Zircon: the metamorphic mineral

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INTRODUCTION

A mineral that forms under conditions as variable as diagenesis to deep subduction, melt crystallization to low temperature alteration, and that retains information on time, temperature, trace element and isotopic signatures is bound to be a useful petrogenetic tool. The variety of conditions under which zircon forms and reacts during metamorphism is a great asset, but also a challenge as interpretation of any geochemical data obtained from zircon must be placed in pressure-temperature-deformation-fluid context. Under which condition and by which process zircon forms in metamorphic rocks remains a crucial question to answer for the correct interpretation of its precious geochemical information.

In the last 20 years there has been a dramatic evolution in the use of zircon in metamorphic petrology. With the advent of in situ dating techniques zircon became relevant as a mineral for age determinations in high-grade metamorphic rocks. Since then, there has been incredible progress in our understanding of metamorphic zircon with the documentation of growth and alteration textures, its capacity to protect mineral inclusions, zircon thermometry, trace element patterns and their relation to main mineral assemblages, solubility of zircon in melt and fluids, and isotopic systematics in single domains that go beyond U-Pb age determinations. Metamorphic zircon is no longer an impediment to precise geochronology of protolith rocks, but has become a truly indispensable mineral in reconstructing pressure-temperature-time-fluid-paths over a wide range of settings. An obvious consequence of its wide use, is the rapid increase of literature on metamorphic zircon and any attempt to summarize it can only be partial: in this chapter, reference to published works are intended as examples and not as a compilation.

This chapter approaches zircon as a metamorphic mineral reporting on its petrography and texture, deformation structure and mineral chemistry, including trace element and isotopic systematics. Linking this information together highlights the potential of zircon as a key mineral in petrochronology.

PREAMBLE: THE MANY FACES AND NAMES OF METAMORPHIC ZIRCON

Various terms have been used, more or less loosely, to describe features and processes that form zircon in metamorphic conditions. Different authors may have used the same term differently, causing additional confusion. Any classification has to be based on texture, crystal structure and zircon composition and requires understanding of the formation process, which is not always the case in published studies. Within this contribution a generic terminology is adopted that uses three principal terms for metamorphic zircon: alteration, replacement/recrystallization and new growth. Examples of texture of these three categories are shown in Figure 1 and an attempt to summarize zircon features distinctive of particular metamorphic environments and processes is presented in Table 1.

(i) Alteration is a process that partly overprints and disturbs a relict mineral and where textural and chemical vestiges of the relict are preserved.

Alteration is often, but not necessarily, associated with metamictization as the damaged zircon domains are particularly prone to alteration by interaction with fluids. Alteration is the term used, for example, for old relict cores that have only partly lost their U-Pb and other isotopic signatures, and may have ghost or fuzzy zoning.

(ii) Replacement is an in situ process that changes the chemical composition of an existing domain, occurs at sub-solidus conditions and is commonly aided by fluids. Recrystallization is another term that is often used to describe this process. Replaced/recrystallized zircon domains show evidence of complete resetting of the chemical/isotopic system, a sharp boundary with inherited domains, and lack regular growth textures (shape or internal zoning), suggesting the domain formed in replacement of pre-existing zircon. One of the best investigated and widely recognized replacement processes that forms metamorphic zircon in sub-solidus conditions is in situ dissolution-precipitation (Geisler et al. 2003a; Tomaschek et al. 2003; Geisler et al. 2007; Rubatto et al. 2008; Putnis 2009).

(iii) Overgrowth or new growth indicates a new crystal domain that shows sharp boundaries with any existing relict core and regular growth textures (shape or internal zoning). These domains have distinct chemical and isotopic compositions that are generally homogenous within a single domain. This type of zircon is commonly found in melt or fluid-rich systems and is caused by crystallization from a melt or precipitation from a fluid. Overgrowths on detrital zircon grains at very low grade would also be included in this category.

This terminology has to be taken as zircon specific, and may not apply to other minerals. While many zircons in metamorphic rocks can be described with these three categories, it is evident that individual cases exist that do not clearly fit a single category as multiple processes may affect the same zircon population, and the distinction between one and another may be blurred (Spandler et al. 2004; Tichomirowa et al. 2005; Zheng et al. 2005; Chen et al. 2011; Gao et al. 2015).

PETROGRAPHY OF ZIRCON

Textural relationships and inclusions

Metamorphic petrology is grounded on careful textural observations to establish mutual relationships between minerals. Defining which mineral is coexistent with others (paragenesis) based on textural equilibrium, inclusion relationships and composition is the backbone of metamorphic petrology. Textural criteria are often questionable when small accessory and refractive minerals like zircon are involved (Fig. 2). Small zircons are commonly included in larger grains, but this does not mean that the host and the inclusion are in equilibrium. A common observation under the optical microscope is the presence of inherited zircons included in key metamorphic minerals, that despite the apparent equilibrium texture with straight grain boundaries, have no petrological relationship with the host mineral (Fig. 2B). Zircon in gneisses,

eclogitic metagabbros, and amphibolites that are included in metamorphic garnet, pyroxene or amphibole may be inherited and unrelated to metamorphism. Textural relationships between major minerals and zircon (and refractory accessory minerals in general) alone are not a robust criterion for age interpretation, particularly at low to medium metamorphic grade. A more robust link between the stability of major minerals and zircon can be established based on mineral inclusions in zircon (see below).

Petrography has proven a powerful and necessary tool to identify low-grade metamorphic zircon that overgrows detrital grains (Rasmussen 2005; Hay and Dempster 2009b). The small size and sawtooth-shape of these overgrowths is so characteristic that the texture alone is a strong evidence of metamorphic growth (Fig. 1A). Similarly, petrography is crucial in identifying micro-zircon that may form by exsolution or metamorphic reactions during cooling and breakdown of Zr-rich minerals. Examples are micro zircons in cordierite coronas around garnet (Fig. 2C, Degeling et al. 2001) or micro zircon around ilmenite and rutile (Bingen et al. 2001; Ewing et al. 2013). Unfortunately the size of these zircons is commonly below the common spatial resolution of microbeam dating techniques (10-30 μm, Fig. 1N and 2C), but their presence still provides important information on the petrogenesis of the rocks.

Particularly important is the use of petrography to recognize and characterize mineral inclusions in zircon. These inclusions are not only valuable for relating zircon ages to metamorphic assemblages, but may also provide unique petrological information on the *P-T* evolution of the host sample. The most striking example is from high and ultra-high pressure rocks (UH*P*), were prograde to peak mineralogy is easily replaced during decompression. Coesite is a key indicator mineral for ultra-high pressure metamorphism, but a robust container, such as garnet or zircon, is often needed to preserve coesite in natural rocks. Additionally, during decompression of felsic UH*P* rocks at T >700°C, phengite melting occurs leading to a pervasive recrystallization of the main rock-forming minerals (Hermann et al. 2006c). For this reason, relicts of UH*P* metamorphism in felsic rocks are most commonly found in refractory minerals such as garnet or zircon. In the subducted continental rocks of the Kokchetav Metamorphic Complex, diamonds in gneisses and marbles are mainly found as inclusions in zircon and garnet (Shatsky and Sobolev 2003). The spectacular record of peak to retrograde inclusions in zircon has proven a key tool for age interpretation (Hermann et al. 2001; Katayama and Maruyama 2009). In the vast Dabie-Sulu orogen, the extent of the crust subducted to UH*P* conditions could only be demonstrated through the widespread occurrence of coesite inclusions in zircon from gneisses (Ye et al. 2000) that otherwise preserve little or no relict of UH*P* assemblages.

Petrography of mineral inclusions in zircon must however deal with the possibility of secondary inclusions (Fig. 3). Altered and metamict zones in inherited zircon cores have been proven to contain secondary inclusions, as for example high pressure minerals in "magmatic" zircon (Gebauer et al. 1997; Zhang et al. 2009a; Gauthiez-Putallaz et al. 2016). These secondary inclusions may be identified because of disturbed cathodoluminescence zoning, fractures, porosity and evidence of metamictization in the zircon around the inclusions. More controversial is the finding of white mica inclusions (Hopkins et al. 2008;

Rasmussen et al. 2011) and carbon-phase inclusions (Menneken et al. 2007) in Early Archean zircons from the Jack Hills quartzite, where the debate is ongoing to what extent these inclusions are primary or secondary (see discussion in Harrison et al. 2017).

Internal zoning

It is impossible to overstate the importance of characterizing internal zoning in metamorphic zircon: recognizing the presence of detrital cores, relict protolith magmatic zircon, and multiple domains formed during metamorphism is a fundamental step in the correct interpretation of any zircon geochemical information and eventually age. This is most commonly achieved with panchromatic cathodoluminescence (CL) or back-scattered-electron (BSE) imaging, which have become ubiquitous tools in zircon studies. Since the early applications to metamorphic zircon it became clear that CL and BSE images reveal internal structure otherwise invisible in light microscopy or etching (e.g. Hanchar and Miller 1993; Hanchar and Rudnick 1995; Vavra et al. 1996). CL and BSE emission are both proxies for chemical signals and are broadly anti-correlated because intrinsic CL attributed primarily to Dy is suppressed by the heavy element U, which increases the BSE signal (Rubatto and Gebauer 2000; Poller et al. 2001). Composition is however not the only player in CL emission, which is also controlled by structural parameters such as crystallinity or the presence of defect centers (Nasdala et al. 2002). The application of CL to metamorphic zircon has revolutionized its use in metamorphic petrology, making it easy to identify distinct growth zones and, to some degree, deformation features.

There have been a few attempts to categorize zoning (particularly CL zoning) of metamorphic zircon (Rubatto and Gebauer 2000; Corfu et al. 2003; Rubatto and Hermann 2007b), but more commonly every case has been presented in separate studies. The variety of textures in zircon is extremely wide, but some general systematics exist (Fig. 1, Table 1). It is commonly recognized that metamorphic zircon domains (including zircons forming in anatectic melts, which are considered metamorphic in this paper) have weak zoning when compared with the marked oscillatory and sector zoning of magmatic zircon (see a review in Rubatto and Gebauer 2000; Corfu et al. 2003). Zircon formed in sub-solidus conditions most commonly shows no regular zoning, having either a homogeneous CL/BSE emission or a cloudy and irregular zonation. However exceptions exist particularly for zircons attributed to fluid-related processes like in metamorphic veins or jadeitites. Weak internal zoning also characterizes metamorphic zircon that crystallized in high-grade rocks, likely from anatectic melts. In this case, weak oscillatory, sector, or fir-tree zoning is more common (Vavra et al. 1996; Schaltegger et al. 1999; Corfu et al. 2003; Claesson et al. 2016). High grade metamorphic zircon often displays a relatively low CL emission, possibly related to a high U content (see also section on Th-U composition), but the opposite has also been observed (Vavra et al. 1996; Corfu et al. 2003; Fu et al. 2008). Notably low-U zircon domains that are irregular in shape and form embayments into magmatic zircon, and thus look quite similar to metamorphic domains, are also formed during late-magmatic processes (Corfu et al. 2003). While CL, and to a lesser extent BSE imaging remains a powerful tool to

recognize different growth domains, additional data are often required to determine the growth environment of metamorphic zircon.

Zircon imaging by more advanced techniques such as Electron Back Scattered Diffraction (EBSD), Transmission Electron Microscopy (TEM), and element mapping is more time consuming than CL and BSE imaging. These advanced techniques are applied to cases where deformation or particular chemical information is targeted (Reddy et al. 2008; Austrheim and Corfu 2009; Reddy et al. 2010; Timms et al. 2011; Piazolo et al. 2012; Vonlanthen et al. 2012). It has been proposed that magmatic and metamorphic zircon can be distinguished based on Raman spectra (Xian et al. 2004), but this application remains limited and widely untested. The analytical approach for Raman identification has indeed been contested (Nasdala and Hanchar 2005) because it is based on a laser-induced photoluminescence peak. Given the possible difference in trace element composition between magmatic and metamorphic (i.e lower in rare earth elements – REE – and Th) zircon, it is plausible that in some cases a distinction based on spectroscopy may work. The greatest use of Raman spectroscopy is in the documentation of completely to partly metamict zircon, where the amorphisation process leads to changes in the wavenumber and half-width of the Raman bands (Nasdala et al. 2003).

The superior spatial resolution of TEM analyses (McLaren et al. 1994; Hay and Dempster 2009b; Hay et al. 2010; Vonlanthen et al. 2012) and, more recently, atom probe (Valley et al. 2014) are promising investigative tools, but they require advanced sample preparation and are partly destructive. Their future application to recrystallization fronts and domain boundaries within metamorphic zircon may be particularly interesting for the understanding of processes of metamorphic zircon formation.

Deformation

There is no regional metamorphism without deformation and thus the effect of deformation on metamorphic zircon systematics must be taken into account. Evidence of crystal-plastic deformation of zircon crystals affecting composition and most importantly U-Pb systematics mainly come from high temperature shear zones (Reddy et al. 2006; Timms et al. 2006; Austrheim and Corfu 2009; Piazolo et al. 2012), although reports from unfoliated rocks also exist (Timms et al. 2011). Large zircon crystals (mm in size) in rocks that deformed under amphibolite- to granulite-facies conditions (>700°C) display intragrain crystallographic miss-orientation of 2–20° at the crystal tips (Reddy et al. 2006; Timms et al. 2006; Reddy et al. 2007; Piazolo et al. 2012). This miss-orientation correlates with panchromatic CL emission (reduced CL at the loci of low angle boundaries), REE composition (increase in total REE and of middle-REE – MREE – with respect to heavy-REE – HREE) or increase in Th/U (Timms et al. 2006; Piazolo et al. 2012). In some cases, deformation results in microfractures that define small subgrains that are misoriented by up to 10° and contain less Ti than the original crystal (Timms et al. 2011; Piazolo et al. 2012). Planar deformation features have been observed in zircon from pseudotachylytes (Austrheim and Corfu 2009). While these features are common in impact-related minerals, in this case they have been attributed to extreme strain rate during seismic deformation.

Studies agree that the dislocations and deformation features act as fast diffusion pathways for trace elements, U, Th and Pb. The creation of subgrains may also enhance chemical exchanges with any alteration fluid due to high surface area (Piazolo et al. 2012). How much this deformation disturbs the age is not always clear because its detection depends on the relative timing of crystallization versus deformation. Partial to complete resetting of U-Pb ages in the deformed domain is observed in some cases (Timms et al. 2011; Piazolo et al. 2012).

