

# Reaction textures and fluid behaviour in very high-pressure calc-silicate rocks of the Münchberg gneiss complex, Bavaria, Germany

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**ABSTRACT** Calc-silicate rocks occur as elliptical bands and boudins intimately interlayered with eclogites and high-pressure gneisses in the Münchberg gneiss complex of NE Bavaria. Core assemblages of the boudins consist of grossular-rich garnet, diopside, quartz, zoisite, clinozoisite, calcite, rutile and titanite. The polygonal granoblastic texture commonly displays mineral relics and reaction textures such as post-kinematic grossular-rich garnet coronas. Reactions between these mineral phases have been modelled in the CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub>O system with an internally consistent thermodynamic data base. High-pressure metamorphism in the calc-silicate rocks has been estimated at a minimum pressure of 31 kbar at a temperature of 630°C with  $X_{\text{H}_2\text{O}} \leq 0.03$ . Small volumes of a CO<sub>2</sub>–N<sub>2</sub>-rich fluid whose composition was buffered on a local scale were present at peak-metamorphic conditions. The *P*–*T* conditions for the onset of the amphibolite facies overprint are about 10 kbar at the same temperature.  $X_{\text{CO}_2}$  of the H<sub>2</sub>O-rich fluid phase is regarded to have been <0.03 during amphibolite facies conditions. These *P*–*T* estimates are interpreted as representing different stages of recrystallization during isothermal decompression. The presence of multiple generations of mineral phases and the preservation of very high-pressure relics in single thin sections preclude pervasive post-peak metamorphic fluid flow as a cause of a re-equilibration within the calc-silicates. The preservation of eclogite facies, very high-pressure relics as well as amphibolite facies reactions textures in the presence of a fluid phase is in agreement with fast, tectonically driven unroofing of these rocks.

**Key words:** calc-silicate rocks; fluid behaviour; *P*–*T* path; reaction textures; Variscan basement; very high-pressure metamorphism.

## INTRODUCTION

The eclogite facies, high-pressure rocks of the Münchberg gneiss complex are part of the Central European Variscides. Three distinctive types are present (mafic eclogites, pelitic to psammitic gneisses, and subordinate calc-silicate rocks), all of which experienced a common tectono-metamorphic evolution. The formation of the mafic eclogites under high-pressure conditions has been investigated by Franz *et al.* (1986), Klemd (1989, 1993a, b) and O'Brien (1993), and the rare high-pressure relics in intercalated gneisses have been described by Blümel (1986), Klemd *et al.* (1991) and Klemd (1993a,b). The presence of eclogite facies calc-silicate rocks has been reported recently (Klemd *et al.*, 1992a). These rocks occur as elliptical lenses and bands ranging in thickness from several millimetres to centimetres and are intimately interlayered with mafic eclogites and gneisses.

Mineral assemblages and reaction textures in eclogite facies calc-silicate rocks have rarely been used for *P*–*T* estimates and reconstructions of uplift paths (an exception is Franz & Spear, 1983). Therefore, the aim of this paper

is to describe and interpret such high-pressure relics and reaction textures for the calc-silicate rocks of the Münchberg gneiss complex and to emphasize the general significance of calc-silicate rocks for the investigation of fluid behaviour during high-pressure metamorphic evolutions.

## GEOLOGICAL SETTING

The Münchberg gneiss complex is situated in the NE Bavarian Variscan basement, which forms the north-western margin of the Bohemian Massif in SE Germany (Fig. 1). It is considered to be a nappe pile resting on the autochthonous, anchi-metamorphic Palaeozoic sequences of the Thuringian lithofacies in the south-eastern Frankenwald (Fig. 1; e.g. Behr *et al.*, 1982; Franke, 1984). The uppermost unit of the nappe pile, the 'Hangendserie', contains amphibolite facies metasediments, banded amphibole gneisses, amphibolites and marbles; eclogites as well as metasediments and interlayered calc-silicate bands and lenses with high-pressure relics form the basal parts of the 'Hangendserie'. The next two lower units, the

