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Zr-in-rutile thermometry of eclogites from the Karakaya Complex in NW Turkey: Implications for rutile growth during subduction zone metamorphism

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ABSTRACT

Eclogites occur as a tectonic slice within a metabasite-phyllite-marble unit of the Karakaya Complex in northwest Turkey. The high-pressure mineral assemblage in eclogite is mainly composed of garnet + omphacite + glaucophane + epidote + quartz. Trace element characteristics of rutile and Zr-in-rutile temperatures were determined for eclogites from the Karakaya Complex. Core-rim analyses of rutile grains yield remarkable trace element zoning with lower contents of Zr, Nb and Ta in the core than in the rim. The variations in Zr, Nb and Ta can be ascribed to growth zoning rather than diffusion effects. The Nb/Ta and Zr/Hf ratios increase with a decrease in Ta and Hf contents, which could be ascribed to the effect of metamorphic dehydration in subduction zones on rutile Nb/Ta differentiation. The rutile grains from eclogites in the Karakaya Complex are dominated by subchondritic Nb/Ta and Zr/Hf ratios. It can be noted that subchondritic Nb/Ta may record rutile growth from local sinks of aqueous fluids from metamorphic dehydration.

The Zr contents of all rutile grains range between 81 and 160 ppm with an average of 123 ppm. The Zr-in-rutile thermometry yields temperatures of 559–604 °C with an average temperature of 585 °C for eclogites from the Karakaya Complex. This average temperature suggests growth temperature of rutile before peak pressure during the subduction. However, some rutile grains have higher Zr contents in the outermost rims compared to the core. Zr-in-rutile temperatures of the rims are about 20 °C higher than those of the cores. This suggests that the outermost rims would have grown from a distinct fluid at higher temperatures than that of the cores. Moreover, Zr contents and calculated temperatures in both inclusion rutile and matrix rutile from eclogites are identical, which suggests that eclogites within the Karakaya Complex belong to the same tectonic slice and underwent similar metamorphic evolution.

1. Introduction

Temperature estimates for eclogite-facies metamorphic rocks are crucial to better understand the formation and evolution of high-pressure (HP) eclogites and related metamorphic rocks in subduction zones. Conventional methods based on Fe-Mg exchange thermometry between garnet and clinopyroxene have been undertaken in the past three decades (e.g. Ellis and Green, 1979; Ganguly, 1979; Krogh, 1988; Ai, 1994; Pattison and Newton, 1989; Ravna, 2000). The Fe-Mg exchange thermometry yielded reasonable temperatures for eclogites formation, which have been widely used in reconstruction of P-T paths for HP and UHP metamorphic rocks in subduction zones. However, geothermometry based on element exchange reactions between two phases such as the Gr-Cpx Fe-Mg exchange geothermometer is very susceptible to post-peak diffusional resetting and thus may underestimate peak temperatures, especially for HP to UHP conditions (Pape et al., 2016). Zr-in-rutile thermometry is an excellent alternative method for estimating temperature of metamorphism which is based on the temperature-dependent incorporation of Zr as a trace element into rutile, coexisting with quartz and zircon (Zack et al., 2004; Watson et al., 2006; Ferry and Watson, 2007). The pressure dependence was incorporated into this thermometer with the calibration of Tomkins et al. (2007). This revised thermometer has been proven to be a more reliable method for estimating peak temperatures at a given pressure in HP to UHP metamorphic rocks compared to any other exchange thermometer because of the chemical simplicity of the system (e.g. Zheng et al., 2011a; Meyer et al., 2011; Kooijman et al., 2012; Chen et al., 2013; Ewing et al., 2013; Liu et al., 2015; Şengün

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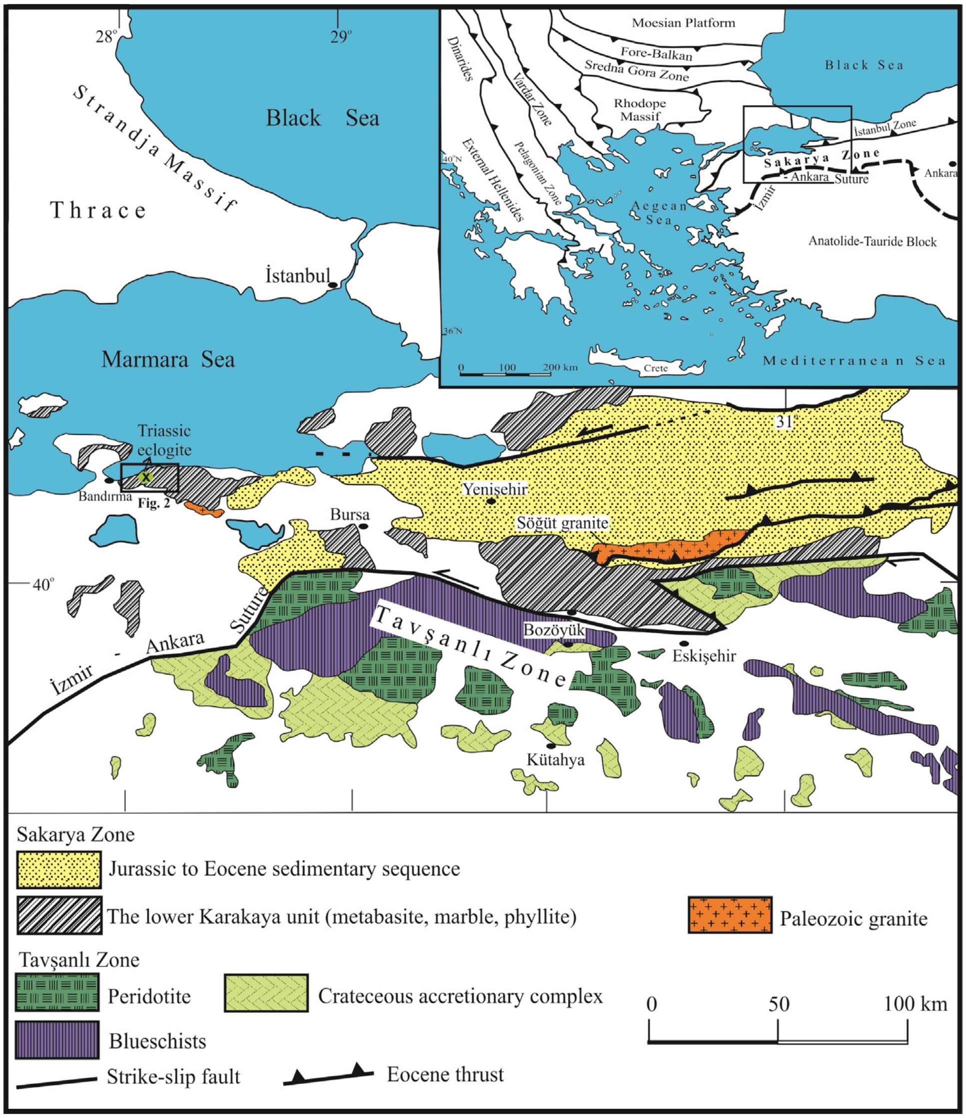

