The current state and future of accessory mineral research

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Abstract

Over the past decade, there have been many significant advances in the area of accessory minerals research, notably permitted by the development of imaging and in situ measurement techniques. In this paper, we review some recent developments and suggest areas on which to focus future research.

The magmatic stability of key accessories like zircon and monazite is now reasonably well known and the past decade has seen a large improvement of the knowledge on the metamorphic stability of monazite, epidote, sphene, and zircon. However, other stability domains such as supergene and hydrothermal conditions remain poorly known. Such data are nevertheless essential as the occurrence or transformations of accessory minerals are being increasingly used as probes of the conditions and timing of their host rock transformations. The stability of accessories plays also a key role on the mobility of geochemically important trace elements, often predominantly hosted by these phases in rocks.

The recent years have also seen extended efforts to improve our knowledge on the crystal chemistry, crystallographic substitutions, and the mechanisms of element mobility within accessory mineral lattices, based both on natural cases and experimental studies. Zircon, monazite, and apatite were the main targets of these investigations. These researches resulted in the derivation of new metamorphic geothermometers, allowed to improve our knowledge of the behaviour of radiometric systems hosted by accessory minerals, and investigated the nature and quantity of nuclear waste that could be stored in ceramic waste forms with structures and compositions similar to those of monazite or zircon, for example. Much remains to be done in this area, however.

Geochronology is another major incentive for accessory mineral research. Recent years have shown the multiplication of geochronological investigations carried out in situ with combined microtextural and microchemical investigations. These researches illustrated the wealth of chronological information locked in accessory minerals. This is, however, a rapidly evolving field, which will strongly benefit from improved understanding of internal mineral textures, mechanisms of element mobility within crystals, and future development of in situ analytical techniques like Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and ion microprobe.
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1. Introduction

Although some minerals are called "accessory" because of their low modal abundance in crustal rocks, usually on the order of less than 0.1% (e.g., Gromet and Silver, 1983; Ward et al., 1992; Bea, 1996; Foster et al., 2002), they are nevertheless becoming increasingly studied because they appear to be key tracers for many geological processes. For instance, numerous chemical elements of geological and geochronological interest, such as the rare earth elements (REEs) U, Th, Pb, Ti, Nb, V, and Ta, are contained in these minerals (e.g., Gromet and Silver, 1983; Ward et al., 1992; Bea, 1996). Much of what we know about Earth's early history comes from in situ stable and radiogenic isotope measurements of minerals such as zircon ($ZrSiO_4$) and apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) (Bowring and Housh, 1995; Buick et al., 1995; Wilde et al., 2001; Mojzsis et al., 1996, 2001). The trace element and isotopic composition of accessory minerals are useful petrogenetic indicators to unravel complex geologic histories preserved in igneous and metamorphic rocks (e.g., DeWolf et al., 1993; Bea, 1996; Bea et al., 1994; Guo et al., 1996; Schaltegger et al., 1999). Ceramics structurally and chemically similar to accessory minerals such as monazite ((Ce,La,Nd,Th)PO_4), apatite, or zircon are also being seriously considered as potential forms for immobilisation of high-level radioactive industrial and military waste (Boatner and Sales, 1988; Ewing, 2001; Read and Williams, 2001). In this paper, our intent is to review some key advances in accessory mineral studies over the past decade, and to highlight areas of research where progresses are likely to be made in the future. We sequentially review the areas of mineral stability and transformation in various geological conditions, then present some recent advances made in accessory crystal chemistry with implications for nuclear ceramics, and finally survey geochronological and isotope studies of accessory minerals, with a specific emphasis on in situ investigations, which became especially important in the past decade. Examples of current accessory mineral research are provided with the subsequent papers enclosed in this second special issue of *Chemical Geology* devoted to accessory minerals, following the first one published nearly 10 years ago (1993, volume 110).

2. Accessory mineral stability and transformations

2.1. Magmatic and metamorphic conditions

The occurrence of accessory minerals, like major phases, can give clues with regard to the petrogenesis of their host rock. Perhaps the most famous example is magma geothermometry, and saturation inferred from zircon (Watson and Harrison, 1983), apatite (Harrison and Watson, 1984), or monazite (Rapp and Watson, 1986; Rapp et al., 1987; Montel, 1993) solubilities and dissolution kinetics in silicate melts. The importance of accessories in the control of trace elements during magmatic differentiation is now well recognised (e.g., Gromet and Silver, 1983; Ward et al., 1992; Bea, 1996; Hoskin et al., 2000), but the partition coefficients database necessary for proper quantitative magmatic differentiation modelling is far from being complete and still needs to be expanded (Bea et al., 1994; Ewart and Griffin, 1994; Asavin, 1995; Guo et al., 1996; Foley et al., 2000; Tiepolo et al., 2002). The common inclusion of accessories in rock-forming minerals (e.g., biotite), however, makes the direct use of partition coefficient during partial melting processes difficult if the host mineral does not melt (Bea, 1996).

Recently, metamorphic geothermometry based on the partitioning of the REE, notably Gd and Y, among coexisting monazite and xenotime was proposed (Heinrich et al., 1997; Gratz and Heinrich, 1997, 1998) and applied to samples from the Himalaya by Viskupic and Hodges (2001). Further refinements were subsequently proposed. Seydoux-Guillaume et al. (2002a, 2002b) illustrated the effect of the monazite Th content on geothermometric estimations. Pyle et al. (2001) proposed use of Y contents from garnet instead of xenotime, thus expanding the applicability of this geothermometer to metapelites lacking xenotime. All of these studies rely on a strong experimental background with a subsequent application to natural samples. Although studies using natural samples should be the starting point to give a full picture of natural conditions (e.g., temperature, pressure, magma or fluid composition, gas fugacities), under which a given accessory phase is stable (cf. for monazite under metamorphic conditions, Smith and Barreiro, 1990; Kingsbury et al., 1993; Bingen et al., 1996; Franz et al., 1996; Lanzirotti and Hanson, 1996;

Pan, 1997; Simpson et al., 2000; Cabella et al., 2001; Foster et al., 2002), only experimental work permits a systematic quantitative evaluation of these parameters. As an illustration, the most quantitative estimates of accessory mineral stabilities, besides the examples discussed above, are largely based on experimental work, as shown by our present extended knowledge of epidote (Liou, 1993) or titanite (Frost et al., 2001) stability conditions. Nevertheless, experimental data are still lacking on the stability in magmatic and metamorphic conditions of important accessory phases such as allanite. This mineral is indeed a major repository for REE in crustal rocks (e.g., Gromet and Silver, 1983; Sawka, 1988; Bea, 1996), and a better understanding of its boundary stability conditions would certainly ease our understanding of REE behaviour during major geodynamic processes, such as subduction (Sorensen and Grossman, 1993; Tribuzio et al., 1996).