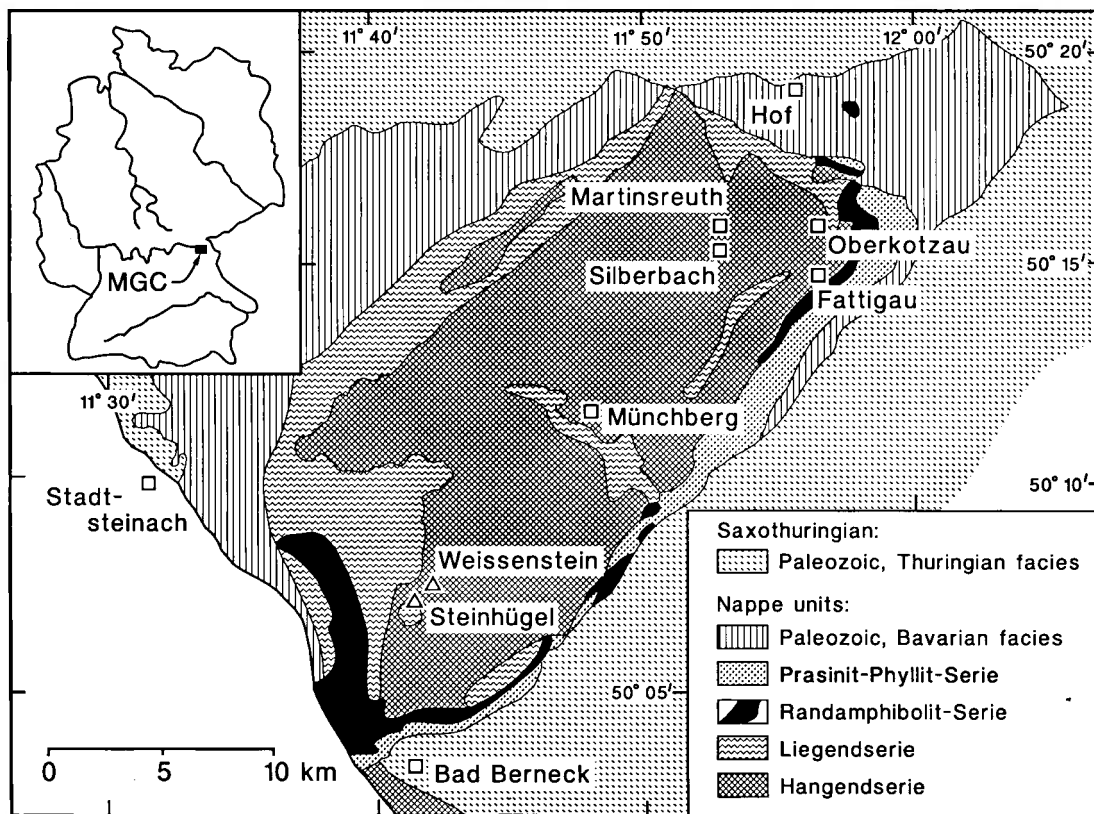


Fig. 1. Geological sketch map of the Münchberg gneiss complex (MGC), based on the Geological Map of Bavaria 1:500 000 (modified after Klemd *et al.*, 1991).

'Liegendserie' and the 'Randamphibolitserie', consist mainly of amphibolite facies ortho- and paragneisses and of amphibolites, respectively. The next underlying tectonic unit, the 'Prasinit-Phyllit-Serie', exhibits greenschist facies mineral assemblages. The lowermost nappe unit comprises the Palaeozoic rock sequences of the Bavarian lithofacies (e.g. Wurm, 1961; Behr *et al.*, 1982). Owing to poor exposure, it has been difficult to establish the eclogite/country-rock relationships. Therefore, a 230-m-long research hole was drilled through the Weissenstein eclogite body (Fig. 1) in order to obtain more information concerning the contact relationships between the different rock types (Matthes *et al.*, 1974). The drill core consists of interlayered eclogites with amphibolites and metasedimentary gneisses of variable composition, the latter including calc-silicate bands and lenses which range in thickness from several millimetres to centimetres (Fig. 2). The transitions between mafic eclogite layers and intercalated gneisses are typically marked by tectonic contacts, but sections with small-scale layering appear to be tectonically undisturbed (Matthes *et al.*, 1974, figs 5 & 6; Klemd *et al.*, 1991, fig. 3). This relationship and the occurrence of high-pressure relics in outcrops of metasediments (Blümel, 1986) and in gneissic interlayers from the drill core (Klemd *et al.*, 1991) suggest that the mafic eclogites and associated country rocks have undergone a common tectono-metamorphic history with an earlier eclogite facies

metamorphism and a subsequent amphibolite facies overprint.

