain inclusions rich in REE that are typical of crustal rocks. The fact that, for these latter rocks, there is little or no improvement in Sm/Nd ratio from their leaching protocol is, therefore, no surprise.

Garnet dating in metamorphic rocks suffers from a further problem. All minerals used in radio-isotope chronometry incorporate a finite amount of the daughter element when they grow. For U–Pb dating of zircon and monazite the amount of such a 'common' daughter element is very low. For garnet, the amount of 'common' Nd incorporated at growth forms a substantial part of the total Nd measured. As such, any isotopic age must be obtained by referencing the isotopic composition of the mineral of interest against some initial isotopic composition for this common daughter element. For zircon and monazite the U/Pb ratio is so high that this correction is often not critical and model crustal values (e.g. Stacey & Kramers 1975; Kramers & Tolstikhin 1997) are often used for common Pb in zircon. For garnet, this is not the case so that either the Sm–Nd systematics of the whole rock or those of other metamorphic minerals are used with those of the garnet in an isochron to extract both the age and the initial Nd isotope composition. This approach requires that the garnet and the other mineral used, or the whole rock, were in isotopic equilibrium at the time of garnet growth. In many cases, and particularly for metapelitic rocks, either or both of these approaches is adequate (e.g. Vance & O'Nions 1990; Burton & O'Nions 1991, 1992; Vance *et al.* 1998*b*; Vance & Harris 1999; Stowell *et al.* 2001; Thöni 2002; Stowell & Tinkham 2003). However, it has been known for some time (Jagoutz 1988; Thöni & Jagoutz 1992; Luais *et al.* 2001; Thöni 2002) that in (mainly coarse-grained) high pressure metabasic rocks this is often not the case. Perhaps this is because the low temperatures often involved are not

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conducive to the attainment of isotopic equilibrium. Or perhaps it is because the mineral reactions involved, e.g. igneous low pressure pyroxene to high pressure metamorphic pyroxene, do not require a pervasive redistribution of the elements and isotopes participating in them. Whatever the reason, in high pressure metabasic rocks, textural and chemical equilibrium between two mineral phases does not necessarily imply isotopic equilibrium. The question then arises as to what, if any, phase can be used to generate an isochron age with garnet.

Zheng *et al.* build on earlier work (Zheng *et al.* 2002) that uses oxygen isotope temperatures in high pressure rocks as a measure of isotopic equilibrium. The approach is based on the idea that, if oxygen isotope equilibrium exists between mineral phases then the oxygen isotope temperatures recorded by those minerals should be the same as temperatures obtained by other, petrological, thermometers. If this is the case, then the oxygen isotope thermometers record the temperature at which chemical and textural equilibrium was attained. And if the transport rates of oxygen and the chronologically relevant trace elements in the rock are similar, then the isotopic dates should also *date* the attainment of this isotopic, chemical and textural equilibrium. The paper in this volume presents new oxygen isotope data for ultrahigh-pressure (UHP) rocks from the Dabie terrane in east central China. However, given the importance of transport processes to this issue, the authors begin their paper with a review and compilation of diffusion rates in metamorphic minerals that is later used to interpret the isotopic data. The Dabie high pressure rocks have been the subject of previous geochronological studies which showed that Sm–Nd isotope systematics – mainly based on garnet – preserves Triassic ages (213–246 Ma) that are in close agreement with lower intercept zircon U–Pb ages (226–237 Ma) while Rb–Sr, mainly based on biotite–plagioclase isochrons, mainly preserve Jurassic ages (161–174 Ma). The oxygen isotope data show that these rocks also preserve two sets of temperatures. Minerals on which the Sm–Nd ages are based (garnet and omphacite) record quartz–mineral oxygen isotope temperatures around 630–720 °C, in agreement with petrological estimates for the temperature reached during the >28 kbar UHP metamorphism. On the other hand, minerals on which Rb–Sr isochrons are based (biotite, plagioclase, epidote) record quartz–mineral oxygen isotope temperatures of 420–540 °C, which are associated with a later amphibolite-facies retrogression. The exception is phengite, which gives Rb–Sr ages with whole rocks or garnet of 219–220 Ma and which also preserves high oxygen isotope temperatures. All these observations can be rationalized in terms of the diffusivities of Sr and Nd in these various minerals or the absence of retrogression in the samples, and the approach represents an extremely useful additional tool to the geochronologist trying to better link isotopic ages with petrological data.