While full characterization of deformation features (best done by EBSD) and degree of chemical and isotopic resetting may not always be possible, panchromatic CL images can give a first hint on the presence of deformation. In all cases reported, a general correspondence between low-angle boundaries and low CL emission exists and such features should be a warning for any isotopic analysis. This correspondence is in agreement with observed recovery of CL emission by annealing of crystal defects (Nasdala et al. 2002).

MINERAL CHEMISTRY

There are several chemical indicators that have been commonly used in identifying metamorphic zircon and to create links between measured ages and metamorphic conditions (see also Table 1). Chemical criteria that can relate zircon composition to metamorphic assemblages are particularly useful for age interpretation. This however requires that the chemical (trace elements including Th and U) and isotopic (Pb) systems are equally robust. Experimental studies indicate that diffusion of the large divalent Pb^{2+} ion is comparable to that of trivalent REE and orders of magnitude faster than tetravalent ions like Th and U, which are essentially immobile under most geological conditions (Cherniak and Watson 2003). Additionally, radiogenic Pb is internally produced and may not be bonded in the crystal lattice in a structural site, and this might enhance its capacity to escape the crystal. Decoupling of U-Pb ages and element abundances has been reported for samples that have experienced high temperature (Kusiak et al. 2013a), metamictization or intense deformation (Reddy et al. 2006; Timms et al. 2006; Timms et al. 2011). Kaczmarek et al. (2008) reported zircon from deformed metagabbros that preserved magmatic REE patterns, but whose apparent ages varied between that of the protolith and of later metamorphism. Zircons from the Dabie-Sulu high pressure rocks commonly contain relicts of magmatic zircon, that may still have their original high Th/U or steep REE patterns, but whose U-Pb system has been reset to the age of metamorphism (Zheng et al. 2005; Xia et al. 2009). Studies of natural samples that suggest diffusional re-equilibration of REE, but not of Th and U, as predicted by diffusion experiments, are lacking.

Th/U systematics

The Th-U composition of zircon is routinely measured during dating and thus has become an easy-to-acquire and widely used criteria for zircon classification. The Th/U of metamorphic zircons is generally < 0.1, but exceptions do exist (see below). This criteria was proposed based on the study of low temperature, high pressure zircons (Rubatto and Gebauer 2000), and it has been proven valid in

countless cases. Exemplary are numerous studies of eclogite-facies zircon, and zircon in migmatites and granulites (Fig. 4). In general terms, the robustness of this simple chemical criteria appears to be independent of the process that led to zircon formation, from solid-sate replacement to crystallization from anatectic melts (Zhao et al. 2015). It is also important to note that the opposite is also true: most magmatic zircons have Th/U > 0.1 unless altered (e.g. Belousova et al. 2002; Grimes et al. 2015).

It has been demonstrated that metamorphic zircon does not always have low Th/U. The most occurrences of metamorphic zircon with Th/U > 0.1 are from high and ultra high temperature (>900°C) samples [(Vavra et al. 1996; Schaltegger et al. 1999; Möller et al. 2003; Kelly and Harley 2005) see also a discussion in (Harley et al. 2007)]. The incorporation of Th in zircon is primarily controlled by the availability of Th and U in the system and partitioning with other phases. The common presence in crustal metamorphic rocks of Th-rich phases such as monazite and allanite is an obvious reason for low Th/U in coexisting metamorphic zircon in eclogite, amphibolite and granulite facies rocks. The absence of these phases in some crustal rocks (either by melting under ultra-high *T* – UH*T*, or because of composition) should produce metamorphic zircon with high Th/U.

A compilation of Th/U versus U content of metamorphic zircon in different tectonic settings shows some interesting systematics (Fig. 4, ca. 1400 analyses). Data are grouped in 4 categories representing different metamorphic conditions. (A) Relatively low temperature, high-pressure rocks of various compositions from mafic eclogites and leucogabbros, to micaschists and metamorphic veins (Rubatto and Gebauer 2000; Rubatto and Hermann 2003; Spandler et al. 2005; Bauer et al. 2007; Rubatto et al. 2008; Gordon et al. 2012; Ganade de Araujo et al. 2014; Phillips et al. 2015; Rubatto and Angiboust 2015). In all cases metamorphic temperatures are below the solidus and there is no evidence of melting in the rocks. According to the studies, most metamorphic zircon in these samples formed under HP conditions. In such "cold" eclogites Th/U of metamorphic zircon is mostly, but not restricted to <0.1, with values between 0.001 to 0.6. U contents are also variable from a few to 1000s of ppm, but mostly below 1000 ppm. The variability in zircon Th-U composition of HP rocks overall is large compared to any other category. The large range reflects the variety of rock types but also the lack of a dominant buffering phase. Monazite is not a common mineral in these rocks, but allanite is present in many samples. Another secondary effect that influences Th/U in these samples may be the temperature dependence of Th incorporation in zircon: the relatively larger Th^{+4} ion may fit proportionally less in a lower T crystal structure than the smaller U^{+4} ion (Rubatto and Gebauer 2000).

(B) In mafic and felsic crustal rocks that underwent UH*P* conditions and thus higher temperatures of re-equilibration, metamorphic zircon Th-U composition is more restricted. U ranges between 10–2500 ppm (at least in the selected samples) and Th/U is mainly below 0.2, with less than 10% of data (total analyses 524) higher than this value. As documented by Stepanov et al. (2016b) for some UH*P*-*T* gneisses of the Kokchetav metamorphic complex, the relatively high solubility of monazite in ultrahigh temperature melts (Stepanov et al. 2012; Stepanov et al. 2014) will allow zircon crystallization with high Th/U in some

rocks. Indeed, in one Kokchetav sample it has been documented that prograde metamorphic zircon cores with low Ti-contents have Th/U<0.1, consistent with coexisting monazite, whereas peak metamorphic zircon domains with high Ti contents have Th/U of 0.4–0.6 and formed at 1000°C, 5 GPa when monazite was completely dissolved in the partial melt. Zircon rims with low Ti that formed during retrograde crystallization of melts, when monazite is again present in the assemblage, show a low Th/U<0.1 (Stepanov et al. 2016a). Zircons in gneisses from the Bohemian Massif UH*P* unit have a restricted composition (Th/U 0.02-0.1, Kylander-Clark et al. 2013). UH*P* mafic eclogites from the Western Gneiss Region (Root et al. 2004; Kylander-Clark et al. 2013) and from the Dora Maira whiteschists (Gebauer et al. 1997; Gauthiez-Putallaz et al. 2016) also have zircon Th/U consistently below 0.1. Zircon rims from the Sulu UH*P* mafic and felsic rocks show higher values up to 0.4 (Zhang et al. 2009b).

(C) Zircon in migmatites, where a significant amount of leucosome is preserved, consistently has Th/U at 0.1 or below. This is independent of metamorphic temperature or pressure, from the 800°C and 9 kbar of the Himalayan Higher Crystalline (Rubatto et al. 2013), to the water assisted melting at 650–700 °C, 5–13 kbar in the Central Alps (Rubatto et al. 2009) and Alaska Chugach complex (Gasser et al. 2012), including low pressure migmatites of central Australia. Most of these samples are metapelitic migmatites, where monazite is always an abundant accessory mineral in both paleosome and leucosome. In metatonalites from the central Alps, allanite is a nearly ubiquitous accessory (Rubatto et al. 2009). Notably, in the metapelites the U content of metamorphic zircon is also quite restricted, never below ~100 ppm, whereas it can be as low as 10 ppm in the migmatitic tonalites. In migmatites of intermediate composition where neither allanite nor monazite are stable then higher Th/U are expected (see an example in the Lewisian granulites of Norhern Scotland Whitehouse and Kemp 2010). The remarkably consistent Th-U composition of zircons in many migmatites may be also related to the presence of partial melts, which are a Th and U bearing phase. Experimental studies show that the relative partitioning of Th and U between zircon and granitic melt does not significantly change with T in the range 800-1050 °C (Rubatto and Hermann 2007a). In very oxidized environments, some of the U might occur as 5+ or even 6+ cation, which are significantly more incompatible than U^{4+} (Burnham and Berry 2012). As Th remains as 4+ cation this might potentially contribute to high Th/U in highly oxidizing environments.

(D) UH*T* rocks (T>900°C) are a distinct case in Th-U metamorphic zircon composition, as the majority of data plot above Th/U of 0.1 with values as high as 3. Samples include the pigeonite-bearing granulites from the Rogaland anorthosite complex (Möller et al. 2002), the saffirine-bearing orthogneiss and charnokite of the Napier Complex in Antarctica (Kelly and Harley 2005), enderbite and migmatitic gneisses of the Eastern Ghats belt in India (Korhonen et al. 2013), and metapelitic rocks of the lower crustal section of the Ivrea Zone (Vavra et al. 1996; Ewing et al. 2013). Note that some of the UH*P* samples from the Kokchetav massif plotted in category B also recorded T of 900-1000°C and Th/U can be >0.1. Lower crustal metapelites that did not reach temperatures >850°C and where monazite is stable are plotted in Figure 4D for comparison (Hojazo and Malenco, Cesare et al. 2003; Hermann and Rubatto 2003); these

relatively lower T granulites have very low Th/U (0.001–0.01) and U content is above 100 ppm. Zircon from ultramafic rocks where there is no stable Th-phase are also included in this plot and indeed they show Th/U of 0.1–1. Examples are metamorphic zircons from a HP metapyroxenite (López Sánchez-Vizcaíno et al. 2001) and zircon from the Duria garnet peridotite (Hermann et al. 2006b).

Rare earth elements

Rare earth elements (REE) and particularly mid to heavy REE (M-HREE, Sm–Lu) can also be used for recognizing metamorphic zircons. The principle is based on partitioning with co-existing minerals that sequester M-HREE in the metamorphic assemblage (Fig. 5). Garnet is commonly a main host of HREE in medium to high-grade mafic to pelitic metamorphic rocks. Zircon that grows in a garnet-rich assemblage, where HREE are sequestered in garnet, will show a relatively flat HREE pattern compared to the HREE enrichment in magmatic zircon. This low HREE signature has been widely reported for metamorphic zircon in garnet-bearing eclogitic and granulitic rocks (Schaltegger et al. 1999; Rubatto 2002; Hermann and Rubatto 2003; Rubatto and Hermann 2003; Whitehouse and Platt 2003; Bingen et al. 2004; Gilotti et al. 2004; Hokada and Harley 2004; Root et al. 2004; Kelly and Harley 2005; Hermann et al. 2006a; Rubatto et al. 2006; Wu et al. 2008a; Wu et al. 2008b; Rubatto et al. 2013; Fornelli et al. 2014; Whitehouse et al. 2014; Gauthiez-Putallaz et al. 2016).

Similarly, Eu deficiency relative to other REE in zircon (i.e negative Eu anomaly) has been attributed to the presence of feldspars that sequester Eu (Schaltegger et al. 1999; Rubatto 2002). The fact that zircon mainly incorporates Eu^{3+}, whereas feldspars take up mainly Eu^{2+} is a further complication (see also a discussion in Kohn 2016). Two main metamorphic conditions have been related to changing Eu anomaly in metamorphic zircon. (i) In eclogite facies assemblages, where albite breaks down to jadeite and quartz, zircon commonly has a weak or no Eu anomaly, at least in rocks that have no strong bulk Eu anomaly. As eclogitic assemblages also commonly yield garnet, the lack of a negative Eu-anomaly is coupled to a relatively flat HREE pattern (Fig. 5A) (Rubatto 2002; Rubatto and Hermann 2003; Baldwin et al. 2004; Gilotti et al. 2004; Wu et al. 2008a; Wu et al. 2008b; Gauthiez-Putallaz et al. 2016) (ii) In migmatites, melting reactions involving micas produce peritectic K-feldspar that incorporates all the available Eu^{2+}. Metamorphic zircon (and monazite) growing from anatectic melts acquires a stronger negative Eu anomaly relative to their protolith or sub-solidus counterpart (Fig. 5B, Schaltegger et al. 1999; Rubatto et al. 2006; Rubatto et al. 2013). Similarly, metamorphic zircon growing in an assemblage rich in L-MREE phases such as titanite, allanite or monazite can develop a particularly light-REE (La-Nd) depleted pattern (Fig. 5C). This has been observed for example in zircon from the amphibolite-facies migmatites of the Central Alps, which are rich in accessory allanite and titanite (Rubatto et al. 2009).

It is important to bear in mind that, as already stated for Th/U, these REE signatures are not absolute and depend on a number of factors: (i) bulk rock composition, e.g. in rocks strongly enriched in HREE, both garnet and metamorphic zircon will have relatively high HREE; zircon growing in a feldspar-free, HP assemblage may still have a negative Eu anomaly if the bulk rock is Eu-

depleted [e.g. HP zircon in some Kokchetav gneisses (Hermann et al. 2001) and Dora Maira whiteschists (Gauthiez-Putallaz et al. 2016)]. (ii) The volume percent of the HREE or Eu controlling phase: rocks in which garnet is only a minor phase may still have metamorphic zircon with high HREE contents. (iii) The presence of other phases controlling the HREE or Eu budget, as for example abundant orthopyroxene that can accommodate significant HREE (Fornelli et al. 2014) and will increase the HREE depletion in granulite facies zircon.