The high-pressure metamorphic conditions for the eclogites are estimated at minimum pressures of about 20–26 kbar at temperatures of  $620 \pm 50^\circ \text{C}$  (Klemd, 1989; O'Brien, 1993). The  $P$ - $T$  estimates are based on several phase equilibria and mineral thermometers (e.g. garnet-omphacite, garnet-phengite). The possible presence of coesite as discussed in Smith (1984) and Okrusch *et al.* (1991) may imply even higher pressures. The eclogite facies event was followed by an amphibolite facies overprint between 6 and 12 kbar in the same temperature range in both the mafic eclogites and the associated metasedimentary country rocks (Matthes *et al.*, 1974; Franz *et al.*, 1986; Klemd *et al.*, 1991; Klemd, 1993a, b; O'Brien, 1993). These latter  $P$ - $T$  estimates were derived largely from experimentally determined reaction positions, since thermobarometric investigations based on the amphibolite facies mineral assemblages gave inconsistent results due to disequilibrium conditions (Franz *et al.*, 1986; Klemd *et al.*, 1991; Klemd, 1993a, b).

A relatively simple structural history is preserved in high-pressure rocks of the Münchberg gneiss complex (e.g. Behr, 1983; Franke, 1984). The oldest structure identified in these rocks is a metamorphic banding (S1), only preserved in a few eclogite bodies. A younger mylonitization (D2) led to the formation of a pervasive S2 cleavage



Fig. 2. Partly boudinaged (arrowheads) calc-silicate layers in gneisses which display porphyroblastic garnets (sample depth: 160 m).

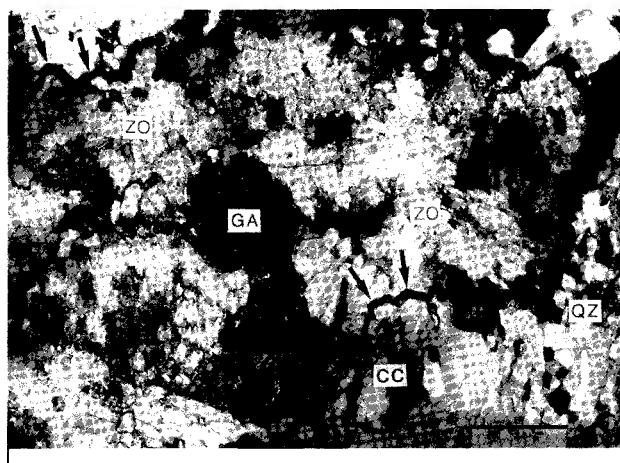


Fig. 3. Corona of grossular-rich garnet (arrows) separating zoisite (ZO) from quartz (QZ) and calcite (CC). GA = relics of the formerly porphyroblastic garnet (sample 754, depth: 165.05 m; scale bar = 0.3 mm; crossed polarized light).

in the less competent metasedimentary country rocks, but spared the more competent eclogite bodies. The competent calc-silicate bands and lenses were boudinaged during D2 deformation (Fig. 3). Last, a weak axial plane crenulation cleavage (S3) is present in some of the metasedimentary country rocks.

The age of high-pressure metamorphism ranges between 380 and 395 Ma, as deduced from concordant Sm/Nd and Rb/Sr mineral isochron ages for the Weissenstein eclogite (Stosch & Lugmair, 1990). These dates coincide with Ar–Ar plateau ages of about 390 Ma on coarse 3T-phengites from the light Oberkotzau eclogite (Kreuzer & Seidel, 1989). The subsequent amphibolite facies overprint is dated at around 380 Ma based on K–Ar mineral ages (Kreuzer *et al.*, 1989). Hammerschmidt & Franz (1992) obtained a 300 Ma age component related to thermal overprinting during the intrusion of late Variscan granites.