2.2. Sedimentary and supergene domains

Less is known about low-temperature stability of accessory minerals. Possible reasons include metastability problems associated with slow reaction kinetics. A good illustration of this is the controversy concerning the relationship between rhabdophane (hexagonal $(Ce,La,Nd,Th)PO_4)·xH_2O$) and monazite (monoclinic $(Ce,La,Nd,Th)PO_4$) (Akers et al., 1993), or the debated suggestion that monazite may decompose during high-temperature diagenesis, but grow again during prograde metamorphism once the greenschist facies is passed (Smith and Barreiro, 1990; Kingsbury et al., 1993; Ohr et al., 1994; Cabella et al., 2001). Monazite and rhabdophane are found associated in metamorphic rocks (Nagy and Draganits, 1999; Nagy et al., 2002), the latter resulting probably from the alteration of the former, but the exact relative $P–T–X$ stability fields of these REE phosphates remain to be clarified. Another reason for our limited knowledge in the low-temperature range might be that the "accessory mineral" concept initiated from the investigation of magmatic and metamorphic rocks, and the subsequent behaviour of the so-called called "heavy minerals" during the erosion and sedimentation cycles has attracted less attention.

Nevertheless, accessory phases like zircon, monazite, xenotime, allanite, ilmenite, rutile, and apatite

tend to weather less rapidly than rock-forming minerals (e.g., Morton, 1992; Morton and Berge, 1995). This, together with their higher densities, yields heavy mineral concentrates in stream and river sediments, which have been used for decades by mineral exploration geologists (e.g., Parfenoff et al., 1970). In tropical areas where outcrops are rare, heavy mineral studies from detrital sediments combining mineralogical, in situ elemental, and geochronological analyses are often the only reliable way to decipher the igneous and metamorphic history of a region (e.g., Ludden et al., 1995; Machado et al., 1996). In other, more favourable geological contexts, Knudsen et al. (2001) used in situ Hf isotopes (by Laser Ablation MultiCollector Inductively Coupled Plasma Mass Spectrometry, LA-MC-ICP-MS) and U–Pb geochronology (by LA-ICP-MS) to constrain the provenance of detrital zircons from a Devonian sedimentary basin from Greenland.Wilde et al. (2001) used the REE chemistry and oxygen isotope composition, both measured by ion microprobe (Secondary Ion Mass Spectrometry, SIMS), to constrain the protolith composition of an Archean zircon crystal from Jack Hills, Australia. Hoskin and Ireland (2000), however, presented results suggesting that the REE composition of zircon may be in some cases misleading for provenance characterization. Clearly, more research needs to be done in this area. With progresses in quadrupole and multicollector LA-ICP-MS instruments, there will most likely be significant advances in the knowledge of trace element and isotopic geochemistry of zircon and other accessory minerals in the future.

Other studies have shown the importance of accessory phases like apatite, zircon, monazite, rhabdophane, or thorianite on REE and Th behaviour in soils, which eventually largely determine the concentrations of these elements in continental waters (Braun et al., 1998), and may lead to elevated $^{234}U/^{238}U$ or $^{206}Pb/^{204}Pb$ ratios due to preferential leaching from decay damaged minerals (e.g., Davis and Krogh, 2001).

Phosphates like monazite, xenotime, and apatite are known to be relatively stable in sedimentary environments. Under such conditions, they typically display a specific habit and mineral composition. For example, monazite forms irregularly shaped grey nodules especially enriched in middle REE (MREE)

but depleted in Th (e.g., Read et al., 1987). Apatite is the main constituent of phosphorites and its REE content was investigated in the view of palaeoenvironmental reconstructions (Grandjean-Lécuyer et al., 1993; Jarvis et al., 1994). More recently, Stille et al. (1996) used Nd isotopes from these phosphorites as a tracer of the evolution of palaeocurrents in the Atlantic and Tethys Oceans during the past 180 Ma. This is certainly an area where promising findings are to be expected provided that any possible subsequent post-depositional perturbation of the geochemistry of these phosphates can be properly evaluated and discounted (e.g., Evans and Zalasiewicz, 1996; Reynard et al., 1999). The recent debate on the claim of the finding of biogenic carbon isotope signatures in 3.8-Ga-old apatites is a good illustration of this (Mojzsis et al., 1996, 1999; Sano et al., 1999a), and clearly shows that more research needs to be done in this area to gain better understanding of issues related to early life on Earth.

2.3. Fluid–mineral interactions

Another area where future research efforts should be focused concerns fluids and accessory mineral interactions. Although there is a growing body of field-based studies reporting the behaviour of accessory phases during their interactions with fluids (e.g., Pan et al., 1993; Poitrasson et al., 1996, 2000a; Geisler and Schleicher, 2000; Wood and Ricketts, 2000; Mathieu et al., 2001; Townsend et al., 2001; Poitrasson, 2002), experimental studies in this area remain scarce. No experimental determination of the aqueous solubility of an accessory mineral as essential as monazite has yet been published, apart from few preliminary data (Ayers and Watson, 1991; Devidal et al., 1998; Poitrasson et al., 2000b). This also holds true for structurally, and chemically, more complicated phases such as allanite. Further, basic thermochemical data (enthalpies, entropies, free energies, heat capacities, etc.) for accessory minerals are still scarce (see Ushakov et al., 2001, however, for a recent effort on REE orthophosphates). Hence, published monazite aqueous solubility estimates (Wood and Williams-Jones, 1994) are based on old thermodynamic data of limited reliability, derived from solubility experiments carried out on more or less crystallized rhabdophane. Such knowledge is never-

theless essential to understand the hydrothermal mobility of the trace elements hosted by accessory minerals (e.g., Ward et al., 1992; Poitrasson et al., 1996; Smith et al., 1999; Förster 2000, 2001) or to interpret properly geochronological and isotopic data from accessory minerals from altered rocks (see, e.g., Poitrasson et al., 1998).

Several recent studies have been conducted to better characterize low-temperature zircon–water interaction mechanisms. Balan et al. (2001a) used first principles quantum mechanical calculations to investigate the adsorption of water on the (100) surface of zircon. In that study, the authors determined that the high resistance of zircon to dissolution is a function of the strong acidity of the $Zr-O-Si$ bridging O atoms, which inhibits hydrolysis reactions. Trocellier and Delmas (2001) determined the solubility of zircon crystals from Brazil and Madagascar using a variety of analytical methods to analyze the solutions resulting from the leaching experiments.

In a higher-temperature domain, Harlov et al. (2002b) studied the relation between apatite and monazite in the Kiirunavaara magnetite–apatite deposit in northern Sweden, and highlighted the importance of late magmatic and hydrothermal fluids on the accessory phosphates textures and geochemistry. Their proposed scenario for a fluid-induced genesis of monazite inclusions in apatite is backed by experimental investigations (Harlov et al., 2002a,b).

Further complications arise with our limited knowledge of activity coefficients of end-member constituents in solid solutions such as monazite or allanite. Case studies using natural samples have shown that fluid–accessory mineral interactions may result in a variety of mechanisms, often characterised by incongruent dissolution, as observed for monazite (Poitrasson et al., 1996, 2000a) or allanite (Wood and Ricketts, 2000; Poitrasson, 2002). Recent experimental studies on zircon (Geisler et al., 2001a, 2002; Chen et al., 2002) and monazite (Oelkers and Poitrasson, 2002; Seydoux-Guillaume et al., 2002a) confirm that incongruent dissolution of these phases in aqueous solutions is common.