Fig. 1. Tectonic map of northwest Turkey showing the distribution of Upper Triassic accretionary complexes.
(modified from Okay et al., 2006; Meinhold et al., 2010)

and Zack, 2016). Previous studies indicate that temperatures calculated by the Zr-in-rutile thermometer might reflect progressive growth (Spear et al., 2006; Zhang et al., 2010; Zheng et al., 2011a; Kooijman et al., 2012), peak metamorphism (Zack and Luvizotto, 2006; Zhang et al., 2010), or retrograde equilibration (Chen and Li, 2008; Zhang et al., 2010). Therefore, the method could reveal different stages of subduction zone metamorphism. Rutile is an important accessory mineral in a variety of magmatic and metamorphic rocks, and is commonly found in high-grade metamorphic rocks from oceanic and continental subduction zones (e.g. Foley et al., 2002; Zack et al., 2002; Meinhold, 2010; Ding et al., 2013). Rutile also participates in the main metamorphic reactions that can readily be attributed to pressure-temperature (P-T) conditions.

Rutile is an important carrier for the high field strength elements (HFSE's) and dominates the Nb, Ta and Ti budgets of many rocks in subduction zone systems (Brenan et al., 1994; Green, 1995; Foley at al., 2000; Rudnick et al., 2000; Ding et al., 2013). Nb/Ta ratios of rutile have been used for geochemical tracing of crust-mantle differentiation through subduction zone metamorphism (Schmidt et al., 2009; Ding et al., 2009; Meinhold, 2010). Since all the known mantle and crustal reservoirs have primarily subchondritic Nb/Ta and Zr/Hf ratios (e.g. Green, 1995; Foley et al., 2000; Rudnick et al., 2000; Zack et al., 2002; Ding et al., 2009), Nb/Ta ratio of rutile usually corresponds to that of the initial rock and is a useful indicator for the reconstruction of eclogite paragenesis (e.g. Schmidt et al., 2009; Liang et al., 2009).

In this paper, Zr-in-rutile thermometry has been applied to estimate metamorphic temperatures and investigate if the Zr-in-rutile data could potentially provide reliable and meaningful temperature estimates for eclogites. The Zr-in-rutile thermometer is examined to check how well it fits with conventional Fe-Mg exchange thermometers, with the aim of assessing how reliable this thermometer is for subduction systems. This study focuses on the trace element composition of rutile and application of Zr-in-rutile thermometry to eclogites from the Karakaya Complex in the northwest of Turkey (Fig. 1). The purpose of this study is to demonstrate the robustness of the Zr-in-rutile thermometer and provide first insights into the growth of rutile during subduction zone metamorphism.

2. Geological setting

Turkey is commonly subdivided into several tectonic terrains separated by ophiolitic suture zones representing the closure of branches of Tethyan ocean basins during the Mesozoic and Cenozoic (e.g. Şengör and Yılmaz, 1981; Okay and Tüysüz, 1999; Moix et al., 2008). These are, from north to south, the Sakarya Zone (Okay, 1984), the İzmir-Ankara-Erzincan Zone (Şengör and Yılmaz, 1981), and the Tavşanlı Zone (Okay, 1986). The Sakarya Zone in northwest Turkey extends from the Aegean in the west to the Eastern Pontides in the east (Fig. 1). It is bordered by the Strandja Massif and Istanbul Zone to the northwest and by the Black Sea in the northeast. To the south, the Sakarya Zone is in contact with the Taurides and their metamorphic equivalents of the Anatolides along the Izmir-Ankara-Erzincan suture zone. The pre-Jurassic basement of the Sakarya Zone is generally characterized by Variscan metamorphism-magmatism, Permo-Triassic Paleo-Tethyan accretion-subduction complexes, collectively called the Karakaya Complex (Tekeli, 1981; Okay et al., 1996) and clastic products of a Liassic regional unconformity (Fig. 1).

The Karakaya Complex lies in the Sakarya Zone and is traditionally subdivided into two units (Okay and Göncüoğlu, 2004): (i) the lower Karakaya units (LKU); and (ii) the upper Karakaya units (UKU). The LKU, broadly referred to as the Nilüfer unit, is composed of an imbricated and foliated sequence of phyllite, schist, serpentinite and recrystallised limestone that is mixed with green and partly thick-bedded metabasic rocks with metagabbro and metadiabase. The LKU was mainly metamorphosed under greenschist-facies conditions, and includes eclogites and blueschist facies slices with Late Triassic (208-203 Ma) Ar–Ar phengite ages (Okay and Monié, 1997). The metabasic rocks of the LKU are interpreted as a Triassic oceanic seamount with their anorogenic alkaline and tholeiitic signatures (e.g. Pickett et al., 1996; Pickett and Robertson, 2004; Sayit et al., 2010; Robertson and Ustaömer, 2012). The Permo-Triassic subduction-accretion series of the lower Karakaya Complex (Okay and Göncüoğlu, 2004) with Late Triassic blueschist and eclogites (Okay and Monié, 1997; Okay et al., 2002) forms part of the Paleo-Tethys oceanic crust that was accreted to the southern margin of Laurussia during the Late Permian to Triassic (Stampfli and Kozur, 2006; Moix et al., 2008). The UKU comprises several tectonostratigraphic units: (i) the upper Permian-Lower Triassic unit, dominated by alkaline volcanics and neritic carbonates; (ii) an upper Permian unit with terrigenous sedimentary rocks and debris-flow deposits, which underwent only very low-grade metamorphism (Federici et al., 2010; Tetiker et al., 2015); (iii) the Triassic unit consisting of MORB (mid-ocean ridge type basalts), radiolarites, sandstone turbidites; and (iv) an accretionary mélange, assembled and emplaced during Late Triassic time (e.g. Pickett et al., 1996; Pickett and Robertson, 2004; Federici et al., 2010; Robertson and Ustaömer, 2012). The maximum depositional age of the terrigenous sandstone of the UKU is Carnian-Norian (Ustaömer et al., 2016). A series of strongly deformed siliciclastic and volcanic rocks including exotic blocks of Permian and Triassic limestones and radiolarian cherts tectonically lie on the lower Karakaya unit (Okay and Göncüoğlu, 2004). The eclogites occur as a tectonic slice in the metabasic rocks of the LKU located in the eastern part of the town of Bandırma (Fig. 2). The metabasic rocks are intercalated with minor marble and phyllite, and have a thickness of more than 5 km (Okay and Monié, 1997). The rocks show a distinct foliation and isoclinal folding, and underwent greenschist-facies metamorphism forming the mineral assemblage of actinolite + albite + epidote + chlorite + titanite. High pressure metamorphic slices with eclogite assemblages are elliptical: approximately 100 m thick and 200 m long. These slices are aligned parallel to the NE-trending foliation in the metabasic rocks. The eclogites are weakly foliated and have homogenous textures. Metabasic rocks only show greenschist-facies metamorphism. Tectonic slices of greenschist-facies metagabbro and serpentinite occur in the vicinity of eclogites (Fig. 2).

