Rutile and its applications in earth sciences

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Abstract

Rutile is a naturally occurring titanium dioxide polymorph and is widely distributed as an accessory mineral in metamorphic rocks ranging from greenschist to eclogite and granulite facies but is also present in igneous rocks, mantle xenoliths, lunar rocks and meteorites. It is one of the most stable heavy minerals in the sedimentary cycle, widespread both in ancient and modern clastic sediments. Rutile has a wide range of applications in earth sciences. It is a major host mineral for Nb, Ta and other high field strength elements, which are widely used as a monitor of geochemical processes in the Earth’s crust and mantle. Great interest has focused recently on rutile geochemistry because rutile varies not only by bulk composition reflected, for instance, in its Cr and Nb contents but also by the temperature of crystallisation, expressed in the Zr content incorporated into the rutile lattice during crystallisation. Rutile geochemistry and Zr-in-rutile thermometry yield diagnostic data on the lithology and metamorphic facies of sediment source areas even in highly modified sandstones that may have lost significant amounts of provenance information. Rutile may therefore serve as a key mineral in sediment provenance analysis in the future, similar to zircon, which has been widely applied in recent decades. Importantly, rutile from high-grade metamorphic rocks can contain sufficient uranium to allow U–Pb geochronology and (U–Th)/He thermochronology. Furthermore, in situ Lu–Hf isotope analysis of rutile permits insights into the evolution of the Earth’s crust and mantle. Besides that, rutile is also of great economic importance because it is one of the favoured natural minerals used in the manufacture of white titanium dioxide pigment, which is a major constituent in various products of our daily life. Heavy mineral sands containing a significant percentage of rutile are therefore the focus of exploration worldwide.

This paper aims to provide an overview of the applications of rutile in earth sciences, based on a review of data published in recent years. After giving a summary of various rutile-bearing lithologies, the focus lies on rutile geochemistry, Zr-in-rutile thermometry, O isotope analysis, U–Pb geochronology, (U–Th)/He thermochronology and Lu–Hf isotope analysis. A final outline of the economic importance of rutile highlights the demand for further rutile-related research in earth sciences.

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1. Introduction

With an estimated TiO₂ concentration of about 0.7 wt.% (Rudnick and Fountain, 1995), rutile is the ninth most abundant element of the Earth's continental crust. The most important titanium minerals are rutile (TiO₂), ilmenite (FeTiO₃) and titanite (CaTiSiO₅)(Figs. 1 and 2). Rutile is an accessory mineral in a variety of metamorphic and igneous rocks and occurs as a detrital mineral in clastic sediments. Although the main formula of rutile is TiO₂, there are commonly several possible substitutions for titanium, for example, Al, V, Fe, Zr, Nb, Sn, Sb, Hf, Ta, W and U (e.g. Graham and Morris, 1973; Hassan, 1994; Fett, 1995; Murad et al., 1995; Smith and Perseil, 1997; Rice et al., 1998; Zack et al., 2002; Bromiley and Hilairet, 2005; Scott, 2005; Carruzzo et al., 2006). Variations in the geochemical composition are host rock specific and allow the rutile source to be traced and the chemical and physical properties during rutile formation to be characterised.

Great interest has focused on rutile geochemistry, because rutile is a major host mineral for high field strength elements (HFSE), amongst others Nb and Ta, which are widely used as geochemical fingerprints of geological processes such as magma evolution and subduction-zone metamorphism (e.g. Foley et al., 2000; Rudnick et al., 2000). For many years, the significance of Nb and Ta concentrations and Nb/Ta values of crustal and mantle rocks and the Earth's hidden suprachonelines (e.g. Foley, 1993; Foley et al., 2000; Rudnick et al., 2000; Kalfoun et al., 2002; Zack et al., 2002; Xiao et al., 2006; Miller et al., 2007; Aulbach et al., 2008; Baier et al., 2008; Bromiley and Redfern, 2008; Schmidt et al., 2009).

Besides that, the Cr and Nb contents of rutile allow discrimination between various rutile source lithologies such as metapelitic rocks (e.g. mica-schists, paragneisses and felsic granulites) and metamafic rocks (e.g. eclogites and mafic granulites) (Zack et al., 2004b; Triebold et al., 2007; Meinhold et al., 2008). Furthermore, the incorporation of Zr into the rutile crystal lattice has a strong dependence on temperature and pressure, which has allowed the development of Zr-in-rutile geothermometers (Zack et al., 2004a; Watson et al., 2006; Tomkins et al., 2007). Several studies have already shown that Zr-in-rutile thermometry is an attractive method to calculate temperatures of high-grade and ultrahigh-grade metamorphic rocks (e.g. Spear et al., 2006; Zack and Luvizotto, 2006; Baldwin and Brown, 2008; Luvizotto and Zack, 2009). Moreover, rutile geochemistry combined with Zr-in-rutile thermometry can help to constrain the sediment provenance and has therefore already been applied successfully to sedimentary strata from the Precambrian to the Holocene worldwide (e.g. Zack et al., 2004b; Stendal et al., 2006; Triebold et al., 2007; Meinhold et al., 2008; Morton and Chenery, 2009).

Rocks exposed on the Earth's surface are prone to weathering and erosion. These processes have continuously modified the Earth's surface for probably more than 3.9 billion years producing clastic sediments. Some of the key pieces of evidence for that may record detrital zircons as old as 4.4 Ga from metamafic and metaconglomerates of the Yilgarn Craton, Western Australia (Moizsis et al., 2001; Wilde et al., 2001). Clastic sediments are composed of various minerals (e.g. quartz, feldspar and mica) and lithic fragments and additionally contain a minor amount of heavy minerals. The sediment composition is primarily affected by the mineralogy of the primary source rock and by a complex set of parameters such as weathering, transport, deposition and diageneis that modify the sediment during the sedimentary cycle (e.g. Morton, 1985; Morton and Hallsworth, 1999).

Besides whole-rock petrography and heavy-mineral analysis, geochemical studies of whole rock and specific detrital minerals are powerful tools in provenance characterisation. Understanding clastic sediment provenance is important for exploration of mineral resources, basin analysis and palaeotectonic reconstructions. The most common heavy minerals such as zircon, tourmaline, garnet and chrome spinel have long been used as provenance indicators by virtue of their geochemical and isotope signatures (e.g. Morton, 1991; von Eynatten and Gaupp, 1999; Morton et al., 2004, 2005; Mange and Morton, 2007). The exception is rutile, which received only minor attention until 2002 (Götze, 1996; Preston et al., 1998, 2002). However, rutile geochemistry, geothermometry and geochronology yield diagnostic data on source-rock lithology and metamorphic facies even in highly modified sandstones that may have lost significant amounts of provenance information. Rutile may therefore serve as a key mineral in sediment provenance analysis in the future, similar to zircon, which has been widely applied in recent decades.

Studying the geochemical and physical parameters of rutile is not only of scientific value. Rutile is an economically important mineral
because of its use in the manufacture of white titanium dioxide pigment (Stanaway, 1994; Korneliussen et al., 2000), which is a component in products of our daily life such as paint, paper, plastics, toothpaste and sunscreen cream (Pearson, 1999; Carp et al., 2004; Gambogi, 2008). Mineral sands containing large percentages of rutile are therefore a focus of exploration worldwide (e.g. Goldsmith and Force, 1978; Force, 1991; Pirkle et al., 2007; Schützer, 2008).

Recently, the search for secondary standards of natural rutile to assess measurement methods and demonstrate the quality of acquired geochemical data (Luvizotto et al., 2009b) has also been a focus of scientific study. Hence, the scope of this paper is to provide an overview of the applications of rutile in earth sciences, introduced with an outline of the physical properties and geochemical composition of rutile and a brief overview of various source lithologies for rutile. The latter part is relative brief because Force (1991) already gave a comprehensive overview of specific rutile sources, except for extraterrestrial material.

The current paper has the following structure: Section 1 states the objectives of this work; Section 2 presents a review of the physical properties and geochemical composition of natural rutile and other TiO₂ polymorphs; Section 3 provides an overview of possible source lithologies including metamorphic rocks, igneous rocks, mineralisation, sedimentary rocks and extraterrestrial rocks; Section 4 discusses the applications of rutile geochemistry and Zr-in-rutile thermometry.

Both methods are evaluated in unravelling specific source characteristics and in use as a chemostratigraphic indicator. Furthermore, oxygen isotope analysis using the quartz–rutile mineral pair is discussed. In the past, powerful new analytical methods such as in situ U–Pb and Hf isotope analyses have been developed, which significantly contribute to unravelling the geological history of natural rutile and its host lithologies and are therefore addressed here too. Finally, Section 5 summarises the economic importance of rutile and shows the need for further rutile-related scientific research.

2. Physical properties and geochemical composition

2.1. General description

Abraham Gottlob Werner created the name rutile (Ludwig, 1803), which he assigned to a mineral originally known as “red schorl”. The first description of “red schorl” is commonly attributed to Romé de l’Isle (1783); however, von Born (1772), as pointed out by Papp (2007), already mentioned “red schorl” a few years earlier. Klaproth (1795) used “red schorl” (rutile) for the description of the element titanium, which he named after the Titans of Greek mythology. Note that William Gregor originally discovered titanium (which he named menakante) in ilmenite in 1791 (Trenogoe, 1792).

Although it has long been thought that Horcajuelo (also called Cajuino) in the province of Burgos in Spain is the type locality of rutile, a thorough study by Papp (2007) has recently revealed that the type locality of rutile is Revúca in Slovakia.

The name “rutile” is derived from the Latin rutilus because of the deep red colour observed in some specimens in transmitted light. Rutile can be translucent or opaque. Yellowish and brownish colours are also very common. A rarity is natural rutile with blue colour, which has only been described so far as needle-like inclusions in garnet from ultrahigh-pressure metasedimentary rocks of the Greek Rhodope Massif (Mposkos and Kostopoulos, 2001). In reflecting light rutile with bluish colour has been reported from several meteorites (El Goresy, 1971). The blue colour of meteoritic rutile may be due to a stoichiometric deficiency of oxygen in the rutile structure (El Goresy, 1971). Experiments on synthetic rutile have shown that blue colours occur in rutile samples grown or annealed under reducing conditions (Bromiley and Hilairet, 2005). Khomenko et al. (1998) demonstrated that the colour of blue rutile is mainly due to intervalence charge...
2.2. Crystal structure

In nature, titanium dioxide mainly occurs in three structural states: rutile, anatase and brookite (Fig. 2). Together they form the TiO₂ end-member of the ternary system FeO–Fe₂O₃–TiO₂ (Fig. 3). Rutile is a high-pressure and high-temperature polymorph and is isostructural with stishovite, a high-pressure silica polymorph (Fig. 5). Stishovite is a major phase in subducting oceanic crust under lower mantle conditions (Ono et al., 2001) and has also been described from impact-related rocks (Chao et al., 1962) and meteorites (Sharp et al., 1999). The behaviour of rutile at high and ultrahigh pressures therefore offers an analogy to explore post-stishovite phase transitions (El Goresy et al., 2001; Bromiley et al., 2004). The low-temperature polymorphs of titanium dioxide are anatase (tetragonal) and brookite (orthorhombic). Under relatively low temperatures and pressures, rutile is metastable with respect to anatase when the TiO₂ crystal size is less than ~14 nm, because the surface energy of rutile is then much higher than that of anatase (see Smith et al., 2009 for discussion).

Besides rutile, anatase and brookite, there are at least three additional TiO₂ polymorphs (Table 1). The TiO₂(B) polymorph has a structure closely related to that of VO₂(B) (Marchand et al., 1980), the TiO₂(II) polymorph has an α-PbO₂-type structure (Simons and Dachille, 1967), and the TiO₂(H) polymorph has a hollandite-type structure (MacChesney and Muan, 1959).

### Table 1

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
<th>TiO₂(B)</th>
<th>TiO₂(II)</th>
<th>TiO₂(H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm⁻³)</td>
<td>4.23–5.5</td>
<td>3.82–3.97</td>
<td>4.08–4.18</td>
<td>3.64</td>
<td>4.33</td>
<td>3.46</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P4₂/mmm</td>
<td>P4₂/mmm</td>
<td>Pbca</td>
<td>C2/m</td>
<td>Pbca</td>
<td>Pbcm</td>
</tr>
<tr>
<td>Unit cell parameters (Å)</td>
<td>a = 4.594, c = 2.959</td>
<td>a = 3.785, c = 9.514</td>
<td>a = 9.184, b = 5.447, c = 5.145</td>
<td>a = 12.16, b = 3.74, c = 6.51</td>
<td>β = 107.29°</td>
<td>a = 10.18, a = 4.59, a = 2.97</td>
</tr>
<tr>
<td>Comment</td>
<td>Reference</td>
<td></td>
<td></td>
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<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
<td>(6)</td>
</tr>
</tbody>
</table>

References: (1) Cromer and Herrington (1955), Baur (1956), Deer et al. (1992); (2) Cromer and Herrington (1955), Deer et al. (1992); Howard et al. (1991); (3) Baur (1961), Deer et al. (1992); (4) Marchand et al. (1980); (5) Simons and Dachille (1967), Hwang et al. (2000); (6) Latroche et al. (1989).
and the highly metastable TiO$_2$ (H) polymorph has a hollandite-type structure (Latroche et al., 1989). For several decades, the last two were only known from synthetic polymorphs. However, Hwang et al. (2000) described an epitaxial (about 8 nm thick) slab of the TiO$_2$ (II) polymorph between twinned rutile bicrystals as inclusion in garnet of diamondiferous quartzofeldspathic rocks from the Saxonian Erzgebirge, Germany, which was the first natural TiO$_2$ (II) polymorph found on Earth. This occurrence was explained by Hwang et al. (2000) to have formed during ultrahigh-pressure prograde metamorphism close to the rutile–α-PbO$_2$ phase boundary in the diamond stability field at depths of at least 130 km. The rocks containing this TiO$_2$ (II) polymorph may have equilibrated at pressures in excess of 70 kbar (Withers et al., 2003) (Fig. 5). Another natural TiO$_2$ (II) polymorph was reported in omphacite from a coesite-bearing eclogite in the Dabie Mountains, China (Wu et al., 2005). Wu et al. (2005) suggested subduction of continental material to depths of over 200 km. El Goresy et al. (2001) discovered a natural shock-induced TiO$_2$ (II) polymorph from shocked garnet–cordierite–sillimanite gneiss clasts of the Ries crater, Germany. Its petrographic setting is entirely different from that of the epitaxial slab in the Saxonian diamondiferous gneisses (see description in El Goresy et al., 2001 for further details). Another natural shock-induced TiO$_2$ (II) polymorph has been identified in breccias from the Chesapeake Bay impact structure in Virginia, U.S.A. (Jackson et al., 2006).

