# Ti- and Zr-minerals in calcite-dolomite marbles from the ultrahigh-pressure Kimi Complex, Rhodope mountains, Greece: Implications for the *P-T* evolution based on reaction textures, petrogenetic grids, and geothermobarometry

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#### ABSTRACT

Rutile, titanite, and zircon formed as relatively coarse-grained accessory minerals in several samples of high-grade calcite-dolomite marble with an early ultrahigh-pressure history. These minerals decomposed to a texturally complex set of secondary minerals during subsequent stages of retrograde metamorphism. The reactions involve several generations of geikielite-ilmenite as well as zirconolite [(Ca,Th,U)Zr(Ti,Fe,Nb,Ta)<sub>2</sub>O<sub>7</sub>], kassite/cafetite [CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub>/CaTi<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O], Ti-bearing humite group minerals, thorianite, and sometimes euxenite [(Ca,U,Th,REE)(Nb,Ta,Ti)<sub>2</sub>(O,OH)<sub>6</sub>]. Stable coexistence of zircon and olivine is observed and stably coexisting titanite with olivine and/or humite-group minerals is reported here for the first time outside of carbonatites, kimberlites, or lamprophyres. Petrogenetic grids constructed for Ti- and Zr-bearing olivine/antigorite-saturated calcite-dolomite marbles show that geikielite is stable at highest pressures, followed by titanite and rutile, and that baddeleyite + diopside replaces zircon + calcite to higher pressures. The observed reaction textures are consistent with an earlier derived P-T path for the Kimi Complex. They corroborate a period of heating during decompression from 25 to 20 kbar and ca. 800 °C, where the assemblage olivine-diopside-spinelrutile-zircon formed. This assemblage partially re-equilibrated during subsequent decompression and cooling, thus forming the observed reaction textures. Even though no memory of the UHP path is preserved in the accessory minerals, their reaction relationships turn out to be potentially very useful for geothermobarometry over a large range of metamorphic conditions.

Keywords: Ti-minerals, zirconolite, kassite, cafetite, impure calcite-dolomite marbles

## INTRODUCTION

Zr- and Ti-minerals in carbonate rocks are rarely discussed in the context of regional metamorphism. Their low modal abundance and the fact that reactions among them are characterized by very slow reaction rates-rims of ilmenite or titanite around rutile are a very common feature in metabasites or metapelitesmakes them very difficult to use for geothermobarometry or the mapping of isograds on a regional scale. A notable exception exists in the field of contact metamorphism: Ferry (1996) mapped isograds of Ti- and Zr-minerals around the Ballachulish contact aureole in Scotland. In a follow-up study, Ferry et al. (2002) calibrated the breakdown of rutile + magnesite to geikielite and of zircon + magnesite to baddeleyite + forsterite experimentally. Fraser et al. (2004) then dated baddeleyite from the Ballachulish aureole to determine the age of the reaction zircon + dolomite = baddeleyite + forsterite + calcite + CO<sub>2</sub>. Marble-hosted zircons have been used in several cases for dating (e.g., Liu et al. 2006; Garnier et al. 2006) and for inclusion studies, e.g., for finding ultrahigh-pressure mineral inclusions in zircons from diamondbearing marbles in Kokchetav (Katayama et al. 2002), but only Ferry and co-workers have yet been using it as an actual participant in metamorphic reactions with other Zr-minerals. Titanite is a typical mineral in regional or contact metamorphic calcite marbles. Rutile is less commonly reported from marbles, but can be found—particularly in those cases where pieces of marble are dissolved in hydrochloric acid and the insoluble residues investigated (e.g., Sastna and Prikryl 2009). The two minerals are related by the reaction

$$rutile + calcite + quartz = titanite + CO_2$$
(1)

which is valid for calcite-dolomite marbles, too, as long as they are quartz-bearing. Titanite in quartz-free calcite-dolomite marbles is very rare and has not yet been observed coexisting with diopside or even olivine (Dunn 2005). Rutile has been reported as part of the assemblage forsterite + clinochlore + calcite + dolomite + spinel + graphite in a marble xenolith in a diorite pluton (Young and Morrison 1992), but the usual Ticarrier in a forsterite-bearing marble is humite-group mineral,

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often Ti-clinohumite (e.g., Franz and Ackermand 1980; Ehlers and Hoinkes 1987; Tropper et al. 2007, etc.)

The main focus of this contribution is a description of the reaction textures and products generated by a multi-stage breakdown of Zr-bearing rutile in a calcite-dolomite marbles, the construction of petrogenetic grids for Ti- and Zr-bearing calcite-dolomite marbles to establish a general understanding of stability fields, and geothermobarometry that includes Ti- and Zr-minerals for a more detailed and refined understanding of the metamorphic evolution of these rocks.

Among the less common minerals involved are zirconolite, euxenite, geikielite, and kassite/cafetite, and the accompanying U/Th-minerals U-pyrochlore and thorianite (Th,U)O<sub>2</sub>. Out of these, zirconolite has received much attention from applied mineralogists due to its capacity to accommodate and store radioactive elements and is one of the components in "Synroc" ceramics for nuclear waste management (URL: http://www. world-nuclear.org/info/inf58.html. Accessed: 2014-05-13. Archived by WebCite at http://www.webcitation.org/6PXAdIuFg).

In natural samples, the Ca-Zr-titanate zirconolite with the ideal formula CaZrTi<sub>2</sub>O<sub>7</sub> is a relatively rare accessory mineral that has been reported from ultramafic to intermediate Si-undersaturated magmatic rocks including kimberlites and carbonatites, from some high-grade marbles and granulites as well as several lunar samples (e.g., from Apollo 17 sample-norite 78235; Zhang et al. 2012). A detailed review about zirconolite occurrences is given by Gieré et al. (1998) who also summarize the range of compositional variations as follows: The M8 site of Ca can also be occupied by actinides (ACT, mainly U<sup>4+</sup> and Th<sup>4+</sup>) and rare earth elements (REE). The M7 site of Zr4+ is of course also used by Hf4+ and rarely by small amounts of actinides and REE. The M5,6 sites of Ti show a broad range of substitutions by Me<sup>2+</sup>, Me<sup>3+</sup>, and Me<sup>5+</sup> ions, and in rare instances also by Zr<sup>4+</sup> or W<sup>6+</sup>.  $Me^{2+} = Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ;  $M^{3+} = Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ;  $Me^{5+} = Al^{3+}$ Nb<sup>5+</sup>, Ta<sup>5+</sup>. Natural zirconolites can be described by the five end-members CaZrTi<sub>2</sub>O<sub>7</sub>, CaZrMe<sup>5+</sup>Me<sup>3+</sup>O<sub>7</sub>, ACTZrTiMe<sup>2+</sup>O<sub>7</sub>, REEZrTiMe3+, and REEZrMe5+Me2+O7. Zirconolites from contact and regional metamorphic metacarbonate rocks have been described by Purtscheller and Tessadri (1985), Gieré (1986, 1989), Williams and Gieré (1988), Kato and Matsubara (1991), Stucki et al. (2001), Nishio and Minakawa (2004), Tropper et al. (2007), and Pascal et al. (2009). According to Gieré et al. (1998), zirconolites from metacarbonate rocks are low in Nb and Ta and can be described by the two main substitutions ACTMe<sup>2+</sup>Ca<sub>-1</sub>Ti<sub>-1</sub> and REEMe<sup>3+</sup>Ca<sub>-1</sub>Ti<sub>-1</sub>.

Geikielite (ideally MgTiO<sub>3</sub>) is the Mg-equivalent of ilmenite with which it forms a complete solid-solution series. Hence, members of this series with  $X_{Mg} > 0.5$  are called geikielite, those with  $X_{Mg} < 0.5$  are ilmenite. It is a typical mineral for high-grade metamorphic dolomitic marbles and also occurs in carbonatites, kimberlites, and serpentinized ultramafic rocks. Significant amounts of Mn (end-member pyrophanite MnTiO<sub>3</sub>) can also be present.

Kassite [ideal formula  $CaTi_2O_4(OH)_2$ ] and its polymorph cafetite (ideal formula  $CaTi_2O_5 \cdot H_2O$ ) are rare hydrous Timinerals, which were first described from the Afrikanda pyroxenite massif, Kola peninsula, Russia (Evans et al. 1986, and references therein), where they occur as fillings of miarolithic

cavities in alkali pegmatites, apparently as breakdown products of precursors like perovskite, rutile, and ilmenite. Mitchell and Chakhmouradian (1998) describe kassite as a replacement product of perovskite in a kimberlite and Popova et al. (1998) and Grey et al. (2003) describe chromian kassite as a secondary mineral from a chromite deposit in the Northern Urals. If the present mineral can be confirmed as kassite or cafetite, it would be to our knowledge the first report of such a mineral from a regional metamorphic marble.

## **GEOLOGICAL CONTEXT AND SAMPLE PETROGRAPHY**

In the Rhodope mountains of northeastern Greece (Fig. 1) microdiamond-bearing gneisses have been reported from the high-grade metamorphic Kimi Complex, indicating a Jurassic ultrahigh-pressure history (Mposkos and Kostopoulos 2001; Perraki et al. 2006; Baziotis et al. 2008; Bauer et al. 2007). The Kimi Complex consists of various rock-types: leucocratic orthogneisses, paragneisses, and micaschists, serpentinites, mafic granulites, eclogites, and amphibolites as well as marbles with a complex tectonometamorphic history lasting from at least 180 to 65 Ma (Mposkos and Krohe 2006; Bauer et al. 2007; Krenn et al. 2010). The marbles are predominantly white and very pure calcite marbles, but subordinate calcite-dolomite marbles have been found near the village of Organi and were studied with regard to their metamorphic record by Mposkos et al. (2006) and Proyer et al. (2008). All calcite-dolomite marbles contain additional phlogopite and most of them also olivine and diopside, where olivine replaces a first generation of rarely preserved diopside-1 and is overgrown itself by a thin corona of diopside-2. Spinel and Ti-clinohumite can be present as additional "peak metamorphic" phases, whereas slightly aluminous tremolite, chlorite, and serpentine have partially or completely replaced the aforementioned minerals during exhumation (Proyer et al. 2008). Zr- and Ti-bearing minerals (other than Ti-clinohumite) were observed in only four of these marble samples.