Another important step in quantitative geochemical fluid–rock interaction modelling involves the integration of the processes observed at the mineral scale to

the whole rock scale. Due to their small size, usually on the order of tens to hundreds of micrometers, accessory mineral specific occurrence within a given mineral type governs their geochemical exchanges with fluids. They will be less altered if they occur as inclusion in weakly permeable minerals (e.g., quartz), where they will be protected from fluid inter-action, than if they are included in more easily alterable phases, like phyllosilicates or feldspar, or especially at mineral grain boundaries acting as preferential fluid pathways. This is illustrated by the differential alter-ation of allanite according to its mineral neighbours in Fig. 1, as it has been already shown for monazite (Poitrasson et al., 1996, 2000a). Hence, the integration of fluid–mineral geochemical exchanges at the whole rock scale requires the development and use of image processing methods applied to backscattered electron (BSE), cathodoluminescence (CL) images or maps, or electron microprobe X-ray composition maps from polished slabs or rock thin sections to determine quantitatively the mineralogical neighbours of the accessories of interest and their likelihood to exchange with fluids.

Besides fluid–rock geochemical modelling, the study of accessory mineral alteration can be useful, like for metamorphism (Heinrich et al., 1997; Gratz and Heinrich, 1997, 1998), to constrain the fluid–rock interaction temperature. In a comprehensive study of natural examples of hydrothermally altered monazite from granites, Poitrasson et al. (2000a) found that an inverse correlation exists between hydrothermal alter-ation temperatures and the relative HREE enrichment
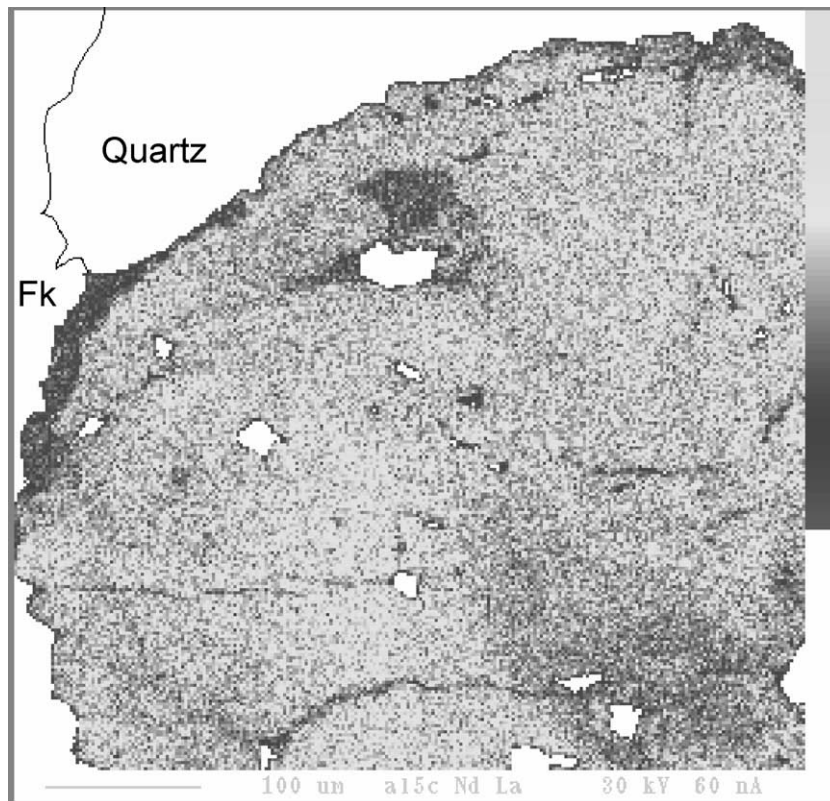

Fig. 1. Neodymium electron microprobe map of an altered allanite from the Mantelluccio granite, Corsica. The altered areas are depleted in Nd (darker zones) and tend to be the crystal margins located against alkali feldspar (Fk). In contrast, those parts of the mineral against quartz appear to be less altered, presumably because quartz acted as a shield for allanite against fluid interaction.

in the altered zones of the monazites studied. This is further illustrated here by relative Yb variations between fresh and altered monazite zones (Fig. 2). This alteration trend depicts a decreasing role for crystallographic site specificity in the chemical exchange as temperature increases, consistent with an increase of the system entropy. At 260 °C, the strong enrichment in HREE with alteration results from the substitution:

$$REE^{3+} + P^{5+} \Longleftrightarrow Th^{4+} + Si^{4+} \tag{1}$$
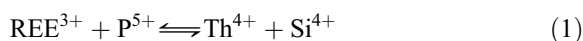
involving both the P and REE crystallographic sites of monazite.

At 290 °C, the relative enrichment in HREE is more limited, with REE site contraction resulting from a preferential removal of Th. At 340 °C, the alteration process is a monoclinic-to-hexagonal structure transition accompanied by chemical exchanges, or dissolution and replacement by allanite with little impact on the REE fractionation. At this higher temperature, the minor influence of crystallographic site constraints results in the lack of significant HREE enrichment in the altered areas with respect to the unaltered parts of the monazite.

These variations of the HREE in monazite with temperature (Fig. 2) can be described by the relation:

$$Yb_{alt.}/Yb_{unalt.} = 114500e^{-0.0346T} \tag{2}$$

where $Yb_{alt.}$ and $Yb_{unalt.}$ are the Yb concentrations in parts per million determined by LA-ICP-MS in the monazite altered and fresh zones, respectively, and T is the temperature in degrees Celsius. Further natural case studies of different temperatures as well as experimental investigations are required before this can become a fluid–rock geothermometer.

3. Crystal chemistry, diffusion, and implications for nuclear waste disposal

3.1. Crystal chemistry

In order to understand ionic substitutions and define crystallographic sites characteristic of accessory minerals, a starting point in this area of research involves the study of the chemical composition of major, minor, and trace elements of natural and
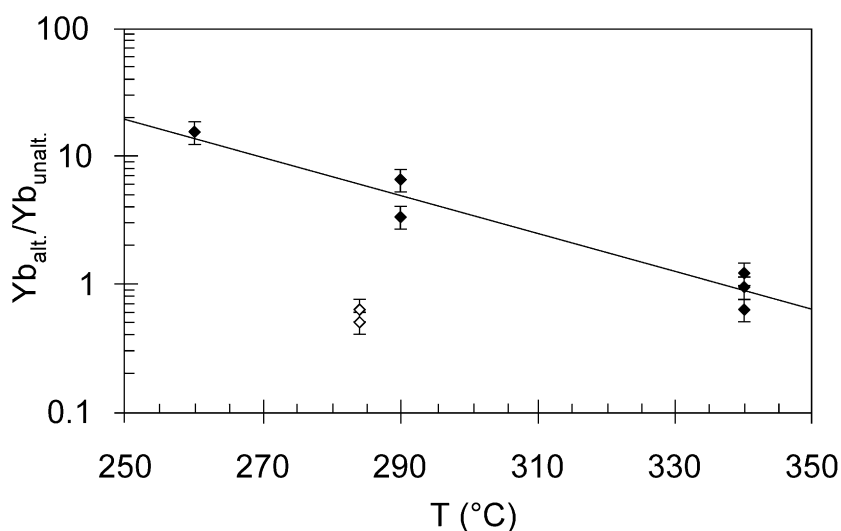