The use of HREE in linking metamorphic zircon to garnet in the co-existing assemblage can be exploited further if the equilibrium partitioning between zircon and garnet is known for different temperatures and garnet compositions. In samples with zoned garnet and multiple metamorphic zircon growth this could lead to identifying which specific garnet and zircon growth are in equilibrium (Hermann and Rubatto 2003). Experimental and empirical trace element zircon/garnet equilibrium partitioning vary over an order of magnitude, particularly for the HREE (Table 2) (Rubatto 2002; Hermann and Rubatto 2003; Rubatto and Hermann 2003; Hokada and Harley 2004; Kelly and Harley 2005; Buick et al. 2006; Rubatto et al. 2006; Rubatto and Hermann 2007a; Taylor et al. 2014). Element partitioning between two phases is firstly controlled by temperature, and secondarily by composition, whereas pressure is likely to have a negligible effect (Rubatto and Hermann 2007a). The published values cover metamorphic temperatures from 550–1000°C for natural samples and 800–1000°C for experiments, and variable garnet compositions from 0 to 8 wt% CaO (subset of studies for which the garnet composition is provided). In this wide range of conditions, variations are expected. Taking as an example Yb, the most abundant HREE in both minerals and thus relatively easy to measure, correlations between these parameters can be seen (Fig. 6). The zircon/garnet partition coefficient for Yb shows a negative correlation with T when the experimental studies are considered. This T-dependence is confirmed by some natural samples at 1000°C that have a low zircon/garnet partition coefficient for Yb of 0.4-1.2, whereas granulites at ~800°C have a Yb partition coefficient of 5-17. Both experimental studies and natural samples at these T are equilibrated with melts. Notably, the three samples that recorded lower metamorphic temperatures, where melt was not present, fall off the trend defined by melt-present samples/experiments. For the subset of studies that report garnet composition, most data also show a correlation between zircon/garnet Yb partitioning and grossular component in garnet. This highlights an additional complexity in the application of equilibrium partitioning as garnet major element composition varies widely, whereas zircon major composition remains constant. More systematic studies are needed to fully map out the effects of temperature and garnet composition on HREE partitioning.

In samples where garnet is zoned and zircon has multiple growth zones partition coefficients could be used to recognize equilibrium versus disequilibrium growth. In general, it is easier to detect when garnet and zircon are clearly not in equilibrium than when they potentially are. The partitioning can be strongly affected by lack of preservation of growth zones and original REE composition. Resorption of garnet or zircon during decompression or melting would impede correct partitioning determination. In rocks that reach relatively high temperatures, garnet commonly grows during the prograde evolution,

whereas zircon is more likely to form during melt crystallization upon cooling, and thus the two phases are not necessarily in trace element equilibrium. An additional complication is diffusional re-equilibration, which can affect particularly the garnet composition: it has been shown that above 700-900°C, diffusional equilibration of trace elements in garnet occurs over geological timescales, whereas zircon still preserves prograde growth stages (Stepanov et al. 2016b). As it is not trivial to detect resorption or diffusion in garnet and zircon, and textural coexistence is not a valid argument to prove chemical equilibrium, the use of HREE zircon/garnet partitioning for a direct link between metamorphic zircon and garnet growth zones must be carefully evaluated case by case. However, the general rule that metamorphic zircon has flat HREE in garnet-rich assemblages, and variable Eu depending on the presence of feldspar has been observed in numerous studies and remains a useful tool for relating metamorphic zircon to assemblages and ultimately metamorphic conditions.

Ti-in-zircon thermometry

The Ti-in-zircon thermometer is based on the principle that, in a buffered assemblage, the incorporation of Ti in zircon depends on *T* (Watson and Harrison 2005; Ferry and Watson 2007). One of the main attractions of this single mineral thermometer is that it can yield temperatures from isolated zircon crystals because in most crustal rocks the activity of SiO_2 is high and a Ti-phase is present. First applied to Early Archean detrital zircons of magmatic origin (Watson and Harrison 2005), the Ti-in-zircon thermometer has since proved a seemingly simple tool for petrology and its application has quickly spread from detrital to magmatic and metamorphic zircon. For temperature-dominated metamorphism the capacity to relate an age to a temperature in the *P-T* path is certainly appealing. Countless studies have applied this thermometer obtaining reasonable metamorphic temperatures, especially in upper amphibolite facies to lower granulite facies conditions, where zircon starts to be reactive and full buffering by quartz and a Ti-phase is achieved. Under lower and higher metamorphic grade, caution is needed in the application of the Ti-in-zircon thermometer as discussed below.

Metamorphic zircons that have formed under low temperature in sub-solidus conditions (<600°C) have low Ti as predicted by the thermometer (<2 ppm, unpublished data, Tailby et al. 2011). Tailby et al. (2011) have shown that different sectors in a fir-tree zoned zircon from a vein containing rutile and quartz have variation in Ti contents that would correspond to variations of ~40°C. This cannot be reconciled with T oscillations during growth and indicates that crystallographic sectors have some influence on Ti content rather than solely crystallization temperature. This effect may be particularly relevant at very low Ti contents, i.e , low temperature, but zircon is hard to react under such conditions and thus very few cases exist to test this issue. For example Ti-thermometry of diagenetic or low-grade zircon has never been achieved. At low Ti concentrations, any contamination during analysis from Ti-bearing micro-inclusions, neighboring phases or fractures could be serious (Harrison and Schmitt 2007). This demands particular cautions during analysis of Ti in potentially low temperature zircons. Additionally, it is much more difficult to prove that a buffer assemblage was reactive at low metamorphic temperatures.

On the other end, under extreme metamorphic temperatures, Ti content in zircon is higher and easier to measure (18–90 ppm at 800–1000°C). The Ti-in-zircon thermometer can indeed record T of 900-1000°C, as shown in some Kaapvaal xenoliths containing two stages of zircon growth (Baldwin et al. 2007). Extreme T is recorded by zircons from the Kokchetav diamondiferous rocks where Ti-in-zircon thermometry returns T of 910–1080°C (Stepanov et al. 2016b), corroborating peak conditions of UH*P* metamorphism. In high grade rocks, which commonly undergo partial melting, a major issue can instead be that zircon crystallizes upon crystallization of melt during decompression and cooling and not at the T peak. For example, in the Anápolis-Itauçu Complex in central Brazil, samples with UH*T* assemblages that recorded metamorphic temperature of ~1000°C, contain metamorphic zircon that record Ti-in-zircon temperatures mainly in the range 800-950°C (Baldwin et al. 2007). Obtained T and textural relationships between zircon and other minerals were used to conclude that the zircon formed mainly during prograde and retrograde reactions and not at the UH*T* peak. The lower crustal section of the Ivrea Zone, Italy, contains metapelitic septa within gabbros that recorded metamorphic T of 900–1050°C according to Zr-in-rutile thermometry (Ewing et al. 2013). In these rocks Ti-in-zircon thermometry records lower temperatures around 750-800°C, likely because zircon crystallized only upon cooling. Ti-in-zircon temperatures below the peak T (700–850°C versus ~900°C) are also reported for metamorphic zircon in leucosomes of the Bohemian Massif (Kotkova and Harley 2010). Therefore, in the case of zircon crystallization from a partial melt, the T of Zr saturation and thus zircon crystallization can be significantly lower than the peak T experienced by the rocks, but also well below the T of melting (see details in thermodynamic modeling by Kelsey et al. 2008; Yakymchuk and Brown 2014; Kohn et al. 2015).

As any successful petrological tool, Ti-in-zircon thermometry has its limitations. Hofmann et al. (2009) pointed out possible problems of this thermometer due to non-equilibrium effects in Ti incorporation in zircon, the effect of other substituting elements, and the contamination of Ti analyses from edges and fractures (see also Harrison and Schmitt 2007; Hiess et al. 2008). Others have highlighted the issue of underestimation of crystallization temperatures in magmatic zircon (Fu et al. 2008). In applying Ti-in-zircon thermometry to metamorphic rocks there are other potential limitations to be considered. (1) Equilibrium with a Ti-phase is a prerequisite for the correct application of the thermometer (Ferry and Watson 2007). In metamorphic rocks where more than one metamorphic assemblage is preserved establishing the presence of a Ti-phase at the stage when zircon formed may not be trivial. Most commonly this leads to an underestimation of the real Ti-activity and thus the temperature of zircon crystallization. (2) The effect of pressure on Ti incorporation in zircon remains unconstrained. The Ti-in-zircon thermometer (Ferry and Watson 2007) was calibrated for pressures close to 10 kbar (Ferry and Watson 2007). Tailby et al. (2011) showed that Ti substitutes for Si at these pressures and proposed that at high pressure the solubility of Ti should decrease. As a result, the Ti-in-zircon thermometer may underestimate temperature. On the other hand, it is expected that under low pressure conditions (< 5 kbar), the thermometer likely overestimates temperatures. Ferriss et al. (2008) suggested that with increasing pressure, Ti might

additionally substitute into the Zr site, in turn increasing Ti solubility in zircon. Testing on natural samples is limited, but Ti-in-zircon temperature estimates for at least the UH*P* Kokchetav rocks are close to the peak *T* estimated by other thermometers (Stepanov et al. 2016b), indicating that, with pressure, decreasing amounts of Ti on the Si site might be compensated by increasing Ti concentration on the Zr site. Until a better understanding of the effect of pressure on this thermometer is gained, it is safer to use Ti-in-zircon temperatures in (U)H*P* rocks as a relative *T* indicator, as suggested by Stepanov et al. (2016b). (3) Deformation under high temperature can modify zircon chemical composition, generally inducing loss of Pb, REE and Ti or redistribution of elements (Reddy et al. 2009); application of the thermometer to highly deformed rocks has to be done with caution or supported by EBSD analysis and chemical mapping of the zircon crystals (see section on Deformation).

ISOTOPE SYSTEMATICS

Since the very early days of geochronology, zircon has been a prime target for U-Pb isotopic investigations in order to obtain crystallization ages. In the last decades Lu-Hf and oxygen isotope investigations in zircon domain have been developed and primarily applied to magmatic or detrital crystals. In metamorphic settings, the use of isotopic tracers to understand zircon petrogenesis and assist in U-Pb age interpretation is less widespread, but increasing. Correlations between different isotopic system (U-Pb, Lu-Hf and oxygen) and chemical signatures acquired from the same growth domain remain underexplored, but have already demonstrated some valid concepts that are summarized below. For any isotopic systematic it is important to consider diffusivity (see also Kohn and Penniston-Dorland 2017), robustness to metamorphic resetting/alteration and thus possible decoupling of different systems.

U-Pb isotopes

Zircon is the most widely used mineral for U-Pb age determination also in metamorphic rocks. U-Pb geochronology (Th is not sufficiently abundant in zircon to be a useful chronometer) in metamorphic zircon has increased dramatically since the development of micro-beam techniques that can measure U-Pb isotopic ratios at the 10-50 μm scale, namely high resolution ion microprobes and Laser Ablation ICP-MS (Kylander-Clark 2017; Schmitt and Vazquez 2017). Whereas these methods may not reach the sub-1% age precision of thermal ionization mass spectrometry (TIMS, Schoene and Baxter 2017) they can spatially resolve the internal growth zones typical of metamorphic zircon.

Zircon alteration and replacement under sub-solidus conditions are difficult to date accurately. In altered zircon domains the U-Pb system is disturbed and measured dates are commonly a mix between the age of the inherited grain and that of metamorphic disturbance. Several examples of these systematics exist in eclogite of the Dabie-Sulu orogenic belt, where altered zircon cores yield a range of spurious dates (Zheng et al. 2005; Xia et al. 2009; Chen et al. 2011; Sheng et al. 2012). Textures also suggests that alteration affects zircon at a micron scale below the spatial resolution of micro-beam geochronology (10-50 μm) and thus

mixing of domains is a common problem in analyzing altered zircon. Alteration that produces spurious dates is not limited to sub-solidus conditions, but can also occur in higher grade samples (Tichomirowa et al. 2005). Metamictization of zircon domains commonly results in dark, mottled CL emission (Table 1) and is present in all metamorphic environment from diagenesis (Hay and Dempster 2009a) to high grade (Tichomirowa et al. 2005). Reversely discordant dates are commonly measured in metamict, altered domains where there has been Pb mobility (Tichomirowa et al. 2005; Kusiak et al. 2013a). Additional indications of zircon alteration are (i) high initial Pb contents and (ii) homogeneous Lu-Hf and oxygen isotopic composition in domains whose ages scatter (see sections on Lu-Hf and oxygen isotopes). Complete metamorphic replacement of zircon domains does achieve resetting of the U-Pb system: such domains (commonly zircon rims) have poor zoning, homogeneous chemistry and yield accurate and reproducible ages. In sub-solidus rocks, metamorphic zircon commonly has low U content and relatively high initial Pb content, which can limit age precision. Eclogite-facies rocks that were subducted along a cold-geotherm yield this type of zircon (Rubatto et al. 1999; Baldwin et al. 2004; Spandler et al. 2005; Rubatto et al. 2011). Replacement/recrystallization may proceed along a well defined front (Hoskin and Black 2000), but it can also be more localized and randomly distributed to generate sub-domains where CL-zoning is chaotic (Rubatto et al. 2008). Where pristine, altered and replaced domains are combined at a micron scale, age determination results in mixed ages. Most other chemical signals are analyses at the same scale as ages and thus will also be mixed.

Metamorphic zircon forms more readily in high-grade rocks where it commonly constitutes overgrowths on inherited magmatic or detrital cores. Chronology of migmatites and granulites that crystallized zircon from melts is relatively straightforward: metamorphic zircon domains are texturally and chemically distinct from the inherited cores and record faithfully the age of crystallization, at least below UHT conditions. Common Pb is generally not an issue in such zircon as Pb strongly partitions in the melt during crystallization. Reproducible and concordant dates are commonly achieved for zircon overgrowths and their chemistry can assist in age interpretation. However, even under conditions where Pb diffusion/mobility, strong deformation or later fluid alteration do not disturb the zircon formation age, it is possible to obtain a spread in zircon ages. This is not necessarily poor geochronology, as this spread can have a geological significance indicating a long-lasting process. Indeed, in several terranes it has been demonstrated that melting and high-grade metamorphism can persist for 10s of million years and thus zircon can form over a period of time. However, during protracted metamorphism the environment of zircon growth changes because of metamorphic reactions or new melt injections and thus zircon grows metamorphic domains that are distinct in chemistry and internal texture (Vavra et al. 1996; Hacker et al. 1998; Schaltegger et al. 1999; Rubatto et al. 2001; Möller et al. 2002; Hermann and Rubatto 2003; Montero et al. 2004; Root et al. 2004; Tichomirowa et al. 2005; Hermann et al. 2006a; Gerdes and Zeh 2009; Rubatto et al. 2009; Kotkova and Harley 2010; Gordon et al. 2012; Gordon et al. 2013; Korhonen et al. 2013; Kylander-Clark et al. 2013; Rubatto et al. 2013; Harley and Nandakumar 2014; Young and Kylander-Clark 2015). In such samples, the presence of distinct metamorphic domains that are internally homogeneous, suggests that zircon grows in discrete, relatively brief episodes.