#### ANALYTICAL CONDITIONS

The mineral chemical analyses of lower precision level (Table 1) were carried out using a JEOL JSM 6310 high-resolution scanning electron microscope with an energy-dispersive system (EDS) and wavelength-dispersive (WDS) at the Institute of Earth Sciences, Karl-Franzens-University, Graz, Austria. Analytical conditions were: acceleration voltage 15 kV, beam current 6 nA, beam diameter  $1-4 \mu m$  and time for data acquisition 100 s. Na, F analyses were obtained using the WDS system with counting times of 20 s on the peak and 10 s on the lower and upper background. Mineral standards, used for the normalization of the elements were: calcite (Ca), magnesite (Mg), siderite (Fe), and rodochrosite (Mn) for the carbonates, garnet (Mg, Fe), corundum (Al), quartz (Si), adularia (K), titanite (Ca, Ti), rhodonite (Mn), jadeite (Na), and F-phlogopite (F) for the silicates and oxides. The 1 $\sigma$  standard deviations range between 0.08 wt% for transition elements to 0.16 wt% for Si and Al, and 0.28 wt% for Mg (all EDX) and 0.06 for Na (WDX) for high concentrations and are always less than 1.5% of the analyzed value.

Additional electron-microprobe analyses of samples were performed in the wavelength-dispersive mode using the JEOL JXA-8500F (Hyperprobe) at the Deutsches GeoForschungsZentrum in Potsdam, Germany. Operating conditions involved an accelerating voltage of 15 or 20 kV, a beam current of 20–40 nA, and a beam diameter of 1  $\mu$ m. *Ka*-lines were used for Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe; *La*-lines for Y, Sr, Zr, Nb, La, Ce, Yb, Lu, Ta, and W; *Lβ*-lines for Pr, Nd, Sm, Gd, Dy, Ho, and Hf; *Ma*-line for Th; and *Mβ*-lines for Pb and U. The counting times on the peaks were 20–100 s for the elements and, in each case halftime for background counts on both sides of the peak. X-ray lines and background offsets were selected so to minimize interference between elements during analysis. Standards for calibration were well-characterized natural and synthetic materials

TABLE 1a. Selected SEM (EDS) analyses of geikielite, ilmenite, spinel, chlorite, olivine, and diopside

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Sample	Fig. 4c	Fig. 4c	Fig. 4c	5K6a1	5K6a2	5K6b	5K6a1	5K6a2	4RA28	4RA28	5K6a2	5K6a2	5K6a2	4RA28
Mineral	gk-1	gk-2l	gk-3	ilm-3	gk-3	spl	chl	ol	ol	chl	срх	срх	срх	срх
SiO <sub>2</sub>	n.d.	n.d.	8.35	0.26	1.04	n.d.	30.70	42.35	40.70	34.36	56.42	55.58	54.41	56.25
TiO <sub>2</sub>	64.50	64.16	38.56	54.50	49.00	n.d.	0.39	n.d.	0.05	0.04	n.d.	n.d.	0.36	n.d.
$AI_2O_3$	n.d.	n.d.	0.74	n.d.	0.41	70.46	20.09	n.d.	n.d.	14.58	0.00	0.89	1.83	0.20
$Cr_2O_3$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.
FeO	7.03	8.22	27.05	37.16	9.24	1.81	0.57	1.74	11.75	4.63	0.26	0.20	0.28	1.38
MnO	0.00	0.00	2.72	2.43	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	0.01
MgO	28.48	27.71	9.89	4.21	26.00	27.78	36.21	56.15	47.66	34.91	18.74	18.49	18.19	18.37
CaO	n.d.	n.d.	0.27	0.10	0.36	n.d.	0.12	0.00	0.05	0.02	25.06	25.58	25.25	24.98
Na₂O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.05	n.d.	0.00
Total	100.01	100.09	87.58	98.66	86.05	100.04	88.08	100.25	100.31	88.63	100.48	100.79	100.32	101.19
Si	-	-	0.21	0.01	0.02	-	2.83	1.00	1.00	3.20	2.02	1.99	1.96	2.01
Ti	1.00	1.00	0.74	1.01	0.87	-	0.03	-	-	-	-	-	0.01	-
Al	-	-	0.02	-	0.01	1.98	2.18	1.60	-	0.04	0.08	0.01		
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe <sup>2+</sup>	0.12	0.14	0.51	0.76	-	0.01	0.04	0.03	0.24	0.36	0.01	0.01	0.01	0.04
Fe <sup>3+</sup>	-	-	0.07	-	0.18	0.02	-	-	-	-	-	-	-	-
Mn	-	-	0.06	0.05	-	-	-	-	-	-	-	-	-	-
Mg	0.88	0.86	0.38	0.15	0.91	0.99	4.97	1.97	1.75	4.84	1.00	0.99	0.97	0.98
Ca	-	-	0.01	-	0.01	-	0.01	-	-	-	0.96	0.98	0.97	0.96
Na	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SumCat	2.00	2.00	2.00	1.99	2.00	3.00	10.06	3.00	3.00	10.00	3.98	4.00	4.00	3.99
Note: n.d.	= not dete	cted, n.a. = r	not analyze	d; chl = chl	orite, cpx =	clinopyroxe	ene, gk = ge	ikielite, ilm	= ilmenite	, ol = olivin	ie, spl = spi	nel.		

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TABLE ID.	Selected SEIV	i iedoj analyses o	i phiodobite.	amphibole,	Kassile, l	itanite, ai	ia numite drou	o minerais

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Sample	5K6a1	5K3	5K6a2	5K6a2	5K6b	4RA28	4RA28	5K6a2	5K6a1	Fig. 4e	5K6b	Fig. 4g	Fig. 3a	Fig. 3d	5K3
Mineral	phl	phl	amp	amp	amp	amp	amp	kst	ttn	ttn	ttn	ttn	Ti-chu	Ti-cho	Ti-hu
SiO <sub>2</sub>	39.87	41.24	44.10	43.98	44.63	58.40	59.53	0.43	30.63	30.42	30.20	30.74	38.83	35.22	36.83
TiO <sub>2</sub>	0.61	0.70	1.00	0.61	0.72	n.d.	n.d.	66.12	38.82	38.02	38.37	38.34	3.22	7.17	4.52
Al <sub>2</sub> O <sub>3</sub>	17.31	13.12	14.05	15.48	14.47	0.85	n.d.	n.d.	1.95	1.88	1.81	1.89	n.d.	n.d.	n.d.
$Cr_2O_3$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	0.80	0.81	0.89	1.01	0.80	1.98	1.72	n.d.	n.d.	n.d.	n.d.	n.d.	1.54	1.64	1.47
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	27.58	27.17	19.33	19.31	19.39	22.48	23.27	0.54	n.d.	n.d.	n.d.	n.d.	55.06	55.01	55.90
CaO	n.d.	n.d.	13.12	13.34	13.12	12.92	13.06	22.67	28.82	28.39	28.29	29.02	n.d.	n.d.	n.d.
Na₂O	0.48	n.d.	3.20	2.87	3.24	0.23	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.
K <sub>2</sub> O	10.33	10.62	1.18	1.10	1.11	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.
F	0.24	0.56	0.63	0.50	0.66	0.32	0.33	0.29	0.39	0.32	0.52	0.23	1.03	1.26	1.02
0-	-0.10	-0.24	-0.27	-0.21	-0.28	-0.13	-0.14	-0.12	-0.16	-0.13	-0.22	-0.10	-0.17	-0.18	-0.16
Total	97.12	93.98	97.23	97.99	97.86	97.16	97.88	89.93	100.45	98.90	98.97	100.12	99.50	100.12	99.58
Si	2.74	2.93	6.26	6.16	6.28	8.01	8.07	0.02	1.00	1.00	1.00	1.00	4.00	2.00	3.00
Ti	0.03	0.04	0.11	0.06	0.08	-	-	1.98	0.95	0.94	0.95	0.94	0.25	0.31	0.28
Al	1.40	1.10	2.35	2.56	2.40	0.14	-	-	0.08	0.07	0.07	0.07	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe <sup>2+</sup>	0.05	0.05	0.07	-	0.06	0.23	0.08	-	-	-	-	-	0.13	0.08	0.10
Fe <sup>3+</sup>	-	-	0.03	0.16	0.04	-	0.12	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	0.01	0.01	-	-	-	-	-	-	-	-
Mg	2.83	2.88	4.09	4.03	4.07	4.60	4.70	0.03	-	-	-	-	8.46	4.66	6.79
Ca	-	-	1.99	2.00	1.98	1.90	1.90	0.97	1.00	1.00	1.00	1.01	-	-	-
Na	0.06	-	0.88	0.78	0.88	0.06	0.01	-	-	-	-	-	-	-	-
К	0.91	0.96	0.21	0.20	0.20	0.01	-	-	-	-	-	-	-	-	-
F	0.05	0.13	0.28	0.22	0.29	0.14	0.14	0.02	0.04	0.03	0.05	0.02	0.34	0.23	0.26
SumCat	8.01	7.96	15.99	15.95	15.97	14.95	14.88	3.00	3.02	3.02	3.02	3.03	12.84	7.04	10.17
Note: n.d.	= not det	ected, n.a	. = not and	alyzed; am	o = amph	ibole, cho =	= chondrodi	ite, (c)hu =	= (clino)hu	mite, ks t=	kassite, p	ohl = phlog	opite, ttn =	titanite.	

including albite (Na), periclase (Mg), corundum (Al), zircon (Si, Zr), orthoclase (K), wollastonite (Ca), nutile (Ti), rhodonite (Mn), hematite (Fe), strontianite (Sr), REE-phosphates (P, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Yb, and Lu), HfO<sub>2</sub> (Hf), vanadinite (Pb), and metals (Nb, Ta, W, U, and Th). The matrix corrections were employed according to the Armstrong-CITZAF method (Armstrong 1995). Average 1 $\sigma$  standard deviations for each element are given in the last column of Table 2 and range between 40 and 580 ppm.