Fig. 2. Inverse correlation between the ratio of Yb in monazite-altered zones ($Yb_{alt.}$) with respect to Yb in the unaltered parts of the mineral ($Yb_{unalt.}$) as a function of temperature. The Yb concentrations were determined by LA-ICP-MS (data from Poitrasson et al., 1996, 2000a). These examples come from altered parts of the Carnmenellis granite (Cornwall, SW England), Skiddaw granite (Lake District, NW England), and St. Nectaire Granite (Massif Central, France). Excluding data for the chloritized Carnmenellis granite (open diamonds), the correlation coefficient, r, equals 0.97. The chloritized Carnmenellis granite data depart from this trend probably because of a relatively high concentration of fluorine in the hydrothermal fluid altering the monazite, which enhanced the HREE solubility (Wood, 1990).

synthetically grown samples, combined with high-precision X-ray diffraction measurements (Ni et al., 1995; Podor and Cuney, 1997; Podor et al., 1995; Finch et al., 2001; Hanchar et al., 2001; Montel et al., 2002). By this approach, Montel et al. (2002) have shown the capability of the monazite structure to incorporate a large range of cations with variable charge and ionic radii. This flexibility of the phosphate crystalline lattice, also deduced from natural cases studies (Poitrasson et al., 2000a; Poitrasson, 2002), is promising with regard to the incorporation of nuclear wastes with variable and complex chemistries. It may also explain the much lower annealing temperature of phosphates compared to silicates (Meldrum et al., 1998a).

An alternative promising approach involves ab initio calculation of crystalline properties otherwise difficult to measure directly in natural samples or on experimental products. For example, Meis et al. (2000) used such numerical simulations to study Pu and Cs incorporation in a Nd-rich apatitic structure.

In the case of the largely studied zircon because of its widespread occurrence and potential use as petrogenetic marker, trivalent REEs and Y may substitute for Zr^{4+} together with P^{5+} substituting for Si^{4+}:

$$Zr^{4+} + Si^{4+} \Longleftrightarrow REE^{3+} + P^{5+}. \qquad (3)$$
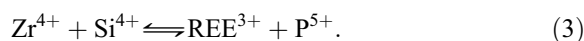
As pointed out by Hinton and Upton (1991) and Hoskin et al. (2000), usually the trivalent REEs are in greater abundance (on an atomic basis) than P in natural zircons, which strongly suggests that other element(s) must participate in charge balancing the trivalent REEs in the zircon structure.

Hanchar et al. (2001) reported similar results in an experimental study involving REE and P incorporation in zircon. In doing Secondary Ion Mass Spectrometry (SIMS) analyses of the REE- and P-doped zircon crystals, Hanchar et al. (2001) determined that minor amounts of Li and Mo were incorporated from the flux in the synthetic zircon crystals. These flux elements assisted in charge balancing the excess of REEs, and most likely resided in an interstitial site in the zircon structure. Finch et al. (2001), in a single crystal X-ray diffraction study of the same REE- and P-doped zircon crystals, found that the strain from P substituting for Si was significant and most likely played a role in the amount of REE^{3+} that could

substitute for zirconium in the *Zr site* in the synthetic zircon crystals. One area of future research is to develop analytical routines for other light and trace elements in zircon to better understand this type of substitution in both natural and experimental systems.

3.2. Internal zoning

Several recent papers have discussed the nature of zoning and overgrowths in accessory minerals, especially zircon. Hoskin (2000), using CL images, investigated the nature of oscillatory zoning (called "oscillatory zonation distribution patterns") in zircon and explained this phenomena using fractal statistics. This author determined that the zoning, and thus the distribution of trace elements, is a function of several factors including melt dynamics at the zircon/melt interface involving cation substitution, diffusion, melt polymerisation, and structure.

Several recent studies have discussed the response of zircon to high-grade metamorphic and anatectic events and hence whether internal metamorphism patterns have been preserved or not in this mineral. One possibility is that the zircon does not participate in the metamorphism (Roberts and Finger, 1997) and thus no evidence of the metamorphism is recorded in this phase. Another possibility is that during high-grade metamorphism, some sort of ripening mechanism occurs in which the zircon material contained in small crystals is transferred to larger grains, thereby forming overgrowths (Hanchar and Miller, 1993; Hanchar and Rudnick, 1995; Nemchin et al., 2001). The dissolution and growth kinetics of zircon need to be better understood for evaluating the general plausibility of this type of coarsening mechanism.

An alternative explanation to the nature of metamorphic growth in zircon involves the recrystallization of preexisting zircon along chemical reaction fronts migrating from the outer surface towards the interior of the zircon crystals (Schaltegger et al., 1999). Hoskin and Black (2000) also presented results from a study of the formation of metamorphic overgrowths on zircon by way of solid-state, closed system recrystallization of preexisting zircon. They presented evidence for the partial resetting of the Th/U ratios, U–Pb, and Pb–Pb ages as a consequence of the recrystallization. On the other hand, because of the sluggish diffusivities of Hf and Lu, Lu–Hf ages were

inferred to remain undisturbed by the recrystallization. Pidgeon et al. (1998) proposed that recrystallization is more likely to occur in regions within zircons that contain high concentrations of trace elements because of the strain they impose onto the crystalline lattice. In either processes, growth or recrystallization, the U–Th–Pb systems are opened and the radiogenic lead is released.

3.3. Diffusion

Over the past decade, there have been several studies investigating the diffusion of cations and anions in accessory minerals. Smith and Giletti (1997) determined the diffusion of Pb in monazite using the depth-profiling capability of SIMS to measure diffusion profiles in natural monazite crystals. Martin et al. (1999) determined the diffusivities of La and Eu in hydroxyapatite using ion implantation to introduce the diffusants, and Rutherford Backscattering Spectrometry (RBS) to measure the diffusion profiles. Cherniak (1993, 1995) used also the RBS technique to determine Pb, Sr, and Nd diffusion in sphene. The application of RBS allows for extremely short diffusion profiles (e.g., tens of Angstroms) to be measured and from which diffusion coefficients may be extracted.

Cherniak et al. (1997a,b) used ''in-diffusion'' experiments, by which the diffusant is introduced into the crystal from the external medium, and RBS to determine the diffusion coefficients for selected trivalent REEs and U, Th, and Hf in synthetic and natural zircon crystals. Lee et al. (1997) measured diffusion coefficients, using the depth profiling technique with SIMS for Pb, U, and Th in a natural zircon from Sri Lanka. Cherniak and Watson (2001) also determined the diffusion coefficients for Pb in natural and synthetic zircon using both ''in-diffusion'' and ''out-diffusion'' experiments and RBS to measure the diffusion profiles. ''Out-diffusion'' experiments consist in the study of the diffusion out of the crystal of a doped element, like Pb in zircon in this example. Meis and Gale (1998) did a computational study of volume diffusion of tetravalent U and Pu in zircon. The results of this work are in good agreement with existing experimental data. A good summary of diffusion in zircon can be found in Cherniak and Watson (2001).

A clear understanding of diffusion in an accessory mineral such as zircon, monazite, or apatite is important not only for geochronology, but also for designing ceramic storage materials for long-term Pu and other actinide radioactive waste. It should be noted that all of the diffusion measurements discussed above were done, for obvious reasons, on crystalline material. Once zircon becomes metamict, other mechanisms for diffusive transport may override volume diffusion (e.g., grain boundary diffusion along cracks formed via structural swelling of the zircon from volume changes due to accumulated radiation damage) and must be considered. Most likely, once zircon becomes significantly metamict, the diffusivities of most elements of interest will be enhanced (Cherniak and Watson, 2001; Geisler et al., 2002).