One key advance with garnet dating has, however, not been with geochronology but with petrology. Metamorphic petrology generally has benefited enormously from a dramatic amelioration in the number and quality of well-constrained basic thermodynamic quantities for mineral phases (e.g. Holland & Powell 1998) and in our ability to model the chemistry of natural samples to extract quantitative P–T paths (e.g. Powell *et al.* 1998). In essence, these advances have turned metamorphic petrology into a genuinely predictive science. This improved modelling ability has been coupled with isotope geochemistry (Vance & Mahar 1998; Vance *et al.* 1998b; Vance & Harris 1999) to establish a combined approach of pseudosection analysis and garnet Sm–Nd dating that can produce quantitative P–T–t paths for metamorphic belts. In a case study, **Stowell & Tinkham** apply this combined approach to polyphase contact and regional rocks from the western Cordillera of North America. The authors present new isotopic and petrological data and integrate it with existing data (Stowell *et al.* 2001) to investigate a terrane with a polyphase history involving plutonism and thrusting related to terrane accretion at 100–60 Ma and three or four contact and regional events. The paper is notable in documenting textures involving the aluminosilicates that are complex but which also provide an abundance of information that is very useful in interpreting the P–T history on pseudosections. The high quality petrology is combined with Sm–Nd ages for cores and rims of garnet (cf. Christensen *et al.* 1989, 1994; Vance & O'Nions 1990, 1992; Vance *et al.* 1998*b*; Vance & Harris 1999) which leads to the distinction in time of contact and regional metamorphic events that are only 5–6 Ma apart. The ability to do this arises from the ability of garnet to preserve a reliable record of both pressure and time so that the timing of loading during regional metamorphism is extractable.

The mineral titanite is intermediate in character between garnet (and other major minerals used in chronology) and accessory minerals like zircon and monazite. Compared with zircon and monazite, titanite contains small amounts of U (Frost *et al.* 2000; Rubatto & Hermann 2001; Castelli & Rubatto 2002) but its

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ratio of uranium to common Pb is far in excess of any major metamorphic mineral. On the other hand, while titanite is more a minor mineral than an accessory phase in many rocks, unlike garnet its relationship to the chemistry of the major metamorphic phases is not entirely straightforward. **Romer & Rötzler** present U–Pb data for titanite from ultra-high pressure and temperature granulites from the Saxon Massif, Germany. These data illustrate rather nicely the two faces of titanite outlined above. Titanite in these rocks grew from reactions involving clinopyroxene, rutile, quartz and plagioclase to produce garnet and titanite so that it can be regarded as part of the main assemblage. But it is only a marginal participant with the main assemblage really depending on reactions like clinopyroxene + plagioclase = garnet + quartz and albite = jadeite + quartz. Nonetheless, textural equilibrium is preserved between titanite and the major minerals in many cases. The main point of the Romer & Rötzler paper is that the U–Pb isotopic systematics of titanite can be quite complex. Despite all the samples studied having experienced an identical P–T history in the Variscan, with peak conditions occuring at *c.* 342 Ma, the U–Pb ages of the titanites span a large range, with a few grains preserving ages up to 500 Ma and many being younger than 342 Ma. The authors use these data to illustrate two problems. The first is the possible inheritance of common and radiogenic Pb from older phases, in this case dominantly rutile. Because, and unlike zircon and monazite, U/Pb ratios of titanite are rather low the ages obtained are sensitive to the incorporation of common Pb and the isotopic composition of that Pb. This issue is analogous to the incomplete re-equilibration observed for the Sm–Nd system in garnet (see above) but is rather surprising in this case as these rocks experienced temperatures in excess of 1000 °C. The authors' point, that if isotopic disequilibrium exists in rocks that have attained these high temperatures then there may be little chance of isotopic equilibrium at lower temperatures, is well made. The second problem relates to the ages that are younger than the apparent peak. Here the authors again make use of the trace element chemistry of the phases they date. The peak aged titanites have high Al concentrations and $X_F = 0.8-1$. In the retrogressed, younger titanites both are lower. All these grains are in apparent *textural* equilibrium with the peak phases yet some are chemically and isotopically younger. In this case, re-equilibration is apparently chemical as well as isotopic – X_F and Al change as well as the isotopic ages – and is aided by deformation and fluids.

Texturally controlled (*'in-situ'*) chronometry

This section primarily focuses on the 'low-temperature' (in comparison to U–Pb and Sm–Nd dealt with in previous sections) chronometers Rb–Sr and K–Ar (or $^{40}Ar/^{39}Ar$, its methodological advance) because it is in this area that two new possibilities arise for integrated P–T–X–t studies. These are made possible by two closely related technical developments, which now facilitate texturally controlled dating at the $\geq$10–100 μm scale.