Extreme conditions with T>1000°C and P up to 50 kbar are documented in metamorphic rocks and such conditions might persist for long geological times (10s Ma). In order to understand ages obtained from zircon in UHT rocks it is thus important to discuss the robustness of the U-Pb system in zircon under these conditions. Experimental studies indicate that Pb diffusion in zircon is not significant at T<900°C even for geological times of several million years (see a review in Cherniak 2010). Metamorphism, however, can reach extreme temperatures up to 1050°C, where even a perfectly crystalline zircon could diffuse Pb over geological time scales (Cherniak and Watson 2003). Inherited zircon (detrital or magmatic cores/grains) that still retain pre-metamorphic ages are preserved in various terranes that underwent extreme *T* for long periods of time. Examples are the Rogaland sapphirine-granulites (peak and decompression at 950–1000°C between 7.5 and 5.5 kbar, Möller et al. 2003; Drüppel et al. 2013), and the lower crustal rocks of the Ivrea Zone (900-1000°C, 6-10 kbar, Vavra et al. 1996; Ewing et al. 2013). Rare inherited cores with pre-metamorphic ages are also preserved in crustal rocks from the Kokchetav metamorphic belt in Kazakhstan, where peak *T* was around 1000°C at elevated *P* of 40-50 kbar. The existence of inherited zircons in some UH*P*-*T* samples imply that zircon was a stable phase even under extreme conditions and that U-Pb ages can at least partially survive such high T, even when associated with deformation and melting. In the Kokchetav belt, the duration of UH*P*-*T* metamorphism was only a few million years (Claoué-Long et al. 1991; Hermann et al. 2001; Katayama et al. 2001; Stepanov et al. 2016b), Zircons in some Kokchetav samples have dates scattering over 20 Ma that do not correlate with the zircon internal zoning texture or composition (Stepanov et al. 2016b). This observation was interpreted as partially reset during peak temperature of 1000 °C in zircon that do not show any evident sign of metamictization. What it is hard to establish is if any age disturbance under these extreme metamorphic conditions is due to diffusional Pb loss or dissolution-precipitation of zircon in several stages during metamorphism.

A particular case of Pb mobility is documented in the Archean zircons of the Napier Complex, Antarctica, which underwent UH*T* metamorphism at > 900°C. The discovery of reversly discordant ages ($^{206}Pb/^{238}U$ age older than the $^{207}Pb/^{206}Pb$ age) led to postulate the presence of unsupported radiogenic Pb in some zircon domains (Williams et al. 1984). More recent studies imaged in detail the distribution of Pb isotopes in these zircons and proved the patchy distribution of radiogenic Pb at the micron scale. Pb forms forms nuggets of Pb metal and its distribution is mostly unrelated to U content (Kusiak et al. 2013a; Kusiak et al. 2013b; Kusiak et al. 2015) and has no correlation with Th/U, REE or oxygen isotopes either. The mobility of radiogenic Pb caused apparent $^{207}Pb/^{206}Pb$ dates within a modified domain to vary over 500 Ma, with the oldest dates being spurious and older than the formation of the crystal. Kusiak et al. (2013a) proposed that extreme metamorphic temperatures in a dry environment caused Pb mobility within the crystal, without net Pb loss. This process of within-crystal Pb mobility has been also identified in the UH*T* rocks of southern India (Whitehouse et al. 2014). Such reports will likely increase with the development of atom probe analysis and ion microprobe mapping. Deformation under relatively high temperature has also been found to cause Pb mobility (see section on deformation).

Pb diffusion profiles in pristine zircon (not metamict, nor deformed) have so far never been measured, but increased spatial resolution in modern analytical techniques (atom probe, NanoSIMS analysis and SIMS depth profiling) may eventually resolve diffusion at a submicron scale. The bulk of available evidence indicates that loss of Pb by volume diffusion in non-metamict zircon is not an important factor even under extreme metamorphic conditions.

Lu-Hf isotopes

Hafnium isotopes in zircon have become a widely used petrogenetic tool in magmatic and sedimentary rocks for crustal evolution studies. For this isotopic system, the role of metamorphism is primarily a negative one, as metamorphism can cause Pb loss and thus compromise the veracity of calculated epsilon Hf values and model ages (see a review in Vervoort and Kemp 2016). The application of Hf isotopes to metamorphic zircon has been directed to understand zircon petrogenesis and resetting of the U-Pb system. Decoupling of the U-Pb and Lu-Hf systems in zircon during metamorphism and alteration has been documented in natural samples (Zheng et al. 2005; Gerdes and Zeh 2009; Xia et al. 2009; Zhao et al. 2015) and by experimental work (Lenting et al. 2010). While variable U-Pb dates can be the product of alteration/resetting and be unrelated to geological events (see above), distinct $^{176}Hf/^{177}Hf$ signature are expected if zircon domains formed during different episodes of the rock evolution (Gerdes and Zeh 2009). The plot in Figure 7A illustrates the different evolution in $^{176}Hf/^{177}Hf$ over time of components (bulk rock, magmatic zircon, metamorphic zircon, garnet) of a metagabbro over a 160 Ma period. Because of the high Hf contents, there is insignificant ingrowth of radiogenic Hf into the magmatic zircon. For other minerals and the bulk rock, radiogenic ingrowth depends on the Lu/Hf ratio. As most of the Hf is locked away in zircon, the "reactive" bulk rock Hf isotopes will evolve much faster than the bulk Lu/Hf. Let's consider a prograde metamorphic event producing garnet 100 Ma after the protolith crystallization, when magmatic zircon was not reactive. Given the high Lu/Hf of garnet, even within a few million years of a metamorphic cycle, garnet can evolve highly radiogenic $^{176}Hf/^{177}Hf$. Metamorphic zircon that forms at peak metamorphic conditions a few million year after prograde garnet can potentially acquire any $^{176}Hf/^{177}Hf$ in between the value of the protolith zircon and the highly radiogenic value of the garnet depending on which reservoir (protolith zircon, bulk rock, bulk without zircon, or garnet) the new zircon equilibrated with. Zircon that forms after dissolution of some protolith zircon and some garnet will acquire an intermediate $^{176}Hf/^{177}Hf$, higher than the protolith zircon. The same effect can be produced by dissolution of other high Lu/Hf phases such as apatite (Valley et al. 2010).

In metamorphic gneisses and mafic eclogites of the Dabie-Sulu HP terrane, inherited magmatic cores, whose ages were partly reset during metamorphism, still preserve high $^{176}Lu/^{177}Hf$ and Th/U relative to metamorphic zircon (Zheng et al. 2005; Xia et al. 2009; Gao et al. 2015). Even when metamorphic disturbance of the U-Pb age and Th/U system is nearly complete (spongy textures, modified CL, apparent ages close to lower intercept and low Th/U) the Lu/Hf system of the protolith zircon remains undisturbed (Xia et al. 2009). On the contrary, zircon grown during metamorphism has not only new U-Pb age and Th-U

compositions but also consistently lower $^{176}Lu/^{177}Hf$ (2-10 times lower) than the protolith zircon value (Fig. 7B). Some of the zircon domains that crystallized during metamorphism also have higher $^{176}Hf/^{177}Hf$, which points to release of radiogenic Hf from other sources, most likely garnet. The low $^{176}Lu/^{177}Hf$ and high $^{176}Hf/^{177}Hf$ in some metamorphic zircon implies that, at the time of zircon growth, garnet was present as a Lu sink (see section on REE), but recrystallized releasing radiogenic $^{176}Hf/^{177}Hf$ (Zheng et al. 2005; Xia et al. 2009). Even more complicated $^{176}Lu/^{177}Hf$ versus $^{176}Hf/^{177}Hf$ trends can be created in metamorphic zircon if multiple Hf sources are identified, such as dissolution in anatectic melts of much older detrital zircon of various age and multiple metamorphic events overprinting each other (Gerdes and Zeh 2009; Zhao et al. 2015). In the process of U-Pb and Lu-Hf decoupling, there is a fundamental role for aqueous fluids and melts in redistributing and transporting these elements. The decoupling of the U-Pb and Lu-Hf systems can also be used to identify analyses mixing inherited cores and metamorphic rims, which produces a correlation between the two systems (Xia et al. 2009; Zhao et al. 2015).

Oxygen isotopes

Oxygen isotopes can be readily measured in single zircon growth zones by ion microprobe to a precision of 0.2‰ (Valley 2003). A common application of this isotopic system is tracing the source of zircon grains, particularly in magmas and sediments, to reconstruct crustal reworking. This strategy applies equally to inherited and detrital zircons in metamorphic rocks (Rumble et al. 2002; Zhao et al. 2008; Rubatto and Angiboust 2015), and is particularly powerful in recrystallized rocks where relic zircon cores may be the only remnant of the protolith (Zheng et al. 2008; Fu et al. 2010; Chen et al. 2011; Sheng et al. 2012; Gauthiez-Putallaz et al. 2016).

Similarly to the Lu-Hf system, oxygen isotopes can give insight into metamorphic replacement and modification of zircons, as well as partial resetting of the U-Pb system and mixed ages. Natural samples indicate that, at least in some environments, the U-Pb system is easier to reset than the oxygen isotopes and thus partly reset zircon domains may still preserve protolith oxygen isotopic composition (Wu et al. 2006; Martin et al. 2008). This may seem at odds with experimental data that report diffusion of oxygen isotopes faster than that of Pb (Cherniak and Watson 2003), but age resetting during metamorphism is generally not dominated by simple solid state diffusion. In other cases, metamorphic resetting of zircon age and Th/U weakly correlates with changes in $\delta^{18}O$ suggesting that metamorphism eventually affects oxygen isotopes (Petersson et al. 2015; Rubatto and Angiboust 2015). This difference may reflect different processes and degree of resetting. Therefore the use of oxygen isotopes to detect metamorphic disturbance of the age may have to be considered case by case.

While replacement/recrystallization can be an effective way to reset the oxygen isotopic composition of zircon, natural and experimental studies indicate that diffusion of oxygen does not play a significant role (Watson and Cherniak 1997; Page et al. 2007). Oxygen isotope diffusion in zircon is still debated (see also Kohn and Penniston-Dorland 2017) because of disagreement whether “dry” or “wet” diffusion applies in natural rocks and the general lack of data (i.e.,

measurable profiles in natural samples). The point has been made that even in apparently "dry" metamorphic rocks where free fluids may be lacking, the activity of H_2O is still buffered by mineral phases and significant, and thus "wet" diffusion generally applies (Kohn 1999). The potential retentivity of $^{18}O/^{16}O$ isotopic ratio in zircon has been modeled by Cherniak and Watson (2003) using the only experimentally determined wet diffusion data. Compared to Pb, U or other trace elements, oxygen diffusion in zircon is much faster so that oxygen isotope signature of a ~100 μm domain should survive less than 0.1 Ma at temperature of 700°C, and only 5700 years at 900°C. Natural cases, however, suggest higher retentivity of oxygen isotopes in zircon. Inherited, relict zircon cores with very low $\delta^{18}O$ that survived UH*P* metamorphism at ~750°C are common in the Dabie-Sulu gneiss (Chen et al. 2011; Sheng et al. 2012). Bowman et al. (2011) have shown that even zircon that underwent relatively high-grade metamorphism for several 10s of million years preserve sharp $\delta^{18}O$ changes (within the 5-10 μm resolution of the analyses) between inherited cores (~6 ‰) and metamorphic rims (8-10‰). Claesson et al. (2016) suggest that the oxygen isotopic composition of non-metamict zircons that still preserve magmatic-type zoning were modified under high temperature (~700°C) in hydrothermal conditions. They base their conclusion on the finding of unusually high $\delta^{18}O$ in Archean zircons and on previous experimental determination of relatively fast oxygen diffusion under wet conditions (Cherniak and Watson 2003). However, also in this case, no oxygen isotope diffusion profile could be measured in zircon. These examples show that oxygen isotope diffusion in zircon is still far from being resolved and requires future work.

Oxygen isotopic composition of zircon can assist in the challenging task to link zircon ages to metamorphic assemblages. Oxygen fractionation factors between zircon and some major minerals are reasonably well known (Valley 2003). For example, given known metamorphic temperatures, oxygen isotopic equilibrium between zircon and garnet can support a case for metamorphic zircon formation (Martin et al. 2006). Conversely, isotopic disequilibrium between zircon and major phases would suggest that inherited zircons are preserved within metamorphic assemblages, where major minerals are isotopically equilibrated (Zheng et al. 2003). Fu et al. (2010) demonstrated that the mantle-like $\delta^{18}O$ (4.8–5.2 ‰) of zircon and Ti-in-zircon thermometry (600-800°C) in numerous jadeitites are not supportive of hydrothermal zircon formation in a vein, but rather of their oceanic crust protolith. The systematics of oxygen isotopes is more complicated during sub-solidus alteration and partial to complete replacement of zircon. Does a zircon formed by in situ dissolution-precipitation equilibrate with the bulk rock oxygen isotopic signature or inherit the $\delta^{18}O$ of the protolith zircon it replaces? Two examples of metamorphic zircon that did not re-equilibrate with the bulk oxygen signature are presented in Figure 8. In a metabasite from Naxos that experienced metamorphism at 500°C, a number of metamorphic zircon rims yield variable $\delta^{18}O$ that in each grain is identical to the values of the magmatic core (Martin et al. 2006), suggesting that the rims inherited the core isotopic signature. In an eclogitic metasediment from the Sesia Zone in the Italian Alps (Rubatto et al. 1999), metamorphic zircon rims yield different $\delta^{18}O$ than the detrital cores, but still differing one from another. In this case it is postulated that the isotopic composition of the metamorphic zircon equilibrated only locally and not rock-wide. On the other hand, zircon

overgrowths that formed in a metamorphic vein, hosted by the eclogitic metasediment, displays a homogenous oxygen isotope composition, as expected for newly formed zircon that equilibrated with the bulk rock.

Particularly insightful is the use of oxygen isotopes in zircon and co-existing minerals to trace metasomatism and open versus closed system metamorphism. In orthogneisses, significant shifts in $\delta^{18}O$ between relict magmatic cores and metamorphic rims have been interpreted as open system behavior and crystallization of zircons from metamorphic fluids (Chen et al. 2011; Sheng et al. 2012). Zircon within metamorphic veins in the Monviso eclogite, have significantly lower $\delta^{18}O$ than inherited magmatic zircon in the country rock. The zircon oxygen composition and age, together with the variable $\delta^{18}O$ in garnet, reveal deep sea floor alteration as well as metasomatism during high pressure metamorphism (Rubatto and Angiboust 2015). As this example shows, a more convincing argument for metasomatism can be made when the isotopic variation in metamorphic zircon is correlated to the composition of major minerals, such as garnet (Martin et al. 2006; Page et al. 2014; Rubatto and Angiboust 2015).