3.4. Implications for nuclear waste disposal

One important area of current and future of accessory mineral research consists of developing materials with similar chemistry and composition for the immobilisation of high-level radioactive waste, including plutonium from dismantled nuclear weapons (see Boatner and Sales, 1988; Hayward, 1988; Read and Williams, 2001; Ewing, 2001). In attempting to understand the fate of long-term disposition of radionuclides in accessory minerals (called ceramic waste forms outside of geology), there are several types of material that have been considered. A large amount of work has been done on zircon and some highlights will be illustrated here.

Natural samples of zircon that have accumulated radiation damage over extended periods of geologic time have been investigated using high-resolution transmission electron microscopy (HRTEM) (Chakoumakos et al., 1987; Murakami et al., 1991; Nasdala et al., 2002), micro-Raman spectroscopy (Wopenka et al., 1996; Nasdala et al., 1996, 1999, 2001, 2002; Högdahl et al., 2001; Balan et al., 2001b; Geisler et al., 2001b, 2002), and infrared spectroscopy (Zhang et al., 2000; Columbo et al., 1999) in an attempt to better understand the mechanisms involved in metamictization. In a study of natural metamict zircon crystals using diffuse X-ray scattering, Salje et al. (1999) found that within metamict zones, there are regions of crystalline material (see also Geisler et al., 2002).

Another way to approach this problem is to implant ions of Kr^+ into synthetic zircon to create a thin layer of amorphous zircon that can be studied in situ using HRTEM and subsequently anneal the crystals after the ion implantation to restore the crystallinity (Meldrum et al., 1998a,b). A third way is to dope synthetic crystals with radionuclides having relatively short half-lives such as ^{238}Pu or ^{239}Pu (Fig. 3), and to investigate the short-term accumulated radiation damage in the crystals over time (Exharos, 1984; Weber, 1990; Burakov et al., 2002).

In a study of Pu-doped glasses and crystalline ceramics using X-ray absorption spectroscopy, Hess et al. (1998) examined several Pu-doped synthetic polycrystalline zircon samples that were synthesized over 15 years ago to determine the local environment of the Pu ions in those materials. Using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and X-ray Absorption Near Edge Structure (XANES) spectroscopy synchrotron techniques, Hess et al. (1998) determined that in their polycrystalline zircon samples, Pu^{3+} substitutes for Zr^{4+} in the zircon structure, and that the charge deficiency introduced by the trivalent Pu is probably charge-compensated by oxygen defects. Burakov et al. (2002) presented the first results of ^{239}Pu-doped single crystals of zircon. These samples are of interest because unlike previous studies of Pu-doped ceramics, which consisted of polycrystalline material, these single crystals of Pu-doped zircon will be used to constrain the plutonium oxidation state and to determine how the incorporation of Pu affects the structural properties of zircon.

In understanding the incorporation of radionuclides in synthetic ceramics such as zircon or monazite, it is important to know the oxidation state of the radionuclide of interest both during synthesis as well as in the long-term repository geologic environment. In the case of Th, only the tetravalent oxidation state is stable under surficial conditions on Earth, but some actinides such as U have several oxidation states that may coexist (e.g., Langmuir, 1996; Hanchar, 1999). In the future, spectroscopic techniques using synchrotron radiation such as EXAFS and XANES to investigate the coordination, redox state, and local environment of actinide-doped synthetic minerals are likely to be a key area of interest.

Monazite has also attracted significant attention as a prospective ceramic waste form for disposition of
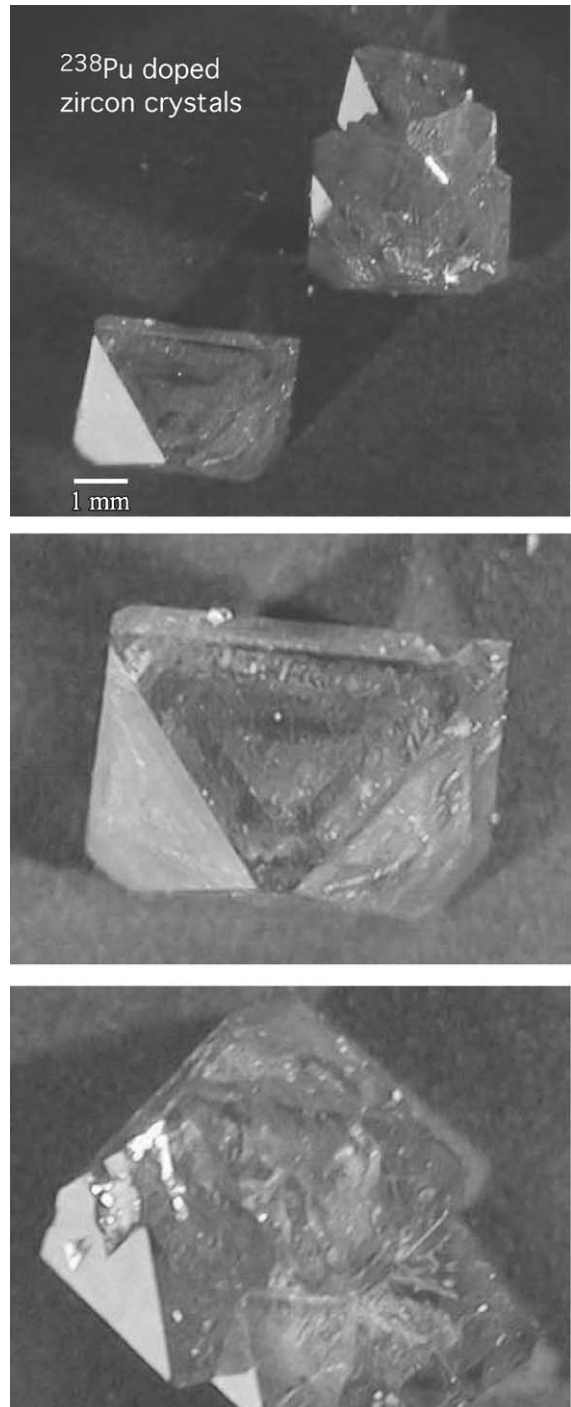

Fig. 3. Optical photomicrographs of synthetic ^{238}Pu-doped zircon crystals.

high-level waste (Boatner and Sales, 1988) due to its stability in various geological environments and because it usually contains in nature tens of weight percent element of La, Ce, and Nd; several weight percent element of Th; and also significant amounts of U, usually on thousands of parts per million (e.g., Franz et al., 1996; van Hemden et al., 1997; Förster, 1998). This, together with a dramatically higher resistance to fluid leaching compared to borosilicate glasses, makes it ideally suited for the containment of actinide based high-level waste in underground repositories (e.g., Read and Williams, 2001).

Other accessory minerals that have been in the past, or are presently, under consideration for immobilization of high-level radioactive waste and Pu include sphene ($CaTiSiO_5[OH]$) (Hayward, 1988), pyrochlore (Ca, $REE[Ti_2O_7]$), zirconolite ($CaZrTi_2O_7$), apatite ($Ca_{4-X}REE_{6+X}[SiO_4]_{6-Y}[PO_4]_Y[OF]_2$), and baddeleyite ($ZrO_2$) (Ewing, 2001).