- Substantial progress has been achieved in the reduction of sample size requirements in geochronology during the past decade, which facilitates the application of microsampling techniques combined with 'conventional' dating, e.g. Rb–Sr microsampling (Müller *et al.* 2000*b*; Cliff & Meffan-Main 2003).
- 'True' *in-situ* dating at high spatial resolution has seen a boost during the late 1990s due to advances in laser-ablation technology, facilitating UV laser-ablation $^{40}Ar/^{39}Ar$ dating (e.g. Kelley *et al.* 1994).

Usually, $\geq$10–100 μm spatial resolution is sufficient for texturally controlled dating (e.g. Müller *et al.* 2000*a*) since it represents the grain size of minerals that can be easily identified optically. It has to be kept in mind, however, that this spatial resolution is still one to two orders of magnitude larger than that of compositional analysis by electron microprobe (EMPA).

The characteristics of Rb–Sr and K–Ar ($^{40}Ar/^{39}Ar$) chronometry allow the dating of major fabric-forming metamorphic minerals, like the micas or amphiboles, due to their generally high parent/daughter ratios. Mica or amphibole ages can be well-integrated into the structural-textural context (e.g. Steiger 1964), and they have been utilized to establish chronologies of metamorphic terranes – with varying success – from the 1950s onwards. Major obstacles for an unequivocal link between those ages and textures have been large sample size requirements in earlier studies (requiring a separation procedure that obliterates textural information), isotopic disequilibria between analysed minerals or whole rocks, low temperature re-equilibration by either diffusion or mineral reaction and the common occurrence of more than one mineral generation (e.g. zoned mineral phases). As a result of these problems, which were increasingly realized during the 1980s, the results of conventional Rb–Sr dating in polymetamorphic terranes, i.e. paired mica–whole rock/feldspar analyses, have

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often been considered unreliable (cf. Frey *et al.* 1976; Müller *et al.* 1999). However, due to the new possibilities provided by Rb–Sr microsampling and UV laser-ablation $^{40}Ar/^{39}Ar$ dating, truly integrated geochronological studies are now feasible. In particular, Rb–Sr microsampling has renewed the interest and confidence of geochronologists in the Rb–Sr geochronometer. In principle, Rb–Sr dating of metamorphic white mica is a powerful technique, because of the high closure temperature ($\geq$550 °C; Cliff 1993; Villa 1998) and the high Rb/Sr ratios of micas, which nowadays allow the dating of single grains (Chen *et al.* 1996; Müller *et al.* 2000*b*). Rb–Sr also allows the dating of other minerals such as chlorite, which cannot be analysed by $^{40}Ar/^{39}Ar$ dating due to low K contents and the associated risk of excess-Ar contamination.

Recently, the Rb–Sr systems in micas and other minerals have been successfully used to study low temperature deformation processes (Inger & Cliff 1994; Müller *et al.* 2000*a*,*b*). In this volume, **Cliff & Meffan-Main** detail their approach for establishing a more reliable chronology in polymetamorphic basement gneisses of the Eastern Alps (Tauern window), mainly using microsampled white mica, which was extracted from rock thick sections after careful optical and electron microscopy. The obtained ages were, in turn, compared to established chronologies in corresponding overlying monometamorphic cover sequences (Inger & Cliff 1994). The augen gneiss samples studied record a two-phase deformation history, which in simple terms comprises an earlier shearing and a subsequent folding event. Cliff & Meffan-Main have used a microdrill to sample small cylinders of different minerals (100–600 μm diameter) out of 150 μm thick sections, which corresponds to sample weights of 10 to 250 μg. The underlying assumption was that by utilizing (adjacent) minerals at the (sub-)millimetre scale, Rb–Sr isotopic equilibration would be more likely to be attained. For the shearing event, two samples indicate a pooled age of 27.3 $\pm$ 0.8 Ma, whereas six crenulated samples record a cluster of ages at 25.5 Ma, with a very good precision of $\pm$0.3 Ma (*c.* 1%), which is interpreted to date the peak of the subsequent folding event. Although the authors demonstrate many examples of isotopic disequilibrium between minerals, most notably involving large feldspars, careful petrographic characterization before microsampling (for Rb–Sr dating) ensures the derivation of the most accurate results. The obtained ages are consistent with field evidence and previous chronology from the cover sequences, and the resultant precision is capable of distinguishing separate events closely spaced in time. Taken together, this example illustrates that meticulous work produces accurate results, even in polymetamorphic basement rocks.