2.1. Petrography

The high-pressure mineral assemblage in eclogite is mainly composed of garnet + omphacite + glaucophane + epidote + quartz (Fig. 3a). Typical accessory minerals are rutile, zircon and titanite. Garnet, omphacite and glaucophane form more than 70% of the rock. Euhedral, relatively large (1–3 mm) porphyroblasts of garnet are scattered through the matrix, and contain inclusions of quartz, epidote, glaucophane, Ca-amphibole and rutile (Fig. 3b). Omphacite is fine-grained and forms up to 0.2 mm long crystals in the matrix. It is surrounded by rims of calcic amphibole, which developed during retrograde overprinting. Sodic amphibole in eclogite is glaucophane in composition and is typically fine-grained and aligned with omphacite in the matrix. Glaucophane inclusions in garnet also show that glaucophane was present as a matrix phase in the eclogite stage. Rutile occurs both as inclusions in garnet and as separate grains in matrix. They are mostly dark brown and have thin ilmenite overgrowths. The grain size of matrix rutile is mostly between 100 and 290 μm with an average of about 200 μm. Inclusion rutile has the grain size of about 20–30 μm. Some rutile grains contain titanite inclusions (Fig. 3c) and have a retrograde rim of titanite (Fig. 3d). Some matrix rutile grains are associated with ilmenite but show a contrasting texture, characterized by partial replacement of rutile by ilmenite. Ca-amphibole and chlorite occur in eclogite as secondary phases that are not in equilibrium with the high-P phases. Pseudomorphic replacement of garnet by chlorite-epidote-amphibole, Ca-amphibole rims around glaucophane, and rutile partially replaced by titanite indicate gradual retrogression to greenschist-facies rocks. The garnet-clinopyroxene Fe–Mg exchange thermometer of Ellis and Green (1979) yielded temperatures of $480 \pm 50\,^{\circ}$C at a pressure of 10 kbar for omphacite-garnet pairs from eclogite samples (Okay and Monié, 1997).

2.2. Analytical methods

Samples were prepared for trace element analyses as polished thin sections of about to 50 μm thickness (1505A, 1511). Rutile grains were backscattered electron (BSE) imaged to identify inclusions and areas of replacement by other phases. BSE imaging was carried out on a Hitachi S-3400N scanning electron microscope (SEM) at the University of Gothenburg to identify inclusions in rutile and document the most suitable spots for analysis. The operation conditions during the BSE imaging were maintained at 20 kV and 6 nA.

The in situ trace element analysis of rutile was performed on prepared thin sections at the Department of Earth Sciences in the University of Gothenburg. All samples were analysed using New Wave NWR 213 laser ablation system coupled to an Agilent 8800 QQQ quadropole ICP-MS. Helium gas, which carries the laser ablated sample aerosol from the sample cell, is mixed with argon carrier gas and nitrogen as additional di-atomic gas to enhance sensitivity, and finally flows into the ICPMS torch. Helium is flushed through the ablation cup at ~1 ml/min. The helium reduces surface deposition during ablation, which increases sensitivity and also reduces fractionation owing to particle size bias (Eggins et al., 1998).

Ablation spot size was set to 30 μm, with the laser energy of ~6.1 J/cm^2 and a frequency of 10 Hz. Signals were recorded over 60 s for each spot. Each analysis involved background acquisition of approximately 20 s followed by 30 s data acquisition from the sample. The last 10 s were used for wash out. ^{27}Al, ^{29}Si, ^{53}Cr, ^{57}Fe, ^{178}Hf, ^{181}Ta, ^{232}Th (10 ms dwell time), ^{49}Ti, ^{93}Nb (5 ms dwell time) and ^{90}Zr, ^{238}U (30 ms dwell time) were analysed for trace element concentration in rutile. Every twelve analyses of unknown rutile grains were bracketed by two analyses of the R10 rutile standard and two analyses of NIST SRM 610 glass standard. Titanium mea-

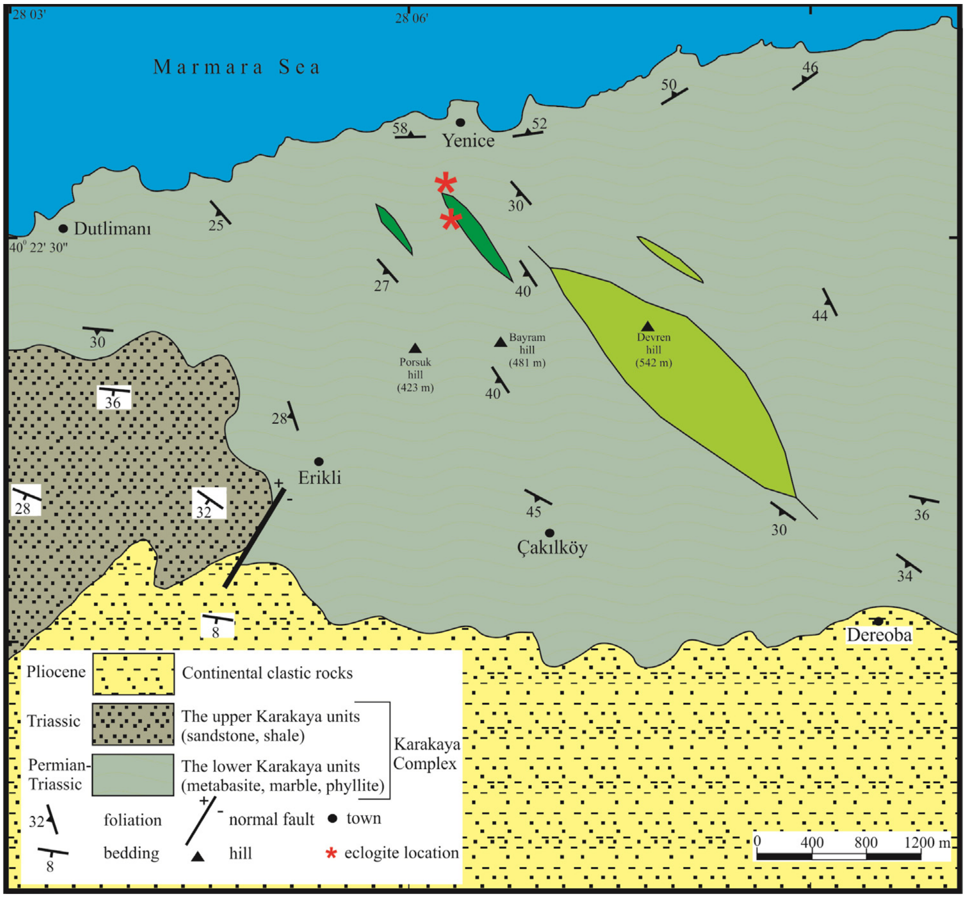

Fig. 2. Detailed geological map of the lower Karakaya unit showing eclogite locality.