Further complications may arise in this field of research for the design of ceramics for nuclear waste produced in countries that have chosen not to reprocess them before storage (e.g., Canada, Russia, US). Such wastes will contain elements with different ionic radius, redox state, and electronic configuration, which will lower the overall stability of the matrix, notably through increased solubility. Future research in this area should focus on physical and chemical characterisation of the different accessory minerals proposed, taking into account the possible complexity of the waste materials if the radionuclides are not separated prior to storage. Studies involving solubility, dissolution, diffusion, doping, and charge balancing should thus be undertaken under a variety of physical conditions.

4. Geochronology and isotope systematics

Minerals like zircon and monazite have been traditionally used for U–Th–Pb dating. This list has been extended over the past decade or so, with minerals like titanite, rutile, baddeleyite, apatite, xenotime, columbite–tantalite, allanite, thorite, perovskite, and many more (e.g., Heaman and LeCheminant, 1993; Heaman and Parrish, 1991; Mezger et al., 1991; Davis et al., 1994a,b; Corfu and Stone, 1998; Schärer et al., 1999). Zircon and monazite, however, remain unique, mainly

due to their high uranium and low initial common lead concentrations and are, as such, the premier minerals of choice for geochronology. This extended list of minerals is currently used to decipher the evolution in magmatic, metamorphic, and hydrothermal mineralising systems.

4.1. Isotopic and chemical heterogeneity

Perhaps the most promising approach for the future of accessory minerals research involves deciphering of the complex chemical and isotopic zoning discussed above, which is often enclosed within these accessory minerals. These phases, which tend to be more stable than major minerals, also have more sluggish diffusivities for actinides, Pb, and the REEs (Cherniak et al., 1997a,b; Cherniak and Watson 2001), and will record a longer portion of the geological history of the host rock. These properties make these accessories particularly interesting. For example, zircon often exhibits internal zoning when studied using BSE and CL imaging (Paterson et al., 1992; Hanchar and Miller, 1993). Hanchar and Miller (1993) and Hanchar and Rudnick (1995) noted that both imaging techniques usually show complementary internal zonation and that usually CL reveals finer detail. Connelly (2001) used CL images and U–Pb isotopic measurements to determine relative degree of Pb diffusion in zircon as related to the internal zoning preserved in these crystals.

Zircon cores inherited from the host rock protolith provide an obvious record of the rock early geological history. This implies that these cores survived at least a high-temperature magmatic event, as detected by U–Pb geochronology, and more recently by Sm–Nd systematics (Paterson et al., 1992; Li, 1994; Poitrasson et al., 1998). Even more complex internal structures are observed in zircon, sometimes unexpected (Alexandrov, 2001), which are records of the complex magmatic and metamorphic histories prior to the incorporation into the host rocks that now enclose them (Pidgeon et al., 1998; Schaltegger et al., 1999), as well as postcrystallization overprinting during slow cooling, and thermal or hydrothermal alteration (Vavra et al., 1999). Tichomirowa (2002) illustrates how important is a prior study of zircon morphology and internal structure to properly interpret zircon U–Pb ages from igneous rocks.

The analysis of oxygen and hafnium isotopes of zircon has considerably enlarged the field of possible interpretations and applications in the recent past: oxygen isotope analyses in zircon using infrared laser ablation (Valley et al., 1994) have brought a new perspective in petrogenetic studies of granites (King et al., 1998; Bindeman et al., 2001). Such data put further constrains for the quantification of contamination and source mixing processes, or permit to better resolve different magmatic episodes. Oxygen isotopes in kimberlite zircons were used to constrain the isotopic variability of metasomatized domains within the subcontinental mantle and their products of partial melting (Valley et al., 1998). Studies of Precambrian zircons helped to reconstruct Precambrian crustal growth (Peck et al., 2000) or surface processes in the early hydrosphere of the earth 4.4 Ga ago (Mojzsis et al., 2001; Wilde et al., 2001). High-resolution in situ analyses of oxygen isotopes may in the future tell us about the processes of recrystallization and annealing of decay damage in zircon in fluid-dominated environments, concerning especially the behaviour of the $Si-O-Zr$ bonds. Such data may also help to characterize the geological environment of new zircon growth within polycyclic complex grains.

The isotopic composition of hafnium in zircon offers an extremely powerful tool to decipher large-scale continental evolution within the provenance area of detrital zircon populations (Bodet and Schärer, 2000; Knudsen et al., 2001), or to characterize crustal and mantle components in the genesis of continental and oceanic magmas (e.g., Schaltegger et al., 2002). The Hf isotopic composition may be determined in situ by laser ablation multicollector ICP-MS, which is possible through elevated Hf concentration of zircon at around $1-4$ wt.% element. In addition, zircon is characterized by very low $^{176}Lu/^{177}Hf$ ratios, which directly yield initial Hf isotopic compositions at the time of crystallization for zircons up to ca. 500 Ma old. The Hf fraction of conventional zircon analyses may be analyzed by MC-ICP-MS with great precision and accuracy (Schaltegger et al., 2002). Both precision and accuracy of in situ laser ablation analyses tend to be limited by imprecisely known isotopic composition of Lu, and especially Yb used for interference correction (see Griffin et al., 2000), which will be a subject of analytical development within the next years.

Monazite also exhibits complex growth structures visible with backscattered electrons, which provide some insights into the chemical environment during growth of the crystals and their postcrystallization evolution. The internal growth structures of granulite facies monazites are often homogenized during retrograde cooling from high temperatures, and initial ^{230}Th disequilibrium is obliterated by diffusion during this process (Vavra and Schaltegger, 1999). Combined BSE, ion microprobe, or electron microprobe investigations revealed that monazite often records protracted metamorphic processes (DeWolf et al., 1993) and single minerals have been shown to record more than 700 Ma of geological history (Cocherie et al., 1998). These studies illustrate the power and need of combining microtextural investigations with in situ analytical techniques in the case of monazite also.

4.2. Dating mineralizing systems

The highest diversity of methods is used to date the formation of mineral deposits and their host rocks (for an overview, consult Lambert and Ruiz, 1999). U–Pb, Sm–Nd, or Re–Os is applied either on accessory minerals from host rocks or on ore minerals directly (scheelite, fluorite, phosphate, carbonate, sphalerite, molybdenite: Chesley et al., 1991; Davis et al., 1994a,b; Raith and Stein, 2000). Alteration minerals (sericite, adularia) or secondary supergene products (alunite) may be dated using Ar–Ar techniques (Zheng et al., 1992; Vasconcelos in Lambert and Ruiz, 1999). A challenging task is the resolution of often multiple magmatic, metamorphic, and mineralizing events, requiring highly precise dating results and good knowledge of mineral and isotopic system behaviour under fluid-dominated ambient conditions (Chesley et al., 1993; Ballard et al., 2001). Even more challenging involves the estimation of fluid–rock event duration (Skinner, 1997). In rare favourable cases, the dating of phosphates (monazite and xenotime) may yield ages precise enough to estimate the duration of hydrothermal systems. For instance, Schärer et al. (1999) found that the Trimouns talc deposit was produced by one or several hydrothermal circulations spanning a total period of 15 Ma. The data reflect the moment of precipitation of phosphates from the fluid phase, which is controlled by many factors including the stability of phosphate and REE

complexes in the fluid phase. On the other hand, detailed investigation of porphyry copper and granite-hosted ore deposits points to shorter durations of single mineralizing events in magmatic mineralizing systems (e.g., Chesley et al. in Lambert and Ruiz, 1999; Ballard et al., 2001; Beuchat et al., 2001; Schaltegger et al., 2001).