### PETROGRAPHY AND MINERAL CHEMISTRY OF CALC-SILICATE LENSES

Electron microprobe analyses were carried out using a CAMECA SX50 microprobe with standard operating conditions of 15 kV accelerating potential and about 10 nA sample current. For matrix corrections the PAP-program of CAMECA was used. Peaks as well as backgrounds were measured over 20 s each. The relative error for major elements, determined for the standards, is <1%, for Na <2%. For trace elements, an error of up to 20% must be taken into account. All investigations were conducted on samples from the Weissenstein drill core. Representative microprobe analyses are listed in Tables 2–4; the complete data set is given in Klemd (1993b).

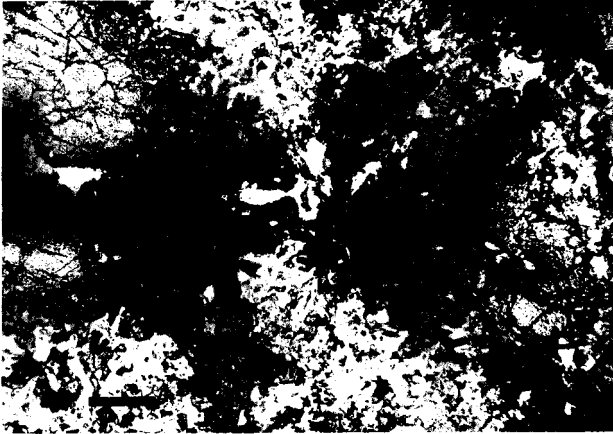
Calc-silicate lenses typically exhibit a concentric mineral zoning from core to rim. The zoning is a reflection of gradients in bulk-chemical composition, probably imposed during or after boudinaging in response to reactions with the adjacent gneisses. Core assemblages such as garnet, diopside, quartz, zoisite, clinozoisite, calcite and titanite are characterized by a polygonal granoblastic texture, which displays mineral relics and reaction textures such as post-kinematic grossular coronas. Grain size ranges from 0.1 to 2 mm. The mineral assemblages from the core of the calc-silicate lenses are listed in Table 1. The rims of the lenses normally consist of quartz, sericite, rare pumpellyite, and fine-grained, saussuritized plagioclase. The rim assemblages are subparallel to the S2 foliation in the surrounding gneisses.

Garnet occurs as porphyroblasts which have been totally or partially replaced by zoisite and titanite (Fig. 3) or subsequently by clinozoisite, calcite and quartz (Fig. 4). Apatite is always associated with these alteration products. This porphyroblastic garnet consists primarily of grossular (78–92 mol.%), andradite (2–17 mol.%) and almandine components (0–10 mol.%); pyrope and spessartine components are generally <5 mol.% (Fig. 5). The TiO<sub>2</sub> content ranges between <0.1 and 0.4 wt.% (Table 2). Schertl *et al.* (1991) and Harley & Buick (1992) describe

**Table 1.** Mineral assemblages in the core of calc-silicate lenses from the Weissenstein drill core.

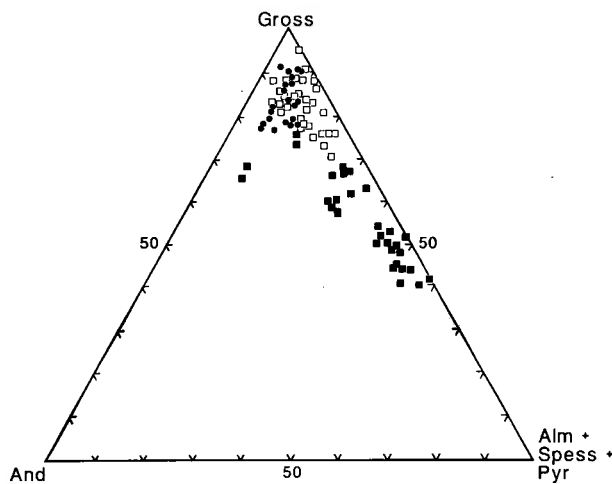
Sample	Depth (m)	Grt	Cpx	Zo	Czo	Cal	Ttn	Rt	Phen	Qtz	Mag
754U	165.40	+, R	+	+	+	+	+	R		+	+
755	165.16	+, R	R	+	+	+	+	R	R	+	+
761	166.20	+, R	+	+	+	+	+	R		+	+
166.02	166.02	+, R		+	+	+	+	R		+	
785	172.0	+, R		+	+	+	+			+	+

+ = present; R = relic; Phen = phengite.