Because the mineral polymorphs of TiO$_2$ cannot be distinguished by their geochemical composition other identification methods such as X-ray diffraction (Spurr and Myers, 1957; Raman and Jackson, 1965) and reflected light microscopy (Mader, 1980) have to be used. The most reliable technique to identify mineral polymorphs is laser micro-Raman spectroscopy. A compilation of Raman bands for the three major structural TiO$_2$ polymorphs is shown in Fig. 6. Rutile can be identified by bands at wavenumbers 143, 247, 447 and 612 cm$^{-1}$ (Porto et al., 1967; Tompsett et al., 1995) and anatase by bands at wavenumbers 144, 197, 400, 516 and 640 cm$^{-1}$ (Ohsaka et al., 1978). Brookite is characterised by several bands. Strong bands are at wavenumbers 153, 247, 322 and 636 cm$^{-1}$ (Tompsett et al., 1995).

### 2.3. Crystal chemistry

Presently, analysis of rutile can be routinely performed by sophisticated techniques such as electron microprobe (EMP), proton microprobe (PIXE) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) so that differences in geochemical composition can easily be identified (Fig. 7). The disadvantage of the LA-ICP-MS technique is that it makes a crater often several tens of micrometres in diameter whereas the first two techniques are nondestructive to the sample, but they have higher detection limits (especially EMP) for the concentration of certain elements compared with LA-ICP-MS facilities. For very tiny rutile crystals analysed in thin sections, it is recommended that the Si content is measured in order to identify beam interferences with adjacent silicate minerals (Carruzzo et al., 2006; Baldwin and Brown, 2008). Smith and Perseil (1997) considered Si substitution in rutile as “highly contentious at non-ultrahigh pressure” and thus if Si is detected in rutile of non-ultrahigh-pressure rocks it is likely to be due to analytical error, microinclusions, or introduction into defective parts of the crystal structure (Smith and Perseil, 1997). Moreover, very fine zircon lamellae can occur in rutile (Schmitz and Bowring, 2003; Downes et al., 2007), which may cause

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**Fig. 5.** Pressure–temperature diagram (after Okamoto and Maruyama, 2004; Baldwin et al., 2004). Phase boundaries for rutile and TiO$_2$ (II) are based on phase equilibrium experiments, nominally dry synthesis experiments and reference data (after Withers et al., 2003). A range of geotherms is also shown. Abbreviations: GS, greenschist facies; AM, amphibolite facies; GR, granulite facies; BS, blueschist facies; EC, epidote facies.

**Fig. 6.** Raman spectra of the TiO$_2$ polymorphs rutile, anatase and brookite. Wavenumbers of main Raman bands are indicated (see text for explanation).
evolved Zr contents if such zircon lamellae-rich rutiles are analysed. Thus, rutile measurements with Si contents >300 ppm showing abnormally high Zr contents should be excluded from the data set (see Zack et al., 2004a; Luvizotto and Zack, 2009 for further discussion). Rutiles from diamondiferous kyanite-bearing eclogites can contain elevated AI contents, which can be explained by several tiny rods of corundum (Sobolev and Yefimova, 2000). Ilmenite and magnetite may also occur as tiny lamellae in rutile. In general, if such mineral rods are smaller than the electron beam size a mixture of them and rutile is analysed. Literature data show a wide range of certain trace elements, in particular AI and Fe, in rutile from crustal and mantle eclogites, which most likely reflects the presence of corundum and ilmenite lamellae (Sobolev and Yefimova, 2000).

Most naturally occurring rutile corresponds to the general formula TiO$_2$, with titanium occurring as Ti$^{4+}$. Note that titanium also exists in pentavalent (Nb$^{5+}$, Sb$^{5+}$ and Ta$^{5+}$), tetravalent (Zr$^{4+}$, Mo$^{4+}$, Sn$^{4+}$, Hf$^{4+}$ and U$^{4+}$), trivalent (Al$^{3+}$, Sc$^{3+}$, V$^{3+}$, Cr$^{3+}$, Fe$^{3+}$ and Y$^{3+}$) and divalent (Fe$^{2+}$, and to a lesser degree Mg$^{2+}$, Mn$^{2+}$ and Zn$^{2+}$) cations (Graham and Morris, 1973; Brenan et al., 1994; Hassan, 1994; Fett, 1995; Murad et al., 1995; Smith and Perseil, 1997; Rice et al., 1998; Zack et al., 2002; Bromiley and Hilairet, 2005; Scott, 2005; Carruzzo et al., 2006). For instance, Fe$^{3+}$ and Nb$^{5+}$ incorporation (Fe$^{3+}$ + Nb$^{5+}$ → 2Ti$^{4+}$) maintaining charge neutrality can compensate for substitution of tetravalent Ti$^{4+}$ ions. Several further examples can be found in the literature (e.g. Urban et al., 1992; Michaelidis, 1997; Smith and Perseil, 1997; Rice et al., 1998; Scott and Radford, 2007). Substitution of Ti$^{4+}$ in the rutile crystal lattice is based on the ionic radius and ionic charge of the substituted cation (Fig. 8). Cathodoluminescence (CL) and backscattered electron (BSE) images of polished rutile grains can reveal complex oscillatory zonation patterns or patchy zoned crystals (e.g. Michailidis, 1997; Carruzzo et al., 2006; Birch et al., 2007), which indicate variations in the geochemical composition in the rutile crystal lattice. Thus, a single-spot analysis may not be representative for the bulk composition of a rutile grain. That is particularly critical for calculating the crystallisation temperatures using Zr-in-rutile thermometry and for in situ isotope analysis.

Rutile is the dominant carrier of HFSE (e.g. Foley et al., 2000; Kalfoun et al., 2002; Zack et al., 2002). For example, in eclogites 1 mol% of rutile can carry more than 90% of the whole-rock content for Ti, Nb, Sb and W and considerable amounts (5–45% of the whole-rock content) of V, Cr, Mo and Sn (Rudnick et al., 2000; Zack et al., 2002). Because rutile dominates the budget of Nb and Ta, Nb + Ta concentrations and Nb/Ta values of rutile should be identical to that of the host rock (Rudnick et al., 2000; Zack et al., 2002; Carruzzo et al., 2006). Schmidt et al. (2009) recently made a critical note on this subject, based on Nb/Ta zoning in eclogitic rutile. In general, the rutile structure can accommodate up to 37 wt.% Nb$_2$O$_5$ in solid solution (Roth and Coughanour, 1955; Tien et al., 1969). Villaseca et al. (2007) suggested that around 10–35% of the whole-rock Zr content of peraluminous granulites could be contained in rutile. The needle-like blue rutile inclusions in garnet from ultrahigh-pressure metasedimentary rocks of the Greek Rhodope Massif contain a small but significant amount of SiO$_2$ (Mposkos and Kostopoulos, 2001) that indicates high-temperature/high-pressure (HT/HP) conditions and represents stishovite component in rutile (H.-J. Massonne, in Mposkos and Kostopoulos, 2001).

Rutile can also contain considerable amounts (tens to thousands of ppm) of H$_2$O, structurally bounded as hydroxyl (OH), which has been reported from both synthetic rutile (Bromiley et al., 2004; Bromiley and Hilairet, 2005) and natural rutile (Rossman and Smyth, 1990; Hammer and Beran, 1991; Vlassopoulos et al., 1993; Zhang et al., 2001). Vlassopoulos et al. (1993) pointed out that rutile is one of the most "hydrous" nominally anhydrous minerals (NAMs: Bell and Rossman, 1992) so far identified. Experimental investigations have shown that OH solubility in NAMs increases with pressure (e.g. Lu and Keppler, 1997; Bromiley et al., 2004; Mierdel and Keppler, 2004; Rauch and Keppler, 2004). Zhang et al. (2001) presented values of about 4300 to 9600 ppm H$_2$O in rutile from eclogites of the Dabie Mountains, China. Therefore, besides pyroxene and garnet, rutile is also an important NAM to recycle water into the mantle (Zhang et al., 2001; Zheng et al., 2003; Bromiley et al., 2004).

3. Occurrences

3.1. Rutile in metamorphic rocks

Rutile is mainly formed during medium- to high-grade metamorphic processes (e.g. Goldsmith and Force, 1978; Force, 1980, 1991) (Fig. 9), but it can also form in low-grade metamorphic rocks (e.g.
chlorite that replaces ilmenite (Fig. 9). Luvizotto et al. (2009a) talline aggregates made of from the Saxonian Erzgebirge, Germany. The rutiles form polycrystalline intergrowths of rutile and ilmenite, rather than being detrital in origin (Bannefeld and Veblen, 1991). Luvizotto et al. (2009a) recently described prograde metamorphism, rather than being detrital in origin (Banfield and Veblen, 1991). Luvizotto et al. (2009a) suggested that rutile has been derived from ilmenite breakdown due to following simplification reaction:

Ilmenite + Silicates + H₂O → Rutile + Chlorite

Rutile in high-grade and ultrahigh-grade metamorphic rocks (e.g. eclogites, granulites) forms mainly single crystals in the matrix but also occurs as inclusion in other minerals such as garnet, pyroxene, amphibole and zircon (Fig. 1). These rutile grains can show euhedral to subhedral forms with oval shapes or irregular shapes, with grain sizes from a few μm up to a few mm (Hills and Haggerty, 1989; Brenan et al., 1994; Zack et al., 2002; Huang et al., 2006; Xiao et al., 2006; Janoušek et al., 2007; Chen and Li, 2008). Brenan et al. (1994) described large (1–5 mm in size), euhedral single crystals of rutile that contain fine exsolution lamellae of ilmenite from an eclogite vein sample of the Rocciafra Massif, Western Alps. Smythe et al. (2008) noted that ilmenite lamellae are abundantly present in mantle-derived rutile.

Eclogite is the major rock type under high-grade metamorphic rocks containing large percentages of rutile (Korneliussen and Foslie, 1985; Liou et al., 1998; Korneliussen et al., 2000; Zack et al., 2002; Chen et al., 2005; Huang et al., 2006; Zhang et al., 2006). Korneliussen and Foslie (1985) suggested that about 90% of the titanium in eclogites of the Sunnfjord region of the Western Gneiss Region (WGR), Norway, is hosted in rutile. Eclogite from the Western Ligurian Alps contains up to 4 vol.% of rutile (Liou et al., 1998). Eclogite is a plagioclase-free metamorphic rock composed of >75 vol.% of garnet and Na-rich clinopyroxene (omphacite) and mainly forms by subduction of gabbroic or basaltic rocks to great depths where rutile crystallises from Fe–Ti oxides and Ti-bearing silicates during metamorphic recrystallisation (Krogh, 1980, 1982; Korneliussen and Foslie, 1985; Liou et al., 1998; Korneliussen et al., 2000; Miller et al., 2007; Figs. 5 and 10). Eclogite has a density of up to 3.6 g cm⁻³ (Hills and Haggerty, 1989; Rudnick and Fountian, 1995), higher than any other crustal rock (Hacker, 1996), even peridotite, which it exceeds by 0.2–0.4 g cm⁻³ (Rudnick and Fountian, 1995). Experimental data suggest that rutile is the main Ti carrier in eclogite below 150 kbar under sub-solidus conditions, even in relatively Ti-poor systems (Okamoto and Maruyama, 2004). However, under ultrahigh-pressure metamorphic conditions close to the coesite–stishovite phase boundary it is more likely to be the TiO₂(II) polymorph instead of rutile (Withers et al., 2003; Fig. 5). In general, the stability of rutile in subducted lithosphere is a complex function of whole-rock composition, temperature and pressure (e.g. Zhang et al., 2003; Klemme et al., 2005; Bromiley and Redfern, 2008; Fig. 10).

Since rutile is a major accessory mineral in eclogite and plays a major role in the Earth’s HFSE budget (in particular Nb and Ta) (see Section 2.3), in the last decade, eclogite has received much attention regarding its whole-rock and mineral geochemical composition (e.g. Rudnick et al., 2000; Zack et al., 2002; Xiao et al., 2006; Miller et al., 2007; Schmidt et al., 2009). In addition, the processes returning
extremely dense eclogite from great depths back to the Earth's surface (e.g. Guilhot et al., 2000; Neufeld et al., 2008), supplemented by geochronological studies (e.g. Baldwin et al., 2004; Goldný et al., 2005; Kylander-Clark et al., 2008), have been much discussed. Unfortunately, the original mineral assemblage of lower crustal rocks such as eclogite and eclogite facies rocks are subject to retrogression during their ascent from great depths to the Earth's surface. For example, in eclogites and eclogite facies rocks from the Western Ligurian Alps, rutile was subsequently replaced by ilmenite and titanite along margins and cracks (Liou et al., 1998). Xiao et al. (2006) described thin titanite (10–20 μm) replacement surrounding rutile and a thin ilmenite (a few μm) rim at the rutile margin from an eclogite and nearby quartz vein, respectively, of the Dabie–Sulu ultrahigh-pressure terrane in east-central China. Note that, under conditions of rapid exhumation (as fast as subduction; Rubatto and Hermann, 2001; Baldwin et al., 2004) the original mineral assemblage is largely preserved and allows insights into the pressure, temperature and geochemical conditions present at great depths. Rutile in eclogitic (E-type) diamonds and diamondiferous eclogites (Prinz et al., 1975; Mvumba Ntanda et al., 1982; Sobolev and Sibolev, 1997; Sobolev and Yefimova, 2000) are accessible at the Earth’s surface due to fast ascent from the Earth’s mantle as xenoliths in kimberlite pipes. The extensive studies of the composition of eclogite in recent years have significantly contributed to the increase of geochemical data for natural rutile, and thus they have opened new ways for rutile characterisation such as rutile geochemistry and Zr-in-rutile thermometry, as outlined in Section 4.