The work of Cliff & Meffan-Main links with those of others in the recent literature. A slightly different approach for the specific purpose of dating fault zones and constraining the duration and rates of faulting was utilized by Müller *et al.* (2000*a*,*b*). They specifically used syndeformationally grown fibrous minerals that formed below their respective temperatures for isotopic closure, either between stretched porphyroclasts or in the strain shadow of large rigid objects. Using newly formed minerals with unambiguous textural relationships avoids problems with isotopic disequilibrium and the incomplete resetting of isotopic systems in minerals during deformation. A key example of this approach includes a mylonitized slate from the northern Pyrenees, which contains quartz–calcite–chlorite fibres grown antitaxially in the strain shadow of large pyrites in response to deformation. These fibres record two distinct stages of deformation related to the northward thrusting of the external Pyrenees (Aerden 1996). For the purpose of Rb–Sr microsampling dating, chlorite + quartz are characterized by elevated Rb/Sr ratios, whereas cogenetic calcite was used to constrain the initial Sr isotopic composition at the time of fibre growth. Four successive increments of fibre growth could be microsampled at a resolution of $\geq$1 mm, which could not be reduced due to the low Sr material used (chlorite, quartz). Subsequent Rb–Sr microsampling dating constrained both duration and rates of faulting and yielded a long duration of shear zone activity of *c.* 37 Ma (87–50 Ma), with a low average strain rate of $1.1 \times 10^{-15}\ s^{-1}$. During one short interval (66–62 Ma), the strain rate increased to $7.7 \times 10^{-15}\ s^{-1}$, which coincided with a change in fibre growth direction and the reorientation of the stress field to renewed horizontal compression (Müller *et al.* 2000*a*).

Rb–Sr microsampling dating still involves low-blank sample dissolution, purification of Sr and Rb via extraction chromatography and, finally, conventional thermal ionization mass spectrometry (TIMS) analysis. **Vanhaecke *et al.*** describe a first step towards the elimination of this time-consuming sample preparation step. At present, separation is still necessary because the isobaric interference from Rb at mass 87 requires complete separation of Rb and Sr before mass spectrometry. Even at highest mass resolution (10 000), current mass spectrometers are unable to separate ^{87}Rb and ^{87}Sr, which would require a resolution power of *c.* 290 000. Vanhaecke *et al.*

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illustrate a possibility for overcoming the spectral interference problem, namely ion-molecule chemistry induced by a reactive gas in a dynamic reaction cell of an ICP mass spectrometer. In this case, CH_3F gas is used, which transforms Sr^+ into SrF^+ ions, but does not convert Rb^+ into RbF^+ ions, because the latter reaction is endothermic and does not proceed (Moens *et al.* 2001). Hence, SrF^+ ions (with F being mono-isotopic) at m/z 103, 105, 106 and 107 are analysed rather than Sr^+, which eliminates the Rb interference on Sr. Vanhaecke *et al.* tested this technique for granitic whole-rock samples and found good agreement with previously reported TIMS data, although TIMS achieves far better precision (*c.* 0.1% for dynamic reaction cell–inductively coupled plasma mass spectrometry (DRC-ICPMS) in contrast to 0.0025% for modern multicollector TIMS). As stated by the authors, a breakthrough would be achieved if the DRC–ICPMS system could be combined with direct solid sampling by laser ablation, which would open up true *in-situ* Rb–Sr dating of minerals with high Rb/Sr ratios, such as micas in differentiated granites or pegmatites (and their deformed counterparts) with typical Rb/Sr ratios of >100. This is currently being worked on by the same authors. It remains to be assessed how accurately parent/daughter ratios can be determined and how mass bias depends on matrix composition. Finally, coupling with a MC–ICPMS would allow for simultaneous collection of all isotopes.

In contrast to Rb–Sr dating, true *in-situ* dating using UV laser ablation $^{40}Ar/^{39}Ar$ analysis is already well-established. The main advantage of extracting Ar with a laser is the ability to perform texturally controlled analysis, with the added benefit of very little sample preparation. Laser-based Ar extraction has been utilized for extraterrestrial samples since the early 1970s and for terrestrial rocks since the early 1980s, but only the use of UV lasers allowed analyses with improved ablation characteristics and sharper resolution (for a review see Kelley 1995). Moreover, only UV lasers facilitate the controlled ablation of transparent minerals such as white mica, feldspars or quartz, which are otherwise poor absorbers of higher wavelength lasers. UV laser ablation potentially has a spatial resolution of ≤ 10 μm and a depth resolution of *c.* 1 μm (Kelley *et al.* 1994), but of course is subject to counting statistics limitations with regard to the smallest useful sample size. The present generation of mass spectrometers requires about 1 pL of radiogenic ^{40}Ar per shot and this corresponds to hundreds or thousands of cubic micrometres of material, depending on the sample's age and K concentration.