## SAMPLE PETROGRAPHY

Sample 4RA28 is almost un-retrogressed, with fresh olivine, diopside (individual grains and rims around olivine), amphibole, and chlorite (Fig. 2a). Accessories are apatite and zircon, which occurs as inclusions in olivine and dolomite, but also in the matrix (Figs. 2b–2e). It forms un-corroded, rounded grains with minor compositional zoning (Figs. 2c–2e), and often contains inclusions of U-Th-oxides (qualitatively determined from EDX spectra). The latter occur also separately in the matrix and might have served as nuclei for zircon growth.

Sample 5K3a is a strongly retrogressed calcite-dolomite marble with antigorite, chlorite, phlogopite, and talc as the main silicate phases. Olivine, diopside, and Ti-bearing humite group minerals have been found as sometimes well-preserved relics, but no amphibole. Olivine is intergrown with or overgrown by diopside and Ti-humite (Fig. 3a). Diopside has rare inclusions of Mg-poor calcite (Fig. 3b), is sometimes intergrown with Ti-clinohumite and replaced at a late stage by serpentine and calcite. Titanite is relatively coarse-grained and occurs as numerous well-preserved rounded inclusions in calcite and dolomite (Fig. 3c) but also in intergranular space where it can show various degrees of corrosion and replacement. An early type of replacement is overgrowth by Ti-bearing humite group

TABLE 2. Selected electron microprobe analyses of zirconolite, euxenite, thorianite, rutile, and geikielite

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Mineral	zlt-1	zlt-2	zlt-3	zlt-4	zlt-5	zlt-6	zlt-7	eux	eux-8	tht-9	tht	rt	gk	rt	1σ(ppm)
Na <sub>2</sub> O	0.02	0.02	0.01	n.d.	n.d.	n.d.	n.d.	0.14	0.31	n.d.	n.d.	n.d.	0.01	0.01	140
FeO	2.37	2.47	3.22	3.07	2.40	2.41	2.43	0.97	0.16	0.04	0.02	0.44	9.36	0.20	96
K <sub>2</sub> O	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.20	0.11	n.d.	n.d.	0.01	0.01	0.06	46
ZrO <sub>2</sub>	30.19	30.53	28.62	29.98	30.68	29.89	30.33	0.05	0.33	0.24	0.31	0.21	n.d.	0.24	251
CaO	11.86	12.63	11.41	11.76	12.75	12.20	12.41	4.47	15.52	0.26	0.06	0.16	0.11	0.05	30
$La_2O_3$	0.04	0.03	0.01	n.d.	n.d.	n.d.	n.d.	0.09	0.03	n.d.	0.01	n.d.	n.d.	n.d.	289
TiO <sub>2</sub>	34.84	36.82	33.09	34.31	37.16	35.94	36.52	28.54	26.42	0.01	n.d.	96.76	63.72	98.33	79
SiO <sub>2</sub>	0.40	0.48	0.03	0.33	0.37	0.34	0.29	n.d.	n.d.	0.35	0.19	0.21	0.21	0.28	124
Nb <sub>2</sub> O <sub>5</sub>	0.76	0.85	1.89	1.32	0.91	0.85	0.87	9.89	1n.d.	n.d.	n.d.	0.04	n.d.	0.03	96
$Ce_2O_3$	0.05	n.d.	0.05	n.d.	0.06	0.18	0.03	0.44	0.32	0.10	0.11	0.05	0.02	0.05	248
Ta₂O₅	0.39	0.20	0.97	0.46	0.36	0.28	0.19	5.85	3.14	n.d.	n.d.	n.d.	n.d.	n.d.	215
$AI_2O_3$	0.99	0.92	0.40	0.53	0.88	0.97	1.00	0.08	0.12	0.11	0.16	0.09	0.07	0.07	50
PbO	n.d.	0.02	0.02	0.04	n.d.	n.d.	n.d.	0.10	0.09	0.11	0.31	n.d.	0.01	n.d.	78
Gd₂O₃	n.d.	0.02	0.06	0.16	n.d.	n.d.	0.03	0.23	n.d.	0.05	n.d.	0.06	n.d.	0.01	299
Pr₂O <sub>3</sub>	0.15	0.01	n.d.	n.d.	0.04	n.d.	n.d.	0.21	0.06	n.d.	n.d.	0.03	n.d.	0.03	324
Y <sub>2</sub> O <sub>3</sub>	0.04	0.05	0.05	0.09	0.04	0.04	n.d.	0.16	0.18	0.01	n.d.	n.d.	n.d.	n.d.	114
ThO <sub>2</sub>	11.35	9.84	13.98	11.67	9.40	10.63	10.15	3.47	3.28	89.61	73.15	n.d.	n.d.	0.01	65
Dy <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	0.16	0.22	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	0.10	n.d.	0.01	0.02	305
$Nd_2O_3$	0.26	0.11	0.02	0.08	0.08	n.d.	0.11	0.34	0.29	n.d.	0.04	n.d.	0.01	n.d.	292
SrO	0.05	0.06	n.d.	n.d.	0.06	0.08	0.07	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	103
Lu <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	0.06	0.01	0.07	n.d.	0.07	0.05	0.03	0.07	n.d.	0.01	n.d.	n.d.	177
Sm <sub>2</sub> O <sub>3</sub>	0.06	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.03	n.d.	n.d.	0.01	n.d.	n.d.	293
MgO	2.04	1.86	2.00	2.19	1.68	1.83	1.78	0.43	0.36	0.32	0.57	0.74	28.90	0.66	43
MnO	0.05	0.02	0.03	0.06	0.02	0.03	0.01	0.04	n.d.	0.04	n.d.	0.02	0.11	n.d.	99
HO <sub>2</sub> O <sub>3</sub>	0.15	n.d.	0.02	n.d.	0.07	0.15	0.02	0.02	n.d.	80.0	0.02	n.d.	n.d.	0.02	310
Yb <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	0.09	n.d.	0.08	0.08	0.04	n.d.	0.01	0.01	n.d.	n.d.	n.d.	0.02	202
	0.85	0.48	1.50	0.87	1.08	0.81	0.84	n.a.	n.a.	0.10	0.06	0.01	0.12	0.14	167
$P_2O_5$	n.a.	0.03	0.02	0.01	n.a.	0.02	0.02	0.05	0.01	n.a.	n.a.	n.a.	n.a.	n.a.	584
00 <sub>2</sub>	2.82 n.d	2.22 n.d	1.40 n.d	2.13 nd	1.89 n.d	2.51	2.3 I	28.03	20.79 nd	0.18 nd	14.10	n.a.	n.a.	n.a.	220
WO₃ Total	n.u. 00.76	00.70	00.12	00.20	100.06	00.25	00.61	02 07	07.50	07.60	0.05	0.00	102.69	100.22	228
iotai	99.70	99.79	99.12	99.30	100.00	99.23	99.01	03.07	07.30	97.09	09.23	90.92	102.00	100.25	
Mineral	zlt-1	zlt-2	zlt-3	zlt-4	zlt-5	zlt-6	zlt-7	eux	eux-8	tht-9	tht	rt	gk	rt	
Na	0.002	0.003	0.001	-	-	-	-	0.019	0.036	-	-	-	-	-	
Fe	0.125	0.128	0.176	0.164	0.124	0.127	0.127	0.058	0.008	0.002	0.001	0.005	0.236	0.002	
K	0.002	-		-		_	-	0.018	0.009		-	-	0.001	0.001	
Zr	0.931	0.920	0.910	0.932	0.922	0.917	0.921	0.002	0.010	0.005	0.007	0.001	-	0.002	
Ca	0.804	0.836	0.797	0.803	0.842	0.822	0.829	0.341	0.984	0.012	0.003	0.002	0.004	0.001	
La	0.001	0.001	-	-	-	-	-	0.002	0.001	-	-	-	-	-	
	1.657	1./11	1.622	1.644	1./22	1.699	1./11	1.529	1.176	-	-	0.971	1.446	0.975	
SI	0.025	0.030	0.002	0.021	0.023	0.021	0.018	-	-	0.015	0.009	0.003	0.006	0.004	
	0.022	0.024	0.056	0.038	0.025	0.024	0.024	0.319	0.268	-	-	0.000	-	0.000	
Ce	0.001	-	0.001	-	0.001	0.004	0.001	0.011	0.007	0.002	0.002	-	-	-	
	0.007	0.003	0.017	0.008	0.006	0.005	0.003	0.113	0.051	-	-	-	-	-	
AI	0.074	0.067	0.031	0.040	0.064	0.072	0.074	0.000	0.008	0.006	0.009	0.001	0.002	0.001	
Cd	-	-	-	0.001	-	-	-	0.002	0.001	0.001	0.004	-	-	-	
Gu Dr	- 0.002	-	0.001	0.005	- 0.001	-	0.001	0.005	-	0.001	-	-	-	-	
PI V	0.005	-	0.002		0.001	0.001	-	0.005	0.001	-	-	-	-	-	
Th	0.001	0.002	0.002	0.005	0.001	0.001	-	0.000	0.008	0 0 7 2	-	-	-	0.000	
	0.105	0.156	0.207	0.109	0.152	0.152	0.144	0.050	0.044	0.075	0.770	-	-	0.000	
Nd	0.006	0 003	0.004	0.003	0 002	_	0.001	0 000	0.006	_	0.001	_	_	_	
Sr	0.000	0.003		0.002	0.002	0.003	0.003	0.009	0.000		0.001		_	_	
Ji Lu	0.002	0.002	0.001		0.002	0.005	0.003	0.001	0.001	0.001			_	_	
Sm	0 001	0.003	0.001	_	0.001	_	0.001	0.001	0.001	0.001	_	_	_	_	
Ma	0.001	0.005	0 1 9 5	0 208	0 1 5 5	0 171	0 165	0.001	0.032	0.020	0.030	0.015	1 300	0.013	
Mn	0.003	0.001	0.002	0.200	0.001	0.002	0.105	0.040	0.052	0.020	0.057	0.015	0.003	0.015	
Но	0.003	0.001	0.002	0.005	0.001	0.002	0.001	0.002	_	0.001	_	_	0.005	_	
Yh	0.005	_	0.002	_	0.001	0.003	0.001	_	_	-	_	_	_	_	
Hf	0.015	0.008	0.022	0.016	0.010	0.002	0.015	_	_	0.001	0.001	0.000	0.001	0.001	
P	-	0.002	0.001	0.001	-	0.001	0.001	0.003	_	-	-	-	-	-	
U	0.040	0.030	0.020	0.030	0.026	0.035	0.032	0,445	0.353	0.059	0.146	_	_	_	
W	-	-	-	-	-	-	-	_	-	-	0.000	0.000	0.000	_	
Total	4.081	4.082	4.077	4.091	4.072	4.076	4.076	3.000	3.000	1.000	1.000	1.000	3.000	1.000	
Note: n.d.	= not dete	cted; zlt =	zirconolite	, eux = ei	uxenite, t	ht = thoriani	te, rt = rut	ile, gk = g	eikielite; nu	nbers indi	cate anal	ysis spots	in Figure 3	3.	

mineral, which is chondrodite in Figure 3d. This would indicate that titanite may well have coexisted once with olivine and the other early silicate minerals. Later-stage replacement of titanite is characterized by fine-grained rutile + calcite ± serpentine (Fig. 3c) or rutile + geikielite + serpentine (Fig. 3e). Serpentinerutile intergrowths are very common and characteristic—rutile is always extremely fine-grained in such a case—and could be pseudomorphs after a former Ti-bearing mineral of the humite group. Figure 3f shows such a possible pseudomorph, which contains additional dolomite with a titanite inclusion in its core.