4.3. Dating metamorphic evolution

The refractory behaviour of accessory minerals opens the way for the reconstruction of protracted geological evolutions, but in some cases hampers the precise and accurate dating of host rock formation. This is especially true for metamorphic rocks, where accessory minerals may not participate in metamorphic mineral reactions (Roberts and Finger, 1997). The use of Pb–Pb stepwise leaching techniques (Frei and Kamber, 1995) or Sm–Nd, Lu–Hf, and U–Pb isotopes using metamorphic minerals like garnet (Vance and O'Nions, 1990; Duchêne et al., 1997) or staurolite (Frei et al., 1995) was thought to overcome these problems. The data from these studies show, however, that lack of knowledge on closure temperature and processes of diffusion versus recrystallization or dissolution/reprecipitation prevents accurate dating for metamorphic mineral assemblage formation.

The response of crystal structures and isotopic systematics to changing ambient parameters (e.g., temperature, pressure, fluid activity and composition, contents of complexing anions) has to be investigated on the basis of both natural (Poitrasson et al., 1996, 2000a; Hawkins and Bowring, 1997; Bingen and van Breemen, 1998; Simpson et al., 2000) and experimental studies (Teufel and Heinrich, 1997; Geisler et al., 2001a, 2002; Chen et al., 2002; Nasdala et al., 2002; Seydoux-Guillaume et al., 2002a). Current concepts are complicated by the fact that the radiogenic daughter products are located at lattice sites modified by the decay damage (or recoil) and are more easily leachable at low temperatures, even for zircon (e.g., Geisler and Schleicher, 2000; Davis and Krogh, 2001). Nevertheless, here also, the future clearly lies with combined microstructural, microchemical, and in situ geochronological measurements (e.g., DeWolf et al., 1993; Zhu et al., 1997; Cocherie et al., 1998; Schaltegger et al., 1999; Poitrasson et al., 2000a; Foster et

al., 2002). The need for such in situ geochronological work on metamorphic rocks has been further illustrated by the occurrence of LREE-rich accessory minerals inclusions in metamorphic garnets, which lead to meaningless Sm–Nd ages when garnet mineral separates are used (Zhou and Hensen, 1995; Prince et al., 2000; Luais et al., 2001).

4.4. In situ dating techniques

The detection of crystalline microstructures and compositional zoning clearly opened the way to in situ spot dating techniques capable of resolving structural and isotopic inhomogeneities. Ion microprobes have been used in the Earth sciences since the late 1970s (Hinton, 1995), and proved to be particularly useful for zircon U–Pb geochronology (Williams, 1998). Ion microprobes are currently used to date ~20-µm spots of zircon, monazite, baddeleyite, titanite, and apatite (Kinny and Friend, 1997; Hacker et al., 1998; Williams, 1998; Sano et al., 1999b; Wingate and Compston, 2000; Stern and Berman, 2000; Rasmussen et al., 2001). Spot sizes as small as 8 µm in diameter have been used to date single growth zones in zircon, such as thin overgrowths representing the last stage of host rock formation (Liati and Gebauer, 1999). Recent studies by Mojzsis et al. (2001), Wilde et al. (2001), and Peck et al. (2001) used the ion microprobe to determine the REE concentrations, oxygen isotope composition, and U–Pb ages to constrain the petrogenesis of zircon grains from Archean metasedimentary rocks from Australia. This type of in situ integrated study is unavoidable to obtain a better understanding of the processes that operated in the early Earth, for which little witnesses are left, apart from resistant accessories like zircon. Nevertheless, ion microprobes remain very sensitive to matrix effects and the use of matrix-matching standards to obtain precise U–Th–Pb ages, especially in the case of allanite (Catlos et al., 2000) or monazite (Stern and Berman, 2000), is unavoidable.

Other developments include total Pb dating of monazite using electron microprobes (Suzuki and Adachi, 1991; Montel et al., 1996; Cocherie et al., 1998; Williams et al., 1999; Geisler and Schleicher, 2000) or micro-XRF (Engi et al., 2002; Scherrer et al., 2002). Electron microprobe is extremely valuable given its excellent spatial resolution, but micro-XRF

offers lower Pb detection limits and thus allows to date monazites of a few tens of millions year only. On the other hand, only total Pb is measured with these techniques and thus the extent of the ^{204}Pb component in the total Pb remains unknown. As such, there is always an uncertainty, depending on whether the dated mineral incorporated large amounts of common Pb during its growth and/or subsequent transformations or not, in the accuracy of the calculated ages with these chemical methods.

An alternative approach involves the use of quadrupole Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), which now permits trace element analysis in accessory minerals with a spatial resolution equivalent to the electron microprobe (ca. 4 μm), while providing isotopic information precise enough to derive useful geochronological data directly on petrographic thin sections (Poitrasson et al., 1996, 2000a). With a larger spot size, Horn et al. (2000) have shown that quadrupole LA-ICP-MS can deliver U–Pb dates with a precision and accuracy close to those of ion microprobes. These laser ablation techniques are, however, not devoid of drawbacks. For instance, a key problem is the chemical fractionation that occurs during laser ablation, even for 193- and 157-nm wavelength Excimer lasers (Eggins et al., 1998; Horn et al., 2000; Russo et al., 2000), because of melting effects. Besides the use continuous laser refocusing (Hirata and Nesbitt, 1995) or short ablation times (Poitrasson et al., 1996, 2000a), beam defocusing (Knudsen et al., 2001), or larger spot sizes (Horn et al., 2000; Bruguier et al., 2001), other authors found that rastering the laser beam across the mineral sample to be analysed minimises elemental fractionation, resulting in more accurate ages (Kosler et al., 2001; Li et al., 2001; Foster et al., 2002). This latter rastering method, though, results in a significant degradation of the spatial resolution.

LA-ICP-MS is, however, an evolving technique and further progresses can be expected with the use of multicollector instruments (Parrish et al., 1999; Foster et al., 2002; Scherrer et al., 2002), for improved in situ isotope ratio measurements, combined with ultrafast lasers to minimise the chemical fractionation effect observed during laser ablation (Russo et al., 1998).

All these in situ techniques have in common the need for high-quality geochronological standards for U, Th, and Pb isotope analysis. This is especially crucial for the ion microprobe to minimize the matrix differences effects between the standards and the unknowns.

4.5. High-precision dating of magmatic rocks

All in situ methods provide very important spatially resolved age information, but they cannot yet challenge the precision and accuracy of conventional isotope dilution thermal ionization mass spectrometry (ID-TIMS) dating of single grains or parts of grains of zircon or baddeleyite (Heaman and LeCheminant, 1993; Heaman and Parrish, 1991; Amelin, 1998). Low-blank microchemical techniques allow dating of low-U zircons from mantle-derived rocks (e.g., Schaltegger et al., 2002) as well as very small amounts of zircon and other minerals from terrestrial and extraterrestrial materials. This remains the reference approach and can fortunately still be applied to a wide range of geological problems for which in situ work is not required, such as precise dating of periods of magmatic activity in a variety of orogenic and anorogenic settings where accessory mineral inheritance problems do not occur. These data may be used for quantitative modelling of orogenic process rates, for instance of burial and exhumation of parts of the lithosphere during compressional and extensional tectonic phases (e.g., Romer and Rötzler, 2001; Schulmann et al., 2002).