Rutile also occurs in the form of oriented, needle-like rods, known as sagenitic texture. Shau et al. (1991) described these from matrix biotite of the Tananao metamorphic complex, NE as sagenitic texture. Shau et al. (1991) described these from matrix biotite of the Tananao metamorphic complex, NE.

Rutile in igneous rocks and mineralisation

3.2. Rutile in igneous rocks and mineralisation

Additional sources of rutile can be quartz veins (e.g. Watson, 1922; Deer et al., 1992), granites (e.g. Force, 1980; Scott, 1988; Force, 1991; Michailidis, 1997; von Quadt et al., 2005), pegmatites (e.g. Force, 1980; Černý et al., 1999; Force, 1991; Rice et al., 1998; Clark and Williams-Jones, 2004; Scott, 2005; von Quadt et al., 2005; Scott and Radford, 2007). The occurrence of large rutile crystals (up to 4 cm in size and larger) is limited to some granitic pegmatites and vein mineralisation (Watson, 1922; Deer et al., 1992; Černý et al., 1999, 2007) and are described from syn-metamorphic quartz veins of eclogite facies (Franz et al., 2001; Gao et al., 2007).

In alpine fissures, rutile can occur as reddish needles in transparent quartz crystals. They are then called rutilized quartz or “flèches d’amour” (“arrows of love”) and are classified as gemstones, with known localities in Brazil, Switzerland and U.S.A. (Pough, 1998).

Blue quartz is another type of rutilized quartz (e.g. Wise, 1981). The “blue” colour of quartz is derived from Rayleigh scattering of light by abundant inclusions of nanometer-scale acicular rutile, but other minerals may also occur as inclusions, for instance, ilmenite (e.g. Wise, 1981; Zolensky et al., 1988). In many cases, acicular rutile in quartz has been formed by exsolution of Ti from the quartz crystal lattice (Černíak et al., 2007a). Rutilized blue quartz has been described, for example, from granites, granodiorites, rhyolites, charnockites and gneisses (Wise, 1981; Zolensky et al., 1988, and references therein), and is restricted in occurrence mainly to the Precambrian, in particularly to middle to late Proterozoic rocks (Zolensky et al., 1988) of the Grenville province. Note that blue quartz incorporated into detritus eroded from these rocks has proven to be a reliable provenance indicator with stratigraphic significance both in the Scottish Highlands, in western Ireland and in the eastern parts of North America (Phillips, 1973; Fitches et al., 1980; Kline, 1991; Dewey and Mange, 1999; Maria Mange, pers. comm, 2010)

Rutile in granitic rocks can have several origins; it can be a primary igneous, peritectic, xenocrystic, or secondary phase (Carruzzo et al., 2006; Clarke and Carruzzo, 2007). Secondary rutile can form because of hydrothermal alteration (chloritisation) of Ti-rich biotite (Carruzzo et al., 2006), by oxidation of ilmenite (Sakoma and Martin, 2002) or by exsolution from Ti-bearing phases such as clinopyroxene and garnet (Zhang et al., 2003).

Primary igneous rutile can have significant concentrations of HFSE (e.g. Nb and Ta). Niobian rutile (also known as ilmenorutile) is a variety of rutile with an atomic ratio of Nb/Ta > 1, while tantalian rutile (also known as strüvertite) has an atomic ratio of Nb/Ta < 1 (Černý et al., 1964). Both are accessory minerals in peraluminous to peralkaline granitoids and sub alkaline to alkaline intrusive rocks (Černý et al., 1964, 1999; Černý and Chapman, 2001). In both rutile varieties, Fe3+ is always present to accommodate the overcharged (Ti4+, Nb5+ and Ta5+) cation population (Smith and Persiel, 1997).

According to Bailey (1961) and Marvin (1971), in alkaline rocks, carbonates and carbonate veins in particular, rutile tends to be enriched in Nb and poor in Ta. However, primary rutiles from carbonatites can be free of Nb, and have ubiquitous V and elevated Fe contents (Ripp et al., 2006). Chrome-rich rutile in carbonatites is commonly related to mantle-derived xenoliths (Ripp et al., 2006). Anderson (1960) mentioned niobian rutile from the carbonate-rich metamorphic zone of the Idaho batholith. Tollo and Haggerty (1987) described niobian rutile from nodules of the Orapa kimberlite, Botswana. Niobiferous rutile in general has higher Nb/Ta ratios compared with rutile from granites and granitic pegmatites (Tollo and Haggerty, 1987). Metasomatised mantle peridotite and continental lithospheric mantle have Nb/Ta ratios > 17.5, chondritic to supachondritic (Kalfoun et al., 2002). Unmetasomatised peridotites commonly have Nb/Ta ratios < 17.5, subchondritic (Kalfoun et al., 2002).

Michailidis (1997) studied niobian rutile (some with substantial tungsten content) from the Fanos apitite granite, northern Greece. Černý et al. (1999) described niobian rutile from the McGuire pegmatite, Colorado, and its breakdown into secondary minerals such as
pseudo-brookite, ferropseudo-brookite, titanio ferrocolumbite and ilmenite. Further examples of exsolution and breakdown of niobian rutile are found in the literature (Uher et al., 1998; Černý and Chapman, 2001; Černý et al., 2007). Carruzzo et al. (2006) described several rutile types from peraluminous granite of the late Devonian South Mountain Batholith, Nova Scotia. The size of the primary igneous rutile grains ranges from 0.04 to 0.28 mm (with minor larger grains), with rare euhedral to commonly anhedral shapes. Carruzzo et al. (2006) recognised that these grains have increasing concentrations of Fe + Mn, Zr, Nb, Sn, Ta and W with increasing chemical differentiation of the South Mountain Batholith and concluded that rutile is a sensitive monitor of Nb-Ta-Sn–W in the batholith. Rutile with high Nb + Ta concentrations and low Nb/Ta values, reflecting variable partitioning of Nb and Ta into a fluid phase, is commonly associated with granitic pegmatites and in case of the South Mountain Batholith may represent crystallisation during H2O-oversaturated conditions (Carruzzo et al., 2006).

Concentrations of boron and H2O can increase in granite magmas during the late stage of emplacement and can lead to explosive release of volatiles forming tourmaline breccia dykes and pipes, some of which have rutile as the main accessory phase (e.g. Müller and Halls, 2005). Such rutile has highly variable amounts of Ti, V, Fe, Nb, Sn and W (Müller and Halls, 2005). Putnis (1978) and Putnis and Wilson (1978) noted that rutile formed at low temperatures (less than 450 °C, hydrothermal) contains notable Fe concentrations. Such rutile is susceptible to exsolution of a Fe-bearing phase such as hematite (Putnis, 1978; Putnis and Wilson, 1978).

### 3.3. Rutile in sedimentary rocks

The largest sedimentary sources of rutile are fine-grained clastic sediment and heavy mineral sands (placer deposits). For example, Valentine and Commeau (1990) studied the TiO2 whole-rock content of Pleistocene and Holocene sediments from surficial and several core samples of the Gulf of Maine where rutile is the main titanium source present in the silt and clay fraction. Based on their data, the authors estimated the amount of TiO2 to exceed 647 million metric tons (1) and could show that the Gulf of Maine hosts a large titanium resource. Placer deposits commonly contain high percentages of zircon, rutile and ilmenite that are concentrated to economic grade (e.g. Force, 1991; Roy, 1999; Dill, 2007a). Examples are marine placer deposits in southeastern Australia (e.g. Roy, 1999) and along the NW coast of South Africa (e.g. Dill, 2007a; see Section 5). In continental placer deposits, titanium minerals occur mainly in rutile–ilmenite aggregates called “nigrine” (Clark, 1993; Dill, 2007a; Dill et al., 2007). Nigrine is a variety of rutile with high iron concentration (Clark, 1993).

Pseudorutile (Fe2Ti3O9; Temple, 1966; Teuffer and Temple, 1966) is formed by Fe2+ removal during oxidation of ilmenite (FeTiO3) (Teuffer and Temple, 1966; Grey and Reid, 1975; Mücke and Chaudhuri, 1991; Grey et al., 1994). Its status as a distinct mineral phase is still subject of lively debate (Dill, 2007a, and references therein). Removal of Fe2+ from pseudorutile due to leaching and hydrolysis results in leucoxene (Mücke and Chaudhuri, 1991). The latter term, introduced by Gümbel (1874), had long been applied to alteration products with high Ti concentration. In present usage, leucoxene refers to a mineral concentrate with about 65–90 wt.% TiO2 (Fig. 2) and is a mixture of pseudorutile and rutile (Grey et al., 1994; Reyneke and Wallmach, 2007). In conclusion, pseudorutile and leucoxene indicate more oxidising supergene or hypogene conditions in the provenance area (Dill, 2007a).

In sedimentary rocks rutile, anatase and brookite can form diagenetically from Ti-rich pore-solutions, which may derive from alteration of ilmenite, titanite and biotite (Mader, 1980; Morad, 1986; Valentine and Commeau, 1990). Paine et al. (2005) ascribed alteration of ilmenite to pseudorutile and anatase in Pliocene placer deposits of southeastern Australia to postdepositional weathering. The TiO2 polymorphs are commonly alteration endmembers of Fe–Ti oxides (Reyneke and Wallmach, 2007). Authigenic rutile can often be identified by its polysynthetic twin lamellae (Mader, 1980).

Rutile has also been described from extraterrestrial material such as lunar rocks and meteorites. Extraterrestrial rutile can have several origins, such as reduction from ilmenite, exsolution from chromite and primary crystallisation as a minor accessory mineral (Buseck and Keil, 1966; Harper, 1996). Rutiles from lunar rocks were described, for example, in Apollo 11, 12, 14 and 17 samples (Keil et al., 1970; Wood et al., 1970; Marvin, 1971; Slava et al., 1972; Hill et al., 2006). They occur within ilmenite as thin exsolution lamellae of less than 2 μm (Keil et al., 1970) and 2–5 μm (Wood et al., 1970) in size. They also occur as small anhedral grains less than 20 μm in diameter adjacent to or enclosed by ilmenite (Keil et al., 1970; Marvin, 1971; Slava et al., 1972). Marvin (1971) identified a niobium-enriched mineral from lunar rocks and soils, which was a niobian rutile (6.4% Nb2O5) in a microbreccia fragment of an Apollo 12 sample. That rutile was also enriched in Ta, La and Ce. Slava et al. (1972) found niobian rutile (7.1% Nb2O5) in a lithic fragment of KREEP composition (K = potassium,
REE — rare earth elements and P — phosphorus) with basaltic texture in an Apollo 14 sample.

One of the pioneers studying meteoritic rutile was Paul Ramdohr who identified rutile in the Mt. Browne chondrite and in several mesosiderites (Ramdohr, 1963, 1965). El Goresy (1965) mentioned a euhedral rutile crystal enclosed in trolite of the Odessa iron meteorite and accessory rutile in the Dalgaranga iron meteorite. Buseck and Keil (1966) described rutile associated primarily with ilmenite and chromite from several meteorites (Allegan, Bondoc, Esterville, Farmington and Vaca Muerta) (see Kimura et al., 1991). Rutile is most abundant in the Farmington L-group chromite where it occurs in fine lamellae in polycrystalline ilmenite (Buseck and Keil, 1966). Referring to Ramdohr (1963, 1965), Buseck and Keil (1966) suggested that this rutile was derived from ilmenite breakdown due to the following reaction:

$$2\text{FeTiO}_3 \rightarrow 2\text{TiO}_2 + 2\text{Fe} + \text{O}_2$$

Experimental studies revealed that ilmenite could not coexist with rutile and remain stable at high temperatures as they react to form FeTiO$_3$ (Fig. 3), a mineral in the pseudobrookite solid solution series (MacChesney and Muan, 1959; Buseck and Keil, 1966). During cooling pseudobrookite decomposes to rutile + ilmenite at and below 1140 ± 10 °C (Lindsley, 1965), indicating that the mineral assemblage observed in the Farmington meteorite formed below that temperature (Buseck and Keil, 1966).

In the Vaca Muerta mesosiderite the rutile occurs together with ilmenite and chromite, both in thin bands within ilmenite (Kimura et al., 1991) and in fine lamellae in chromite, as well as in individual grains of up to 65 μm in diameter (Buseck and Keil, 1966). Nazarov et al. (2002) reported rutile from the Dhofar 303 lunar highland meteorite. El Goresy (1971) described Nb-rich rutile from the Tolucia iron meteorite in both silicate-bearing and silicate-free sulphide inclusions. Later, Harper (1996) also analysed niobian rutiles from this meteorite and discovered formerly live $^{92}$Nb, which forms in supernovae by p-processes (Harper, 1996) and decays by electron capture to $^{92}$Zr with a half-life of about 36 Ma (Nethaway et al., 1978). Extraterrestrial rutile may therefore bring quantitative data for the initial abundance of short-lived, now extinct, radionuclides (e.g. $^{92}$Nb) in the solar system's parental molecular cloud, which has been the subject of recent discussion (Schönbächer et al., 2002, 2005; Wadhwa et al., 2007, and references therein). The most interesting application of short-lived radionuclides is their potential usage as fine-scale chronometers to study processes in the early solar system (Harper, 1996; Wadhwa et al., 2007).