Fresh zircons were found as inclusions in phlogopite; another single grain shows development of a reaction rim of Th-zirconolite (Fig. 3g); in most cases zircon forms larger grain aggregates or skeletal grains intergrown with zirconolite, thorianite, and rare euxenite (Figs. 3h and 3i). One titanite inclusion in calcite is accompanied by Th-bearing zirconolite



**FIGURE 1.** Geotectonic map of the Greek part of the Rhodope mountains. Diamond-bearing gneisses of the Kimi-UHP-unit indicated by black diamond symbols. The calcite-dolomite marble location near Organi village is indicated by the square symbol.

(Fig. 3j). Zirconolite single crystals are rare, idiomorphic to xenomorphic, with the most prominent zonation in Th-content (Fig. 3k) and sometimes enrichment of U along some rim portions, as well as marginal growth of euxenite.

Two thin sections were cut from sample 5K6a. 5K6a-1 is a strongly retrogressed calcite-dolomite marble with serpentine, chlorite, amphibole, and spinel as the main additional constituents. No olivine or diopside is preserved, as in the other samples. Rutile is observed both as a matrix phase and as an inclusion in spinel (Fig. 4a). Whereas rutile entirely included in spinel is "fresh" and even a rutile grain found in serpentine (former olivine) is completely unaltered, one rutile grain formerly included in spinel and now in contact with the matrix shows minor transformation into geikielite (Fig. 4b). In the matrix, rutile is invariably overgrown and replaced by a first generation of geikielite (geikielite-1, Figs. 4c–4f).

Texturally, there seem to be three different types of geikielite (Fig. 4c): Geikielite-1 directly replaces rutile and sometimes hosts inclusions of a first generation of zirconolite (zirconolite-1, Th-poor). Geikielite-2 is medium-grained and intergrown with chlorite and sometimes subordinate amounts of additional phlogopite, calcite, and serpentine (Fig. 4c, top right). Geikielite-3 has quite variable BSE contrast, a

very fine-grained, "spongy" texture and is intergrown with equally fine-grained serpentine (Fig. 4c, bottom). In some instances, titanite is observed in a grain size similar to rutile and geikielite1, always adjacent to and intergrown with the former two minerals (Figs. 4e and 4f) but invariably corroded and replaced by geikielite-3.

Chemically homogenous geikielite-1 with or without small inclusions of rutile or zirconolite is the most common Ti-accessory in this sample. Geikielite-2 is similar in composition to geikielite-1 but occupies a clearly distinct textural position at the margin of rutile-geikielite-1±titanite cores and sometimes develops Th-enriched zirconolite-2 at its rim (Table 1). Rare thorianite was also found in the geikielite-2 domain. Geikielite-3 varies in composition from BSE-darker geikielite to BSE-brighter ilmenite and forms a very delicate, spongy, symplectite-type structure within or next to geikielite-2 intergrowths (Figs. 4a and 4c), thus more or less enveloping parts of or even the entire inner core of rutile-geikielite-1-titanite relics. Geikielite-3 is generally Mg-rich around titanite relics (Figs. 4e, 4f, and 4g) and Fe-rich in other domains. It often appears to be pseudomorphic and can even be part of symplectitic coronas around such pseudomorphs (Fig. 4h). The distribution of Mg-rich and Fe-rich varieties in pseudomorphs is uneven (Fig.



25 µm

4i), which invites more than one explanation for their genesis.

The pseudomorphs and coronae can also get very complex in mineralogical composition: the most common constituents additional to geikielite are calcite, serpentine, retrograde rutile-2, and a Ca-Ti-compound with an analytical total of ca. 90 wt%, tentatively classified as kassite or cafetite (Fig. 4j). Less common constituents are zirconolite and titanite. In terms of geikielite evolution, it is interesting that geikielite-1 often forms separate grains in the matrix, with or without a rim of geikielite-3 (Fig. 4j). Geikielite-2 usually develops toward a chlorite matrix (Figs. 4l and 4m). In rare cases titanite appears in the same textural habit as geikielite-2 (Fig. 4m), almost indistinguishable in BSE-grayscale intensity.

5K6a-2 is another section cut from the same sample and



FIGURE 3. Sample 5K3. (a) Olivine overgrown by Ti-clinohumite and partly serpentinized. (b) Diopside with inclusions of Mg-free calcite, contained in dolomite. (c) Matrix titanite, slightly retrogressed to rutile + calcite + serpentine. (d) Titanite replaced by Ti-clinohumite. (e) Late-stage pseudomorphs of rutile + serpentine + geikielite after titanite. (f) Pseudomorphs of serpentine + rutile + dolomite after Ti-clinohumite. (*Continued on next page*)



**FIGURE 3.**—*CONTINUED* (g–j) Zirconolite in various forms of intergrowth with zircon, euxenite, titanite, and thorianite. (k) Zirconolite single crystal (inclusion in a large chlorite) with BSE-zoning mainly due to variable Th-content (color inset: red = high Th, yellow = lower Th). Numbers correspond to points of analyses given in Table 2.





FIGURE 4. Sample 5K6a1. (a) Rutile inclusion in spinel. (b) Rutile partly exposed to the matrix and transformed to geikielite + zirconolite. (c) Rutile near spinel, transformed into three textural types of geikielite/ilmenite. (d) Large rutile grain transformed into geikielite-1 and complex polymineralic pseudomorphs. (e-g) Rutile with three types of geikielite-ilmenite and relics of titanite. (h) Complex double-pseudomorph of type-3 geikielite-ilmenite compositions by BSE contrast. (j) Detail of d showing variability of type-3 geikielite-3 rim. (l) Rutile-geikielite-1 intergrowth with geikielite-2 developing toward chlorite matrix and geikielite-3 toward serpentine (former olivine). (m) Detail of l shows titanite in geikielite-2 textural setting. *(continued on next page)* 



40 µm

also contains calcite, dolomite, diopside, olivine (partly or completely replaced by serpentine), spinel, amphibole, phlogopite, and chlorite. Diopside occasionally forms rims around olivine (Fig. 5a), whereas amphibole coexists with and partly overgrows diopside in turn. Occasionally, it contains numerous sub-idiomorphic inclusions of rutile, perhaps pseudomorphing a former Ti-bearing humite-group mineral (Fig. 5b). The main accessory phases, though scarce, are zircon and titanite. The latter often contains inclusions of rutile and zirconolite (Figs. 5c and 5d) and is often preserved fresh in a coarse-grained carbonate-chlorite-phlogopite-serpentine matrix. In other cases it is partially corroded at the rim by spongy geikielite-3 and some additional ilmenite, in other places by the typical combination kassite/cafetite + serpentine (Figs. 5c, 5d, and 5f). Geikielite-1 was observed once intergrown with rutile as an inclusion in titanite (Fig. 5e). Rutile growth in that site, however, may at least partly be secondary from titanite, together with serpentine and calcite.

Sample 5K6b was collected in close vicinity to 5K6a and also contains relics of olivine, diopside, spinel, amphibole, and phlogopite in addition to retrograde serpentine and chlorite. Diopside also forms rims around olivine, whereas amphibole forms small grains at diopside-olivine interfaces or large blasts in the matrix containing relics of diopside. Fresh rutile in contact with amphibole, dolomite, and serpentine (former olivine) indicates that rutile was stable with amphibole, i.e., the transitions observed in the Ti-minerals postdate amphibole growth. Titanite forms single grains or overgrowths on rutile, which occasionally also contain Th-zirconolite (Fig. 6a). Most titanite grains are slightly corroded by spongy ilmenite-geikielite of type-3 (Fig. 6b) or by late kassite/cafetite + serpentine (Fig. 6c). Geikielite of type-1 was observed once intergrown with rutile next to titanite (Fig. 6c). Medium-sized intergrowths reminiscent of geikielite type-2 consist of rutile (Rt-2), which seems to replace titanite in a reaction texture corresponding to titanite = rutile + calcite (Fig. 6d).

## **MINERAL COMPOSITIONS**

Representative analyses of most minerals are given in Table 1. Zirconolite as well as a few spots on other accessories like rutile, geikielite, euxenite, and thorianite were analyzed for a large spectrum of elements—these data are shown in Table 2.

Clinopyroxene was observed in all samples except 5K6a-1 and is always diopside. Its composition can range from pure to slightly aluminous (up to 2.3 wt% Al<sub>2</sub>O<sub>3</sub> or 0.5 apfu Tschermak-component) in these cases the diopside is also titanoan, with up to 0.7 wt% TiO<sub>2</sub>. All diopsides contain very minor amounts of FeO (<0.4 wt%), with the exception of sample 4RA28, where diopside has up to 1.4 wt% FeO. The  $X_{Mg}$  is 0.99 and 0.96, respectively. Sodium is rarely above detection limit and always less than 0.1 wt% Na<sub>2</sub>O.

Olivine was found in the diopside-bearing samples and is very constant in composition throughout: Ni- and Ca-contents are below detection limit, the  $X_{Mg}$  is consistently 0.98; only 4RA28 olivines are more ferrous with  $X_{Mg}$  of 0.88.