Changes in the oxygen isotopic composition of minerals can change according to temperature, assemblages and external fluids. Therefore the interpretation of oxygen isotope signatures in metamorphic systems in terms of external fluids requires a control on the change in assemblages and temperatures between the protolith and metamorphic stages. Large variations in mineral crystallization and volume of quartz and plagioclase can, for example, shift the $\delta^{18}O$ of metamorphic minerals of a few ‰ within a constant bulk $\delta^{18}O$. This was modeled in metamorphic rocks from Alpine Corsica (France) where Permian granulites (T 650-800°C) composed mainly of garnet, quartz and feldspars were transformed by Eocene high-pressure metamorphism (T 400-500°C) into garnet, amphibole, lawsonite, quartz and phengite (Martin et al. 2014). The shift in $\delta^{18}O$ between the granulitic garnet core (9.9‰) and the high-pressure garnet domains (7.2‰) is significant, but it can be largely reconciled with changes in assemblage and T alone. In that sample, a further stage of metamorphism under high pressure was related to metasomatism by external fluids. While the Corsica rocks may represent a rather extreme case (large variation in T and assemblages between metamorphic cycles), the case highlights that the interpretation of $\delta^{18}O$ in zircon or any metamorphic mineral must be supported by accurate P-T constraints, and that changes in $\delta^{18}O$ between growth zones of up to a couple of ‰ do not necessarily imply external fluids.

Particularly low $\delta^{18}O$ have been reported for metamorphic zircons (Fig. 9) that grew in high-pressure rocks such as mafic eclogites and veins (Fu et al. 2010; Chen et al. 2011; Fu et al. 2012; Sheng et al. 2012; Rubatto and Angiboust 2015). The $\delta^{18}O$ value of these zircons is well below the value of the relict magmatic zircons present in the same or nearby rocks and below the mantle value of 5.3±0.3 ‰, 1SD (Valley 2003). In some cases the low zircon values are also found in coexisting garnet (Rubatto and Angiboust 2015). Two explanations have been proposed for these low $\delta^{18}O$ zircons. In the case of values between 1-5 ‰ in mafic rocks and included veins the low $\delta^{18}O$ has been attributed to ocean floor alteration of the protolith and/or presence of low $\delta^{18}O$ metasomatic fluids generated from nearby altered crust (ultramafic or mafic) during zircon growth. Indeed, bulk rock analyses have proven that altered oceanic crust, even when

subducted to high pressure conditions, generally preserves the $\delta^{18}O$ typical of ocean floor alteration (Putlitz et al. 2000; Miller et al. 2001). However profiles through oceanic crust in Oman report minimum $\delta^{18}O$ values of 3‰ for serpentinization under relatively high temperature (Gregory and Taylor 1981); these values are still higher of what is measured in some metamorphic zircon in eclogites and veins (Fig. 9). Internal fractionation of oxygen isotopes during metamorphism by crystallization of high $\delta^{18}O$ phases could additionally shift the zircon oxygen composition to lighter values. Alternatively, the protolith of subducted oceanic crust could have experienced more extreme high *T* alteration than found in the Oman sequence.

A particularly intriguing case is that of negative $\delta^{18}O$ values (as low as -10 ‰) in metamorphic zircons of the Dabie–Sulu eclogites, veins and gneisses, where inherited zircon are -4 to 3.5‰ in the gneiss and 2-10‰ in the eclogite (Chen et al. 2011; Sheng et al. 2012). These negative values have been interpreted as metamorphic zircon growth from externally-derived negative $\delta^{18}O$ fluids produced by dehydration of gneissic protoliths that were glacial-hydrothermally altered, in a particularly cold clima (the so called "Snowball Earth"). Such extremely light oxygen signature has been extensively documented in the inherited magmatic zircon over a wide section of the South China Craton (Zheng et al. 2008).

PETROGENESIS

Compared to the wealth of petrological knowledge on major metamorphic minerals, understanding the behavior of accessory phases is still in its infancy. Relatively few studies have dealt with the stability of accessory minerals. Zircon is a robust accessory mineral and case studies show that its stability is wide and its reactivity can vary case by case. Only a few reactions that form new metamorphic zircon from major or accessory minerals have been proposed. Processes that produce metamorphic zircon from precursor zircon by replacement/recrystallization at the solid state, dissolution (re)precipitation in situ aided by fluids, or melting and crystallization in leucosomes have been recognized as significant.

In this section the complex topic of the petrogenesis of zircon in metamorphic rocks is discussed for four main processes/environments roughly corresponding to increasing metamorphic grade: (i) diagenesis and low *T* metamorphism, (ii) zircon replacement or dissolution-precipitation in sub-solidus conditions and in the presence of aqueous fluids, (iii) zircon in melt-dominated metamorphic systems and (iv) zircon-forming reactions involving major/minor minerals under amphibolite to granulite facies conditions. An overview of typical zircon types under variable metamorphic conditions is shown in Figure 1.

Diagenesis and low *T* metamorphism

What may happen to zircon in the early stages of metamorphism is best shown by the study of lightly metamorphosed sandstones (Hay and Dempster 2009a). During burial at <100°C, detrital zircons in these sediments show signs of alteration and new metamorphic zircon is formed. Delicate textures of zircon

showing alteration have been documented under such conditions (Fig. 1A): they are unlikely to have survived the depositional process, and thus represent diagenetic/metamorphic modifications. The modification is driven by fluids and affects particularly radiation-damaged zones (Fig. 1B), as predicted by experimental studies (Geisler et al. 2003a). The altered zones are enriched in elements such as Ca, Al, Fe, Mn and LREE that do not enter the zircon structure (Geisler et al. 2003b; Hay and Dempster 2009a), and show porosity and fractures. These zones are similar to what observed in zircons in hydrothermal altered granites (Geisler et al. 2003b). The altered zones are progressively replaced by new crystalline zircon that also forms jagged, sawtooth-shaped zircon overgrowths of a few microns in thickness (Hay and Dempster 2009a), which become relatively more abundant in lower greenschist facies samples (200-400°C) (Rasmussen 2005; Hay and Dempster 2009b). The formation of low-grade metamorphic xenotime, even finely intergrown with zircon, is commonly associated to these first metamorphic zircon overgrowths (Rasmussen 2005; Hay and Dempster 2009a; Hay et al. 2010). The mechanisms that have been proposed to be dominant at this low grade are dissolution-precipitation and solid-state reaction (Hay and Dempster 2009a).

The sawtooth-shaped zircon overgrowths are generally absent (see an exception in Franz et al. 2015) from higher grade rocks (upper greenschist to lower amphibolite facies, Rubatto et al. 2001; Hay and Dempster 2009b) and thus it is likely that later dissolution or Ostwald ripening is erasing this early record. Zr released by dissolution of small zircon overgrowths during prograde metamorphism could be accommodated in other growing metamorphic minerals (Kohn et al. 2015) explaining why metamorphic zircon is generally absent in greenschist to lower amphibolite facies rocks. Partly altered, porous and metamict zircon domains, which are the likely source of Zr for low-grade zircon growth, are partly dissolved during early metamorphism, but can also be preserved at higher grade.

Metamorphic zircon and fluids at sub-solidus conditions

Zircon replacement and modification by fluids has been identified in a variety of metamorphic settings from diagenetic environments (see above) to granulite facies metamorphism, and particularly in rocks that record high pressure metamorphism (see also a review in Rubatto and Hermann 2007b). A variety of textures have been attributed to fluid-driven alteration/replacement of zircon (Fig. 1, Table 1, see also Corfu et al. 2003). One of the lowest *T* reported for zircon alteration in metamorphic rocks is from Spandler et al. (2004), who proposed that relict zircon cores preserved in schist from New Caledonia underwent alteration by fluids during sea floor alteration of the mafic protolith at T< 100°C, based on their inclusion assemblage and texture (Fig. 1C). Such process expelled trace elements from the original zircon, increased porosity, and produced mottled and patchy zoning. These features have many similarities to the dissolution-precipitation process described in zircon from rocks at 400-600°C (Tomaschek et al. 2003; Rubatto et al. 2008). Similar alteration and replacement processes have been described for other accessory minerals such as apatite and monazite and reproduced in controlled experiments (Hetherington

et al. 2010; Harlov et al. 2011; Seydoux-Guillaume et al. 2012). For a more general description of mineral replacement see also Putnis (2009) .

More extensive alteration leads to full replacement of domains that are texturally discordant with the original zoning and often marked by a recrystallization front (Hoskin and Black 2000; Vonlanthen et al. 2012). These replaced domains are chemically and microstructurally different from the cores: they commonly have a lower trace element content, they lack any elements typical for alteration zones such as LREE, Ca, Al and Fe, and they are inclusion poor. TEM investigation of these domains shows that they are relatively free of defects (Vonlanthen et al. 2012). Most studies of natural samples report that during this process the chemical composition and isotopic systematics of the replaced zircon is totally reset. However, remnants of the chemical and isotopic composition of protolith zircon have been reported in such domains when analyses were performed with a spatial resolution of ~20 microns (Hoskin and Black 2000). This indicates that the replacement process is not always complete and that "islands" of altered zircon are preserved at the micro to nanoscale. Such micro-relicts have been identified in zircon where the replacement/recrystallization process led to micro-zircon formation (Rubatto et al. 2008).

It has been proposed that dissolution-precipitation can proceed efficiently even with minimum free fluid, and with low Zr solubility in that fluid (Tomaschek et al. 2003; Geisler et al. 2007). The process does not require transport of Zr and other zircon-forming elements outside the zircon itself, and can proceed in a virtually closed system (Hoskin and Black 2000). This implies that this process, that cannibalizes inherited zircon and resets its isotopic and chemical composition to form metamorphic zircon, is not necessarily communicating with the reactive bulk rock and can occur independently of Zr solubility or metamorphic reactions. It requires aggressive fluids and it is enhanced by temperature and the presence of metamict zircon (Geisler et al. 2003a).

Zircon with textures suggestive of metamict state is preserved up to high metamorphic conditions. For example, porous zircon domains that contain very low-grade (<100°C) mineral inclusions have been recovered in blueschist- to eclogite-facies rocks (Spandler et al. 2004). A whiteschists that recorded ultra high pressure metamorphism (35 kbar and 750°C) preserves altered zircon cores from the precursor granite that contain prograde to peak metamorphic mineral inclusions in healed alteration zones (Gauthiez-Putallaz et al. 2016). These reports suggest that dissolution of metamict zircon domains by metamorphic fluids that provides Zr and other essential elements for metamorphic zircon formation can occur under diverse conditions.

Preservation of metamict zircon up to high grade conditions is supported by experimental work and calculations. Zircon is predicted to stop accumulating radiation damage at ~250°C, the T above which amorphisation will no longer occur, because annealing becomes faster than damage accumulation (Meldrum et al. 1999; Ewing et al. 2003). The process of recovery damage and structural re-organisation of zircon, as described in Ewing et al. (2003, and references therein) occurs in stages over a T range and is particularly low in zircon compared to any

related phase. In experiments, the first stage of recovery occurs below ~700°C (recovery of point defects and short length damage). The second stage of re-organisation occurs above the ~700°C and, full structural re-organisation has been documented at 900°C or above (Geisler et al. 2001b). During this process, islands of recovered material are intercalated by still amorphous domains until damaged material is not longer detectable (by Raman or TEM investigation). The recovery process is dominantly a diffusion process and thus T and time dependent (Ewing et al. 2003). Calculations indicate that it would take Ma to fully recover the structure of metamict zircon at 700°C (Geisler et al. 2001a), but the process is significantly more efficient under hydrothermal or wet conditions conditions (Geisler et al. 2001b).

Experimental investigations have shown very low solubility of Zr in aqueous fluids, that increases with increasing Si contents and alkalinity of the fluids (Ayers et al. 2012). Both, Si contents and alkalinity in aqueous fluids increase significantly with increasing pressure (Hermann and Rubatto 2014). This might explain why abundant metamorphic zircon occurs in high-pressure crustal rocks that record metamorphic temperatures below the solidus <700°C, as for example in Alpine eclogites. Examples are large metamorphic zircon in the omphacite-garnet-rutile veins within the Monviso eclogites (Rubatto and Hermann 2003) and the intense zircon dissolution-precipitation process in the jadeite-leucogabbro of the Lanzo Massif (Rubatto et al. 2008). Metamorphic zircon in jedeitites could also form by precipitation from alkaline-rich fluids (e.g. Mori et al. 2011). The abundance of metamorphic zircon in the HP rocks of the Dabie-Sulu region has also been largely attributed to the activity of aggressive fluids (Zheng et al. 2005; Zhang et al. 2009b; Zhao et al. 2015). In contrast, metamorphic zircon is very rare in greenschist to amphibolite facies crustal rocks that record Barrovian metamorphism at similar *T*.

If fluids are the driver of zircon dissolution-precipitation, zircon reactivity would be much less dependent on T, but rather enhanced by the release of fluids in the rock system. Thus, metamorphic zircon formation can occur even while T is increasing, unlike what indicated by thermodynamic models that require equilibrium among all phases (Kohn et al. 2015). Prograde metamorphic zircon have been for example documented in the Dora Maira schists (Gauthiez-Putallaz et al. 2016), where zircon domains have been related to episode of fluid release by dehydration reactions (see texture in Fig. 1F). Such cases of prograde zircon must be considered when interpreting zircon ages.

Metamorphic zircon and melts

The most common form of metamorphic zircon is overgrowth on detrital or inherited magmatic grains during partial melting. Field studies that looked at prograde metamorphic sequences, mainly of pelitic/arcosic compositions, show that new zircon formation under sub-solidus conditions is virtually absent, but becomes abundant as soon as partial melting is observed (Rubatto et al. 2001; Williams 2001). Such metamorphic overgrowths on zircon cores are more abundant in leucosomes than melanosomes (Rubatto et al. 2001).