(modified from Okay and Monié, 1997)

sured as ^{49}Ti was used as internal standard element for all analyses. The glass reference material NIST SRM 610 (Jochum and Nehring, 2006) and R10 (Luvizotto et al., 2009) rutile were used for external calibrations. The concentrations of elements were determined using "GLITTER version 4.4.4" software program (online interactive data reduction for LA-ICPMS microprobe, Van Achterbergh et al., 2000). Titanium content during data reduction was assumed to be 100 wt% TiO_2.

Zr-in-rutile temperatures were calculated using the calibration of Tomkins et al. (2007) with pressure correction, since the investigated eclogites have been metamorphosed under HP conditions.

3. Results

3.1. *Trace element geochemistry*

Trace element concentrations of rutile grains from two eclogite samples (1505A, 1511) are given in Table 1. Rutile occurs as two different textural types in the studied samples. It occurs as single grains in the matrix between rock-forming minerals and as inclusions in garnet. The different textural rutile types in eclogites and the associated range of Zr concentrations are summarized in Table 2. Small cracks in garnet grains include retrograde minerals such as chlorite, epidote and biotite, showing possible pathways for trace element transfer during retrogression. Zr concentrations from sample 1505 A range from 96 to 294 ppm. Ta contents from the sample range from 16 to 28 ppm. Nb and Hf range in concentration from 203 to 416 ppm and from 5 to 8 ppm, respectively. Rutile from sample 1511 has Zr and Hf contents of 81–159 ppm and 3–7 ppm, respectively. The Nb and Taconcentrations vary from 141 to 400 ppm and from 11 to 26 ppm. Although Fe contents of all rutile grains from eclogite samples range between 2812 and 7685 ppm, one rutile grain occurring in the matrix from sample 1511 shows the highest Fe concentration of 16320 ppm.

Rutile grains commonly display compositional zoning for some trace elements (Table 1; Fig. 4). The core of the matrix rutiles has low contents of Zr (96–110 ppm), Nb (213–216 ppm) and Ta (16–18 ppm). In contrast, the rims yield relatively variable and generally high contents of Zr (127–160 ppm), Nb (304–416 ppm) and Ta (17–28 ppm).

One rutile grain from sample 1505A has an unexpectedly high Zr content of 294 ppm. Detailed investigation of BSE images and EDS (energy dispersive spectroscopy) analyses revealed tiny, often submicron-sized inclusions in rutile. It is difficult to avoid micron and submicron-sized inclusions, especially those below the surface due to the relatively big LA-ICPMS spot (30 μm). In the time-resolved LA-ICPMS count diagram (Fig. 5b, c), rutile grains with unexpectedly high Zr content show different Zr and Hf, which proves involvement of baddeleyite inclusions.

The correlation between concentrations and element ratios changes from sample to sample, and is more pronounced for Nb and Ta than for Zr and Hf elements. Nb and Ta from two eclogite samples exhibit a strong positive correlation (Fig. 6a). Zr and Hf also indicate a positive correlation (Fig. 6b). On the other hand, Ta and Zr show a negative correlation (1511), but Ta and Zr from sample 1505A are randomly distributed (Fig. 6c).

Rutile in all analysed eclogite samples has Nb/Ta ranging from 11 to 19 with an average of 15. Zr/Hf ratios of rutile from eclogites range between 15 and 29 with an average of 21. The cores of rutile grains from sample 1505A are generally characterized by low con-

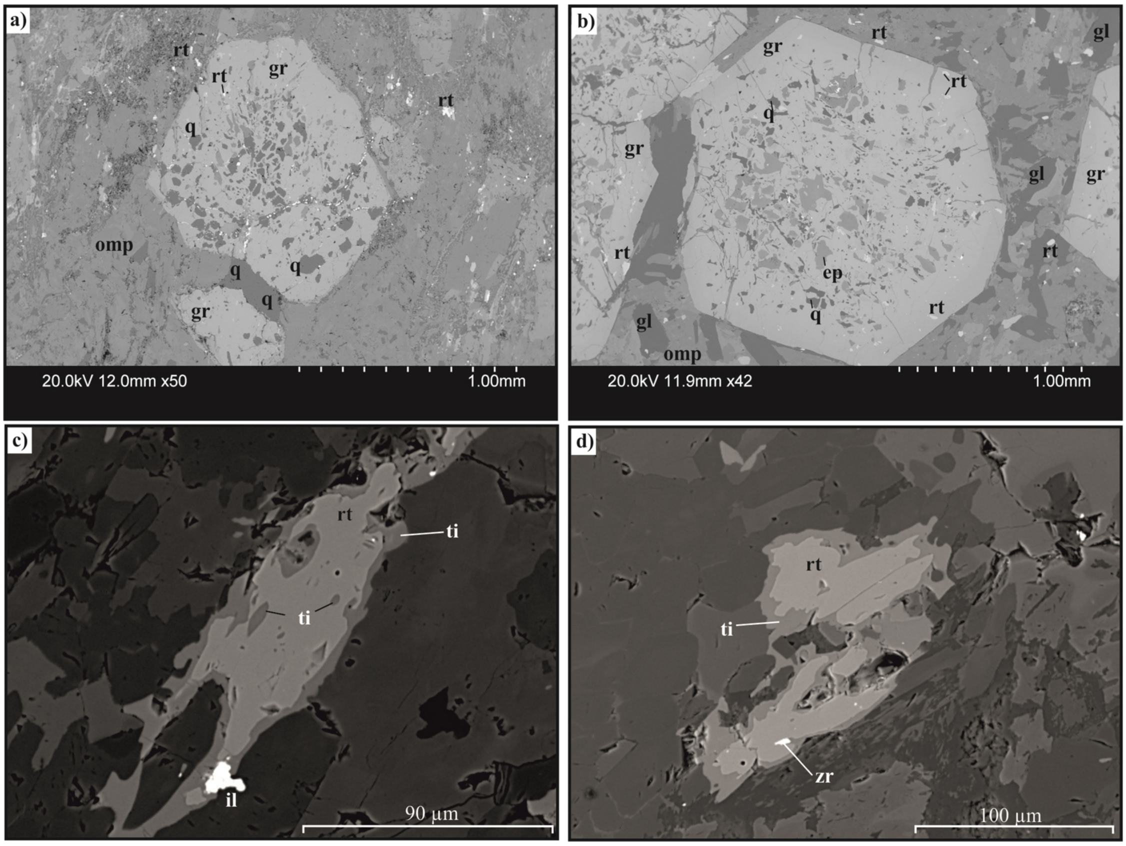

Fig. 3. BSE images of typical eclogite paragenesis and textures, (a) Eclogitic paragenesis with garnet, omphacite, and glaucophane, (b) Garnet porphyroblasts contain glaucophane, epidote, quartz and rutil inclusions, (c) Titanite inclusions in rutile, (d) Rutile grains are mantled by titanite (gr: garnet, omp: omphacite, ep: epidote, gl: glaucophane, il: ilmenite, q: quartz, rt: rutile, ti: titanite, zr: zircon).