4. Applications of rutile in earth sciences

4.1. Rutile geochemistry

4.1.1. Introduction

Rutile is a major host mineral for Nb, Ta and other HFSE, which are widely used as geochemical fingerprints of geological processes such as magma evolution and subduction-zone metamorphism (e.g. Foley et al., 2000; Rudnick et al., 2000). Although Nb/Ta values of crustal and mantle rocks have been studied for a long time, processes that lead to the fractionation of Nb and Ta and to the formation of the Earth’s hidden supachondritic Nb/Ta reservoir are still the subject of a lively debate, as outlined in Section 4.1.3.

Besides its application in igneous and metamorphic petrology, rutile geochemistry can also be applied in sedimentary provenance studies. Banfield and Veblen (1991) were one of the first who suggested that rutile geochemistry may be useful in determining the provenance of rutile. Nevertheless, until 2002, only a few papers related to the mineral geochemistry of rutile and its application to sedimentary provenance studies (Götze, 1996; Preston et al., 1998, 2002) were published. This was probably because of the lack of major-element composition, in conjunction with a scarcity of rutile geochemical data from potential source lithologies. For example, Götze (1996) suggested that rutile with elevated concentrations of Sn and W implies ore-bearing source rocks. Preston et al. (1998, 2002) demonstrated that detrital rutile in Triassic continental red-beds in the Beryll Field, North Sea, comprises almost pure TiO$_2$, with only a small proportion containing appreciable Nb$_2$O$_5$ or FeO.

More recently, however, rutile has attracted a lot of interest as new studies have demonstrated the high potential of the trace-element signature of rutile, including Zr-in-rutile thermometry, for characterising sediment source areas and hence for quantitative provenance analysis, as will be shown in the following sections.

4.1.2. Fe content

The Fe content has been suggested to be an indicator of metamorphic origin since metamorphic rutile contains mostly >1000 ppm Fe (Zack et al., 2004a). However, lamellae-rich regions in rutile can show considerable Fe enrichment (Banfield and Veblen, 1991; Liou et al., 1998; Sobolev and Yefimova, 2000). Therefore, careful examination of rutile at the microscopic scale is necessary to ensure that measurements yielding elevated Fe contents were carried out in a homogeneous part of the grain, as discussed in Section 2.3.

Banfield and Veblen (1991) recognised that the Fe content in rutile generally increases with metamorphic grade, although they cautioned that this observation needs further research to determine whether the correlation is independent of whole-rock composition and other aspects of metamorphic history. They suggested the potential of such a correlation might be applicable as a thermometer in rocks that have experienced temperatures less than 500 °C. However, rutile formed at low temperatures (less than 450 °C, hydrothermal) also contains high FeO and remains tightly coupled during chemical processes within the crust—mantle system. This should lead to relatively constant Nb/Ta ratios of metamorphic rutile.

Dawson and Smith (1977) assumed that their mica–amphibole–rutile–ilmenite–diopside (MARID) group of xenoliths resulted from crystallisation of an oxidised magma in the uppermost mantle, and that all the Fe in rutile from these rocks is trivalent. Sobolev and Yefimova (2000) noted that the Fe content in rutile from crustal and mantle eclogites and diamond inclusions depends on whole-rock composition, oxygen fugacity ($f$O$_2$) and pressure and temperature conditions. Hence, it is worthwhile to calculate the ferric Fe content of rutile by either partitioning the measured total iron content into Fe$_2$O$_3$ and FeO using the stoichiometric method of Droop (1987) or by using Mössbauer spectroscopy. The Fe$^{3+}$ content is controlled by $f$O$_2$ (e.g. Buddington and Lindsley, 1964), and thus, presence of Fe$^{3+}$ indicates high $f$O$_2$ during crystal growth. For example, many ultrahigh temperature (UHT) terrains contain oxidised (high $f$O$_2$) mineral assemblages (Harley, 2008, and references therein). Zhao et al. (1999) used $f$O$_2$ as barometer for rutile–ilmenite assemblages in mantle xenoliths from kimberlites.

4.1.3. Nb and Ta contents

Nb and Ta have the same oxidation state and nearly identical ionic radii (Shannon, 1976; Tiepolo et al., 2000; Fig. 8) and thus should remain tightly coupled during chemical processes within the crust–mantle system. This should lead to relatively constant Nb/Ta ratios of minerals and rocks, close to the chondritic value of about 17.65 (McDonough and Sun, 1995). However, continental crust, island arc volcanic rocks and many oceanic basalts are characterised by subchondritic Nb/Ta values (e.g. Green, 1995; Rudnick and Fountain, 1995; Rudnick et al., 2000; Foley et al., 2002; Schmidt et al., 2009). A geochemically complementary reservoir is therefore required to accommodate the mass imbalance in Nb and Ta between continental crust and depleted mantle (McDonough, 1991; Rudnick et al., 2000).
The processes leading to major fractionation of Nb and Ta, and thus to subchondritic Nb/Ta values, have been the subject of prolonged debate because they are important for understanding the formation of the continental crust (e.g. Foley et al., 2002; Xiao et al., 2006). As outlined in Section 3.1, rutile is a major accessory mineral in eclogite, which mainly forms by subduction of gabbroic or basaltic rocks to great depths. During metamorphic recrystallisation, rutile crystallises from Fe–Ti oxides and Ti-bearing silicates. It dominates the budget of Nb and Ta in eclogite, and thus Nb/Ta of whole-rock eclogite reflects this ratio in rutile (Rudnick et al., 2000; Zack et al., 2002). Experimental studies by Brenan et al. (1994) have shown that a small amount of rutile (∼0.2 wt.%) is enough to prevent HFSE enrichment in the mantle wedge by fluids generated during subduction zone metamorphism. Thus, rutile has long been regarded as a major factor controlling the slab-to-mantle flux of HFSE (e.g. Brenan et al., 1994; Green, 1995). Subchondritic Nb/Ta of the continental crust and island arc volcanic rocks has been ascribed to melting of subducted slabs in the presence of rutile (e.g. Rudnick et al., 2000). Rudnick et al. (2000) suggested that refractory eclogite produced by slab melting is the “missing reservoir” to accommodate the mass imbalance in Nb/Ta between continental crust and depleted mantle. This reservoir possibly exists in the Earth’s deep mantle (Rudnick et al., 2000). Alternatively, it may be in the Earth’s core (Wade and Wood, 2001).

Experimental studies on the partitioning of Nb and Ta between rutile and melts have shown that rutile favors Ta over Nb (e.g. Foley et al., 2000, 2002; Klemme et al., 2005). Consequently, partial melting of subducted rutile-bearing eclogite with chondritic Nb/Ta results in melts with suprachondritic Nb/Ta and a residue depleted in Nb that cannot be the “missing reservoir” with suprachondritic Nb/Ta (e.g. Foley et al., 2002; Klemme et al., 2005).

Xiao et al. (2006) studied Nb and Ta in eclogites from the Dubi–Sulu UHP metamorphic belt in east-central China and suggested the following model: During the early stage of subduction, hotter regions of the subducting slab will experience significant dehydration in the presence of amphibole and absence of rutile (<15 kbar; Fig. 10), which leads to suprachondritic Nb/Ta in the residual amphibole eclogites with complementary subchondritic Nb/Ta in the released fluids. A large proportion of these fluids (containing Nb, Ta, Ti, etc.) can be retained in cold regions inside the subducting slab, forming hydrated cold eclogites with subchondritic Nb/Ta. Subduction continues and the slab, consisting of these hydrated cold eclogites, reaches greater depths where rutile finally appears (>15 kbar; Fig. 10) and controls the Nb and Ta budget. Thus, melting of these hydrated cold eclogites will form magmas with negative Nb and Ta anomalies and subchondritic Nb/Ta values. Because early-dehydrated slab with suprachondritic Nb/Ta cannot be melted, refractory residual eclogites have highly variable Nb/Ta from subchondritic to suprachondritic (Xiao et al., 2006). Nonetheless, Xiao et al. (2006) suggested that they form the geochemically complementary reservoir to the continental crust since their overall average Nb/Ta is suprachondritic.

4.1.4. Cr and Nb contents

Zack et al. (2002, 2004b) suggested that Cr and Nb abundances in rutile (Fig. 11a) can effectively distinguish between metamafic and metapelitic source lithologies. For simplification, Triebold et al. (2007) introduced log(Cr/Nb) values to discriminate between metamafic and metapelitic source lithologies (“1:1” line; Fig. 11b). This method is applicable except for low Cr and low Nb contents. Based on literature data of Nb/TiO2 ratios of whole rock for pelites, Zack et al. (2002, 2004b) calculated that rutile in metapelites contains 900–2700 ppm Nb. Combined with reference data, Meinhold et al. (2008) proposed that the lower limit of Nb in metapelitic rutiles should be set at 800 ppm and that the discriminant boundaries between metamafic and metapelitic source lithologies should therefore be modified as shown in Fig. 11c. Rutiles with Cr>Nb accompanied by Nb>800 ppm are interpreted to be derived from metapelitic rocks (e.g. mica-schists, paragneisses, felsic granulites). Rutiles with Cr>Nb and those with Cr<Nb, the latter however accompanied by Nb<800 ppm, are interpreted to be derived from metamafic rocks (e.g. eclogites and mafic granulites). Rutiles from amphibolites plot in both fields because the protoliths of amphibolites are of either sedimentary or mafic igneous origin.

4.1.5. Other trace elements

Smythe et al. (2008) noted that Mg and Al contents distinguish rutile derived from crustal and mantle sources (Fig. 12), and Al, Cr and Nb contents further allow distinction between various mantle-derived rocks such as eclogite, metasomatic rutile-dominated nodules and mica–amphibole–rutile–ilmenite–diopside (MARID: Dawson and
4.1.6. Examples

As outlined in Section 4.1.3, Nb and Ta concentrations in rutile allow tracing the formation and evolution of the continental crust. Hence, a large number of publications exists discussing Nb and Ta values and Nb/Ta ratios of crustal and mantle rocks and the Earth’s hidden suprachondritic Nb/Ta reservoir. Here, the reader is referred to a selection of recent literature for further information (e.g. Xiao et al., 2006; Aulbach et al., 2008; Baier et al., 2008; Bromiley and Redfern, 2008; Schmidt et al., 2009).

Since the work of Zack et al. (2004b), rutile geochemical constraints on sediment provenance have been included in several publications related to sedimentary strata from the Neoproterozoic to the Holocene worldwide.

Stendal et al. (2006) used rutile geochemistry to establish that the rutiles in young alluvial and eluvial heavy mineral deposits of the Yaoundé region in southern Cameroon were derived from the adjacent Neoproterozoic micaschists of the Yaoundé Group.

Triebold et al. (2007) analysed detrital rutile from Early Palaeozoic metasedimentary rocks and Holocene river sediments of the Erzgebirge, Germany. They demonstrated that rutile compositions in river sediments mirror those of the surrounding country rocks. This led them to conclude that rutile is an accurate tracer of source rock characterisation in sedimentary provenance studies.

Uher et al. (2007) analysed niobium–tantalum mineral assemblages (including Nb–Ta-rich rutile) from alluvial placer deposits in southwest Slovakia, which were most likely sourced from granitic pegmatites of the Bratislava Granitic Massif.

Meinhold et al. (2008) investigated detrital rutile from Carboniferous to Early Triassic sandstones of Chios Island, Greece. They recognised a change in source rock lithology from the Carboniferous with dominantly metamafic rutile to the Early Triassic with more metapelitic rutile. Zr-in-rutile thermometry has confirmed this change in the sediment source, which was explained by plate-tectonic reorganisation during the subduction of Palaeotethys at the southern margin of Laurussia in the Late Palaeozoic (Meinhold et al., 2008).

Morton and Chenery (2009) studied the rutile source of Jurassic to Palaeocene sandstones in hydrocarbon exploration wells of the Norwegian Sea. Their rutile data confirm the presence of five distinct sand types sourced from different parts of the Norwegian and Greenland landmasses to the east and west of the basin, established by previous studies, concentrating on provenance-sensitive heavy mineral ratios, garnet geochemistry, tourmaline geochemistry and detrital zircon geochronology (Morton and Chenery, 2009). Moreover, these authors demonstrated the importance of rutile geochemistry as a provenance tracer, since the method yields diagnostic data on source rock lithology and metamorphic facies even in highly modified sandstones that may have lost significant amounts of provenance information. This is because of the ultrastable nature of rutile under both diagenetic and surficial weathering conditions (Pettijohn, 1941; Hubert, 1962; Morton and Hallsworth, 1999, 2007).

Although the successful application of rutile geochemistry to single-mineral provenance studies has been shown above, there are at least two publications that clearly demonstrate that the discrimination diagrams based on Cr and Nb may not be strictly valid. Bakun-Czubarow et al. (2005) pointed out that the Cr–Nb discrimination

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Table 2

List of natural rocks containing rutile with economically important elements (compiled from Williams and Cesbron, 1977; Scott, 1988; Urban et al., 1992; Clark and Williams-Jones, 2004; Scott, 2005). For example, elevated concentrations of W and Nb in rutile strongly suggest a source from a mesothermal gold deposit (see Fig. 13). The V content in rutile can be used as a guide to mineralisation even in highly weathered rocks (Scott, 2005). Geochemical data of rutile from ancient and modern clastic sedimentary rocks can therefore provide useful fingerprints to identify the type of mineralisation.