Zr solubility in anatectic melts ranges from 10s to 100s of ppm according to temperature and melt composition (Boehnke et al. 2013). A few studies have

attempted to model the behavior of zircon and monazite in migmatites using thermodynamic databases (Kelsey et al. 2008; Kelsey and Powell 2011; Yakymchuk and Brown 2014; Kohn et al. 2015). These models agree that in migmatites, most of the bulk Zr will be either stored in the melt or locked in undissolved inherited zircon. They also predict that zircon crystallization will occur significantly during cooling when Zr saturation is reached in leucosomes or in interstitial melt. A common conclusion is that most of the new zircon will crystallize in leucosomes compared to melanosomes or restitic portions. The solubility models also predict that, in felsic compositions, zircon dissolution and thus crystallization from a melt is less effective than that of monazite, and thus relict zircon will survive to higher metamorphic grade than monazite. The models consistently predict that anatectic zircon should grow during cooling when Zr solubility decreases in the melt or the solidus is reached (Kelsey et al. 2008; Kelsey and Powell 2011; Kohn et al. 2015).

The thermodynamic models all make significant assumptions that may differ from natural cases. A common assumption to all models is that all zircon and monazite crystals are in contact with the melt over the entire *P-T* evolution (Kelsey et al. 2008; Kelsey and Powell 2011; Yakymchuk and Brown 2014; Kohn et al. 2015). In natural rocks, shielding of inherited grains from contact with the melt (or fluids) is often the case. The observation that metamorphic zircon rims even in migmatites are variable in size from grain to grain, with the common presence of grains that are lacking overgrowths, support this scenario. Therefore any attempt to model the Zr budget in metamorphic rocks has the limitation that a variable but significant proportion of Zr may remain shielded from the melt. A second assumption in some models is that no melt loss from the system occurs. The pioneering modeling of Kelsey et al. (2008) mainly considered closed system behavior, with one episode of melt loss. Melt loss is undoubtedly a complication in natural rocks and successive models demonstrated that such behavior will reduce the amount of melt generated, and thus the solubility of Zr and the production of new zircon (Yakymchuk and Brown 2014). Ignoring the effect of Zr-release and uptake from other Zr-bearing phases in thermodynamic models (Kelsey et al. 2008; Yakymchuk and Brown 2014) does not seems to affect the general conclusions compared to studies that budgeted for Zr in minerals such as garnet, rutile and amphibole (Kelsey and Powell 2011; Kohn et al. 2015).

Crystallization from a Zr saturated melt upon cooling, as predicted by the models, is not the only process to form zircon overgrowth at high-grade metamorphic conditions. Some studies concluded that zircon in migmatites or granulites can form during prograde or peak metamorphism (Hermann and Rubatto 2003; Baldwin et al. 2007; Gordon et al. 2013; Rubatto et al. 2013). Arguments are based on zircon inclusions, trace element composition, Ti-in-zircon-temperatures and different zircon ages from continuous sequences. In the most compelling cases, a change in REE composition has been observed between relatively older and younger metamorphic zircon domains (Hermann and Rubatto 2003; Gordon et al. 2013; Rubatto et al. 2013). When the change in zircon REE composition has been related to the abundance of coexisting phases (particularly garnet and feldspars, see discussion above) and in turn to the *P-T* path, prograde to peak zircon growth was proposed. Such examples span different tectonic setting and *P-T* evolutions from collisional Barrovian

metamorphism (Rubatto et al. 2013), UH*P* metamorphism (Gordon et al. 2013) and lower crustal melting in extensional settings (Hermann and Rubatto 2003). In the case of fluid-induced melting in the central Alps, Rubatto et al. (2009) observed that zircon growth from melt occurred at different times (million of years apart) in segregated leucosomes sampled only meters from each other. Some migmatites contain multiple growth zones (Fig. 1) that have distinct age and composition, within single samples or even zircon grains. The intermittent availability of water for fluid-induced melting has been proposed by Rubatto et al. (2009) as a mechanism to explain multiple zircon growth zones in the same crystal and with age differences of several million years. These observation provide strong evidence that dissolution-precipitation of zircon in the presence of a melt can occur at any stage – prograde or retrograde – as long as melt is present.

Zircon forming reactions

Textural observations in natural samples that support metamorphic zircon growth from the breakdown of another phase have been reported for ilmenite (Bingen et al. 2004), rutile (Ewing et al. 2013; Pape et al. 2016) and garnet (Fraser et al. 1997; Degeling et al. 2001); see textures in Fig. 1N and Fig. 2C. In some cases the textural observations are supported by trace element mass balance considerations (Degeling et al. 2001; Ewing et al. 2013). The main idea is that, in a metamorphic reaction, there is a decrease of Zr solubility in source minerals (rutile, garnet etc...) and the expelled Zr results in the precipitation of metamorphic zircon. It has been suggested that garnet plays a minor role in the Zr budget of crustal rocks (Kelsey and Powell 2011), and thus garnet breakdown reactions might result in the formation of new zircon. A recent compilation of Zr content in major minerals (Kohn et al. 2015) identified rutile, ilmenite, titanite, garnet and hornblende as carriers for Zr: such minerals contain a few to 100s of ppm of Zr, and even 1000s of ppm in the case of rutile. A review of own data on Zr content in garnet (320 analyses, 20 samples) in rocks metamorphosed from 500 to 1000°C where metamorphic zircon is found, show Zr contents of only 5–20 ppm Zr in garnet. Zr concentrations in minerals increase with increasing temperature. Thus, the reaction of magmatic minerals such as pyroxene, amphibole and ilmenite, but also volcanic glass to lower temperature metamorphic minerals provides a mechanism to form metamorphic zircon.

The storage capacity of Zr in rock forming minerals can be considered in a simple example: A garnet-amphibolite with 20% garnet, 20% hornblende with contents of 3, 30 or 100 ppm Zr, that also contains 2 % of rutile with 40, 1500 or 3500 ppm Zr (T of 500, 700 and 900°C, respectively) would provide a maximum of 2, 42 or 110 ppm Zr for the bulk, respectively. Thus, Zr release at low temperature of 500°C from these minerals is irrelevant, whereas is more significant when very high temperature minerals are affected. As modeled by Kohn et al. (2015) for a basaltic and metapelitic composition, Zr released from major and accessory minerals during prograde metamorphism is expected to be entirely taken up by other minerals, at least as long as the *T* is increasing. Particularly in rutile-bearing rocks, any Zr release in the reactive bulk can be taken up by growing rutile (Kohn et al. 2015). Therefore zircon-forming reactions will be mainly related to decompression when rutile transforms to

ilmenite or titanite, or related to retrograde replacement of garnet by minerals that have a lower capacity to store Zr (cordierite, biotite or chlorite).

CONCLUSIONS AND OUTLOOK

The investigation of metamorphic zircon has dramatically increased since the development of in situ analytical methods that allow measuring diverse chemical and isotopic signals in distinct zircon domains. Combined with essential imaging of internal textures, geochemical information has provided the necessary base for metamorphic petrology of zircon.

Metamorphic zircon forms by a series of processes from the lowest grade to extreme metamorphism. At low grade, fluid alteration and solid-state replacement are dominant mechanisms affecting zircon. During partial melting zircon is particularly reactive with high solubility in the melts and crystallization of overgrowths. Under extreme conditions metamorphic zircon remains stable, but different elements and isotope systems are likely to be affected in different ways. The most prominent process is the loss of incompatible Pb that occurs in altered, deformed or metamict zircon, whereas the REE and HFSE trace element chemistry and Hf systematics are generally preserved. The behaviour of oxygen isotopes in zircon under extreme conditions remains uncertain.

Linking U-Pb ages to metamorphic conditions for correct age interpretation requires the combination of multiple information, including internal zoning, deformation features, inclusions, Ti-thermometry, trace element patterns, Lu-Hf and/or oxygen isotopes. These different systems may have different retentivity and thus are not always coupled, and their comparison provides additional information. Zircon is not only a robust geochronometer, but also a mineral relevant for the petrogenesis of metamorphic rocks that can provide details on protolith, temperature evolution, deformation, fluids and melts and assists the reconstruction of crustal processes.

Current and future analytical developments will increase our capability to collect geochemical information with a greater spatial resolution, that in turn will allow resolving element and isotopic diffusion, fine scale alteration and replacement/recrystallization. The systematics of numerous trace elements hosted in zircons remains underexplored (e.g. H, Li, Nb, Ta, Sc) and requires systemic studies. Trace element partitioning with other phases and melts of different compositions have to be further investigated over a range of *P*-*T* to fully exploit the capacity of zircon to monitor geochemical differentiation. Ti-in-zircon thermometry is lacking studies on the effect of pressure and Ti activity. Diffusion of crucial elements, for example oxygen, requires further investigation both experimentally and of natural samples. Petrogenesis of metamorphic zircon will gain from additional knowledge of Zr and Hf distribution in metamorphic minerals and fluids, and of zircon forming reactions. The complex processes of zircon alteration, replacement, dissolution, precipitation and modification in general should be approached through simulations, experiments and systematic studies in natural samples.

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Table 1. Summary of metamorphic zircon characteristics

	Characteristic	Metamorphic conditions	Process and/or cause
zoning	Regular polygonal zoning, oscillatory or sector, generally weak, and mostly euhedral external shape	Anatexis, granulite facies and hydrothermal conditions	Crystallization from a melt or precipitation from a fluid
	Patchy, mosaic zoning	Subsolidus	Metamictization, fluid alteratioin, initial stages of replacement
	Unzoned or weak convolute zoning	Subsolidus above greenschist facies	Replacement including dissolution-precipitation
microstructure	Sawtooth overgrowths	Diagenesis to low greenschist facies < 400°C	Dissolution-precipitation
	Intragrain crystallographic missorientation and formation of subgrains	Amphibolite to UHT	High strain rates and milonitization
	Microzircon around major minerals (rutile, ilmenite, garnet)	Cooling from high temperatures	Expulsion fo Zr during mineral breakdown or recrystallization
anomalous composition	Porosity and inclusions of Th and U phases	Subsolidus	Dissolution-precipitation
	Presence of non-formula elements (Ca, Al...)	From diagenesis to extreme conditions	Metamictization and fluid alteratioin
	Pb nuggets	Ultra high temperature >900°C	Pb mobilization
chemistry	Low Th/U	Subsolidus to migmatites, less common in UHT and mafic compositions	Coexistence with Th-rich phase such as monazite or allanite
	Flat HREE pattern	Amphibolite, eclogite and granulite facies to extreme *P-T*	Coexistence with garnet
	Strong LREE depletion and steep REE pattern	Amphibolite to granulite facies	Coexistence with abundant LREE-rich phases such as titanite, allanite, monazite
	Absence of negative Eu-anomaly	Eclogite facies (or assemblages lacking feldspar)	Lack of significant amount of feldspars in the assemblage
	Decoupling of U-Pb and Hf systematics	Subsolidus to granulite	Alteration and incomplete replacement

Table 2. Zircon/garnet partition coefficient for middle to heavy REE obtained from natural rocks and experiments. The major element garnet composition for each sample is reported when available.

Rock type	Reference	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	T in °C	XGrs	XAlm	XPrp	XSpess
HP vein	Rubatto & Hermann 2003	1.6	1.6	2.1	2.9	3.6	4.5	5.3	6.0	3.4	550	0.15	0.55	0.30	0.001
HP schist	Rubatto 2002	0.3	0.4	0.7	1.0	1.2	1.5	1.8	2.1	1.3	600	0.14	0.68	0.16	0.018
Gneiss	Buick et al. 2006	2.3	2.5	3.8	5.6	8.2	10.9		15.5		800	0.016	0.63	0.35	0.006
Granulite	Hermann & Rubatto 2003	0.8	1.0	1.3	1.7	2.6	3.9	5.8	8.2	2.1	750	0.18	0.63	0.18	0.008
Granulite	Rubatto 2002	1.6	1.8	2.6	4.3	7.1	11.1	17.3	23.9	4.8	800	0.017	0.81	0.16	0.015
Granulite	Rubatto 2002	0.9	0.9	1.3	2.0	3.2	5.2	8.6	12.1	2.3	800	0.023	0.82	0.13	0.026
Granulite	Rubatto et al. 2006	0.7	0.8	1.1	1.6	2.4	3.4	4.6	6.3	1.9	800	0.031	0.84	0.1	0.027
Granulite	Whitehouse & Platt 2003	0.5	0.7	0.8	0.8	1.0	0.7	0.7	0.8		700				
UHT gneiss	Hokada & Harley 2004	1.3	0.9	0.7	0.7	0.7	0.7	0.6	0.7		1000	0.024	0.52	0.46	0.003
UHT gneiss	Kelly & Harley 2005	0.7	0.7	0.7	0.8	0.9	0.9	1.0	1.2		1000				
Experiment	Rubatto & Hermann 2007	1.0		2.8		5.5		8.4	11.6	3.9	800	0.22	0.5	0.3	0.0
Experiment	Rubatto & Hermann 2007	1.0		1.3		2.1		2.9	3.5	1.8	900	0.11	0.52	0.37	0.0
Experiment	Rubatto & Hermann 2007	0.8		0.6		0.8		1.2	1.4	0.7	1000	0.06	0.47	0.47	0.0
Experiment	Taylor et al. 2014	0.6	0.5	0.5	0.5	0.5	0.6	0.7	0.8		900	0.0	0.53	0.47	0.0
Experiment	Taylor et al. 2014	0.7	0.6	0.6	0.6	0.7	0.8	1.0	1.2		950	0.0	0.56	0.44	0.0
Experiment	Taylor et al. 2014	0.7	0.6	0.6	0.6	0.7	0.8	0.9	1.1		950				
Experiment	Taylor et al. 2014	0.9	0.8	0.7	0.8	0.9	1.0	1.1	1.5		950				
Experiment	Taylor et al. 2014	0.7	0.5	0.5	0.4	0.4	0.4	0.4	0.5		1000	0.0	0.55	0.45	0.0
Experiment	Taylor et al. 2014	0.8	0.6	0.5	0.5	0.5	0.6	0.6	0.7		1000				