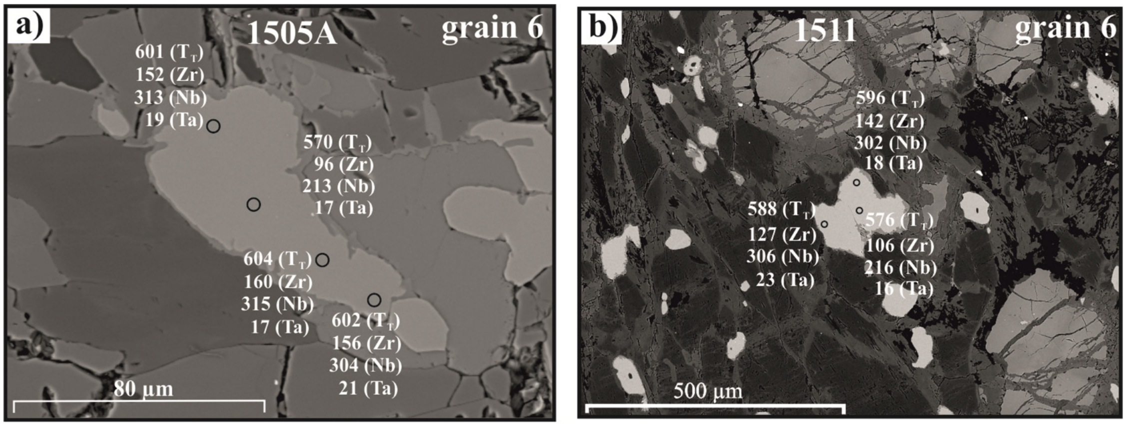

Fig. 4. BSE images of rutile from sample 1505A (grain 6) and 1511 (grain 6) used for multiple measurements. (a-b) the core of rutile grain has low contents of Zr, Nb and Ta but the rim is enriched in Zr, Nb and Ta. Circles mark the location of the spots analysed. The numbers give T_T in °C and the contents of Zr, Nb and Ta in ppm.

tents of Zr, Nb and Ta with low Nb/Ta ratios of 12–13, whereas the rims show relatively high contents of Zr, Nb and Ta with partly elevated and dispersive Nb/Ta ratios of 14–19. The cores of rutile grains from sample 1511 are characterized by low contents of Zr, Nb and Ta with low Nb/Ta ratios of 14, whereas the rims show relatively high contents of Zr, Nb and Ta with Nb/Ta ratios of 13–16. Both Nb/Ta and Zr/Hf increase with a decrease in Ta and Hf concentrations (Fig. 7a, b). Rutile compositions mostly display subchondritic Nb/Ta values (chondritic value 19.9, Münker et al., 2003) and Zr/Hf values (chondritic value 34.3 ± 0.3, Münker et al., 2003) (Fig. 7c). However, one rutile grain from sample 1505A has suprachondritic Nb/Ta and Zr/Hf values.

3.2. Zr-in-rutile thermometry

The measured Zr concentrations of rutile grains and corresponding Zr-in-rutile temperatures are given in Table 1. The Zr contents of rutile grains range between 81 and 160 ppm with an average of 123 ppm. One grain from sample 1505A with the highest Zr content (294 ppm) was excluded from calculation of temperatures due to baddeleyite inclusions in rutile. The temperatures were calculated using the pressure-dependant Zr-in-rutile thermometer of Tomkins et al. (2007). A minumum pressure of 10 kbar estimated from the jadeite content of the sodic pyroxene (Okay and Monié, 1997) was used to calculate temperature estimates. In detail, eclog-

Table 1
LA-ICPMS trace element concentrations and estimated temperatures of rutile by Zr-in-rutile thermometry.

Element (ppm)	Grain no	Cr	Fe	Zr	Nb	Hf	Ta	Nb/Ta	Zr/Hf	T °C
Sample no										
1511	1	659	16320	94	400	5	25	16	21	568
	4	566	4162	140	297	7	18	16	20	595
	5–1	623	5408	104	302	5	19	16	21	574
	5–2	693	3935	101	294	6	16	18	17	573
	6–1	560	5511	142	302	7	18	16	22	596
	6–2	481	3873	106	216	5	16	14	21	576
	6–3	436	5446	127	306	6	23	13	22	588
	11	696	5128	81	316	6	19	17	15	559
	12	554	4967	101	296	4	20	15	25	573
	13	582	7685	159	223	6	16	14	26	604
	14	930	3282	157	141	7	11	13	22	603
	17	619	4113	111	334	5	18	19	22	579
	18	293	5835	92	391	3	26	15	29	567
	19	562	3043	82	223	4	20	11	21	559
	21	249	4034	132	279	7	18	15	19	591
									Ave	**580**
1505A	1	688	5100	133	317	7	17	19	18	591
	6–1	603	5501	152	313	7	19	16	22	601
	6–2	514	2812	96	213	5	17	13	19	570
	6–3	651	6272	160	315	8	17	19	20	604
	6–4	516	6438	156	304	7	21	14	22	602
	8–1	338	5826	157	416	8	28	15	20	603
	8–2	437	3028	110	214	7	18	12	16	578
	8–3	505	5202	133	321	6	21	15	22	591
	9	485	3466	118	211	5	16	13	24	583
	10	393	3472	112	203	5	16	13	22	579
	11	539	7353	150	316	7	22	14	21	600
	13	252	3062	113	281	7	19	15	16	580
	14	376	2899	294	216	8	17	13	37	649
	15	396	4044	116	210	7	16	13	17	582
									Ave	**590**

Temperatures were estimated according to the thermometry of Tomkins et al. (2007) at 10 kbar.