<table>
<thead>
<tr>
<th>Type of deposit</th>
<th>Characteristic elements in rutile</th>
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<tr>
<td>Volcanogenic massive sulphide Cu–Zn deposits</td>
<td>Sn (W and/or Cu)</td>
</tr>
<tr>
<td>Mesothermal and related gold deposits</td>
<td>Sb, W and/or V</td>
</tr>
<tr>
<td>Magmatic–hydrothermal Pd–Ni–Cu deposits</td>
<td>Ni, Cu</td>
</tr>
<tr>
<td>Granite-related Sn deposits</td>
<td>Sn, W</td>
</tr>
<tr>
<td>Granite–pegmatite Sn–W deposits</td>
<td>Sn, W, Nb, Ta</td>
</tr>
<tr>
<td>Porphyry and skarn Cu and Cu–Au deposits</td>
<td>Cu, W (and sometimes V)</td>
</tr>
</tbody>
</table>

Fig. 13. Summary of Ti, Fe, Cr, V and W contents of rutile from variably metamorphosed mesothermal gold deposits (after Clark and Williams-Jones, 2004).
diagram of Zack et al. (2002, 2004b) is not applicable for rutile from the Sudetes Fe–Ti-rich eclogites, which plot in the metapelitic field. Rutiles from eclogite of the ultrahigh-pressure metamorphic area at the Sädenbach reservoir of the Erzgebirge in Germany (Massonne, 2001) also plot in the field of metapelitic source lithologies (Triebold et al., 2007; their fig. 5). Based on whole-rock geochemical data, Massonne and Czambor (2007) suggested that the protoliths of the Saidenbach eclogites were basaltic to trachyandesitic in composition and formed in a within-plate geotectonic setting with a relatively low degree of melting. The Sädenbach eclogites have high Nb/Ti ratios. Rutiles from eclogite of the ultrahigh-pressure metamorphic area at the Sudetes Fe–Ti-rich eclogites, which plot in the metapelite Nb discrimination diagram, as it stands now, is useful and should be applied in sediment provenance analysis until more rutile data of various source rock lithologies are available to place better constraints on its discrimination boundaries.

4.2. Zr-in-rutile thermometry

4.2.1. Introduction

The partitioning of zirconium (Zr) into rutile coexisting with zircon or other Zr-rich phases has a strong dependence on temperature (T) (Zack et al., 2004a; Watson et al., 2006; Tomkins et al., 2007). Zack et al. (2004a) were the first presenting an empirically calibrated Zr-in-rutile thermometer (Fig. 14), expressing temperature as:

\[ T(°C) = 127.8 \times \ln(Zr_{ppm}) - 10 \]

with an error of ±50 °C. The calibration is based on analyses of rutile grains from 31 metamorphic rocks with rutile–quartz–zircon assemblages spanning a temperature range from 430 to 1100 °C.

Watson et al. (2006) presented a revised Zr-in-rutile thermometer based on experimental data (at ~10 kbar) and constrained by natural rutiles from metamorphic rocks (Fig. 14), expressing temperature as:

\[ T(°C) = \frac{4470}{7.36 - \log_{10}(Zr_{ppm})} - 273 \]

with an error of ±20 °C. The two thermometers intersect at a temperature of about 540 °C but diverge significantly both at lower and higher temperatures (Fig. 14). Watson et al. (2006) considered this behaviour to indicate possible pressure dependence and emphasised the need for further investigation.

\[ T(°C) = \frac{83.9 + 0.410 \times P}{0.1428 - R \times \ln(Zr_{ppm})} - 273 \]

in the β-quartz field

\[ T(°C) = \frac{85.7 + 0.473 \times P}{0.1453 - R \times \ln(Zr_{ppm})} - 273 \]

and in the coesite field

\[ T(°C) = \frac{88.1 + 0.206 \times P}{0.1412 - R \times \ln(Zr_{ppm})} - 273 \]

with P in kbar, and R is the gas constant, 0.0083144 kJ K⁻¹. An obvious input parameter in their equation is the pressure. Hence, this thermometer is suitable for rutiles of known source, meaning of known pressure during rutile crystallisation. For detrital rutile, however, the pressure under which the source rock had formed is commonly unknown. To avoid speculation about the input parameter ‘pressure’, the equation of Watson et al. (2006) should be used for detrital rutile or for rutile of unknown origin in general. Although it was originally thought that the Zr-in-rutile thermometer is only valid for metapelitic rutile (Zack et al., 2004a), recent studies have demonstrated that it is also valid for rutile from metamafic lithologies (e.g. Zack and Luvizotto, 2006; Triebold et al., 2007) and for detrital metamafic rutile (e.g. Meinhold et al., 2008; Morton and Chenery, 2009).

Chen and Li (2008) have shown that the Zr-in-rutile thermometers by Watson et al. (2006) and Tomkins et al. (2007) yield similar shapes of the frequency histograms of temperatures (Fig. 15). However, the Zr-in-rutile thermometer of Watson et al. (2006) gives about 70 °C lower temperatures compared with the Zr-in-rutile thermometer of Tomkins et al. (2007) for eclogitic rutile from the central Dabie UHP metamorphic zone. The thermometer of Zack et al. (2004a) shows a wider spread in the frequency histograms of temperatures. The differences in shape and range of the frequency histograms of temperatures reflect the different approaches of the various Zr-in-rutile thermometers to calculate the temperature. Hereby, the pressure dependence of Zr incorporation into the rutile crystal lattice is an important factor to be considered, which is well illustrated in Fig. 14. The thermometers of Zack et al. (2004a) and Watson et al. (2006) intersect at a temperature of about 540 °C but diverge significantly both at lower and higher temperatures. The
thermometer of \( T_{Z} \) was calculated from Eq. (3) in \( T_{Z} \) and \( T_{W} \) correspond to the Zr-in-rutile thermometer of \( T_{T} \) was calculated at 28 kbar. Besides histograms, some statistical parameters are also given. \( n \) — number of data used, \( \text{Min} \) — minimum value, \( \text{Max} \) — maximum value, \( \text{Med} \) — Median, \( \text{Avg} \) — average (arithmetic mean), \( \text{SD} \) — Standard deviation (1σ), \( \text{Sk} \) — Skewness, \( \text{Ku} \) — Kurtosis.

**Fig. 15.** Frequency histograms (bin width = 25 °C) showing calculated formation temperatures for eclogitic rutile from the central Dabie UHP metamorphic zone with data from Chen and Li (2008). Abbreviations \( T_{Z} \), \( T_{W} \), and \( T_{T} \) correspond to the Zr-in-rutile thermometers of Zack et al. (2004a), Watson et al. (2006) and Tomkins et al. (2007) respectively. \( T_{Z} \) was calculated from Eq. (3) in Zack et al. (2004a); \( T_{W} \) was calculated at 28 kbar. Besides histograms, some statistical parameters are also given. \( n \) — number of data used, \( \text{Min} \) — minimum value, \( \text{Max} \) — maximum value, \( \text{Med} \) — Median, \( \text{Avg} \) — average (arithmetic mean), \( \text{SD} \) — Standard deviation (1σ), \( \text{Sk} \) — Skewness, \( \text{Ku} \) — Kurtosis.

In general, overestimation of temperature with Zr-in-rutile thermometry is only possible where mineral assemblages in equilibrium with rutile are quartz-free while underestimation can occur by absence of zircon and/or in partly reset mineral assemblages (Zack et al., 2004a; Baldwin and Brown, 2008; Harley, 2008; Luvizotto and Zack, 2009). Although Tomkins et al. (2007) noted that “Zr-in-rutile thermometry is not going to be a magic bullet in thermometry”, clearly it is an attractive method to calculate temperatures of high-grade and ultrahigh-grade metamorphic rocks (Spear et al., 2006; Zack and Luvizotto, 2006; Miller et al., 2007; Baldwin and Brown, 2008; Harley, 2008; Luvizotto and Zack, 2009). In the case of detrital rutile, Zr-in-rutile thermometry is an important technique in sediment provenance analysis especially in highly modified sandstones that may have lost significant amounts of provenance information (Morton and Chenery, 2009).

4.2.2. Examples

The reliability of the new Zr-in-rutile thermometers of Zack et al. (2004a) was demonstrated, for example, for eclogites and granulites from the Sudetes of SW Poland (Bakun-Czubarow et al., 2005) and for a wide variety of eclogites from Germany, Greece, Italy, Norway, Switzerland and Turkey (Zack and Luvizotto, 2006). Spear et al. (2006) showed the successful application of the Watson et al. (2006) calibration on blueschist facies rocks from Sifnos Island, Greece and Vaggelli et al. (2007) on high-pressure rocks from the Western Alps, Italy.

Zack et al. (2004b) first applied the combined use of detrital rutile geochemistry and Zr-in-rutile thermometry for quantitative sediment provenance analysis. Subsequent studies by Triebold et al. (2007) and von Eynatten et al. (2005) have demonstrated that the trace element composition of detrital rutile is unrelated to the grain size of the host sediment. They furthermore revealed that high-grade metamorphic rutile might preserve its geochemical signature to much lower temperatures, suggesting that rutile may survive metamorphic conditions on a retrograde path below 550 °C. Stendal et al. (2006) have also shown that relic rutile can retain its original composition during low- to medium-grade metamorphism, indicating that it can survive temperatures as high as 620 °C. Thus, the generally accepted views of rutile breakdown during low-grade metamorphism at greenschist facies and formation during medium-grade metastable metamorphic conditions (Force, 1980; Zack et al., 2004b) may not be strictly valid. Luvizotto et al. (2009a) who recognised prograde rutile growth from ilmenite in low- to medium-grade metasedimentary rocks of the Erzgebirge, Germany, as outlined in Section 3.1, have recently addressed this subject.

Morton and Chenery (2009) successfully used Zr-in-rutile thermometry to characterise the rutile source of Jurassic to Palaeocene sandstones in hydrocarbon exploration wells of the Norwegian Sea, accompanied with application of rutile geochemistry, as outlined in Section 4.1.6.

Note that for provenance identification of detrital rutile the possibility of polyphase recycling has to be kept in mind.

4.2.3. Zr diffusion

Cherniak et al. (2007b) studied the Zr diffusion in natural and synthetic rutile and provided evidence that Zr concentrations in rutile
can be affected by later thermal disturbance, although, based on observations made by Watson et al. (2006), this is not likely to be as rapid as Sasaki et al. (1985) suggested. Cherniak et al. (2007b) pointed out that Zr diffusion in rutile is significantly slower than diffusion of divalent and trivalent cation substitutions and seems little affected by variations in trace element composition. The authors, however, made a cautionary remark that under a broad range of geological conditions, the Zr-in-rutile thermometry is less resistant to resetting than Ti-in-zircon and Zr-in-titanite thermometry. They demonstrated that Zr diffusion in rutile depends on the grain size and the cooling rate (Fig. 16). For example, a rutile grain formed under ultrahigh-temperature (UHT) metamorphic conditions at about 945 °C with a 500-μm radius will preserve its Zr signature only under the cooling path. For illustration purposes, the field of ultrahigh-temperature (UHT) metamorphism (Harley, 1998) is marked in grey.

Fig. 16. Zr centre-retention criteria for rutile of different radii cooling at a linear rate from a range of maximum temperatures (after Cherniak et al., 2007b). The critical cooling rate depends on the maximum temperature, grain radius and diffusion parameters. When cooling rates are slower than this critical value, the peak-temperature Zr signature in the centre of a rutile grain is not preserved over the cooling path. For illustration purposes, the field of ultrahigh-temperature (UHT) metamorphism (Harley, 1998) is marked in grey.

Observations made by Watson et al. (2006), this is not likely to be as rapid as Sasaki et al. (1985) suggested. Cherniak et al. (2007b) pointed out that Zr diffusion in rutile is significantly slower than diffusion of divalent and trivalent cation substitutions and seems little affected by variations in trace element composition. The authors, however, made a cautionary remark that under a broad range of geological conditions, the Zr-in-rutile thermometry is less resistant to resetting than Ti-in-zircon and Zr-in-titanite thermometry. They demonstrated that Zr diffusion in rutile depends on the grain size and the cooling rate (Fig. 16). For example, a rutile grain formed under ultrahigh-temperature (UHT) metamorphic conditions at about 945 °C with a 500-μm radius will preserve its Zr signature only under the cooling path. For illustration purposes, the field of ultrahigh-temperature (UHT) metamorphism (Harley, 1998) is marked in grey.

4.3. Oxygen Isotopes

4.3.1. Introduction

The oxygen (O) isotope composition of minerals can yield information regarding the extent and nature of fluid–mineral interactions and the temperature at the time of crystallisation or alteration (e.g. Matthews et al., 1979; Agrinier, 1991; Zheng, 1991; Chacko et al., 1996; Moore et al., 1998; Zheng et al., 1999, 2003). Many studies have shown that O isotopes are a good fingerprint to identify the derivation of certain minerals from juvenile mantle-derived magmas, which contrast with those from “contaminants” that experienced low temperature and surficial process such as hydrothermal alteration and sedimentary recycling and hence have elevated δ18O values (e.g. Mozdziak et al., 2001; Wilde et al., 2001; Valley, 2003; Valley et al., 2005). The isotopes used are 16O and 18O, which are incorporated into the lattice during crystallisation. In current studies, oxygen isotope analyses on minerals are commonly performed by secondary ion mass spectrometry (SIMS) (e.g. Valley, 2003) and various laser techniques (e.g. Li et al., 2003; Valley, 2003; Zhang et al., 2006). The O isotope composition of a mineral is reported in delta notation (δ18O) relative to VSMOW (Vienna Standard Mean Ocean Water), which has an 18O/16O value of (2005.2±0.45)×10–6 (Gonfiantini, 1978). The corresponding equation is as follows:

\[ \delta^{18}O = \left( \frac{^{18}O / ^{16}O}_{\text{sample}} / \frac{^{18}O / ^{16}O}{\text{VSMOW}} - 1 \right) \times 10^3 \]

with δ18O values in per mil (‰).