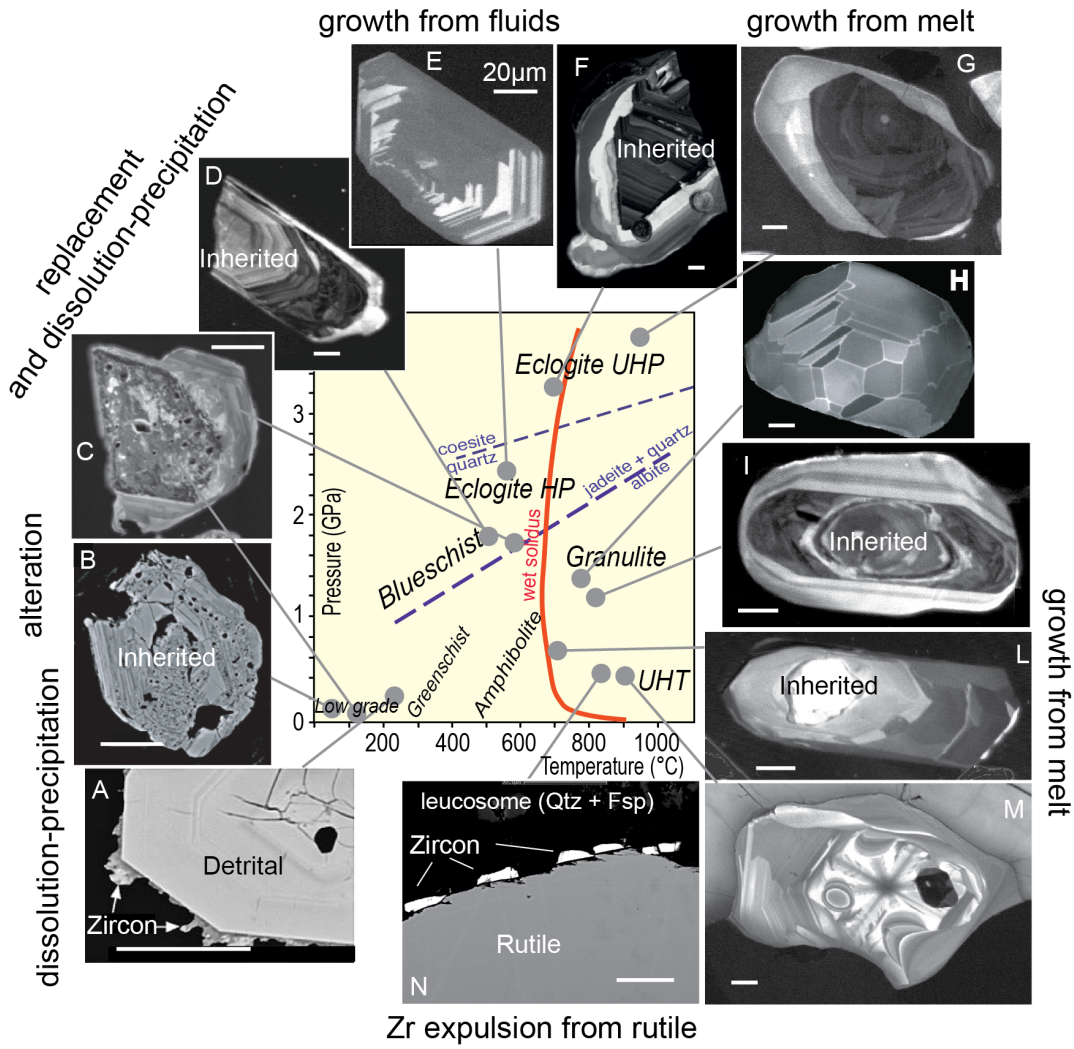

Figure 1. Typical internal zoning and textures of zircons from different metamorphic grades. Images in A, B and N are BSE, others are CL images. Horizontal scale bar in all images is 20 microns. Labels on the outside of images indicate the main process responsible for zircon growth or disturbance. The central diagram summarizes the main metamorphic facies. A) Zircon overgrowth on detrital core in greenschist facies shale [used by permission of Springer, license 3930810283470, from Rasmussen et al. (2005), Contributions to Mineralogy and Petrology, Vol. 150, Fig. 3k, p. 149]. B) Altered inherited zircon in digenetic sandstone [used by permission of John Wiley and Sons, license 3930080281612, from Hay and Dempster (2009), Sedimentology, Vol. 56, Fig. 4A, p. 2181]. C) Zircon with core altered during sea-floor alteration and rim formed during high-pressure metamorphism, same sample as described in Spandler et al. (2004). D) Zircon with inherited core and two metamorphic rims from eclogitic micaschist [used by permission of Nature Publishing Group, from Rubatto et al. (2011), Nature Geoscience, Vol. 4, Fig. 2a, p. 339]. E) Zircon formed in a fluid vein within eclogite [used by permission of Elsevier, from Rubatto and Hermann (2003), Geochimica et Cosmochimica Acta, Vol. 67, Fig. 4b, p. 2179]. F) Zircon with inherited core and two metamorphic rims from UH*P* whiteschist

[used by permission of Springer, license 3930090407326, from Gauthiez-Putallaz et al. (2016), Contributions to Mineralogy and Petrology, Vol. 171, Fig. 3a, p. 15]. G) Zircon grown under UH*P* to granulite facies metamorphic conditions in a Kokchetav gneiss, courtesy of A. Stepanov. H) Fir-tree sector zoning in metamorphic zircon from eclogite [used by permission of Elsevier, license 3930810027220, Root et al. (2004), Earth and Planetary Science Letters, Vol. 228, Fig. 3a, p. 330]. In this case the process for zircon formation is unclear. I) Zircon from granulite with two metamorphic overgrowths around inherited core [used by permission of John Wiley and Sons, license 3930090711788, from Hermann and Rubatto (2003), Journal of Metamorphic Geology, Vol. 171, Fig. 3a, p. 15]. L) Zircon from low temperature migmatite with two metamorphic overgrowths around inherited core [used by permission of Springer, license 3930090864124, from Rubatto et al. (2009), Contributions to Mineralogy and Petrology, Vol. 158, Fig. 3l, p. 708]. M) Zircon from a leucocratic vein that records the age of UH*T* metamorphism [used by permission of Oxford University Press, license 930800811618, from Harley and Nandakumar (2014), Journal of Petrology, Vol. 55, Fig. 8b, p. 1978]. Note the feathered texture and a multiphase inclusion in the core. N) Microzircons around rutile grain formed by expulsion of Zr during recrystallization of rutile upon cooling from UH*T* metamorphism [used by permission of Springer, license 3930091093780, from Ewing et al. (2013), Contributions to Mineralogy and Petrology, Vol. 165, Fig. 5d, p. 766].

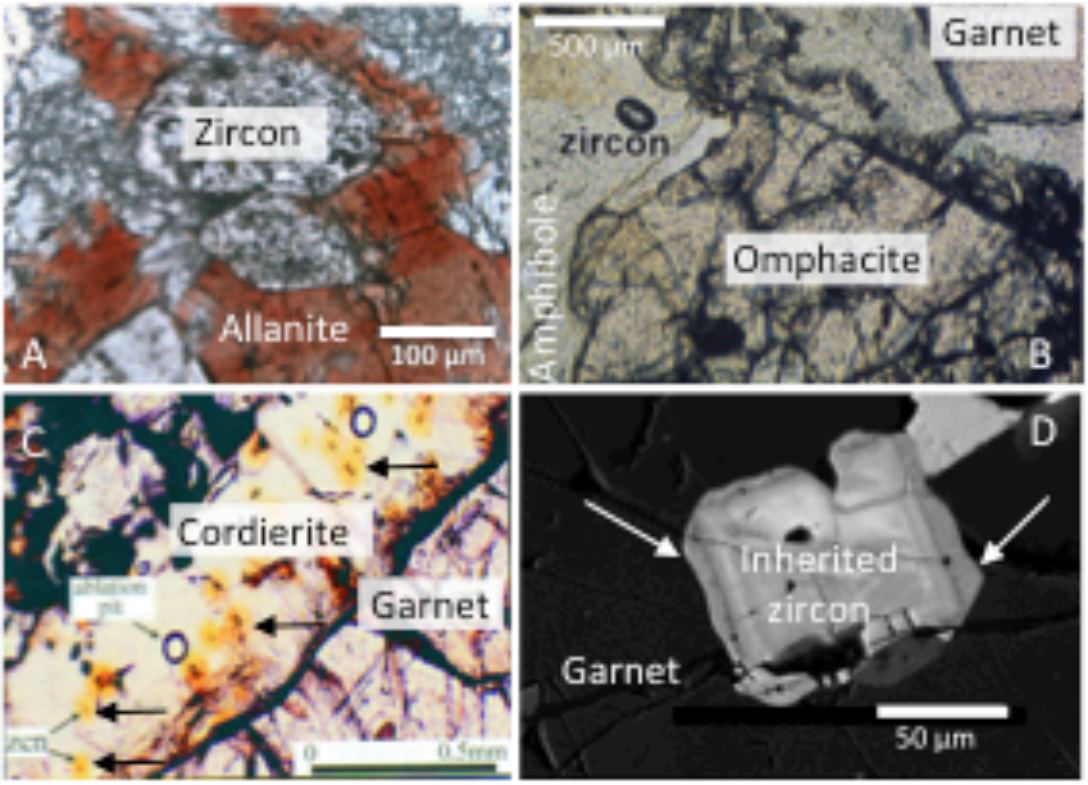

Figure 2. Textural relationships between zircon and other metamorphic minerals. A) Zircon in apparent textural equilibrium with allanite (brown) in an eclogite facies rock; zircon and monazite are both metamorphic but differ in age by 10 Ma [used by permission of Mineralogical Society of America, from Rubatto et al. (2007), American Mineralogist, Vol. 94, Fig. 1, p. 1521]. B) Inherited magmatic zircon included in amphibole in an eclogite. C) Micro-zircons (indicated by arrows) in the cordierite corona around garnet, which formed during decompression from granulite facies [used by permission of Mineralogical Society of Great Britain and Ireland, license 3930121477614, from Degeling et al. (2001), Mineralogical Magazine, Vol. 65, Fig. 2b, p. 752]. D) Zircon included in garnet in amphibolite; most of the zircon is inherited and only the thin rim (indicated by arrows) is metamorphic, same sample as described in Buick et al. (2006).

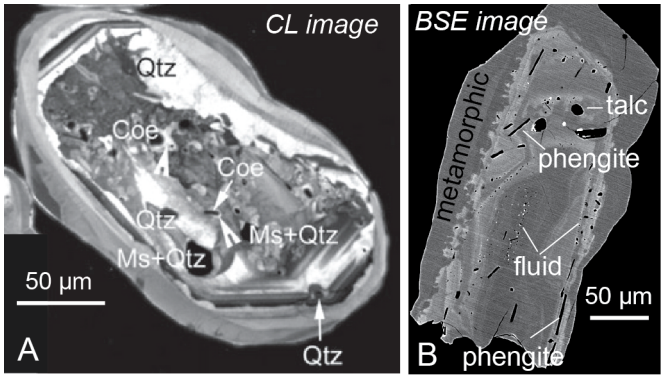

Figure 3. Secondary metamorphic inclusions in inherited zircon cores that underwent high pressure metamorphism. The cores also show disturbance of the original zoning likely due to alteration by metamorphic fluids. A) Zircon from micaschist recovered from the Chinese Continental Scientific Drilling Main Hole in the Sulu orogeny, China [used by permission of John Wiley and Sons, license 3930800210763, from Zhang et al. (2009a), Journal of Metamorphic Geology, Vol. 27, Fig. 3c, p. 321]. B) Zircon from a whiteschist of the Dora Maira unit, Western Alps, Italy [used by permission of Springer, license 3930130984661, from Gauthiez-Putallaz et al. (2016), Contributions to Mineralogy and Petrology, Vol. 171, Fig. 3b, p. 15].

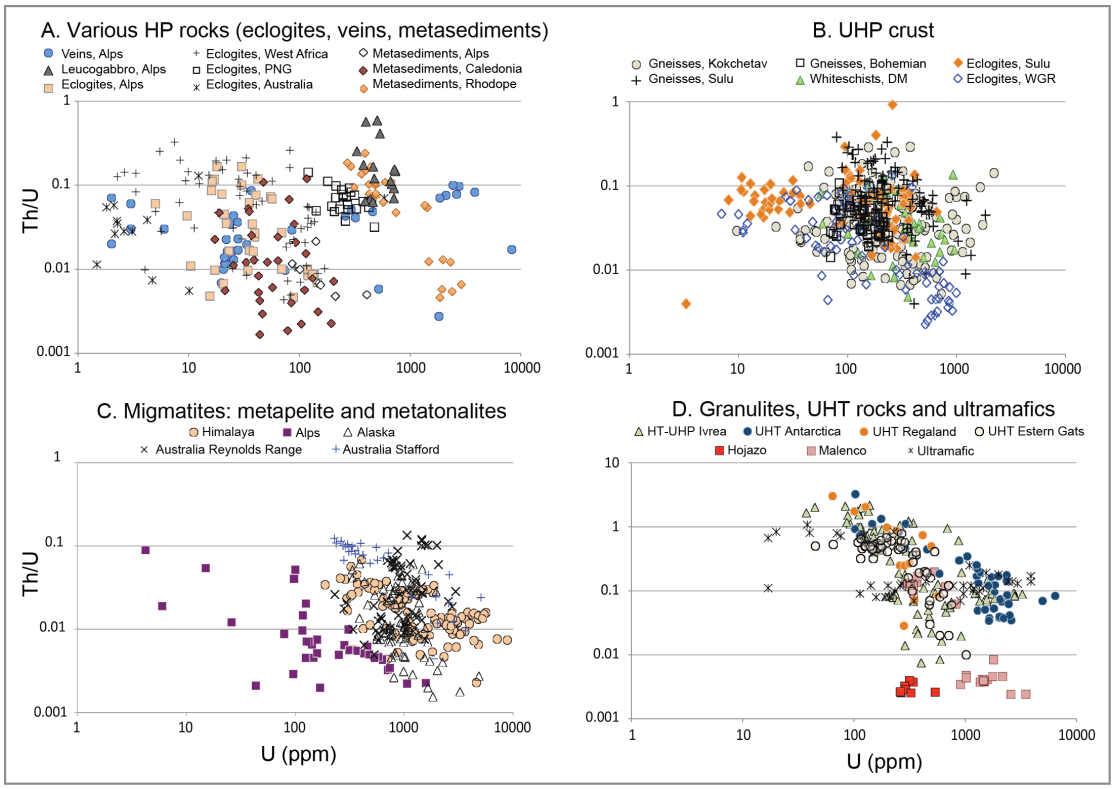

Figure 4. Th/U versus U content (in ppm) of metamorphic zircon from different tectonic settings. The compilation is based on circa 1400 published analyses (Vavra et al. 1996; Gebauer et al. 1997; Rubatto and Gebauer 2000; Hermann et al. 2001; López Sánchez-Vizcaíno et al. 2001; Rubatto et al. 2001; Möller et al. 2002; Cesare et al. 2003; Hermann and Rubatto 2003; Rubatto and Hermann 2003; Root et al. 2004; Kelly and Harley 2005; Spandler et al. 2005; Hermann et al. 2006b; Rubatto et al. 2006; Bauer et al. 2007; Rubatto et al. 2008; Rubatto et al. 2009; Zhang et al. 2009b; Gasser et al. 2012; Gordon et al. 2012; Ewing et al. 2013; Korhonen et al. 2013; Kylander-Clark et al. 2013; Rubatto et al. 2013; Ganade de Araujo et al. 2014; Phillips et al. 2015; Rubatto and Angiboust 2015; Gauthiez-Putallaz et al. 2016; Stepanov et al. 2016b). See text for discussion.