**Fig. 4.** Porphyroblastic garnets (dark) being replaced by a fine-grained mixture (light) of clinozoisite, calcite and quartz (sample 754, depth: 165.05 m; scale bar = 0.2 mm; crossed polarized light).

garnets with similar high  $\text{TiO}_2$  contents in eclogite facies metasediments belonging to the Dora Maira massif (Western Alps) and in granulite facies calc-silicates in the Rauer Group (Antarctica), respectively. No systematic zoning was observed in the porphyroblastic garnets, but Ca



**Fig. 5.** Garnet chemical variations in terms of the grossular (Gross), andradite (And) and almandine + spessartine + pyrope (Alm + Spess + Pyr) end-members (filled circles = garnets I and II; open squares = garnet III; filled squares = garnets IV and V).

decreases near zoisite and Ti decreases adjacent to titanite inclusions.

A younger generation of garnets forms coronas between alteration products (zoisite or quartz and calcite) of the older, porphyroblastic garnet (Fig. 3). The garnet coronas show a wide range in composition (Table 2), with varying grossular (38–95 mol.%), andradite (0–27 mol.%) and almandine contents (2–60 mol.%) (Fig. 5). This variation can be observed between different samples; however, even in individual samples, garnet coronas are heterogeneous and show no systematic chemical zoning. The grossular content decreases dramatically when garnets are in contact with clinozoisite and calcite, indicating a replacement of the garnet coronas during decreasing  $P$ – $T$  conditions by these two minerals. However, the heterogeneous composition of the coronas could also be a result of small-scale bulk-chemical variations (G. Franz, written comm., 1994). Despite repeated calibration and satisfying results of standard checks, some totals are low and suggest the incorporation of a hydrogrossular component (cf. Schertl *et al.*, 1991).

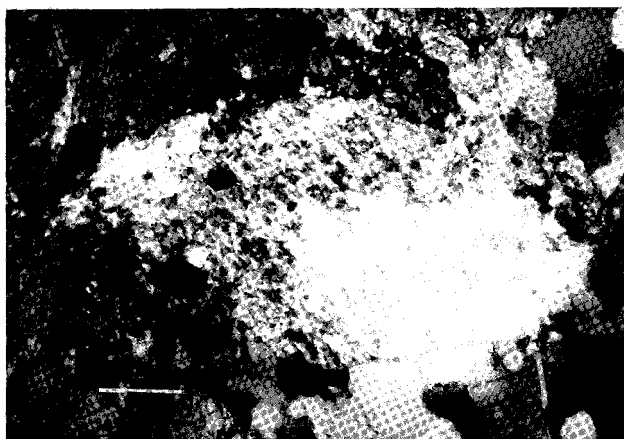
**Clinopyroxene.** Coarse-grained clinopyroxene is either in mutual contact with all other minerals of the calc-silicate cores or is partly replaced by calcite, quartz  $\pm$  magnetite (Fig. 6). The composition is salitic to ferrosalitic (Table 3) with  $X_{\text{Mg}}$  ranging between 0.33 and 0.60. This large variation is mainly due to different degrees of replacement.

**Phengite.** Rare phengite is observed as fine-grained relics in zoisite. We could obtain only two quantitative analyses (Table 3), with Si contents of 3.42 and 3.45 p.f.u., representing the high-pressure stage.

**Titanite, rutile.** Titanite occurs as inclusions in zoisite pseudomorphs after garnet and replaces rutile. Titanite contains almost no  $\text{Fe}^{3+}$  (0–0.1 p.f.u.), while Al values range between 0.6 and 0.12 p.f.u. (Table 3). The Al content is somewhat higher in comparison to amphibolite facies titanites, but much lower than that expected at high- to very high-pressure conditions (Franz & Spear, 1985). This is possibly due to the influence of the bulk-rock composition as suggested by Franz & Spear (1985). On the other hand, Chopin *et al.* (1991), influenced by low Al contents of titanites in the very high-pressure gneisses of the Dora massif (Western Alps), claimed that bulk-rock F contents may be a more important control than pressure on Al incorporation in titanite. In a few samples rutile relics in titanite are preserved (Fig. 7). Chopin *et al.* (1991) observed the same feature in the high-grade gneisses of the