Consequently, there are already a number of truly integrated applications of laser ablation $^{40}Ar/^{39}Ar$ analysis available. These include the dating of deformation (Mulch *et al.* 2002; Sherlock *et al.* 2003), the study of intragrain argon transport processes in minerals (Onstott *et al.* 1990; Reddy *et al.* 1996; Wartho *et al.* 1999), dating of impact-related pseudotachylytes (Spray *et al.* 1995), dating of different stages of one P–T loop (Di Vincenzo *et al.* 2001), dating of K-feldspar cements (Girard & Onstott 1991; Hagen *et al.* 2001), modelling the speed of kimberlite ascent (Kelley & Wartho 2000), modelling magma flow regimes in sills from Ar systematics in host rock micas (Wartho *et al.* 2001), dating of mineral inclusions in porphyroblasts (Kelley *et al.* 1997) and others.

In order to improve our understanding of the evolution of (semi-)brittle fault rocks like fault gouges or pseudotachylytes, both *in-situ* and stepwise-heating (or even better their combined use) $^{40}Ar/^{39}Ar$ dating have recently been applied (Müller *et al.* 2002; van der Pluijm *et al.* 2001). Fault gouges, which predominantly consist of fine-grained clay minerals, pose enormous difficulties for $^{40}Ar/^{39}Ar$ dating. One problem is the recoil-induced redistribution and subsequent loss of reactor-produced ^{39}Ar and ^{37}Ar (Onstott *et al.* 1995), which can be overcome by monitoring the ^{39}Ar loss by vacuum encapsulation and dating of microgram-sized clay samples (Foland *et al.* 1992; Onstott *et al.* 1997). The second issue is that clay samples consist of mixtures between different-aged authigenic and detrital components, which have to be resolved in order to arrive at accurate ages. Two techniques have recently been proposed to overcome the problem. Ages of both clay 'end-member' components can be determined due to differences in thermally activated Ar release between authigenic and detrital clay minerals, as revealed by laser-stepped heating (Onstott *et al.* 1997). Dating combined with detailed X-ray diffraction analysis of several grain size fractions of clays in fault gouges allows for the extrapolation of ages of clay mixtures to both pure authigenic and pure detrital 'end-member' ages (van der Pluijm *et al.* 2001). While considerable complexities exist in the processes governing the authigenic growth of mica, such as Ostwald ripening (Eberl *et al.* 1990; Kübler & Jaboyedoff 2000) and the reaction kinetics of mineral homogenization (Livi *et al.* 2002), these new techniques offer exciting prospects for the complicated dating of fault gouges and our understanding of brittle faults.

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As a complement to spatially resolved (laser microprobe) analyses, the K–Ar system can be exploited in the form of stepwise-heating $^{40}Ar/^{39}Ar$ analysis. The connection between these two analytical approaches requires some explanation. During stepwise-heating, $^{40}Ar/^{39}Ar$ analysis, Ar is sequentially released from the sample by increasing the temperature of a vacuum furnace and analysing the Ar isotopic composition of each step. Stepwise gas release can also be achieved with a defocused laser beam. In the early days of $^{40}Ar/^{39}Ar$ work, stepwise Ar release was considered to primarily reveal information about the spatial distribution of Ar within a mineral (McDougall & Harrison 1999). However, more recent work has demonstrated that hydrous phases especially (micas, amphiboles) are unstable during *in vacuo* heating and yield only limited, if any, information about the intragrain Ar distribution (Gaber *et al.* 1988; Lee *et al.* 1991; Hodges *et al.* 1994; Sletten & Onstott 1998). On the other hand, compositionally heterogeneous minerals or multiphase samples have been shown to release Ar over characteristic stages during a step-heating experiment (Villa *et al.* 2000; Müller *et al.* 2002). Using the direct compositional information from ^{37}Ar, ^{38}Ar and ^{39}Ar produced by neutron reactions from Ca, Cl and K, respectively, individual steps can be related to certain minerals present in chemically non-uniform samples (Villa *et al.* 2000; Villa 2001; Müller *et al.* 2002). EMPA data that can be compared with Ca/K and Cl/K ratios calculated from $^{40}Ar/^{39}Ar$ analyses are crucial for the success of this link. The theoretical spatial resolution of differential Ar release by step-heating is controlled by the reactor-induced recoil redistribution of Ar isotopes, i.e. less than *c.* 0.5 μm (Onstott *et al.* 1995). Using this indirect method for linking time, composition and textures, zoned amphiboles or pseudotachylytes, for example, can be reliably dated (Villa *et al.* 2000; Müller *et al.* 2002). This contrasts with *in-situ* laser ablation $^{40}Ar/^{39}Ar$ analysis, which in the presence of inhomogeneities on the *c.* 10 μm scale may yield inaccurate ages due to mixing of unrelated components, such as very fine-grained inherited clasts present in a pseudotachylyte matrix (Müller *et al.* 2002).