The conventional method is the prime method to be used for high-resolution calibration of biostratigraphic zones using zircons extracted from volcanic tuffs, e.g., at the Precambrian–Cambrian boundary (Bowring et al., 1993; Grotzinger et al., 1995), at the Permain–Triassic boundary (Bowring et al., 1998), and in the Middle Triassic (Mundil et al., 1996; Brack et al., 1996). The detection of small-scale heterogeneities within zircon grains, causing systematic and nonsystematic biases of both precision and accuracy of such results, is a prerequisite for the correct interpretation of the data. Uncertainties caused by effects like ^{206}Pb deficit due to initial ^{230}Th disequilibrium, ^{231}Pa excess, or inheritance/lead loss phenomena are in the 10^5 years' range and can significantly compromise the results of precise age determination (Anczkiewicz et al., 2001; Mundil et al., 2001).

Table 1
Comparison of current U–Th–Pb dating techniques on zircon and monazite

Abbreviation	EPMA	Micro-XRFA	LA-ICP-MS	LA-MC-ICP-MS	SIMS	ID-TIMS
Complete name	electron microprobe analysis	micro X-ray fluorescence analysis	laser ablation quadrupole inductively coupled plasma mass spectrometry	laser ablation multicollector inductively coupled plasma mass spectrometry	secondary ion mass spectrometry	isotope dilution thermal ionization mass spectrometry
Other acronyms	CHIME		LA-Q-ICP-MS	LA-PIMMS	SHRIMP, Cameca ims 1270	
U–Th–Pb dating	chemical	chemical	isotopic	isotopic	isotopic	isotopic
Common lead ^{204}Pb correction	no	no	no	yes	yes	yes
^{207}Pb/^{206}Pb ages	no	no	yes	yes	yes	yes
Average 2σ precision for Palaeozoic ages[a]	$\pm$ 30% not suitable for zircons with less than 100 ppm Pb, better suited for monazite	< $\pm$ 10%	$\pm$ 2–10%	$\pm$ 2%	$\pm$ 2%	$\pm$ 0.3%
Average 2σ precision for Caenozoic ages[a]	too young	$\pm$ 35%	$\pm$ 10%	$\pm$ 2–5%	$\pm$ 5%	$\pm$ 0.5%
Spatial resolution	ø < 5 µm	ø 38 or 90 µm	5–80 µm[b]	50 × 50 × 10 µm	10–25 µm	grain
Beam shape	spot/rectangle	circular, fixed	variable	variable	ellipsoid	–
Penetration depth	< 5 µm, but depends on accelerating voltage	>1000 µm	ca. 10 µm	ca. 10 µm	1–2 µm	–
Destruction during analyses	some radiation damage from electron–solid interactions	none	partial	partial	limited	complete
Repeated measurements	possible	possible	not on same spot	not on same spot	on same spot after repolishing	none
Analysis time (min)	<10, but depends on Pb content	30–240	<2	≤ 5	20	days
Standards						
Mineral	yes	yes	yes	yes	yes	no
NIST glass	no	no	yes	yes	no	no
Tracer solution	no	no	yes	yes	no	yes

[a] Depending primarily on spot size and analysis time.
[b] Worse if the rastering technique is adopted (see text).

The combination of conventional U–Pb and Th–Pb disequilibrium dating allows estimation of zircon residence times in silicic melts (Reid and Coath, 2000; Reid et al., 1997; Brown and Fletcher, 1999). Precise dating results provided much evidence that phenocryst ages cannot be taken as the emplacement age of their host rock, either due to prolonged residence times or remelting of shallow magma chambers (Davies et al., 1994; Heumann and Davies, 1997). This becomes a very important issue when volcanic phenocrysts as well as volcanic glass are used as external standards for precise Ar–Ar or fission track dating, as it is done with several minerals of the Fish Canyon Tuff that are partly shown to be inherited from a plutonic precursor (Schmitz and Bowring, 2001).

U–Th–Pb dating of zircon and monazite is a good example for the benefit of a diversity of analytical techniques, which are much more of complementary than of competitive character. Table 1 presents a compilation of the relative performances of chemical and isotopic, in situ, and bulk dating methods.

5. What does the future store for accessory minerals research?

This short and necessary author-biased overview of current accessory mineral research has listed many unanswered questions and areas where our knowledge remains limited. Although they all deserve investigations, there are questions which appear to need more urgent answers than others because they are often asked for in the literature, or they concern areas of research that appear closer to reach new significant findings now because of the evolution of the ideas or recent methodological/analytical developments.

The first area needing urgent research concerns the stability of accessory minerals under metamorphic conditions. Metamorphism is a key process in geodynamics, which remains relatively less known than, e.g., magmatism or tectonics. This probably results from the complex nature of metamorphism, especially in the frequent cases where fluids are involved. Besides rock-forming minerals, which permit to constrain the main physico-chemical parameters of metamorphism, accessory minerals have been used for long in the attempt to date metamorphic events and, more recently, to give some further information on the metamorphic conditions (i.e., temperature). It is thus expected that the multiplication of well-characterised natural cases studies and experiments of petrological reactions involving accessory minerals will undoubtedly strengthen the usefulness of these minerals in metamorphic geology.

The second main domain meets a societal request. Developed countries found a nearly inexhaustible source of energy, nuclear power, but the current generation of scientists is faced with the eminent challenge of dealing with the nuclear waste produced. Finding the right solutions is a prerequisite for our continued use of nuclear energy, and mineralogists and geochemists can provide critical information concerning the geological repository of nuclear wastes. Ceramics with the structure and composition of accessory phases like monazite or zircon may well be the key answer to unlock the nuclear fuel cycle, but for this, more research on their crystallochemistry and their stability in aqueous solutions is urgently needed.

Finally, after the electron microprobe in the 1960s and the ion microprobe in the 1970s, we are now witnessing the development of plasma source mass spectrometric techniques. This new type of mass spectrometry, compared to the robust thermal ionisation sources, has among other advantages the decisive capability of doing precise in situ isotopic and geochronological measurements using laser ablation, particularly to the heavy-end side of the mass spectrum. Combined with imaging techniques (CL, backscattered electron imaging), in situ spectroscopic approaches (e.g., laser Raman and infrared spectroscopy, high-resolution transmission electron microscopy, focused extended X-ray absorption fluorescence spectroscopy), and ion microprobes unavoidable for in situ light isotopes measurements, in situ plasma mass spectrometry really opens the way to a new dimension for mineralogical and geochemical research: the information of trace element and isotope heterogeneity locked into accessory mineral zoning, which is awaiting discovery.

Acknowledgements

sciences XI symposium devoted to accessory minerals during which most papers appearing in this special issue were presented and discussed. This dynamism prompted the preparation of this review, which we hope will be useful for future work in this area. **[EO]**

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