Almost none of the analyses of humite-group minerals yield a cation ratio that fits one of the defined end-members nicely, so we think that the periodicity of hydrous layers is variable (cf. Ribbe

1982). The analyses listed in Table 1 reflect this situation, and they were labeled clinohumite, humite or chondrodite according to the most closely corresponding cation ratio. The Ti-content ranges between 2.8 and 7.8 wt%. The F-content correlates positively with Ti-content and ranges from 0.87 to 1.27 wt%.

Spinel in thin sections 5K6 is chemically homogenous, with Mn and Zn generally below detection limit. Fe-content is also low (0.02–0.04 apfu), and according to formula recalculation mainly in the ferric state.

Amphiboles in sample 4RA28 are tremolite, those in the other samples are calcic and highly aluminous (pargasite), with significant amounts of K (0.50-1.34 wt% K<sub>2</sub>O or 0.09-0.25 apfu) and Ti (0.61-1.24 wt% TiO<sub>2</sub> or 0.06-0.13 apfu). F-content ranges from 0.50 to 0.66 wt% or 0.22 to 0.29 apfu.

Both chlorite and phlogopite are almost pure Mg-endmembers ( $X_{Mg} = 0.98-0.99$ ) and Al-poor (Al = 2.18-2.34 apfu in chlorite and 1.10-1.40 apfu in phlogopite). Ti-content of phlogopites are significant (0.60-0.70 wt% TiO<sub>2</sub> or 0.03 apfu), F ranges from below detection limit to ca. 0.9 wt% or 0.20 apfu, i.e., an  $X_F$  of 0.10). Only chlorite in sample 4RA28 is again a bit more ferrous, with  $X_{Mg} = 0.93$ .

No compositional zoning is visible in titanite even at highcontrast BSE imaging. However, Al-content varies slightly between grains from 1.4–2.0 wt% Al<sub>2</sub>O<sub>3</sub>, which corresponds to 0.05–0.08 apfu. This goes along with slightly lower F-contents of 0.02–0.05 apfu.

Rutile occurs in samples 5K6a and 5K6-3 but was analyzed in detail only in the former sample, where the large grains (Rt-1) contain significant amounts of FeO ( $\leq 0.44$  wt%), MgO ( $\leq 0.74$ wt%), SiO<sub>2</sub> ( $\leq 0.28$  wt%), and ZrO<sub>2</sub> ( $\leq 0.29$  wt%), as well as minor Al<sub>2</sub>O<sub>3</sub> ( $\leq 0.09$  wt%), CaO ( $\leq 0.16$  wt%), Nb<sub>2</sub>O<sub>5</sub> ( $\leq 0.05$  wt%), Ta<sub>2</sub>O<sub>5</sub> ( $\leq 0.14$  wt%), and some REE.

Geikielite-ilmenite: Type-1 and type-2 geikielites are chemically indistinguishable. The grain-to-grain variation in composition within one thin section, however, can be significant:  $X_{Mg}$  ranges from 0.89 (Fig. 1b) to typical values of 0.85 to 0.83 in some rutile-free grains in the matrix. Ilmentite occurs as type-3 and also along late cracks in type-1 grains with an  $X_{Mg}$ of 0.15–0.30 and significant amounts on manganese ( $X_{Mn}$  up to 0.05 or 2.4 wt% MnO or up to 0.05 apfu).

The identification of kassite/cafetite is tentative, based only on the microprobe analysis of a Ca-Ti-compound with a Ca:Ti ratio of exactly 0.5 and low analytical totals of around 90 wt%, which points to a hydrous Ca-Ti-oxide, that could be kassite  $Ca[Ti_2O_4(OH)_2]$  or its polymorph cafetite  $Ca[Ti_2O_5](H_2O)$ (Krivovichev et al. 2003; Grey et al. 2003). These two minerals can only be distinguished by their structure, which we did not attempt in this study. Mg, Si, and F have occasionally been measured slightly above detection limit, but this could also be due to beam overlap because of the small grain size. A slight spread of the electron beam was necessary to avoid beam damage. A Raman spectrum of the grain shown in Figure 5d has been obtained with a red laser (785 nm) and is shown in Figure 7. After eliminating peaks for adjacent minerals like titanite (Fig. 7, red line), carbonates, and serpentine, the remaining Raman bands are at 283, 372, 396, 451, 677, and 707 wavenumbers. However, there is no good match with any of the rare published spectra of kassite or cafetite (e.g., RRUFF database), so the true nature of



**FIGURE 5.** Sample 5K6a2. (a) Diopside rim around partly serpentinized olivine, with some additional amphibole. (b) Large amphibole with some diopside inclusions and hundreds of small BSE-bright rutile inclusions, perhaps after former Ti-clinohumite. (c) Rutile overgrown by titanite that partly retrogresses to geikielite-3 or rutile-2 (minute BSE-bright streaks and dots) at the margins. (d) Like c, but titanite with zirconolite-inclusion and decomposition to kassite. (e) Rutile+geikielite-1 overgrown by titanite, partly decomposing to ilmenite + calcite + serpentine. (f) Titanite partly replaced by laths of kassite + calcite + serpentine.



**FIGURE 6.** Sample 5K6b. (**a**) Rutile overgrown by titanite + zirconolite. (**b**) Rutile (unaltered) and titanite partly transformed to ilmenite-3 in serpentine. (**c**) Rutile-geikielite-1 intergrowth next to a partial and a complete pseudomorphs after titanite. (**d**) Detail of **c**: type-2 intergrowth of rutile and/or titanite with chlorite, with rutile replacing titanite (left side and in large ellipse).

this mineral remains ambiguous.

The analyses of zirconolite from samples 5K3a and 5K6a-1 cluster close to end-member composition in the Zr-Ca-Ti triangle, with slight deviations toward the Zr-apex (Fig. 8a). A close-up shows that 5K3 is more strongly displaced, indicating a higher degree of substitution on the Ca- and Ti-sites (Fig. 8b). The reason for this displacement is mainly the substitution of divalent cations ( $M^{2+}$ ) together with actinides (ACT) (see Figs. 8c and 8d). The amount of REE is generally low and less important than actinides or pentavalent cations (Fig. 9a). REE in 5K3 zirconolites are lower (mostly <0.015 apfu) compared to 5K6, but generally too low to find a definite substitution correlation relationship (Fig. 9b). The contents of  $M^{5+}$  cations are slightly higher than REE, but they also show no clear correlation with any of the other components, the best "fit" is a poorly defined positive correlation with Fe<sub>tot</sub> (Fig. 9c).

There seems to be a significant deficiency of Zr + Hf in the M7 site, however there is no correlation between Zr and ACT, REE or Ti, the three possible substitution candidates according

to Gieré et al. (1998). The Ti vs. Al diagram (Fig. 9d) shows a contrasting correlation for the two samples, with an uncertain positive slope for 5K3 and a clearer negative one for 5K6.

Euxenite was detected as very tiny (up to a few micrometers in diameter) intergrowth with zircon, zirconolite, and thorianite (Figs. 3h) and contains ca. 10 wt% Nb<sub>2</sub>O<sub>5</sub>, 3-6 wt% Ta<sub>2</sub>O<sub>5</sub>, 26-28 wt% UO<sub>2</sub>, and 3-3.5 wt% ThO<sub>2</sub> (Table 2).

Thorianite grains cover two composition ranges. One is almost pure ThO<sub>2</sub> (with up to  $\sim 6 \text{ wt}\% \text{ UO}_2$ ) and the other contains around to 20–25 wt% UO<sub>2</sub>. The content of other elements is generally low and most likely due to beam overlap with matrix minerals, as the grain size of thorianite is usually also only a few micrometers.

## METAMORPHIC EVOLUTION OF TI- AND ZR-MINERALS

Sample 4RA28 is an olivine-diopside-amphbole-chloritemarble; it contains no Ti-minerals, and zircon is the only Zrmineral. U-Th-oxide occurs both as inclusions in zircon and in the matrix, which means that it rather served as a nucleation



**FIGURE 7.** Raman spectrum of kassite/cafetite (black line) and titanite (red line). The remaining characteristic bands (not belonging to titanite, carbonate, or serpentine or overlapping with these) are underlined.

site for zircon than being a decomposition product of a Zr- and actinide-bearing precursor mineral. The most important aspect of this sample is that zircon can definitely coexist stably with olivine, which is very uncommon for regional metamorphic marbles (but see Ferry 1996). It not only occurs in the intergranular space of the sample, in the vicinity of fresh olivine and diopside, but also as rounded, uncorroded inclusion in olivine itself.

Sample 5K3 is an olivine-diopside-Ti-humite-chlorite-marble with zircon in granular to skeletal growth habits, intergrown with or overgrown by zirconolite. Other less common minerals intergrown with zircon are thorianite and euxenite. Zirconolite also occurs with idiomorphic growth habits and may have been coexisting with and partly replacing earlier zircon.

The textures of Ti-minerals indicate a growth sequence of titanite  $\rightarrow$  Ti-humite  $\rightarrow$  rutile. Titanite is interpreted to have coexisted once with olivine, which is another very uncommon feature. It is obviously directly replaced by a Ti-bearing mineral of the humite group. Different compositions have been measured for the latter, which may be due to variable small-scale intergrowth of different humite-group minerals. These Ti-carriers are replaced during serpentinization of the rock by a fine-grained intergrowth of serpentine + rutile, sometimes with additional dolomite; in one such instance, a titanite relict was still preserved in the core of such a pseudomorph (Fig. 3f).

Despite the great variety of textures observed in the different slices taken from sample 5K6, they have the same "peak metamorphic" mineral assemblage in common: olivine + diopside + spinel + phlogopite + rutile + amphibole. Even though there is a textural age sequence of olivine  $\rightarrow$  diopside  $\rightarrow$  amphibole, all these minerals are considered to have coexisted stably at one point, which is still before the onset of reactions responsible for the multi-stage decomposition of Ti-minerals. According to textural criteria the oldest Ti-mineral is rutile (Rt-1), which is slightly Zr-bearing and perhaps of detrital or early metamorphic origin. A reasonable genetic explanation of Ti-mineral textures may be as follows.