Experimental studies by Moore et al. (1998) on synthetic and natural rutile have shown that the closure temperatures for O diffusion in rutile are high (Fig. 17), with about 650 °C for a crystal with a 100-μm radius and a cooling rate of 10 °C Ma−1. That means a rutile crystal with a 100-μm radius loses its initial core composition only after heating at 600 °C for just over 10 Ma. Moore et al. (1998) finally concluded that rutile retains its O isotope composition during a wide range of thermal events.

Various minerals effectively fractionate the O isotopes. As for all stable isotopes, this fractionation process is a strong function of temperature and is time-independent. For example, quartz, calcite and albite more strongly partition 18O while diopside, hornblende, zircon, almandine and rutile more strongly partition 16O (Matthews et al., 1979; Chacko et al., 1996; Moore et al., 1998, and references therein). Fig. 18 demonstrates the O isotope fractionation in a coesite-bearing eclogite of the Dabie Mountains, with δ18O values of about +1.1‰ for quartz, −2.3‰ for garnet and −6.1‰ for rutile (Li et al., 2003). A compilation of literature data reveals that eclogitic rutile shows δ18O values from −8.9 to +7.1‰, with values from 3.6 to 8.0‰ for oxygen isotope fractionation between quartz and rutile (Fig. 19). Fig. 20 compares the quartz–rutile geothermometers of Agrinier (1991), Zheng (1991) and Chacko et al. (1996). Quartz–rutile geothermometry is a reliable method because both minerals are relatively resistant to post-formation oxygen exchange (Agrinier, 1991; Chacko et al., 1996).
Quartz–rutile geothermometry yields reliable temperatures for blueschist and eclogite facies rocks but may not work for granulite facies rocks due to extensive re-equilibration (Chacko et al., 1996).

4.3.2. Examples

Vogel and Garlick (1970) analysed the O isotope composition of various minerals, amongst others rutile and quartz, from eclogites in Europe, Venezuela and California, and they pointed out that O isotope fractionations between quartz and rutile are relatively large. Thus, the quartz–rutile pair is particularly suitable for geothermometry because analytical errors involved in the determination of $\delta^{18}O$ values would not lead to large errors in the calculated isotope temperatures (Matthews et al., 1979). Hence, Addy and Garlick (1974) and Matthews et al. (1979) carried out experimental studies of O isotope fractionation between rutile and water and tested their quartz–rutile geothermometers on a number of eclogites. Desmons and O’Neil (1978) reported O isotope data of various minerals from eclogites of the Western Alps, Italy, and calculated for these eclogites an average formation temperature of 540 °C, using quartz–rutile and quartz–phengite geothermometry. Studies by Agrinier et al. (1985) have shown that in eclogites of the WGR, Norway, the O isotope fractionation between rutile and quartz is small ($\Delta^{18}O \approx 4.3$–5.0‰), with quartz–rutile geothermometry yielding formation temperatures of about 680 to 715 °C. Zheng et al. (1999) analysed the O isotope composition of various minerals (i.a. rutile and quartz) from HP and UHP eclogites of the Dabie Mountains and calculated formation temperatures using amongst others quartz–rutile geothermometry. Quartz–rutile pairs from some of the eclogites yielded isotope temperatures lower than the temperatures of eclogite facies metamorphism, suggesting O isotope exchange due to retrograde fluid–rock interaction (Zheng et al., 1999). Li et al. (2003) used O isotope analysis of rutile to test the validity of rutile U–Pb isochron dating on coesite-bearing eclogite from the Dabie Mountains. They determined almost identical $\delta^{18}O$ values for different rutile grains from the same specimen (Fig. 18), which suggests attainment of O isotope homogenisation in rutile during eclogite facies metamorphism and preservation during amphibolite facies retrograde metamorphism (Li et al., 2003). Gao et al. (2006) also studied the O isotope composition of mineral pairs in eclogite from the Dabie Mountains, with the quartz–rutile pair yielding an isotope temperature of 530 °C. Chen and Li (2008) emphasised the potential of quartz–rutile geothermometry to place constraints on rutile U–Pb cooling ages since O diffusion in rutile is similar to that of Pb under hydrous conditions (Moore et al., 1998; Cherniak, 2000).

4.4. U–Pb geochronology

4.4.1. Introduction

Rutile typically contains between 3 and 130 ppm of uranium (Mezger et al., 1989) (Table 3; Fig. 21), but higher concentrations also occur, making Pb–Pb and U–Pb dating possible (e.g. Mezger et al., 1989, 1991; Möller et al., 2000; Vry and Baker, 2006). Radiometric dating of rutile is based on the occurrences of unstable (radioactive) uranium isotopes $^{238}$U and $^{235}$U incorporated into the rutile crystal structure, which decay over several stages (decay chain) into stable daughter lead isotopes $^{206}$Pb and $^{207}$Pb, respectively (Jaffey et al., 1971; Table 4). By measuring the parent/daughter ratios and known...
In the natural logarithm, the number of atoms of the parent isotope, the number of atoms of the daughter isotope, the decay constant of the parent isotope, and the closure temperature. The latter is around 600 °C for rutile grains larger than about 0.2 mm in diameter (Cherniak, 2000; Vry and Baker, 2006), which is much higher than previously thought (370–500 °C: Mezger et al., 1989). The mathematical expression to determine the age of a rutile sample, as applied to any closed system, is given as:

\[ t = \frac{1}{\lambda} \ln \left(1 + \frac{D}{P} \right) \]

where \( t \) is the elapsed time, \( \lambda \) the decay constant of the parent isotope, \( D \) the number of atoms of the daughter isotope in the sample, and \( P \) the number of atoms of the parent isotope in the sample.

Measurements to determine the required parent/daughter ratios are performed by conventional isotope dilution-thermal ionisation mass spectrometry (ID-TIMS), secondary ion mass spectrometry (SIMS), of which the sensitive high-resolution ion microprobe (SHRIMP) is an example, and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Rutile has some advantages compared with zircon for U–Pb dating. Firstly, rutile from granulite facies rocks contains almost no Th, allowing common lead correction via 206Pb (Allen and Campbell, 2007; Zack et al., 2008; see also Ireland and Williams, 2003). Secondly, the isotope composition of Pb in rutile is usually highly radiogenic, and U–Pb ages are mostly concordant (Mezger et al., 1989, 1991; Mukasa et al., 1998; Möller et al., 2000; Bibikova et al., 2001). Thirdly, rutile appears to be resistant to subsequent resetting of Pb values (Vry and Baker, 2006).

Rutile has also some disadvantages compared with zircon for U–Pb dating. Rutile usually has lower U contents compared with zircon. Furthermore, there is a lack of large, isotopically homogeneous and commonly available natural rutile standards to assess measurement methods and demonstrate the quality of acquired geochemical data, although this may change in the future (Luvizotto et al., 2009b).

Eclogitic rutile commonly has low U contents (Table 3; Fig. 21), which in turn leads to low radiogenic Pb contents, and can contain a relatively large proportion of common (nonradiogenic) Pb (Cherniak, 2000; Schärer and Labrousse, 2003). Therefore, common Pb correction is important in age calculation, based on the isotope composition of rutile in a single analysis (Cherniak, 2000; Li et al., 2003). Correction for common Pb for the U–Pb data can be made using the measured 238U/206Pb and 207Pb/206Pb ratios following Tera-Wasserburg (1972) as outlined, for example, in Williams (1998). Further possibilities are the use of a Pb growth model (Stacey and Kramers, 1975) and a numerical solution if measurement of 204Pb is not possible (Andersen, 2002). Common Pb correction is also possible by using Pb ratios obtained from leached K-feldspars or the host whole-rock sample (e.g. Mezger et al., 1989). The latter method is only applicable for rutile of known igneous or metamorphic host rocks and not for detrital rutile. The problem of common Pb correction can be avoided if there is the chance to construct an isochron (e.g. Schandl et al., 1990; Li et al., 2003; Stendal et al., 2006). This, however, requires analyses of a sufficient number of coexisting minerals with large U/Pb fractionation (e.g. Mukasa et al., 1998; Li et al., 2003; Schärer and Labrousse, 2003). Fig. 22 schematically illustrates the interpretation of U/Pb ratios of rutile in the conventional (Wetherill) concordia plot and in a U–Pb isochron diagram.

### Table 3

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<th>Lithology</th>
<th>U (ppm)</th>
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<td>Felsic granulite</td>
<td>185</td>
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<tr>
<td>Eclogite</td>
<td>91</td>
</tr>
<tr>
<td>Quartz vein</td>
<td>85</td>
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<td>40</td>
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<table>
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<tr>
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<th>Max</th>
<th>Med</th>
<th>Avg</th>
<th>Std</th>
<th>Ref</th>
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<td>390</td>
<td>170</td>
<td>176</td>
<td>143</td>
<td>(1)</td>
</tr>
<tr>
<td>Eclogite</td>
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<td>7</td>
<td>1</td>
<td>7</td>
<td>10</td>
<td>(2)</td>
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<tr>
<td>Quartz vein</td>
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<td>22</td>
<td>19</td>
<td>27</td>
<td>(3)</td>
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<td></td>
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<tr>
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<td></td>
</tr>
<tr>
<td>Quartz vein</td>
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<td></td>
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### Table 4

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<th>Decay constant</th>
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</thead>
<tbody>
<tr>
<td>238U → 206Pb</td>
<td>4.4633 × 10^9</td>
<td>1.55125 × 10^-10</td>
</tr>
<tr>
<td>235U → 207Pb</td>
<td>0.7031 × 10^9</td>
<td>9.8485 × 10^-10</td>
</tr>
<tr>
<td>232Th → 208Pb</td>
<td>14.01 × 10^9</td>
<td>0.49475 × 10^-10</td>
</tr>
</tbody>
</table>

### 4.4.2. Examples

Radiometric dating of rutile has been successfully carried out for more than two decades (e.g. Corfu and Andrews, 1986; Schärer et al., 1986; Richards et al., 1988). For example, Mezger et al. (1989) applied the rutile geochronometer to reconstruct the pressure–temperature evolution of Archaean and Proterozoic high-grade polymetamorphic terrains in North America. They recognised that within a single hand specimen larger rutile grains give older ages than do smaller ones and explained this observation with volume diffusion directly related to the dimensions of the rutile crystal. Mezger et al. (1989) furthermore defined that at a cooling rate of about 0.5–1 °C Ma^-1 the closure...
temperature for U–Pb diffusion in rutile is about 420 °C for grains with a radius of 90–210 μm and about 380 °C for grains with a radius of 70–90 μm. The significance of these conclusions has been debated, as discussed later in this section.

Romer and Rötzler (2001) analysed rutile grains from granulite facies rocks of the Saxonian Granulite Massif. The grains had low radiogenic Pb contents and yielded a broad range in apparent 206Pb/238U ages, which was interpreted by the authors as being due to initial isotope heterogeneity. Franz et al. (2001) and Chen et al. (2005) had a similar problem with eclogitic rutile from Dabie and Sulu respectively.

Wong et al. (1991) used the ID-TIMS method to carry out U–Pb isotope dating on rutile from Archaean greenstones and gold mineralisation in the Val d’Or region of Quebec. They determined a U–Pb age of 2684 ± 7 Ma, which overlaps within the analytical error with previous 40Ar/39Ar ages on hornblende (2693 ± 17 Ma and 2672 ± 23 Ma) and thus shows the successful application of U–Pb rutile dating. Hydrothermal rutile from the alteration zone around a quartz vein gave a Pb–Pb isochron age of about 2600 Ma that was interpreted as the time of rutile growth during vein emplacement and constrains the age of gold mineralisation.

Bibikova et al. (2001) dated rutile from various rocks of the Archaean domain of the Belomorian Belt and its junction zone with the Karelalian Protocraton of the Baltic Shield. The analysed rutiles gave concordant U–Pb ages between 1740 and 1810 Ma and are about 50–100 Ma younger than the coexisting titanite, with smaller age difference in the junction zone and larger age difference in the main body of the Belomorian Belt. The difference in U–Pb ages may reflect different cooling histories of both units (see Bibikova et al., 2001 for discussion).

Hirdes and Davis (2002) carried out a multigrain ID-TIMS analysis of rutile from garnet-hornblende gneiss of southeastern Ghana. The 206Pb/238U age of 576 ± 2 Ma corrected for common Pb is concordant and was interpreted by them as a younger limit on metamorphism when the cooling isograd passed through the closure temperature of rutile.

Li et al. (2003) reported the first high-precision U–Pb age for metamorphic rutile of about 218 Ma (ID-TIMS) from coesite-bearing eclogite of the Dabie Mountains using conventional U–Pb dating and the isochron dating method (see also Chen et al., 2006). They analysed two colour types of rutile, light red and reddish brown, which showed no systematic difference in the concentrations of U and Pb or of Pb isotope ratios. In addition, they showed that omphacite in eclogite has a low U/Pb ratio and thus suggested that the Pb composition of omphacite can be used for common Pb correction in U–Pb dating of rutile from eclogites.

Flowers et al. (2005) obtained 206Pb/238U ages of rutile (and titanite and apatite) from a Mesozoic magmatic arc in New Zealand to constrain the timing and duration of exhumation. Franz and Romer (2007) dated syn-eclogite facies rutile from the Strona–Ceneri Zone of the Southern Alps using the ID-TIMS method to constrain the tectonometamorphic evolution at the northern margin of Gondwana during Early Palaeozoic time. Further U–Pb ages of rutile (and titanite) were obtained from eclogites of the WGR to assess the style and timing of exhumation and cooling of that UHP terrane (Kylander-Clark et al., 2008). There seem to be fundamental differences in the mechanisms controlling the evolution of large UHP terranes (Dabie–Sulu, WGR) that undergo protracted subduction and exhumation, and smaller UHP terranes (e.g. Dora Maira in the Western Alps) that undergo rapid subduction and exhumation (Kylander-Clark et al., 2008, and references therein).