**Table 2.** Selected microprobe analyses of garnet; formulae calculated on the basis of 24 O.

Type Sample	I 755II/5 rim	I 755II/7 core	I 755II/9 rim	II 755II/6 core	III 755II/8 core	IV 755II/10 rim	III 166.02/1 core	I 166.02/1 rim	I 166.02/1 core	V 166.02/1 core
SiO <sub>2</sub>	38.99	38.01	38.96	38.36	38.59	38.14	38.78	38.67	38.75	37.91
TiO <sub>2</sub>	0.37	0.42	0.15	0.20	0.24	0.15	0.22	0.41	0.12	0.00
Al <sub>2</sub> O <sub>3</sub>	21.59	21.21	21.09	19.98	20.75	21.60	20.5	20.16	20.33	19.28
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	0.81	0.82	1.60	3.10	2.07	0.00	2.02	2.64	2.48	4.10
FeO	2.13	2.13	1.44	4.21	3.36	21.27	6.85	5.05	5.47	5.31
MnO	0.26	0.32	0.36	1.58	0.58	2.77	1.44	1.21	1.27	7.22
MgO	0.04	0.05	0.00	0.00	0.04	1.35	0.16	0.02	0.12	0.00
CaO	35.57	35.17	35.58	32.58	34.19	14.84	29.52	31.36	30.81	25.86
<b>Total</b>	<b>99.79</b>	<b>98.13</b>	<b>99.19</b>	<b>100.01</b>	<b>99.82</b>	<b>100.12</b>	<b>99.49</b>	<b>99.54</b>	<b>99.35</b>	<b>99.68</b>
Si	5.92	5.88	5.96	5.91	5.91	5.99	5.99	5.97	5.99	5.96
Ti	0.05	0.04	0.01	0.02	0.02	0.01	0.03	0.05	0.01	0.00
Al <sup>IV</sup>	0.07	0.11	0.04	0.08	0.08	0.00	0.00	0.03	0.01	0.05
Al <sup>VI</sup>	3.80	3.76	3.76	3.54	3.66	3.99	3.73	3.64	3.69	3.52
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe <sup>3+</sup>	0.10	0.09	0.18	0.36	0.23	0.00	0.24	0.31	0.29	0.48
Fe <sup>2+</sup>	0.27	0.27	0.18	0.54	0.43	2.79	0.89	0.65	0.71	0.70
Mn	0.03	0.04	0.04	0.20	0.07	0.36	0.19	0.16	0.17	0.96
Mg	0.01	0.01	0.00	0.00	0.01	0.31	0.04	0.00	0.03	0.00
Ca	5.79	5.83	5.83	5.38	5.61	2.49	4.89	5.19	5.10	4.35
<b>Total</b>	<b>16.04</b>	<b>16.03</b>	<b>16.00</b>	<b>16.03</b>	<b>16.02</b>	<b>15.94</b>	<b>16.00</b>	<b>16.00</b>	<b>16.00</b>	<b>16.02</b>
Uvar.	0	0	0	0	0	0	0	0	0	0
Andr.	3	3	5	9	6	0	6	9	8	12
Gross.	92	92	91	79	86	42	75	77	77	60
Pyr.	0	0	0	0	0	5	1	0	0	0
Spess.	1	1	1	3	1	6	3	3	3	16
Alm.	4	5	3	9	7	47	15	11	12	12


**Fig. 6.** Replacement of diopside (large light grain) by calcite, quartz and magnetite (sample 755I, depth 165.15 m; scale bar = 0.2 mm; crossed polarized light).

coesite-bearing unit of the Dora Maira massif. These authors regard the possible former presence of almost pure grossular and rutile as the only indication for *very* high pressures in these rocks.

*Zoisite, clinozoisite.* Zoisite (Table 4) replaces porphyroblastic garnet and is typically surrounded by grossular-rich coronas separating it from quartz and calcite; zoisite thus

never occurs in mutual contact with these minerals. The pistacite content [ $\text{Fe}^{3+}/(\text{Al} + \text{Fe}^{3+})$ ], with total  $\text{Fe} = \text{Fe}^{3+}$ , ranges between 0.01 and 0.07.