## Stage 1

Rutile breaks down to geikielite (type-1 and -2) + chlorite, which indicates that the reaction also involves breakdown of spinel. Such a reaction would be:

spinel + 2 rutile + 3 olivine + 4  $H_2O = 2$  geikielite + clinochlore (2)

Whereas geikielite-1 pseudomorphically replaces rutile, geikielite-2 grows toward the matrix, very often toward (former) spinel sites, as indicated by intergrown chlorite. Being compositionally identical, these two textural types most likely developed at the same time. Th-poor zirconolite included in geikielite-1 is preserved from later alteration phenomena, which might have caused a change to more Th-rich compositions (stabilizing effect by passive enrichment) in the matrix-exposed zirconolites associated with geikielite-2. Reaction 2 requires external hydration and was perhaps triggered metastably at the time of fluid infiltration. Where fluid or spinel was scarce or missing near a rutile site, this reaction would only occur partially or not at all.

## Stage 2

Thin sections 5K6a-2 and 5K6b demonstrate that an alternative transformation of rutile to titanite must have occurred in many cases, possibly by the reaction

4 rutile + 3 diopside + dolomite = 2 olivine + 4 titanite + 
$$2 \text{ CO}_2$$
 (3)

or perhaps instead

rutile + olivine + 3 calcite +  $CO_2$  = titanite + 2 dolomite (4)

as there is no indication of a late olivine generation.

In a disequilibrium (reaction overstepping) situation, these reactions might include geikielite of type-1 or type-2 as an additional reactant. There is rare textural evidence that titanite actually replaced geikielite-2 (Fig. 4m) and was later replaced in these sites by rutile-2 + calcite (Fig. 6d). This texture and the fact that the earliest replacement of rutile seems to be by geikielite (Fig. 4b) establish titanite growth as stage 2. But as any of the reactions 2 and 4 strongly depend on the presence of some fluid as a reaction participant, significant amounts of overstepping and even omission of reactions is possible in different parts of the marbles.

Both geikielite-1 and titanite grew directly from rutile and may carry zirconolite-inclusions, that accomodated the Zr, Nb, and Ta released from rutile. As zirconolite has a significant capacity for the uptake of actinides, it may have removed both U and Th from the pore fluid or may have nucleated on and partly resorbed pre-existing U-Th-oxides.



► FIGURE 8. (a) Zr-Ca-Ti-diagram for zirconolites from samples 5K3 (dots) and 5K6a1 (crosses) and (b) detail of the diagram; (c) clear positive correlation of actinides (Th + U) with total Fe and (d) with Mg + Mn.

## Stage 3

Late-stage textures are generally fine-grained: spongy ilmenite or geikielite of type-3 are intergrown with late, finegrained serpentine and form simple to multiply complex overgrowth patterns. As both rutile-geikielite-1 intergrowths and single geikielite-1 grains (Fig. 4k) are rimmed by spongy or symplectite-type geikielite-3, and one would not expect geikielite to be replaced by another generation of geikielite of almost the same composition, we conclude that type-3 intergrowths of geikielite-ilmenite have replaced former titanite. Based on the partial replacement of titanite by either geikielite-3 or kassite + serpentine + calcite in 5K6a-2 and 5K6b, we conclude that this type of replacement is almost complete in thin section 5K6a, which would corroborate the above interpretation of essentially all fine-grained type-3 textures as pseudomorphs after former titanite, following a reaction like:

4 titanite + 10 dolomite + 4  $H_2O = 4$  geikielite + antigorite + 14 calcite + 6  $CO_2$ . (5-1)



The alternative breakdown reactions of titanite to kassite + serpentine and even of titanite to rutile + calcite are often observed in the same location and could be accomplished by very similar model reactions:

4 titanite + 6 dolomite + 4  $H_2O$  = 4 kassite + antigorite + 6 calcite + 6  $CO_2$  (5-2)

and

4 titanite + 6 dolomite + 4  $H_2O = 4$  rutile + antigorite + 10 calcite + 2  $CO_2$ . (5-3)

It is not clear what causes these alternative mechanisms. Desilicification due to transformation of olivine and spinel relics to the more Si-rich antigorite and chlorite, however, could be the main cause for the breakdown of titanite to Si-free Ti-minerals.

The complex intergrowth textures of Zr-minerals in sample

5K3 are interpreted as the result of a continuous replacement of zirconolite by zircon, thorianite, and euxenite according to the reaction:

$$(Ca,Th,U)Zr(Ti,Fe,Nb,Ta)_2O_7 + CaCO_3 = ZrSiO_4 + ThO_2 + (Ca,U,Th)_2(Ti,Nb,Ta)_2O_7$$
 (6)

during which Th, U, Nb, Ta, etc., are enriched in zirconolite, thus stabilizing it. This equation is not exactly mass-balanced. U, Nb, and Ta are strongly enriched in euxenite compared to zirconolite, whereas Zr and most of the Th are released as zircon and thorianite, respectively.

A more complex reaction history, perhaps involving an early generation of zircon (Zr-1) is indicated by the overgrowth of zirconolite on zircon (Fig. 3g). The zircons in sample 4RA28 could be such a first generation.

#### **PETROGENETIC GRIDS**

A thermodynamic analysis of phase relationships in the system  $TiO_2$ -ZrO\_2-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O (TZCMASCH) has been attempted to understand the stability fields of Ti- and Zr-minerals in ultrabasic (olivine/antigorite-dominated) calcitedolomite marbles. The petrogenetic grid for Ti-bearing marbles in Figure 10 shows the most important stable reactions involving the end-members forsterite, antigorite, diopside, tremolite, calcite, dolomite, spinel, clinochlore, rutile, geikielite, titanite, and H<sub>2</sub>O-CO<sub>2</sub> fluid. Stable reactions were found using the software PERPLEX (Connolly 1990, 2005), and the full grid was subsequently developed with the software THERMOCALC version 3.30 (Powell et al. 1998) and the ds55 data set (Holland and Powell 1998, and unpublished updates). For the purpose of reducing complexity and making the grid applicable to the



**FIGURE 9. (a)** Triangular plot of actinides vs. rare earth elements and  $(Nb^{5+} + Ta^{5+})$ . (b) Best correlation found for rare earths is with total Fe. (c) Best correlation found for  $(Nb^{5+} + Ta^{5+})$  is also with total Fe. (d) Best correlation found for Al is with Ti: positive for 5K3 and negative for 5K6a1.





FIGURE 10. Partial petrogentic grid in the system TiO<sub>2</sub>-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O (TCMASCH) for calcite-dolomite marbles with olivine- or serpentine-predominance (SiO<sub>2</sub>-undersaturated), showing the stability fields of geikielite, rutile, and titanite. Mineral abbreviations are according to Whitney and Evans (2010). Invariant points named consecutively as IP1 to IP7. IP3 and IP5 are in the CMSCH subsystem.

most common bulk rock compositions, the carbonates as well as forsterite or antigorite were considered to be in excess and one Ca-Mg silicate (diopside or tremolite) as well. No reactions with three coexisting Ti-minerals are shown. The most important reactions for high-temperature marbles (with spinel as the stable Al-buffer mineral) are grouped around invariant point 1 (IP1) at 19.7 kbar, 803 °C. They show that geikielite is stable mainly at high pressures, followed by titanite in an intermediate stability field and then rutile at the lowest pressures at temperatures below IP1. The temperature range below 500 °C is dominated by titanite, which is replaced by rutile at relatively low pressures. The activities of titanite and tremolite control this strongly pressure-dependent transition. All reactions around IP1 are fluid-absent, or, in other words, fluid-independent. Therefore fluid composition, which is often an unknown variable in geothermobarometry with marbles, is not an issue. Moreover, the reactions shift considerably in pressure and temperature depending on the end-member activities, which makes them highly suitable for geothermobarometry to the degree that activity-composition relationships (activity models) are well known. Figure 11 illustrates how IP1 shifts if the activity of one end-member is changed (along the reaction where this end-member is absent). The effect is strongest for titanite and still considerable for the other end-members. Figure 12 shows the petrogenetic grid for Zr-minerals (zircon and baddeleyite) for olivine/serpentine-dominated calcitedolomite marbles. Due to the lack of thermodynamic data and an activity-composition model for zirconolite, this mineral could not be included in the present analysis. At temperatures above antigorite stability, the assemblage diopside + baddeleyite is stable at elevated pressures, whereas zircon + forsterite covers the lower pressure region, indicating the value of this equilibrium as a useful geothermobarometer.

## GEOTHERMOBAROMETRY

Figure 13 combines the two grids with the results of geothermobarometry and also shows a P-T path derived in a prior study of impure marbles from the same field area (Proyer et al. 2008). The activities derived from measured mineral compositions in sample 5K6a2 were used to calculate P-T conditions of equilibration of the assemblage olivine-chlorite-spinel-geikielitecarbonates-fluid (using THERMOCALC in average-PT mode, Powell and Holland 1994), as shown by a red ellipse in Figure 13. The calculated *P*-*T* conditions converge to a minimum  $2\sigma$ standard deviation (sigfit 0.60) around an  $X_{CO_2}$  of 0.10–0.15 at 763  $\pm$  28 °C and 9.2  $\pm$  2.0 kbar. Average-PT values derived for sample 5K6b are almost identical (776  $\pm$  24 °C and 10.5  $\pm$ 2.4 kbar at an  $X_{CO_2}$  of 0.20). The conditions derived from these two samples are inferred to reflect the main conditions of reequilibration when geikielite formed contemporaneous with the hydration of spinel to form chlorite (reaction 2). It was concluded from the relatively coarse-grained reaction texture that this reaction, even though triggered by external hydration, occurred near equilibrium. The close proximity of the red ellipse to the chlorite-in curve corroborates this conclusion.

*P-T* conditions for the peak reaction assemblage olivineclinopyroxene-titanite-chlorite-titanoan (clino)humite in sample 5K3a are difficult to assess because there is no thermodynamic data for Ti-clinohumite and the humite-group minerals analyzed in this study are not well-crystallized members of the series but instead disordered crystals with changes in the stacking sequence



FIGURE 11. Invariant point 1 (IP1 from Fig. 10) with all possible univariants around it. Points on the univariants show the shift of IP1 with the deviation of one of the end-members from unit activity, illustrating the sensitivity of reaction curves to mineral compositions. Mineral abbreviations like in Figure 10; the numbers indicate activity values.