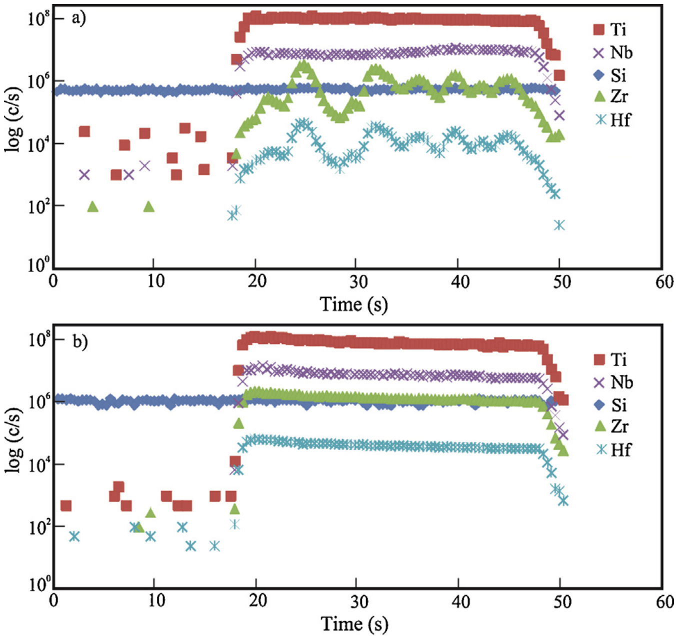

Fig. 5. (a) Time-resolved LA–ICPMS count diagram (with logarithmic coordinates) of sample 1513, showing anomalous Zr and Hf counts with regular Ti, Si and Nb counts (c) A real rutile analysis diagram.

Table 2
Zr concentrations from different positions in rutile grains.

Sample	1505A Zr (ppm)	1511 Zr (ppm)
Rt in matrix	152	142
	96	106
	160	127
	156	159
	157	157
	110	111
	133	94
	118	82
	112	132
	294	
Rt in garnet	133	92
	150	140
	113	104
	116	101
		81
		101

ite sample 1505A has Zr contents of 113–150 ppm for four rutile inclusions in garnet, corresponding to temperatures of 580–600 °C. Nine matrix rutiles have Zr contents of 96–160 ppm corresponding to temperatures of 570–604 °C. Eclogite sample 1511 has Zr contents of 81–140 ppm for six inclusion rutiles in garnet and 82–159 ppm for nine matrix rutiles. Calculated temperatures are 559–595 °C for the inclusion rutiles, and 559–604 °C for the matrix rutiles. Zr contents of both inclusion rutile and matrix rutile are identical, which suggest that all rutiles grew under similar metamorphic conditions. In contrast, the cores of some grains from sample 1505A have Zr contents of 96–110 ppm and Zr-in-rutile temperatures of 570–578 °C. Zr contents of the rims range from 133 to 160 ppm. Zr-in-rutile temperatures gave 591–604 °C. For sample 1511, the core has Zr content of 106 ppm, corresponding to temperatures of 576 °C and Zr content of the rim ranges from 127 to 142 ppm, corresponding to temperatures of 588–596 °C. Zr-in-rutile thermometer shows that the temperatures of the rim are approximately 20 °C higher than the core. When all results are combined, the Zr-in-rutile thermometer of Tomkins et al. (2007) gives 559–604 °C with an average temperature of 585 °C for eclogite from the Karakaya Complex.

4. Discussion

4.1. Trace element characteristics of rutile

Rutile is the main host mineral for Nb and Ta in metamorphic rocks. Nb and Ta dominate the whole rock Nb and Ta budget, and the average Nb/Ta ratio of rutile may be identical to that of the bulk rock. Rutile grains from two eclogite samples have relatively high HFSE contents such as Nb (141–416 ppm), Ta (11–28 ppm), Zr (81–160 ppm), and Hf (3–8 ppm). The Nb and Ta values are almost entirely controlled by the Ti phases, those of Zr-Hf are significantly influenced by zircon as well as garnet and pyroxene (Pfander et al., 2007; Schmidt et al., 2009). The analysis showing the highest Fe content (16320 ppm) resulted from sampling of microscale mineral inclusions in the form of very tiny ilmenite or iron oxide lamellae. One rutile grain from sample 1505A has an unexpectedly high Zr content of 294 ppm caused by the presence of baddeleyite inclusions. Replacement by rutile of a pre-existing Zr-rich mineral like ilmenite is a possible explanation for the formation of these Zr-rich phase separations in rutile (Austrheim et al., 2008; Meyer et al., 2011).

Trace element zonation in rutile from eclogite samples is observed based on the notable increase in Zr, Nb and Ta contents and slightly high Nb/Ta and Zr/Hf ratios from core to rim. Trace element zonation may occur either during growth or by diffusion. Growth zoning is possibly driven by changes in source composition or in pressure-temperature conditions, which result in variation of element partitioning during growth of the mineral (Kohn, 2003; Ding et al., 2009; Gao et al., 2014). Diffusion zoning is caused by a difference in chemical potential; a pre-existing grain is changed in composition by exchange of material with the rock matrix. The diffusive loss of Zr from rutile is not expected during eclogite-facies metamorphism based on the low diffusion rate of Zr in rutile (Cherniak et al., 2007). Experimentally determined diffusion coefficients for Zr, Hf, Nb and Ta in rutile show complete resetting of rutile compositions at 750 °C requires 15.5 My for a small rutile grain with a size of 100 μm and 62.2 My for a large rutile grain with a size of 200 μm (Cherniak et al., 2007; Marschall et al., 2013). Decreasing Zr toward the rims of grains is evidence for diffusive resetting of Zr and is also expected through diffusive resetting of the Zr-in-rutile thermometer (Kohn et al., 2016). Therefore, the Zr, Nb and Ta are significantly enriched in the rim and thus zonation of rutile cannot be attributed to the diffusion effect. Instead, it more probably resulted from growth zoning.

Nb/Ta ratios for rutile rims and cores are different from each other in eclogite samples. The cores of rutile grains from eclogite samples are generally characterized by low Nb/Ta ratios of 12–14 whereas the rims exhibit relatively high Nb/Ta ratios of 13–19. The cores with low Nb/Ta ratios are ascribed to rutile growth from mineralogical reactions in association with eclogite-facies metamorphic dehydration during prograde subduction, whereas the high Nb/Ta ratios in the rims of rutile are attributed to rutile growth from the aqueous solution that is the phase separated product of supercritical fluid during exhumation. The increase in Nb/Ta and Zr/Hf ratios is mainly caused by a decrease in Ta and Hf contents (Fig. 7a, b). This suggests that differential incorporation of Nb and Ta into rutile during its growth is a basic cause of the Nb/Ta differentiation due to a significant difference in their mass. Accordingly, the increase in Nb/Ta ratios with the decreased Ta content can be linked to the effect of metamorphic dehydration in subduction zones on rutile Nb/Ta differentiation (Schmidt et al., 2009; Gao et al., 2014). Dehydration metamorphism is a common mechanism for rutile formation in subduction processes. The breakdown of HP hydrous minerals such as phengite can give rise to the enrichment of water-insoluble incompatible trace elements such as Nb, Ta with slightly high Nb/Ta ratios in the rims of rutile (Stepanov and Hermann, 2013). Phengite in metamorphic rocks preferentially incorporate Nb over Ta. Thus, the aqueous solution of high Nb/Ta ratios can be derived from metamorphic dehydration due to the breakdown of phengite during the exhumation based on the experimental study of Stepanov and Hermann (2013). Rutile grains from two eclogite samples display subchondritic Nb/Ta values (chondritic value 19.9, Münker et al., 2003) and Zr/Hf values (chondritic value 34.3 ± 0.3, Münker et al., 2003) (Fig. 7c). It is probable that the subchondritic Nb/Ta ratios may record rutile growth from local sinks of aqueous fluids formed by metamorphic dehydration. Moreover, low Nb/Ta ratios in rutile would be formed if its growth is associated with prograde eclogite-facies metamorphism during subduction. In contrast, suprachondritic Nb/Ta ratios may suggest rutile growth from supercritical fluids or their products of phase separation into immiscible aqueous fluids and hydrous melts (Zheng at al., 2011b).