Understanding transport processes in rocks

The issue of how fast mineral reactions occur in rocks is one that has exercised petrologists and isotope geochemists alike (e.g. Wood & Walther 1983; Rubie & Thompson 1985; Christensen *et al.* 1989; Vance & O'Nions 1990; Baxter & DePaolo 2000, 2002*a*,*b*). As we have noted earlier, an understanding of the relative rates of attainment of isotopic, chemical and textural equilibrium is one of the main problems barring progress in understanding isotopic ages in a petrological and structural context. On the other side of the coin, however, the quantification of rates of metamorphic reactions has also been an important *objective* in chronological studies themselves (e.g. Christensen *et al.* 1989; Vance & O'Nions 1990; Müller *et al.* 2000; Baxter & DePaolo 2000, 2002*a*,*b*). The importance of this issue extends beyond mere idle curiosity: if rates of reaction are not fast enough to keep up with changes in intensive variables like P, T and the strain environment, then the whole concept of local equilibrium and the P–T–X–d–t data that are based on it are called into question. Disequilibrium – chemical, textural and isotopic – is well-known in metamorphic rocks (and, indeed, used in the extraction of P–T–t paths from zoned minerals like garnet) on larger scales and is increasingly being recognized on smaller scales (e.g. Cooke *et al.* 2000). However, metamorphic petrology simply works too well for unrecognized disequilibrium (at least at the scale of electron microprobe measurements) to be a serious and pervasive problem. It has also been known for some time (see references in Baxter 2003) that the rates of reaction measured in laboratory experiments, if applicable to natural situations, are certainly fast enough to allow local equilibrium in geological timescales. However, **Baxter** points out that the growing natural database, while consistent with the experiments for contact metamorphism, suggests much slower reaction rates in natural regional metamorphic settings than in the laboratory. This is not a new observation (see for example Rubie & Thompson 1985) but Baxter presents a very useful review of recently published constraints on natural reaction rates to sit alongside previously published reviews of the experimental database (Wood & Walther 1983; Rubie & Thompson 1985). The natural dataset is based on techniques as diverse as the analysis of crystal size distributions, isotope exchange modelling of disequilibrium in strontium and oxygen isotopes, garnet growth rate studies, the modelling of chemical gradients in metamorphic rocks and strain rate constraints. All of these approaches document natural reaction rates that are four to seven orders of magnitude slower than those in laboratory experiments.

The paradox highlighted by Baxter mirrors a similar dichotomy that is familiar to the world of

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geochronology, where many instances of contrasts between predictions and observations are known (Cherniak & Watson 2001; Villa & Puxeddu 1994). The common reason appears to be the role of water in laboratory experiments. Water is sometimes added in experimental capsules to stabilize hydrous minerals, but its effect on the reaction rate is detrimental, as it enhances it dramatically (Farver & Yund 1991). Indeed, diffusivity experiments on biotites were initially believed to support very high Ar loss rates (e.g. Harrison *et al.* 1985), until it was shown that the high rates derived from such experiments really pertained to nanometre scale alteration reactions (Lippolt *et al.* 1987) and dissolution/reprecipitation in the capsule (Villa & Puxeddu 1994). The role of water is evident from Baxter's comparison of two kinds of natural systems: regional and contact metamorphic rocks. The former show a large discrepancy by being many orders of magnitude slower than laboratory extrapolations, the latter much less so. Ore geologists owe their livelihood to the fact that a cooling pluton exsolves very large amounts of water, creating an alteration halo. It is therefore self-evident that the rates of contact-metamorphic processes will be dominated by the involvement of aqueous fluids, which are present but not necessarily pervasive in regional metamorphism.