FIGURE 12. Partial petrogentic grid in the system ZrO<sub>2</sub>-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O (ZCMASCH) for calcite-dolomite marbles with olivine- or serpentine-predominance (SiO<sub>2</sub>-undersaturated), showing the stability fields of baddeleyite and zircon.

of the hydrous layers on a micro- to nanoscale. Using measured mineral compositions of olivine, clinopyroxene, and chlorite at an  $X_{CO_2}$  of 0.1 and taking the activity of clinohumite as a variable in average P-T calculations shows that the best estimates within the confidence limit converge around an activity for clinohumite  $(a_{chu})$  of 0.07 and 750 ± 32 °C, 9.2 ± 1.6 kbar (lower green ellipse in Fig. 13). Variation of  $X_{CO_2}$  shows that the minimum for optimum fit (sigfit = 0.72) lies between 0.02 and 0.10  $X_{CO2}$ , and the corresponding *P*-*T* conditions range up to  $782 \pm 30$  °C and  $15.6 \pm 1.8$  kbar ( $a_{chu} = 0.15$ ) for the lower  $X_{CO2}$  (upper green ellipse in Fig. 13). As the main stage of recrystallization in both 5K6a,b and 5K3a are the result of external hydration, both rocks may have reequilibrated at the same time and under very similar P-T-X<sub>CO2</sub> conditions. No statistically significant P-T results could be obtained for sample 4RA28 due to disequilibrium chlorite composition revealed by the average-PT statistical diagnostics.

Whereas zircon occurs as an accessory mineral in samples 4RA28, 5K3a, and 5K6a-2, baddeleyite was not observed in any of the samples. As zircon and baddeleyite are usually close to their end-member composition—the main substitution being Hf for Zr—the actual position of the reaction curve depends on the activities of the other silicates and carbonates involved. The dashed blue curve in Figure 13 was calculated for measured olivine and clinopyroxene compositions in sample 4RA28. Both blue curves are consistent with equilibration of 4RA28 at peak conditions similar to those recorded by samples 5K6a and 5K3a, where zircon is also part of the equilibrium assemblage.

The *P-T* path derived by Proyer et al. (2008) is largely but not entirely consistent with the information derived in this study. Following that path during exhumation, the assemblage would have evolved during the heating episode in the subducted and overthickened lower crust (between 25 and 20 kbar) from an olivine-diopside-chlorite-geikielite-baddeleyite-bearing rock to an olivine-diopside-rutile-spinel-zircon-bearing marble-the assemblage that was identified here as the oldest preserved (peak) assemblage. Partial re-equilibration occurred during reentrance into the chlorite stability field by hydration close to the equilibrium curve. Variable availability of fluorine has partially expanded the stability fields of titanite and titanoan clinohumite, so both minerals became stable at some section of the P-T path instead of geikielite or rutile, thus creating the variations in mineral assemblages and textures observed in some of our samples. The retrograde cooling path may have passed at somewhat lower pressures than estimated in the prior study. Late reaction textures involving fine-grained rutile have developed at relatively low pressures in the antigorite stability field, where rutile also became partly metastable with regard to cafetite/kassite at least in some local environments at the latest recorded stage.

The petrogenetic grids presented in this study allow a re-evaluation of the findings in other contact- or regional metamorphic field studies involving Ti- and Zr-minerals. In particular they allow a differentiation between the effects of an earlier regional metamorphism and a subsequent contact metamorphism, and an understanding of how bulk composition differences influenced the formation of "isograds" at the Ballachulish contact aureole, Scotland (Ferry 1996).

#### ZIRCON AND TITANITE IN OLIVINE-BEARING MARBLES

To our knowledge, coexistence of zircon with olivine in regional metamorphic marbles has been reported only once in the literature (Copjakova et al. 2008). Smooth, uncorroded grain



**FIGURE 13.** Combined petrogenetic grid in TZCMASCH, including *P*-*T* conditions derived for samples 5K6a-2 (red ellipse) and 5K3a (area between and including green ellipses). The dashed blue line shows the shift of the reaction bdy + di + dol = zrn + fo + cal if measured mineral compositions for clinopyroxene and olivine in sample 4RA28 are used. The long thick arrow represents the *P*-*T* path derived by Proyer et al. (2008) for impure marbles from the same field area.

boundaries between olivine and its zircon inclusions in sample 4RA28 are a strong indication for stable coexistence of the two phases in equilibrium, which is in keeping with evidence from (meta-)peridotites, the zircon content of which is regularly used for age dating of both igneous and metamorphic overprint stages and with some experimental evidence (Ferry et al. 2002). The grid presented here fully confirms that zircon can be stable under quartz-undersaturated conditions. Even though reactions like zircon + dolomite = baddeleyite + forsterite + calcite +  $CO_2$ (Ferry 1996) have not yet been determined directly in experiment, the existing field and experimental evidence demonstrates that the stability field of zircon is considerably reduced in quartzundersaturated rocks and baddelyite and other more complex Zr-bearing minerals like zirconolite become stable at metamorphic temperatures, whereas the equilibrium curve for zircon = baddelevite + SiO<sub>2</sub> lies way beyond 1000 °C.

Coexistence of titanite with forsteritic olivine is apparently rare and was so far only reported from exotic magmatic rocks (highly alkaline intrusives, lamprophyres, kimberlites, carbonatites), where titanite is usually not the only Ti-mineral but occurs together with ilmenite, perovskite, titanomagnetite, ulvöspinel, or Ti-andradite (Deer et al. 1982; Mariano 1989). In rare instances, olivine and titanite have also been reported from more basic lavas (Benhallou et al. 2008) and gabbro (Dimitrova et al. 2008; Cabella et al. 1997; Xirouchakis et al. 2001). Titaniteolivine assemblages to our knowledge have not yet been reported from marbles or metamorphic rocks in general. In our samples titanite is either the first preserved Ti-mineral (sample 5K3a) or forms directly from rutile and geikielite and is replaced either by a Ti-bearing mineral of the humite group or by various finegrained late-stage minerals including geikielite-3, rutile, kassite, and serpentine. The coarse grain size of titanite and replacement by humite-group minerals indicates stability at relatively high *P*-*T* conditions, i.e., coexisting with olivine before the onset of serpentinization. The petrogenetic grids constructed during this study demonstrate that both titanite and zircon have large stability ranges in olivine-bearing marbles. They should be much more common and will most likely be found more frequently if carefully looked for. Their usefulness for geothermobarometry and geochronology should make such a search rewarding.

## IMPLICATIONS

Ti- and Zr-bearing accessory minerals record in their reaction textures part of the metamorphic history of a rock and can be included in any geothermobarometric evaluation to obtain refined information about metamorphic paths. Simple petrogenetic grids like the one constructed here for calcite-dolomite marbles with forsterite/antigorite in excess and including those Ti- and Zr-minerals for which thermodynamic data are known (rutile, titanite, geikielite, zircon, and baddeleyite) can be used to delineate the general stability fields. Due to the simple chemical formulas of most of these Ti- and Zr-minerals, many of the univariant reactions are fluid-independent and hence highly suitable for geothermobarometry. In addition, several of these univariants are pressure-sensitive and can provide valuable barometric information that is usually not easy to get from the main mineral assemblage, at least in impure marbles. The lack of thermodynamic data for zirconolite end-members, and for F- and Ti-bearing minerals of the humite group are limitations and perhaps worthwhile fields of future experimental research. Titanite activity in particular has a dominant influence on many equilibria and a better understanding of its activity-composition relationships in the system Ti-Si-Al-Fe-Ca-F-H-O—even though subject of some studies (Tropper et al. 2002; Troitzsch and Ellis 2002)—is still highly desirable.