Besides isotopic dating of rutile from metamorphic rocks, a number of studies have also been already shown the power of radiometric rutile dating in sedimentary successions from the Palaeoproterozoic to the Holocene worldwide.

SHRIMP U–Pb work by Sircombe (1993, 1997) on rutile from mineral sands in eastern Australia has shown a predominance of Late Proterozoic/Early Cambrian grains that are exotic to the local continental hinterland (Williams, 1998).

Harrison et al. (2007) used a SIMS multi-collector facility to determine 207Pb/206Pb ages of detrital rutile from the famous Jack Hills quartzite of Western Australia. They recognised a distinct age peak at 2.5 Ga, which corresponds to regional metamorphism and local granite emplacement in the Archaean Narryer Gneiss Complex.

Stendal et al. (2006) carried out lead isotope analyses using a step-leaching process on rutile grains from alluvial heavy mineral deposits and from a Neoproterozoic garnet–kyanite micaschist of the Yaoundé Group, southern Cameroon. The 207Pb/204Pb and 208Pb/204Pb data for
most rutiles from heavy mineral concentrates yielded scattered plots on the Pb–Pb isochron diagram, with no possibility to define a clear age. However, those from the micaschist defined an age of about 950 Ma, which suggests that rutile in the Yauondé Group formed during early Pan-African metamorphism or was inherited as detrital rutile from an early Pan-African source (Stendal et al., 2006).

Birch et al. (2007) used LA-ICP-MS to date detrital rutile from the Late Cretaceous–Tertiary gold-bearing White Hills Gravel placer deposits of the Victorian uplands in Australia. The analysed rutiles show up to 5.5 wt.% Nb₂O₅ and 2.9 wt.%WO₃ and together with their weighted mean 206Pb/238U age of 393 ± 10 Ma (2σ) suggest an origin associated with granite intrusion in the St Arnaud district (Birch et al., 2007).

Allen and Campbell (2007) analysed rutiles from a sand sample of the lower Mississippi River in the U.S.A. using LA-ICP-MS. They identified a major Appalachian source and noted that some trace elements (i.e. Cr, V and Zr) show strong correlation with age. The latter effect is probably caused by diffusion of cation substitutions for Ti⁴⁺ in the crystal lattice of rutile under slow cooling conditions (see Cherniak et al., 2007b).

Taylor (2008) used an excimer laser system coupled to a quadrupole ICP-MS to date rutile from the North Kimberley Kimberlite province of northwestern Australia and from a present-day stream catchment within the Geogina Basin, Northern Territory, Australia. He identified potential source areas and discussed the application of rutile dating to diamond exploration.

4.4.3. Pb diffusion

The closure temperature for U in rutile is strongly dependent on grain size (Mezger et al., 1991; Cherniak, 2000; see equation below). Thus, if rutile grains of different sizes are dated, as is commonly the case in sedimentary provenance studies, different rutile ages may not necessarily represent different igneous or metamorphic events, but may reflect the cooling history of each individual rutile grain. However, the differences between closure temperatures for rutile grains of different sizes are only of minor significance (few tens of degrees for cooling rates between 1 and 10 °C Ma⁻¹ and grain sizes up to a few millimetres) (Cherniak, 2000). The corresponding mathematical expression to determine the closure temperature (Tc) of rutile, as applied to any other mineral, is given as:

\[ T_c = \frac{E}{R} \ln \left[ \left( \frac{A \times R}{\ln \left( \frac{A \times R}{T_c^2 + D_0/a^2} \right) / E \times C_0} \right) \right] \]

where R is the gas constant, E the activation energy, A the geometric factor, D the factor for diffusion of the relevant species, a the effective diffusion radius and C, the cooling rate (Dodson, 1973). Cherniak (2000) gave examples of closure temperature values of 567 °C for 70 μm-size grains and 617 °C for 200 μm-size grains, for a cooling rate of 1 °C Ma⁻¹ with grains of spherical geometry. Moreover, it is likely that under some conditions of slow cooling, rutile will record significantly younger U–Pb ages compared to coexisting zircon (Cherniak, 2000). Li et al. (2003) pointed out that a number of field-based studies on rutile of slowly cooled terrains have demonstrated younger U–Pb ages compared with coexisting titanite and hornblende Ar–Ar ages (Mezger et al., 1989; Bibikova et al., 2001; Hirdes and Davis, 2002; Schmitz and Bowring, 2003). Although the causes of the disagreement between the experimental Pb diffusion data and the field-based observations remained unclear, Li et al. (2003) expressed their preference for the field-based rutile closure temperature estimates by Mezger et al. (1989).

Kramers et al. (2009) recently discussed the valence state of Pb in zircon and suggested that radiogenic Pb is tetravalent, being similar in ionic charge and effective ionic radius to U and Th, and hence has an extremely low diffusivity. In general, the loss of radiogenic Pb causes younger U–Pb ages. However, “radiogenic Pb cannot be lost from zircon crystals except by being reduced to the divalent state” that can be caused by hydrothermal fluids and natural leaching by groundwater, “after which it would become both incompatible in the lattice and highly mobile in solution” (Kramers et al., 2009). Although data are still pending, it is likely that in rutile radiogenic Pb is also tetravalent. In conclusion, fluids are more likely to affect rutile in slowly cooled than in rapidly cooled terrains. The change from tetravalent to divalent Pb causes loss of radiogenic Pb and thus of “age” (Kramers et al., 2009). This may explain why rutile from slowly cooled terrains often has younger U–Pb ages compared with coexisting titanite and hornblende Ar–Ar ages. The disagreement between the experimental Pb diffusion data and the field-based observations may be because the experiments do not fully reflect the conditions for slowly cooled terrains and hence a change of the valence state of radiogenic Pb does not occur in the experiments.

4.5. (U–Th)/He thermochronology

4.5.1. Introduction

The application of (U–Th)/He thermochronology to rutile is still in its preliminary stages. In general, thermochronology is a temperature-sensitive radiometric dating technique, which constrains low-temperature, upper crustal processes such as timing and duration of mineralisation, rate of exhumation and erosion of igneous and metamorphic rocks (Farley, 2002; Mclnnes et al., 2005; Reiners and Brandon, 2006, and references therein). The method is based on the measurement of radiogenic ⁴He produced from ²³⁸U, ²³⁵U and ²²⁷Th decay (Farley, 2002; Reiners and Brandon, 2006; Table 4). The daughter helium is retained in the rutile crystal lattice until the grain is heated above the closure temperature where the lattice becomes weak for helium loss. Preliminary (U–Th)/He thermochronology on rutile by Crowhurst et al. (2002) has suggested a closure temperature of >180–200 °C, which is about 100 °C higher than the closure temperature for apatite (75–100 °C; Farley, 2002) but in the range of the closure temperature for zircon (171–196 °C; Reiners et al., 2004). Initial step-heating He diffusion experiments by Stockli et al. (2005, 2007) and Wolfe et al. (2007) suggest a closure temperature of about 220–235 °C. As already documented in the previous section, the closure temperature is dependent on a series of parameters such as grain size, shape and cooling rate. In the case of rapid cooling of the sample, the (U–Th)/He age reflects cooling of the sample through its closure temperature and can often be related to a particular geological event (Dodson, 1973; Mclnnes et al., 2005). Slow cooling over a longer time interval, however, will give an age that is not necessarily related to any specific geological event (Mclnnes et al., 2005). Further details about the dependence of closure temperature from cooling rate can be found, for instance, in Reiners and Brandon (2006).

4.5.2. Examples

Only a few applications of (U–Th)/He thermochronology to rutile have been published. Crowhurst et al. (2002) analysed rutile from a metamorphic rock in South Australia and determined an average (U–Th)/He age of 472 ± 20 Ma that they interpreted as later stage cooling related to the Delamerian Orogeny. Mclnnes et al. (2005) presented preliminary rutile and zircon age data of a porphyry copper deposit from Iran, which yielded identical ages within error supporting the predicted similarity in rutile and zircon He closure temperatures. Stockli et al. (2007) analysed rutile from mantle and lower crustal xenoliths from Cenozoic volcanic rocks in the western U.S.A. and demonstrated that the determined (U–Th)/He ages are in excellent agreement with both ⁴⁰Ar/³⁹Ar and zircon (U–Th)/He data. To quantify the position of the rutile He partial retention zone (e.g. Reiners and Brandon, 2006) and to constrain the thermal history of Variscan basement rocks, Wolfe et al. (2007) determined rutile (U–Th)/He ages of amphibolites from the borehole of German Continental Deep Drilling Project, which is, at 9101 m and a cost of about US$350 million, the deepest and most expensive borehole for research in Germany (Emmermann and Lauterjung, 1997; Dunkl and von Eynatten (2009)
used anchizonal–hydrothermal grown rutile crystals from the sub-greenschist facies metamorphosed Mesozoic sandstones of Oman for (U–Th)/He thermochronology, which allowed them to determine fluid and thermal events after Late Cretaceous ophiolite emplacement.

Although the results outlined above are preliminary studies only, it seems obvious that (U–Th)/He thermochronology on rutile can place important constraints on the igneous and metamorphic evolution of a region. Moreover, as already applied for zircon (McInnes et al., 2005, and references therein), combined U–Pb dating and (U–Th)/He thermochronology on rutile grains can provide information on their age of formation and cooling history (Fig. 23). Note at the time of writing this paper no study had been published about (U–Th)/He thermochronology on detrital rutile. Nonetheless, this might change in the future since (U–Th)/He thermochronology seems useful in sediment provenance analysis to reconstruct both the age of potential source lithologies and the timing of tectonic uplift in the source area.

4.6. Lu–Hf isotopes

4.6.1. Introduction

Rutile typically has Hf concentrations between <5 and 120 ppm, but also higher amounts occur (Table 5; Fig. 24), and low Lu/Hf ratios, so that correction for in situ radiogenic growth is negligible. Hafnium isotope studies of single minerals are based on the occurrences of the unstable (radioactive) $^{176}$Lu isotope incorporated into the crystal lattice, which undergoes spontaneous $\beta$-decay to the stable daughter $^{176}$Hf isotope, with a decay constant of $1.93 \times 10^{-11}$ year$^{-1}$ (Sguigina et al., 1982). The decay constant of $^{176}$Lu, however, has currently been under review, which led to proposals of revised decay constants, i.e. $1.865 \times 10^{-11}$ year$^{-1}$ (Scherer et al., 2001), $1.983 \times 10^{-11}$ year$^{-1}$ (Bizzarro et al., 2003) and $1.945 \times 10^{-11}$ year$^{-1}$ (Luo and Kong, 2006). Owing to the large half-life of $^{176}$Lu of about 35–40 billion years, the Lu–Hf system is suitable for tracing the history of the solar system and the evolution of the Earth’s crust–mantle system (Patchett et al., 1981; Patchett, 1983; Salters and Zindler, 1995; Blichert-Toft and Albarède, 1997; Amelin et al., 1999; Griffin et al., 2000; Choukrour et al., 2005; Amelin, 2006; Aulbach et al., 2008).

The Lu–Hf isotope system is generally less disturbed by alteration processes than other isotope systems such as Rb–Sr, Sm–Nd and U–Pb (see discussions in Patchett, 1983; Griffin et al., 2000; Kinny and Maas, 2003). Experimental studies have shown that Hf diffusion is significantly slower than diffusion of divalent and trivalent cation substitutions; for example, it is about an order of magnitude slower than Pb diffusion (Cherniak et al., 2007b). However, Luivizzotto and Zack (2009) have recently shown for granulite facies metapelitic rocks from the Ivrea–Verbano Zone that Hf incorporation in rutile is temperature dependent.

The Lu–Hf isotope system has been widely applied in earth sciences over the last decades. Its application is based on the fact that Lu and Hf partition differently into specific minerals such as garnet, zircon and rutile, and Lu/Hf ratios are thereby strongly fractionated during partial melting, metamorphism and metasomatism (Salters and Zindler, 1995; Amelin et al., 1999; Griffin et al., 2000; Kinny and Maas, 2003). Therefore, the Hf isotope composition of the Earth’s crust–mantle system varies widely between the depleted mantle (Lu/Hf = chondritic), the enriched crust (Lu/Hf = chondritic) and any remaining unfracti- nated source (Lu/Hf = chondritic), as shown in Fig. 25. Different Lu/Hf ratios reflect the long-term evolution of these reservoirs (Patchett et al., 1981; Choukrour et al., 2005). Hafnium preferentially enters the melt phase, which leaves a residuum with relatively higher Lu/Hf ratios for the subcontinental lithospheric mantle. However, metasomatism by melts derived from the asthenospheric mantle can introduce Hf, which produces lithospheric mantle with relatively low Lu/Hf ratios (Chouk- ukrown et al., 2005). The deviations of the Hf isotope composition of a

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Table 5

<table>
<thead>
<tr>
<th>Source Lithology</th>
<th>Hf concentrations (ppm)</th>
<th>Table 5 for references.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Felsic granulate</td>
<td>173</td>
<td></td>
</tr>
<tr>
<td>Eclogite</td>
<td>368</td>
<td></td>
</tr>
<tr>
<td>Quartz vein</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Metasediment</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: n = number of data, Min = minimum value, Max = maximum value, Med = Median, Avg = average (arithmetic mean), Std = Standard deviation (1σ). Ref = References: (1) Luivizzotto and Zack (2009); (2) Zack et al. (2002), Xiao et al. (2006), Gao et al. (2007), Miller et al. (2007), Schmidt et al. (2009); (3) Zack et al. (2002), Xiao et al. (2006), Gao et al. (2007), John et al. (2008); (4) Zack et al. (2002), Luivizzotto et al. (2009a).
The 176Hf/177Hf ratios are used to determine Hf model ages, which are commonly expressed in epsilon units (\( \varepsilon_{\text{Hf}} \)) as function of crystallisation age. The 176Hf/177Hf ratio and the \( \varepsilon_{\text{Hf}} \) value of a sample (calculated for the age of the sample) can be used to produce a growth line that indicates the depleted mantle curve. The intersection yields a depleted mantle (\( T_{\text{DM}} \)) model age. This model age could reflect the time (\( t_1 \)) at which the source of the magma from which a mineral (e.g. rutile) crystallised was extracted from the depleted mantle reservoir. At time \( t_1 \) a variety of possible sources may contribute to newly formed crust.