Trace element analyses in rutile suggest that rutile rims may have crystallized from a kind of geofluid that has a high content of water-insoluble trace elements such as Nb and Ta. The significant enrichment of HFSE in the rutile rims demonstrates that the geofluid could have the property of a supercritical fluid. However, rutile rims were not crystallized directly from the supercritical fluid due to its great capacity to dissolve various elements. It would probably have precipitated from its derivative (i.e. the product of its phase separation into aqueous solution). Fluid-immobile incompatible trace elements such as HREE and HFSE can be dissolved and transported by the supercritical fluid under subduction-zone high-pressure metamorphic conditions (e.g. Tatsumi and Nakamura, 1986; Scambelluri et al., 2001; John et al., 2004; Hermann et al., 2006; Xia et al., 2010; Zheng et al., 2011b; Gao et al., 2014). Rutile grains crystallized prior to peak metamorphic conditions and hence the rock was still subducting.

4.2. Zr-in-rutile temperatures

The application of the Zr-in-rutile geothermometer of Tomkins et al. (2007) requires a pressure estimate for rutile growth which is, however, difficult to assign to individual rutile grains. The larger Zr^{4+} cation would be less able to substitute for the smaller Ti^{4+} due to increasing pressure, and thus the Zr content of rutile decreases with increasing pressure, resulting in lower temperatures. On the other hand, the garnet-clinopyroxene Fe-Mg exchange thermometer has larger uncertainty (usually ± 50 °C even up to ± 250 °C; Proyer et al., 2004) due to the unreliable estimation of Fe^{+3} in clinopyroxene using electron microprobe analyses. This is particularly true in the eclogite facies, where the clinopyroxene is omphacitic and can have a high content of trivalent ions. Eclogites from the Karakaya Complex underwent retrogression and that retrograde fluid was internally buffered in stable isotope compositions. The fluid activity is obvious during the exhumation and allows the reequilibration of element/isotopes in the mineral that formed under the eclogite-facies conditions. Therefore, the temperatures obtained from element/isotope exchange thermometers between coexisting minerals can give lower metamorphic temperatures (Zhang et al., 2010; Zheng et al., 2011a). Thus, Zr-in-rutile thermometry of Tomkins et al. (2007) with a pressure correction is an excellent alternative when researching HP/UHP terranes and investigating their equilibration temperature estimations. Accordingly, the significance of a pressure correction should not be ignored for rocks which not only experienced more pressure but also underwent lower pressure dominated metamorphism. It is noted that pressure used for eclogites was assumed to be 10 kbar in

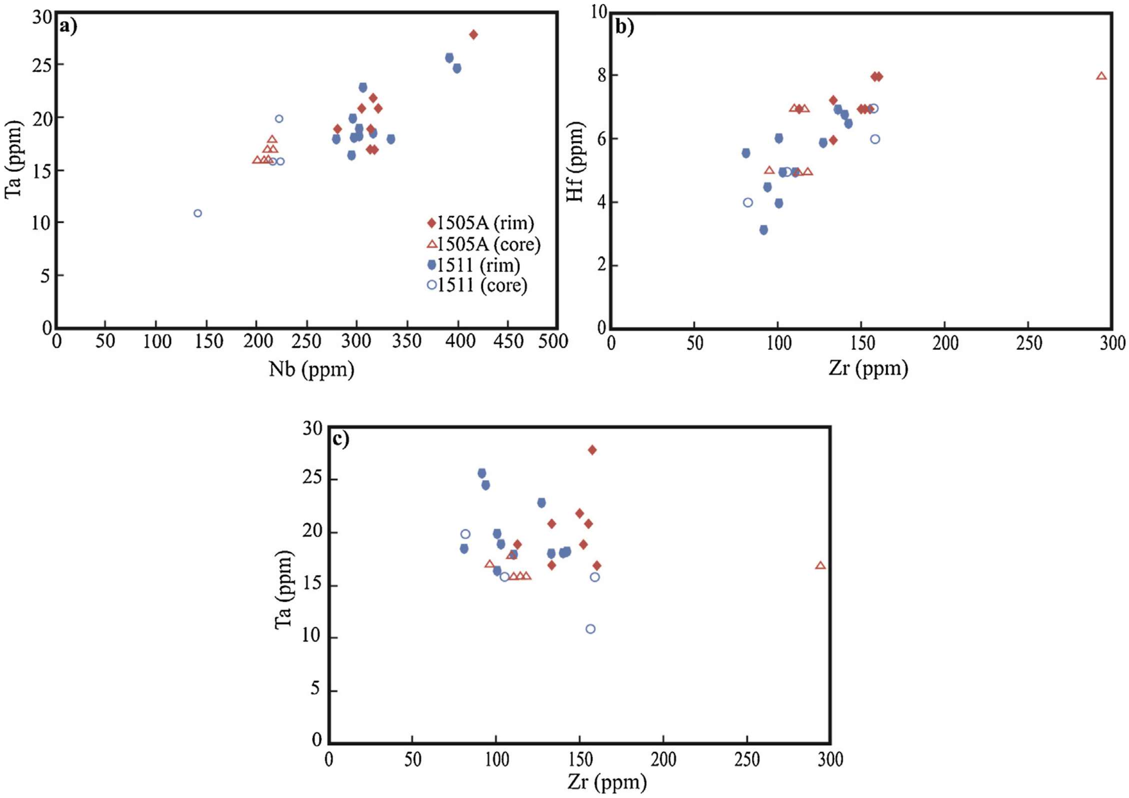

Fig. 6. Results for HFSE concentrations of rutile from eclogites. Points refer to individual analyses. (a) Nb versus Ta indicating a strong positive correlation. (b) Zr versus Hf also shows positive correlation. (c) Zr versus Ta showing negative correlation except one sample (1505A).