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#### **REFERENCES CITED**

- Armstrong, J.T. (1995) CITZAF: a package of correction programs for the quantitative electron microbeam X-ray analysis of thick polished materials, thin films, and particles: Microbeam Analysis, 4, 177–200.
- Bauer, C., Rubatto, D., Krenn, K., Proyer, A., and Hoinkes, G. (2007) A zircon study from the Rhodope metamorphic complex, N-Greece: Time record of a multistage evolution. Lithos, 99, 207–228.
- Baziotis, I., Mposkos, E., and Asimow, P.D. (2008) Petrogenesis of ultramafic rocks from the ultrahigh-pressure metamorphic Kimi Complex in Eastern Rhodope (NE Greece). Journal of Petrology, 49, 885–909.
- Benhallou, A.Z., Azzouni-Sekkal, A., Liegeois, J.-P., and Bonin, B. (2008) Mineralogy of the Cenozoic Manzaz volcanic province (Latea metacraton, Hoggar, Algeria) International Geological Congress 2008, abstract 1344992.
- Cabella, R., Gazzotti, M., and Lucchetti, G. (1997) Loveringite and baddeleyite in layers of chromian spinel from the Bracco ophiolitic unit, Northern Appenines, Italy. The Canadian Mineralogist, 35, 899–908.
- Connolly, J.A.D. (1990) Multivariable phase diagrams: an algorithm based on generalized thermodynamics. American Journal of Science, 290, 666–718.
- (2005) Composition of phase equilibria by linear programming: tool for geodynamic modelling and its application to subduction zone decarbonation. Earth and Planetary Science Letters, 236, 524–541.
- Copjakova, R., Vrana, S., Houzar, S., Cerveny, A., and Malec, J. (2008) Zirconolite, Baddeleyite and geikielite in clinohumite-spinel-forsterite marbles near Horazdivice and Prachatice in southwestern Bohemia. Acta Musei Moraviae, Scientiae Geologicae, 83, 37–51.
- Deer, W.A., Howie, R.A., and Zussman, J. (1982) Rock-Forming Minerals, vol. 1A, Orthosilicates, 2nd ed. Longman, London.
- Dimitrova, D., Mladenova, V, Hecht, L., Kerestedjian, T., and Machev, P. (2008) Accessory Fe-Ti oxides in the Pilatovets Gabbro from the island-arc volcanosedimetary sequence unconformably overlaying the Balkan-Carpathian Ophiolite. International Geological Congress 2008, abstract 1208483.
- Dunn, S.R. (2005) Calcite-graphite isotope thermometry in amphibolites-facies marble. Journal of Metamorphic Geology, 23, 813–827.
- Ehlers, K., and Hoinkes, G. (1987) Titanian chondrodite and clinohumite in marbles from the Ötztal Crystalline Basement. Mineralogy and Petrology, 36, 13–25.
- Evans, H.T. Jr., Dwornik, E.J., and Milton, C. (1986) Kassite from the Diamond Jo quarry, Magnet Cove, Hot Springs County, Arkansas: The problem of cafetite and cassite. American Mineralogist, 71, 1045–1048.
- Ferry, J.M. (1996) Three novel isograds in metamorphosed siliceous dolomites from the Ballachulish aureole, Scotland. American Mineralogist, 81, 485–494.
- Ferry, J.M., Newton, R.C., and Manning, C.E. (2002) Experimental determination of the equilibria: rutile + magnesite + geikielite + CO<sub>2</sub> and zircon + 2 magnesite = baddeleyite + forsterite + 2 CO<sub>2</sub>. American Mineralogist, 87, 1342–1350.
- Franz, G., and Ackermand, D. (1980) Phase relations and metamorphic history of a clinohumite-chlorite-serpentinite-marble from the Western Tauern Area,(Austria). Contributions to Mineralogy and Petrology, 75, 97–110.
- Fraser, G.L., Pattison, D.R.M., and Heaman, L.M. (2004) Age of the Ballachulish and Glencoe Igneous Complexes (Scottish Highlands), and paragenesis of zircon, monazite and baddeleyite in the Ballachulish aureole. Journal of the Geological Society of London, 161, 447–462.
- Garnier, V., Maluski, H., Giuliani, G., Ohnenstetter, D., and Schwarz, D. (2006) Ar-Ar and U-Pb ages of marble-hosted ruby deposits from central and southeast Asia. Canadian Journal of Earth Sciences, 43, 509–532.
- Gieré, R. (1986) Zirconolite, allanite and hoegbomite in a marble skarn from the Bergell contact aureole: implications for mobility of Ti, Zr and REE. Contributions to Mineralogy and Petrology, 93, 459–470.
- ——(1989) Hydrothermal mobility of Ti, Zr and REE: examples from the Bergell and Adamello contact aureoles (Italy). Terra Nova, 2, 60–67.
- Gieré, R., Williams, C.T., and Lumpkin, G.R. (1998) Chemical characteristics of natural zirconolite. Schweizerische Mineralogische und Petrographische Mitteilungen, 78, 433–459.
- Grey, I.E., Mumme, W.G., Pekov, I.V., and Pushcharovsky, D.Yu. (2003) The crystal

structure of chromian kassite from the Saranovskoye deposit, Northern Urals, Russia. American Mineralogist, 88, 1331–1335.

- Holland, T.J.B., and Powell, R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. Journal of Metamorphic Geology, 16, 309–343.
- Liu, F.L., Gerdes, A., Liou, J.G., Xue, H.M., and Liang, F.H. (2006) SHRIMP U-Pb zircon dating from Sulu-Dabie dolomitic marble, eastern China: constraints on prograde, ultrahigh-pressure and retrograde metamorphic ages. Journal of Metamorphic Geology, 24, 569–589.
- Katayama, I., Ohta, M., and Ogasawara, Y. (2002) Mineral inclusions in zircon from diamond-bearing marble in the Kokchetav massif, northern Kazakhstan. European Journal of Mineralogy, 14, 1103–1108.
- Kato, A., and Matsubara, S. (1991) Geikielite, baddeleyite and zirconolite in dolomitic marble from the Neichi mine, Miyako City, Iwate Prefecture, Japan. Bulletin of the National Science Museum, Tokyo, Series C, 17, 11–20.
- Krenn, K., Bauer, C., Proyer, A., Klötzli, U., and Hoinkes, G. (2010) Tectonometamorphic evolution of the Rhodope orogen. Tectonics, 29, TC4001, doi:10.1029/2009TC002513.
- Krivovichev, S.V., Yakovenchuk, V.N., Burns P.C., Pakhomovsky, Y.A., and Menshikov, Y.P. (2003) Cafetite, Ca[Ti<sub>2</sub>O<sub>3</sub>](H<sub>2</sub>O): Crystal structure revision of chemical formula. American Mineralogist, 88, 424–429.
- Mariano, A.N. (1989) Nature of economic mineralization in carbonatites and related rocks. In K. Bell, Ed., Carbonatites, p. 149–167. Unwin Hyman, London.
- Mitchell, R.H., and Chakhmouradian, A.R. (1998) Instability of perovskite in a CO<sub>2</sub>-rich environment; examples from carbonatite and kimberlite. The Canadian Mineralogist, 36, 939–951.
- Mposkos, E., and Kostopoulos, D. (2001) Diamond, former coesite and supersilicic garnet in metasedimentary rocks from the Greek Rhodope: a new ultrahighpressure metamorphic province established. Earth and Planetary Science Letters, 192, 497–506.
- Mposkos, E., and Krohe, A. (2006) Pressure-temperature-time paths of closely associated ultra-high-pressure diamond-bearing crustal and mantle rocks of the Kimi Complex: implications for the tectonic history of the Rhodope Mountains, northern Greece. Canadian Journal of Earth Sciences, 43, 1755–1776.
- Mposkos, E., Baziotis, I., Proyer, A., and Hoinkes, G. (2006) Dolomitic marbles from the ultrahigh-presure metamorphic Kimi Complex, N.E. Greece. Mineralogy and Petrology, 88, 341–362.
- Nishio, D., and Minakawa, T. (2004) Baddeleyite, zirconolite and calcirtite in lateritic rocks from Ryoke and Chichibu Terranes, Japan. Journal of Mineralogical and Petrological Sciences, 99, 42–53.
- Pascal, M-L., Di Muro, A., Fonteilles, M., and Principe, C. (2009) Zirconolite and calcirtite in banded forsterite-spinel-calcite skarn ejecta from the 1631 eruption of Vesuvius: inferences for magma-wallrock interactions. Mineralogical Magazine, 73, 333–356.
- Perraki, M., Proyer, A., Mposkos, E., Kaindl, R., and Hoinkes, G. (2006) Raman microspectroscopy on diamond, graphite and other carbon polymorphs from the ultrahigh-pressure metamorphic Kimi-Complex of the Rhodope Metamorphic Province, NE Greece. Earth and Planetary Science Letters, 241, 672–685.
- Popova, V.I., Popov, V.A., and Kanonerov, A.A. (1998) Chromium-bearing kassite from the Saranovskoye deposit—a first finding from the Urals. Miass, 2, 75–77.
- Powell, R., and Holland, T.J.B. (1994) Optimal geothermobarometry. American Mineralogist, 79, 120–133.

- Powell, R., Holland, T., and Worley, B. (1998) Calculating phase diagrams involving solid solutions via non-linear equations, with examples using THERMOCALC. Journal of Metamorphic Geology 16, 577–588.
- Proyer, A., Mposkos, E., Baziotis, I., and Hoinkes, G. (2008) Tracing high-pressure metamorphism in marbles: Phase relations in high-grade aluminous calcite– dolomite marbles from the Greek Rhodope massif in the system CaO–MgO– Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub> and indications of prior aragonite. Lithos, 104, 119–130.
- Purtscheller, F., and Tessadri, R. (1985) Zirconolite and baddeleyite from metacarbonates of the Oetztal-Stubai complex (northern Tyrol, Austria). Mineralogical Magazine, 49, 523–529.
- Ribbe, P. (1982) The humite series and Mn-analogues. In P.H. Ribbe, Ed., Orthosilicates, 2nd ed., 5, p. 231–274. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Sastna, A., and Prikryl, R. (2009) Decorative marbles from the Krkonose-Jizera terrane (Bohemian Massif, Czech Republic): provenance criteria. International Journal of Earth Sciences, 98, 357–366.
- Stucki, A., Trommsdorff, V., and Günther, C. (2001) Zirconolite in metarodingites of Penninic Mesozoic ophiolites, Central Alps. Schweizerische Mineralogische und Petrographische Mitteilungen, 81, 257–265.
- Troitzsch, U., and Ellis, D.J. (2002) Thermodynamic properties and stability of AlF-bearing titanite CaTiOSiO4-CaAlFSiO4. Contributions to Mineralogy and Petrology, 142, 543–563.
- Tropper, P., Manning, C.E., and Essene, E.J. (2002) The substitution of Al and F in titanite at high pressure and temperature: experimental constraints on phase relations and solid solution properties. Journal of Petrology, 43, 1787–1814.
- Tropper, P., Harlov, D., Krenn, E., Finger, F., Rhede, D., and Bernhard, F. (2007) Zr-bearing minerals as indicators of the polymetamorphic evolution of the eastern, lower Austroalpine nappes (Stubenberg Granit contact aureole, Styria, Eastern Alps, Austria). Lithos, 95, 72–86.
- Whitney, D.A., and Evans, B.W. (2010) Abbreviations for names of rock-forming minerals. American Mineralogist, 95, 185–187.
- Williams, C.T., and Gieré, R. (198) Metasomatic zonation of REE in zirconolite from a marble skarn at the Bergell contact aureole (Switzerland/Italy). Schweizerische Mineralogische und Petrographische Mitteilungen, 68, 133–140.
- Xirouchakis, D., Lidsley, D.H., and Frost, B.R. (2001) Assemblages with titanite (CATiSiO<sub>5</sub>), Ca-Mg-Fe olivine and pyroxenes, Fe-Mg-Ti oxides, and quartz: Part II. Application. American Mineralogist, 86, 254–264.
- Young, E.D., and Morrison, J. (1992) Relations among net-transfer reaction progress <sup>18</sup>O–<sup>13</sup>C depletion, and fluid infiltration in a clinohumite-bearing marble. Contributions to Mineralogy and Petrology, 111, 391–408.
- Zhang, A.C., Taylor, L.A., Wang, R.C., Li, Q.L., Li, X.H., Patchen, A.D., and Liu, Y. (2012) Sims Pb/Pb ages of baddeleyite and zirconolite in Apollo 17 norite 78235: implications for shock histories of extraterrestrial rocks. 43<sup>rd</sup> Lunar and Planetary Sciences Conference, Abstract no. 1036.

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