Sample from that of the chondritic uniform reservoir (CHUR) are commonly expressed in epsilon units (\( \varepsilon_{\text{Hf}} \)) as given by following equation (Patchett et al., 1981):

\[
\varepsilon_{\text{Hf}} = \left[ \frac{176\text{Hf}}{177\text{Hf}} \right]_{\text{sample}} - 1 \times 10^4
\]

Samples with higher than chondritic 176Hf/177Hf at time \( t \) have positive \( \varepsilon_{\text{Hf}} \) values; those with lower than chondritic 176Hf/177Hf have negative \( \varepsilon_{\text{Hf}} \) values, and hence chondrites per definition have \( \varepsilon_{\text{Hf}} = 0 \).

4.6.2. Examples

The use of in situ Lu–Hf isotope analysis has rapidly increased in recent years because of an increase in sophisticated laser ablation multi-collector ICP-MS facilities, which allow precise isotope analysis of samples with HF quantities as low as 25 ng (Blichert-Toft and Albarède, 1997; Amelin et al., 1999). Choukroun et al. (2005) analysed the Hf isotope composition of rutile from MARID xenoliths of the Kimberley area, South Africa. The 176Hf/177Hf ratios are highly variable (0.2811–0.2858, \( \varepsilon_{\text{Hf}} = -55 \) to +110), with much of this range found in single samples and even within single grains. They noted that such a wide range of Hf isotope composition within single samples and within single rutile grains could not be generated by radioactive decay of 176Lu in the rutile within the age of the Earth. Choukroun et al. (2005) therefore interpreted the ranges in Hf isotope composition as reflecting primary interaction of an asthenospheric-derived melt with ancient depleted harzburgitic mantle, which was later overprinted by metasomatism. The authors explained low 176Hf/177Hf ratios still preserved in some MARID rutile grains by mixing between an asthenospheric-derived melt and the ancient subcontinental lithospheric mantle.

Aulbach et al. (2008) analysed 176Hf/177Hf of rutile in eclogite xenoliths from kimberlites of the Lac de Gras area, northern Canada. They received similar, highly variable 176Hf/177Hf ratios (0.28156–0.28568, \( \varepsilon_{\text{Hf}} = -43 \) to +103), with negligible intergrowth of radiogenic Hf in rutile since emplacement of the kimberlite, as shown by low 176Lu/177Hf ratio of 0.000039 ± 0.000077 (1σ). They recognised a correlation between Nb/Ta and minimum 176Hf/177Hf of eclogitic rutiles, and interpreted the low 176Hf/177Hf and suprachondritic Nb/Ta values as acquired during interaction with a component derived from ancient metasomatised subcontinental lithospheric mantle. By contrast, they interpreted rutile with high 176Hf/177Hf and subchondritic Nb/Ta values as having preserved its primary HFSE concentrations and isotope characteristics. Their study clearly shows that Lu–Hf isotope analysis combined with trace element geochemical data of rutile is particularly helpful for a better understanding of the evolution of the Earth's crust and mantle. New studies are under way to improve Lu–Hf isotope analysis on rutile (Ewing et al., 2009).

At the time of writing this paper, no study had been published about Lu–Hf isotope analysis of detrital rutile. However, this might change in the future since the Lu–Hf isotope composition of rutile represents an estimate of the protolith composition at the time of crystallisation and therefore is helpful in tracing potential source rocks in sediment provenance studies.

5. Economic importance of rutile

5.1. Introduction

Although the primary purpose of this paper is to provide information on various applications of rutile in earth sciences, an outline of the economic importance of rutile is essential because the academic issues mentioned above have also important commercial implications.

One of the major subjects for earth scientists is the exploration and evaluation of mineral raw materials, including hydrocarbons, gold, diamonds, chromium, iron, nickel and platinum group metals but also titanium minerals. The world total rutile reserves are estimated to be 45 million t and those of ilmenite are about 680 million t, with ilmenite supplying about 92% of the world’s demand for titanium minerals (Gambogi, 2009). Titanium minerals are commercially important because they are processed to titanium metal, which is used, for instance, in the aerospace industry because of its low weight, high strength and resistance to heat and corrosion. Rutile is one of the favoured minerals for the production of titanium dioxide white pigment, dominantly through the chloride manufacturing process (Stanaway, 1994; Korneliussen et al., 2000). The main applications of
titanium dioxide white pigment are in the manufacture of paint (51% of total production), paper (19%) and plastics (17%) (Pearson, 1999; Carp et al., 2004; Gambogi, 2008). Other uses include ceramics, coated fabrics and textiles, floor coverings, printing ink, roofing granules, food colouring (E171), tablet coating, toothpaste and as a UV absorber in sunscreen cream with high sun protection factors (Carp et al., 2004; Gambogi, 2008, and references therein). Thus, titanium dioxide (rutile) is almost always present in our daily life. Moreover, since Fujishima and Honda (1972) successfully showed the application of TiO₂ as a photoanode to decompose water by visible light, anatase has received much attention in photocatalysis (Carp et al., 2004). This use has also been extended to rutile (e.g. Lu et al., 2004; Chuan et al., 2008), although its reaction rate is a fifth of anatase (Chuan et al., 2008). In contrast to rutile containing, for example, V and Fe, pure rutile shows no photoactivity (Lu et al., 2004). Chuan et al. (2008) used natural V-bearing rutile from a rutile mine in the Shaanxi Province, China, to decompose methylene blue and suggested the application of rutile for large-scale photocatalytic decomposition of organic pollutants in quiet and still waters.

5.2. Economic importance

Most of the natural rutile used in industry comes from heavy mineral sands (placer deposits) enriched in ilmenite and rutile (e.g. Force, 1991; Roy, 1999; Pirkle et al., 2007). The world’s largest sedimentary deposits of rutile and the largest rutile mine are both in Sierra Leone. Before its closure in 1995, the rutile operation in Sierra Leone supplied 137,000 t (Mobbs, 1996), which was about two-thirds of the world’s rutile output in 1994. Although rutile is commercially important, rutile mining causes drastic changes to the environment (Akivumi and Butler, 2008). The Sierra Rutile Mine reopened in 2006, and Sierra Leone may become one of the world’s leading rutile producers in the future. In 2006, 70,360 t of rutile (worth US$28.5 million) was exported (Bermúdez-Lugo, 2008). Other African rutile placer deposits occur in Cameroon (exploited between 1935 and 1955 near Yaoundé, Gambia ( mined in the 1950s), Guinea (deposits not yet exploited), Kenya ( to commence in the future), Malawi (exploration has been conducted in recent years) and Guinea (deposits not yet exploited), Kenya (to commence in the future), Malawi (exploration has been conducted in recent years) and Guinea (deposits not yet exploited), Kenya (to commence in the future), Malawi (exploration has been conducted in recent years) and Sierra Leone (to commence in the near future). Rutile placer deposits are also mined in Australia, India, Ceylon and U.S.A. (Goldsmit and Force, 1978; Force, 1991; Roy, 1999; Force, 2000; Pirkle et al., 2007).

Fig. 26 shows the world largest producers of natural rutile and the trend of growth between 2006 and 2008. For example, in 2008, the world production of natural rutile was about 608,000 t, with Australia (309,000 t), South Africa (121,000 t) and Sierra Leone (95,000 t) being the three largest producers (Gambogi, 2009). However, rutile placer deposits are limited in volume and are rapidly being depleted, and therefore, the current producers may not be able to fulfill the world’s need in the future (Korneliussen, 1980; Korneliussen et al., 2000), with Sierra Leone being an exception. Thus, an alternative source for high-grade TiO₂ ores (such as eclogite) has to be found.

The eclogites of the Western Gneiss Region, Norway, contain several million tons of rutile, and are therefore a large rutile resource (Korneliussen and Foslie, 1985; Korneliussen et al., 2000). The eclogites occur as pods and lenses within amphibolite to granulite facies metamorphosed Proterozoic/sub-Caledonian gneisses and have rutile concentrations in the range of 1 to 4 wt.%, although higher concentrations occur locally (Korneliussen, 1980; Korneliussen and Foslie, 1985). Ilmenite is important in the economic evaluation of rutile-rich eclogite deposits, for two main reasons (Korneliussen and Foslie, 1985). First, intergrowths of less-valuable ilmenite will lower the purity, and accordingly the values of the rutile concentrate that can be produced. Second, an increase in the ilmenite concentration in eclogite will lead to a correspondingly smaller amount of Ti available to form rutile (Korneliussen and Foslie, 1985). Moreover, the grain size of the rutile and the CaO content in the concentrates (should be less than 0.2%) are of considerable importance in the economic evaluation of rutile-rich eclogite deposits (Korneliussen et al., 2000). Further examples of rutile-bearing eclogite deposits are the Sulu deposits, Italy (Force, 1991; Liou et al., 1998), the Shubino deposit, Russia (Force, 1991) and from the Dabie-Sulu deposits, China (Chen et al., 2005; Huang et al., 2006; Zhang et al., 2006). For instance, in the Sulu UHP metamorphic terrane the rutile modal content in eclogite is 2–5 vol.% and can be as high as 8–10 vol.% (Chen et al., 2005).

Minor economically important sources of natural rutile are ore deposits (Czamanske et al., 1981; Clark and Williams-Jones, 2004), amphibolitic rocks (Korneliussen et al., 2000; 40), granitic pegmatites and rare-earth element mineralisation (Scott, 1988; Černý et al., 1999; Černý and Chapman, 2001). Clark and Williams-Jones (2004) discussed anomalous compositions of rutile at certain deposits for their potential as indicators of metallic mineralisation (see Scott, 1988, 2005; Scott and Radford, 2007). Thus, detrital rutile can be used as a mineral indicator mineral in stream sediments to guide the exploration geologists to metallic mineralisation. Table 2 shows a compilation of various rutile-bearing deposits and the characteristic trace elements incorporated into the rutile crystal lattice. Moreover, pyrope garnet, chrome diopside and chrome spinel, rutile can also be used as a kimberlite indicator mineral (Smythe et al., 2008) and therefore plays an important role in diamond exploration.

Table 6
Key elements in natural rutile useful for a wide range of applications in earth sciences (see text for explanation).

<table>
<thead>
<tr>
<th>Key elements</th>
<th>Applications</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr and Nb</td>
<td>Source rock characterisation</td>
<td>These elements allow discrimination between rutile derived from metamorphic lithologies (high Cr, low Nb) or peraluminous lithologies (low Cr, high Nb).</td>
</tr>
<tr>
<td>V, Ni, Cu, Nb, Sn, Sh, Ta and W</td>
<td>Source rock characterisation</td>
<td>Rutile containing these elements is useful as a mineral in stream sediments to identify and trace the type of metallic mineralisation.</td>
</tr>
<tr>
<td>Zr, O</td>
<td>Zr-in-rutile thermometry, O isotopy</td>
<td>Zr in rutile can yield the temperature of rutile crystallisation. O isotopic data can yield information about the temperature of rutile crystallisation and the extent and nature of fluid–mineral interactions.</td>
</tr>
<tr>
<td>U and Pb</td>
<td>U–Pb geochronology, (U–Th)/He thermochronology</td>
<td>U/Pb and Pb/Pb isotope ratios can yield the age of rutile crystallisation. (U–Th)/He isotope ratios are used to calculate an age related to the time the rutile cooled through about 200 °C.</td>
</tr>
<tr>
<td>Lu and Hf</td>
<td>Lu–Hf isotopy</td>
<td>The Hf isotopic composition of rutile allows identifying the magmatic source by reference to an Earth model.</td>
</tr>
</tbody>
</table>

Fig. 26. World production of natural rutile by country between 2006 and 2008, according to data in Gambogi (2008, 2009).
6. Summary

Rutile is widely distributed as an accessory mineral in igneous, metamorphic and sedimentary rocks. Its geochemical composition allows tracing the formation and evolution of the Earth’s continental crust because rutile is a host major mineral for Nb, Ta and other HFSE, which are widely used as a monitor of geochemical processes in the crust and mantle such as magma evolution and subduction-zone metamorphism. Processes influencing the Nb/Ta ratio of minerals (e.g., rutile) and rocks are continuously topics of scientific debate. In recent years, many data have been generated which significantly increased our knowledge about rutile and its host lithologies. Table 6 gives a summary of key elements in natural rutile that are useful for a wide range of applications in earth sciences. For example, elements such as Cr, Nb, Sb and W are used to trace the provenance of rutile. A number of publications have already shown that rutile geochemistry, Zr-in-rutile thermometry and isotope studies of rutile are useful methods in both hard and soft rock geology. Rutile is also of economic importance because of its use in the manufacture of white titanium dioxide pigment, which is a major constituent in various products of our daily life. Heavy mineral sands containing a significant percentage of rutile are therefore the focus of exploration worldwide. Because these mineral sands are limited in volume and are rapidly being depleted, an alternative source for high-grade TiO2 ores has to be found. This clearly shows the growing demand for further rutile-related research in earth sciences. I hope that this review will serve as a good source of reference for earth scientists both in academic research and in industry.

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