In two companion papers, **Kriegsman & Nyström** and **Nyström & Kriegsman** discuss a theme that is directly relevant to that of this book – the calculation of magma extraction rates. In the first, theoretical, paper, **Kriegsman & Nyström** demonstrate the mathematical equivalence of five different numerical models to describe trace element distributions in migmatites. One of these models involves disequilibrium melting followed by *in-situ* crystallization of a non-segregated melt. The operation of this scenario, and the consequent trace element patterns it produces, has been used in the past to suggest very rapid melt extraction rates in high-grade terranes (e.g. Barbey *et al.* 1989; Sawyer 1991). However, the authors suggest that the trace element patterns involved in this scenario can be equally well produced by a variety of other models involving equilibrium or disequilibrium melting, followed by minor equilibrium crystallization and melt escape and/or back reaction of restite with the melt. If this model is correct, then it implies that there is no unique solution to the inverse problem (determining a melt extraction rate from the trace element distribution), so that geochemical estimation of melt extraction rates must rely on other techniques, such as microtextural and microchemical observations combined with better geochronology. **Nyström & Kriegsman** then go on to present a case study that is illustrative of these ideas, involving detailed textural and chemical observations of migmatites in the Palaeoproterozoic Svecofennian Orogen in SW Finland. Garnet (and other minerals) in these rocks is interpreted to have grown as a result of prograde melt reactions. Later retrogression, however, via back-reaction with melt has resulted from the reversal of these prograde reactions. The detailed major and trace element chemistry of the garnet preserves a record of these reactions. In particular, sharp decreases in Mn and trace element contents (Y, HREE, Zr) at the rims suggest release of these elements during the garnet–melt back-reaction. The apparent disequilibrium distribution of these trace elements between melt and restitic material in migmatites has previously been used as evidence of rapid segregation rates (Sawyer 1991). However, the present authors interpret the release of these trace elements from garnet–melt retrograde reactions, along with their textural observations on accessory phases which suggest new growth of zircon and monazite in the restite, to suggest an alternative explanation for apparently disequilibrium features that do not necessitate rapid melt extraction. Indeed, if trace element distributions are to be explained by back-reaction with melt, then that melt must remain in contact with the restite for a prolonged period of time. The data also have direct consequences for a paradox in some of the geochronology literature: why is it sometimes the case that accessory phase ages in restitic material are not dominated by old, inherited zircons but are actually younger than those located in the leucosome? Curious readers should enjoy their discussion as a geological 'whodunit'.

The paper by **Wartho & Kelley** attempts to use isotopic data to constrain the rate of a natural process. It also illustrates extremely well the strength of high spatial resolution UV laser ablation $^{40}Ar/^{39}Ar$ analysis, for both isotopic profiling and *in-situ* dating. They extend their earlier work (Kelley & Wartho 2000) and present additional UV laser ablation $^{40}Ar/^{39}Ar$ analyses of mantle phlogopites to evaluate the significance of recorded core ages, and kimberlite/diatreme ascent rates. Besides Siberian and Pacific (Solomon Islands) examples, they additionally include several South African kimberlites. Because Ar in the mantle effectively only partitions into phlogopite (which also is the only K-bearing phase), it retains Ar apparently quantitatively several hundred degrees Celsius above its nominal closure temperature, until it

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gets entrained into the diatreme magma. There, the degree of Ar loss is governed by the speed of ascent, the depth and initial magma temperature. For at least two localities from both South Africa and the Solomon Islands, the authors are able to demonstrate similar phlogopite core ages from several samples, which in turn are interpreted to reflect geological events. Other examples yield a larger range of core ages, but in most of these cases the Ar loss profiles indicate similar results in terms of diffusional Ar loss (when corrected for grain size effects). When converted into ascent times, both Solomon Islands and South African diatremes recorded times of 0.9–6.9 and *c.* 11 days, respectively. These are significantly slower than the Siberian examples (Kelley & Wartho 2000). A welcome side effect of this result is that Ar in kimberlitic phlogopites can serve as a 'proxy' for diamond resorption during ascent in the kimberlite magma. By measuring Ar zonation in phlogopite phenocrysts by laser microprobe, the authors observe higher radiogenic ^{40}Ar (Ar*) concentration in the grain cores than at the rims. Large differences correspond to higher surface corrosion of diamonds, an undesirable economic flaw. In the past it had been shown that phlogopites from kimberlites were isotopically zoned (Phillips & Onstott 1988) and that, at least in some cases, the chemical zonation suggested the presence of chemically heterogeneous mica generations. Regardless of whether only chemical reaction, or only reaction-free diffusion, or a combination of both, was responsible for the observed spatial distribution of Ar, it is a robust property of all three possibilities that the rate of Ar loss, x, depends exponentially on temperature: $x = K_1 e^{(E_1/RT)}$, where K_1 is a constant, E_1 is the relevant effective activation energy for the process causing Ar loss, and R is the gas constant. On the other hand, the resorption rate of diamonds, k, also obeys an Arrhenian relationship: $k = K_2 e^{(E_2/RT)}$, where K_2 is a constant and E_2 is the activation energy of the resorption reaction. If E_1 and E_2 do not differ by a factor of more than two or three, the magma temperatures at which Ar is transported are quite similar to those at which the diamond surface is resorbed. Thus, it is possible to derive a time-integrated resorption whose relative magnitude is accurate without having to know either the magma temperature T, or the exact diffusivity x, or even the precise mechanism by which Ar is lost, by simply comparing the time-integrated Ar losses xt, or, more rigorously, $\int xT(t)\,dt$.