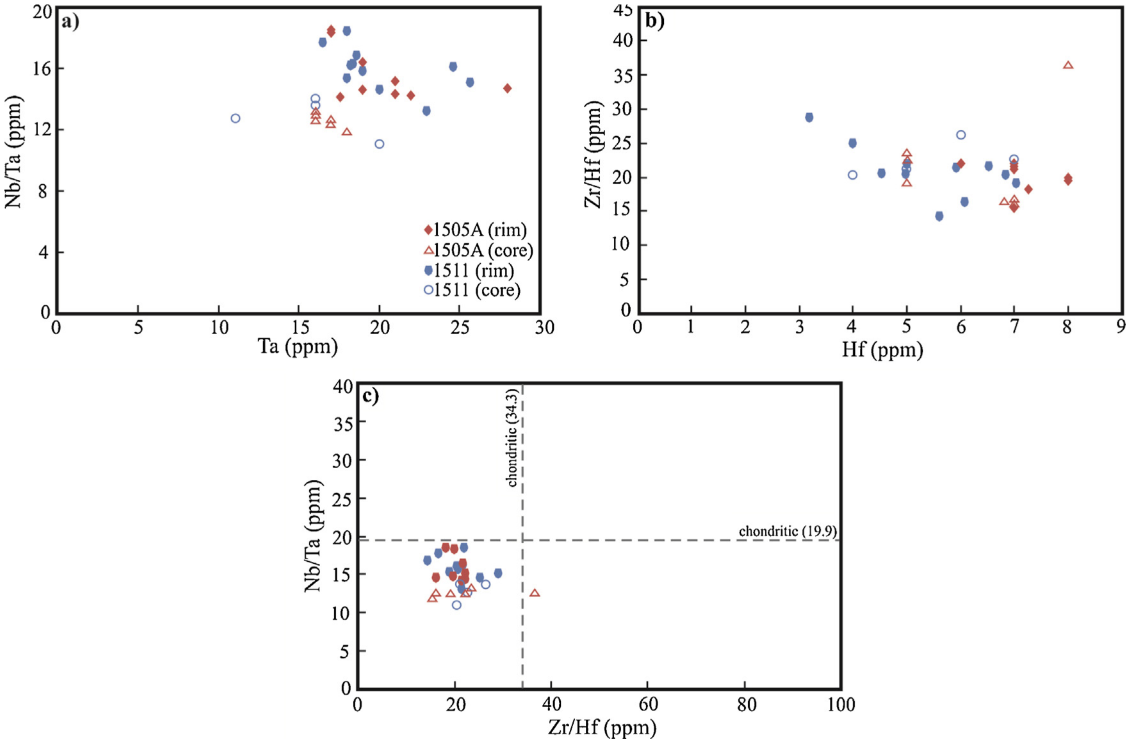

Fig. 7. Element ratio plots. Points represent individual analyses. (a) Ta versus Nb/Ta. (b) Hf versus Zr/Hf. (c) Zr/Hf versus Nb/Ta diagram. Generally, Nb/Ta and Zr/Hf of rutile are subchondritic. Dashed lines refer to chondritic values for Nb/Ta and Zr/Hf (Münker et al., 2003).

the equation of Tomkins et al. (2007) based on a conventional geothermobarometer estimation of 10 kbar for the condition of eclogite-facies metamorphism. The Zr-in-rutile thermometer of Tomkins et al. (2007) gives temperatures of 559–604 °C with an average temperature of 585 °C for eclogites from the Karakaya Complex. This average temperature is interpreted as growth temperature of rutile during subduction before the peak pressure. The corresponding Zr-in-rutile temperature (average 585 °C) is higher than temperature estimations by conventional thermometers based on the mineral assemblage in eclogite.

There are differences in Zr contents between the core and rim of some rutile grains. The core of rutile grains from eclogite samples shows a variation in Zr content from 96 to 110 ppm, corresponding to Zr-in-rutile temperatures of 570–578 °C. The Zr contents of their rims vary from 127 to 160 ppm, corresponding to Zr-in-rutile temperatures of 588–604 °C. These Zr-in-rutile temperatures for the rims are about 20 °C higher than those for the cores. This suggests that the outermost rims grow at higher temperatures than the core. The intergranular Zr variation during rutile growth can result from the preservation of primary Zr concentrations at different temperatures during prograde metamorphism (Luvizotto and Zack, 2009; Pape et al., 2016).

It is noted that both Zr contents and calculated temperatures of inclusion rutile and matrix rutile from two eclogite samples overlap each other (Table 1). This suggests that eclogites occurring in the eastern part of Bandırma (Karakaya Complex) belong to the same tectonic slice and underwent a similar metamorphic evolution. Moreover, rutile inclusion in garnet probably retains its original equilibrated Zr contents, given the very restricted ability to exchange Zr with the host phase during retrogression. The new Zr-in-rutile temperatures of eclogites in the Karakaya Complex show that eclogites were buried to at least 35 km depth within the subduction channel.

5. Conclusions

The following major conclusions are derived from this study of eclogites in the Karakaya Complex:

1) There is a trace element zonation in rutile from eclogite samples with a remarkable increase in Zr, Nb and Ta contents from core to rims. The Zr, Nb and Ta are significantly enriched in the rim and thus zonation of rutile can be ascribed to growth zoning instead of diffusion effects. The enrichment of Nb and Ta in rutile rims suggests local enrichment of water-insoluble incompatible trace elements in metamorphic fluid, which may be the product of phase separation from a supercritical fluid during exhumation.
2) The Nb/Ta and Zr/Hf ratios increase with a decrease in Ta and Hf contents, which could be ascribed to the effect of metamorphic dehydration in subduction zones on rutile Nb/Ta differentiation. The rutile grains from eclogites in the Karakaya Complex are dominated by subchondritic Nb/Ta and Zr/Hf ratios. It can be noted that the subchondritic Nb/Ta ratios may record rutile growth from local sinks of aqueous fluids from metamorphic dehydration. Subchondritic Nb/Ta ratios of rutile would be produced if its growth is associated with prograde eclogite-facies metamorphism during subduction.
3) The rutile grains have higher Zr contents in the outermost rims compared to those in the core. The Zr-in-rutile temperatures of the rims are approximately 20 °C higher than those of the cores. This suggests that the rims grew from a different fluid at higher temperatures than for the core. Therefore, the difference in fluid composition can give rise to the difference in metamorphic temperature.
4) The Zr-in-rutile thermometer of Tomkins et al. (2007) gives temperatures of 559–604 °C with an average temperature of 585 °C for eclogites from the Karakaya Complex. This average temperature suggests the growth temperature of rutile. The corresponding Zr-in-rutile temperature (average 585 °C) is higher than temperature estimations of conventional Fe-Mg exchange thermometers. Therefore, Zr-in-rutile thermometry of Tomkins et al. (2007) with a pressure correction is the best choice for temperature calculation. Furthermore, Zr contents and calculated temperatures of inclusion rutile and matrix rutile from two eclogite samples are identical, which suggests that eclogites within the Karakaya Complex belong to the same tectonic slice and all rutiles grew under the same P-T conditions during the subduction.

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