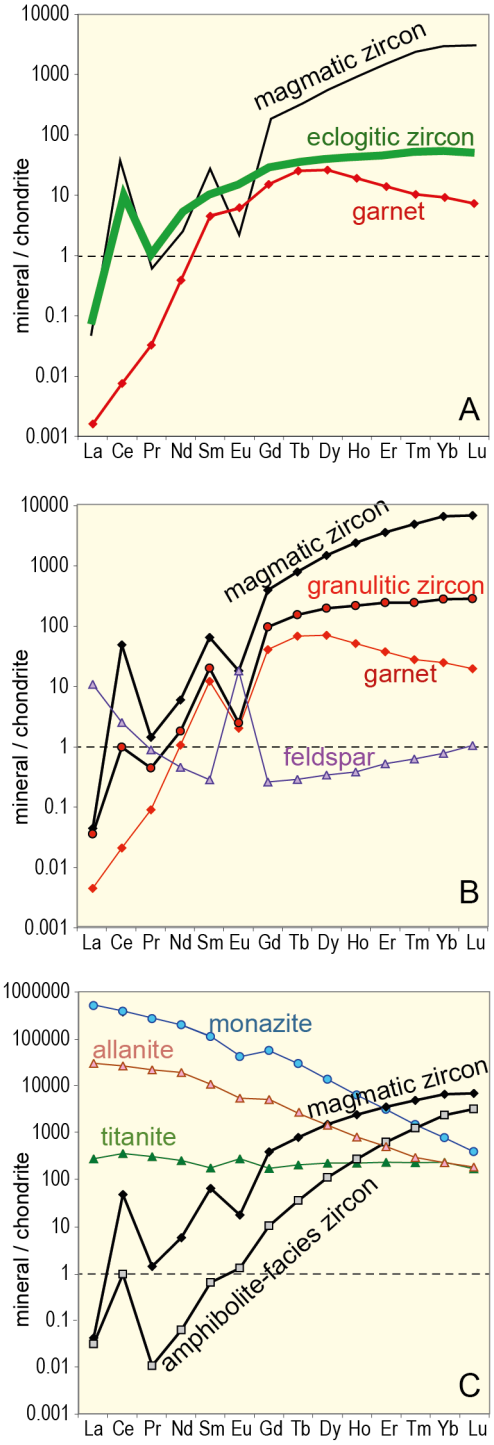

Figure 5. Representative REE patterns of zircon types and other relevant minerals, normalized to Chondrite values. Magmatic zircon is plotted for reference in all diagrams. Relevant REE-bearing minerals coexisting with metamorphic zircon in eclogite (A), granulite (B) and amphibolite facies (C) assemblages are represented in the respective diagrams to illustrate the competition for REE and the consequent REE signature of metamorphic zircon in each assemblage. See text for discussion.

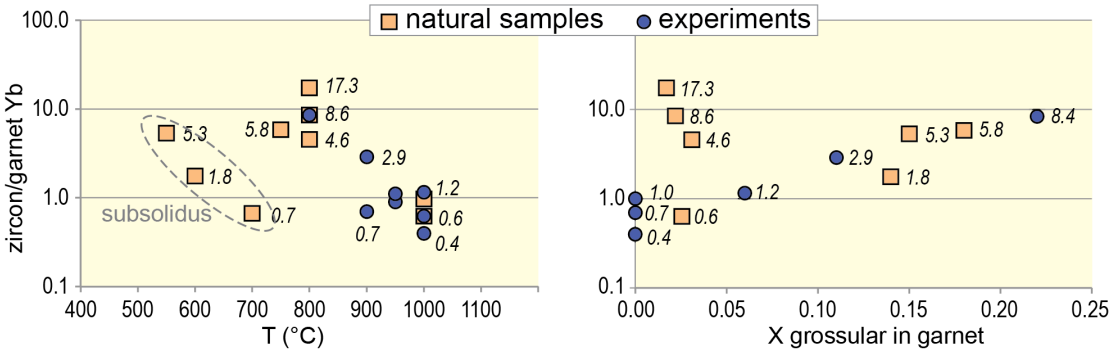

Figure 6. Zircon/garnet Yb partition coefficients from experimental studies and natural samples plotted against *T* (A) and garnet composition represented by molar proportion of grossular (B). The dotted ellipse in A groups natural samples that did not reach melting conditions. The number next to each symbol is the partition coefficient. Data are from Table 2 that also contains the references. See text for discussion.

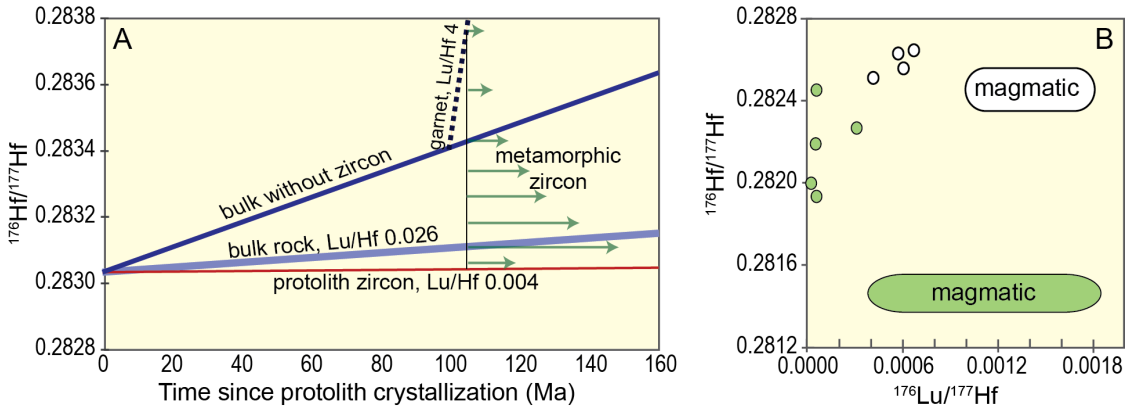

Figure 7. Lu-Hf systematics in metamorphic zircon. A) $^{176}Hf/^{177}Hf$ isotopic evolution over time for different components of a gabbroic rock that crystallized magmatic zircon at time 0 and metamorphic zircon 100 Ma later, in a garnet bearing assemblage. Because zircon is the main host of Hf in the rock, the evolution of the bulk rock where protolith zircon remains isotopically isolated (bulk without zircon) is significantly more radiogenic than that of the protolith zircon. Garnet that forms during prograde metamorphism has a much higher Lu/Hf than the bulk (4 versus 0.026) or the magmatic zircon (Lu/Hf 0.004) and rapidly increases its $^{176}Hf/^{177}Hf$ with time. The $^{176}Hf/^{177}Hf$ ratio of metamorphic zircon that forms a few Ma after garnet (peak to retrograde path) will depend on which component(s) of the system the zircon equilibrates with: only the magmatic zircon, the bulk rock fully equilibrated, the bulk rock without participation of the magmatic zircon, or even only the garnet. The grey arrows indicate the trajectory of new metamorphic zircon depending on its acquired $^{176}Hf/^{177}Hf$, and their variable length represents the likelihood of that composition occurring. Model based on data from Monviso eclogite described in Spandler et al. (2011). B) Difference in $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ systematics between magmatic protolith zircons (large fields) and new metamorphic zircon (small circles) in two HP samples from the Dabie orogeny. Data are from Zheng et al. (2005), white symbols, and Gao et al. (2015), grey symbols. Note the tendency of the metamorphic zircon to higher $^{176}Hf/^{177}Hf$ and lower $^{176}Lu/^{177}Hf$ due to the likely effect of garnet in the metamorphic assemblage.

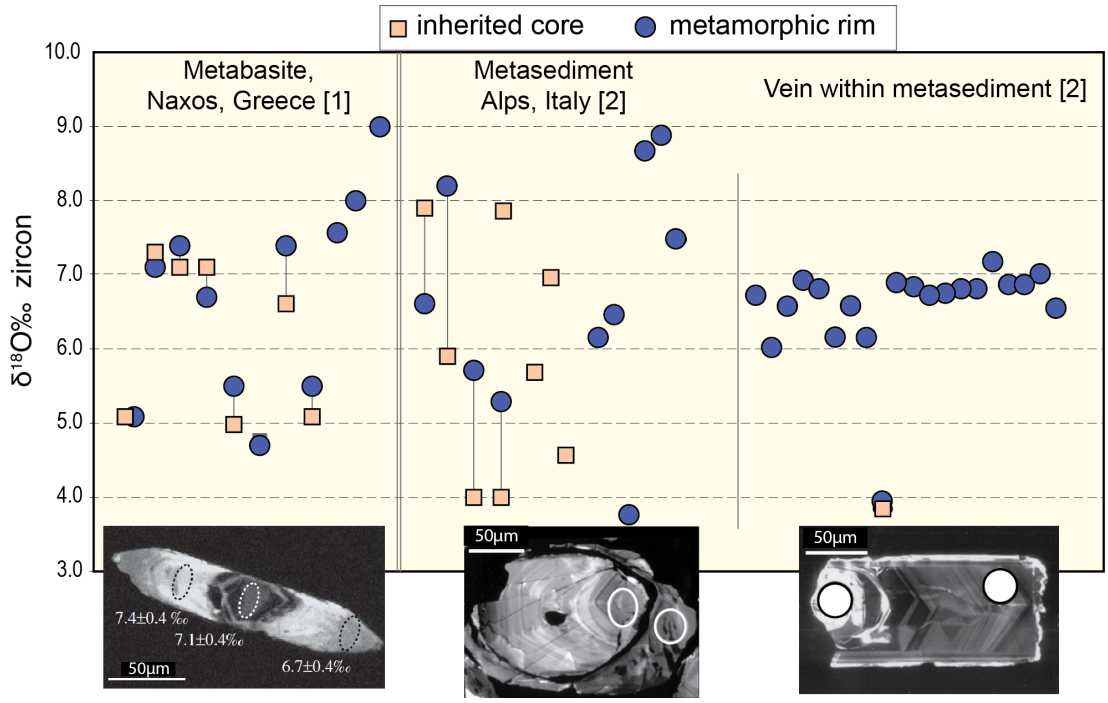

Figure 8. Oxygen isotopic composition of zircon core and rim from two samples that underwent metamorphism at 500-600°C and where zircon rims record the age of metamorphism. Analyses of rim and core from the same crystal are linked by thin vertical lines. In both samples, the zircon rim oxygen isotope composition did not equilibrate with the bulk rock. In contrast, zircon in the metamorphic vein within the micaschist (right) have a uniform oxygen isotope composition. Example of the zircon texture is shown in the CL image below the data. Errors on $\delta^{18}O$ values are not plotted. Data and images are from [1] Martin et al. (2006) and [2] unpublished data from sample MST2 and MST1 described in Rubatto et al. (1999) [Images are used by permission of Elsevier, license 3930790667589, in Martin et al. (2006), Vol. 87, Fig. 7, p.183; license 3930131166344, from Rubatto et al. (1999), Vol. 167, Fig. 2, p. 146]. See text for discussion

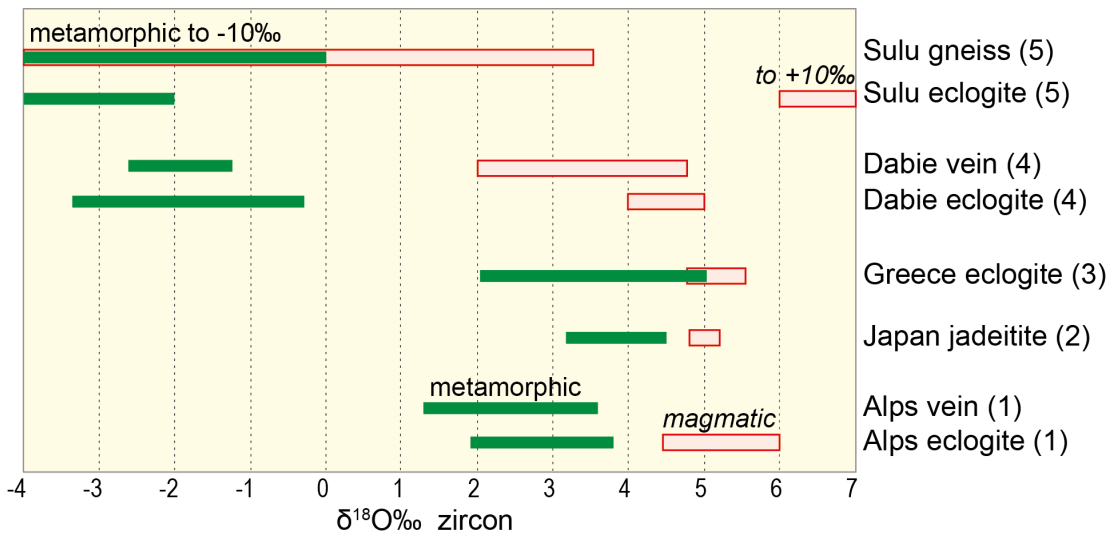

Figure 9. Compilation of low $\delta^{18}O$ values in metamorphic zircon (black bars) compared to protolith zircon of the same sample (empty bars). Data are from (1) Rubatto and Angiboust (2015), (2) Fu et al. (2010), (3) Fu et al. (2012), (4) Sheng et al. (2012) and (5) Chen et al. (2011). See text for discussion.

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