The work presented by **Kramar *et al.*** extends their earlier work on linking the distribution of radiogenic ^{40}Ar in micas to the deformational history of the rock (Kramar *et al.* 2001) and attempts to identify a physical mechanism for deformation-enhanced Ar transport. They use transmission electron micrograph imaging to identify heterogeneously spaced two-dimensional defects, 'stacking faults' as possible pathways for enhanced Ar diffusion, because stacking faults induce a net dilation effect on a crystal lattice and hence reduce Ar retention. Subsequent modelling shows that stacking faults indeed are viable pathways for Ar loss, in addition to other mechanisms involving physical grain size reduction or mineral recrystallization. Moreover, stacking faults are not static but in fact a continuously migrating zone of elevated diffusivity through the mineral lattice. This paper could be the starting-point for a comparison of dislocation densities in porphyroblasts with different apparent ages, different degrees of deformation, and different degrees of chemical disequilibria. The sample shown here, with non-stoichiometric K_2O ranging from 9.9% to 11.0%, hints at even more aspects that may need careful mineralogical-chemical assessment even at the sub-micrometric scale.

Conclusions and outlook

The papers in this volume amply illustrate the difficulty in achieving the key aim of providing a close link between isotopic ages from geochronology and the other information that rocks store in their chemistry and textures. However, they also illustrate the imaginative and innovative ways which geochemists and petrologists have devised to surmount those difficulties. In these concluding remarks, we return to the three key barriers to progress that we identified at the start of the paper and briefly summarize the way forward illustrated by papers in this volume.

The most precise ages available to isotope geochemists come from minerals with high parent/daughter ratios, accessory phases like zircon and monazite. A major effort is currently being invested in attempts to tie these ages more closely to the petrology of major mineral phases (Rubatto 2002; Foster & Parrish 2003; Whitehouse 2003). The most promising approach seems to be the use of common aspects of the chemistry of these two sets of minerals, like the REE and yttrium. This subject is still in its infancy and progress is likely to continue for some time yet. The principal problems with dating major mineral phases, like garnet, are related to the robustness of the chronometer in the face of problems with inclusions of trace-element-rich mineral phases. One of the key purposes of geochronology in the area of

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lithospheric deformation is the testing of numerical models. Such a purpose requires large datasets, which are difficult to obtain in the face of these problems. Developments that make garnet dating more routine (e.g. Anczkiewicz & Thirlwall 2003) will greatly facilitate progress.

The requirement for isotopic information on smaller and smaller scales is very important. The great potential of accessory phase chronometry is that, through *in-situ* techniques such as the ion microprobe and laser ablation, the chronometry can yield data on scales approaching chemical information. Other *in-situ* techniques, such as $^{40}Ar/^{39}Ar$ analysis by laser ablation, hold out that same promise. If the hurdle of coupling a laser system to dynamic reaction cell ICPMS can be overcome (Vanhaecke *et al.* 2003), this development could put Rb–Sr chronology on the same footing as these other *in-situ* techniques.

The final barrier outlined earlier in the paper – that of understanding more completely the details of isotope transport and equilibration in rocks and minerals – is perhaps the most difficult to overcome. However, one thing seems certain: this understanding will most likely come about through developments in the first two areas outlined above. Careful experimental petrology will help, of course, but, as Baxter (2003) illustrates, the real requirement is for isotope geochemists to use their newly won technical prowess at smaller and smaller scales to study real, natural systems and thereby identify the controls on isotope transport and equilibration processes.

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