Xenoblastic clinozoisite usually replaces zoisite and can only be distinguished optically from zoisite by its higher interference colours. Clinozoisite has a higher Fe content than zoisite (Table 4). The pistacite content ranges between 0.12 and 0.29. Clinozoisite and calcite also replace porphyroblastic and corona garnet and rarely zoisite.

*Calcite* is almost pure  $\text{CaCO}_3$ , even when replacing diopside (Fig. 6). Microprobe analyses yielded only up to 2.52 mol.% magnesite, 0.04–3.45 mol.% siderite and 0.09–1.41 mol.% rhodochrosite content.

*Chlorite, pumpellyite.* Chlorite and pumpellyite are observed in only a few of the investigated samples as part of the rim assemblages.

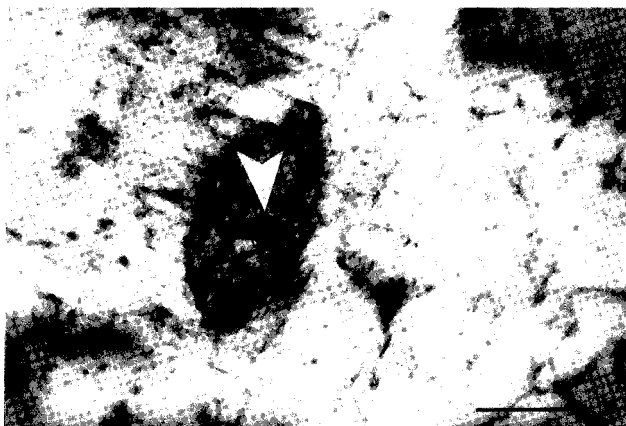
## MINERAL REACTIONS AND METAMORPHIC EVOLUTION

Metamorphic  $P$ – $T$ – $X$  constraints were obtained using the internally consistent thermodynamic data set of Powell & Holland (1988) and Holland & Powell (1990). The mixing model of Hodges & Spear (1982) was used for garnet, but application of the activity models of Moecher *et al.* (1988)

**Table 3.** Selected microprobe analyses of clinopyroxene,\* phengite† and titanite.‡

Grain Sample	Clinopyroxene					Phengite			Titanite		
	2/2 755I	9/18 755III	CPX 1 754 B1	CPX 2 754 B1	CPX 3 754 B1	20 785II	21 785II	20 755I	B4 755I		
SiO <sub>2</sub>	50.25	49.92	51.82	51.05	52.86	SiO <sub>2</sub>	52.95	51.68	SiO <sub>2</sub>	29.62	29.29
TiO <sub>2</sub>	0.05	0.09	0.00	0.00	0.02	TiO <sub>2</sub>	0.01	0.00	TiO <sub>2</sub>	39.19	35.19
Al <sub>2</sub> O <sub>3</sub>	0.38	0.38	0.90	0.50	1.98	Al <sub>2</sub> O <sub>3</sub>	29.14	28.91	Al <sub>2</sub> O <sub>3</sub>	1.72	2.84
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.04	0.00	0.01	0.01	Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	Fe <sub>2</sub> O <sub>3</sub>	0.27	0.21
Fe <sub>2</sub> O <sub>3</sub>	2.72	4.67	0.00	0.00	0.00	FeO	1.56	1.67	CaO	28.55	28.29
FeO	11.98	10.50	14.34	15.10	10.10	MnO	0.00	0.00	Total	99.35	95.82
MnO	0.65	0.40	0.31	0.37	0.23	MgO	2.64	2.59			
MgO	9.12	9.68	8.34	8.31	10.71	CaO	0.17	0.27	Si	1.00	1.00
CaO	23.94	23.61	22.91	23.40	23.04	Na <sub>2</sub> O	0.04	0.00	Ti	1.00	0.90
Na <sub>2</sub> O	0.12	0.29	0.57	0.40	1.04	K <sub>2</sub> O	9.08	9.53	Al	0.07	0.12
K <sub>2</sub> O	0.00	0.01	0.00	0.01	0.00	Total	95.59	94.65	Fe <sup>tot</sup>	0.01	0.01
Total	99.22	99.59	99.19	99.15	99.99				Ca	1.03	1.03
									Total	3.11	3.06
Si	1.95	1.93	2.01	1.99	1.99	Si	6.90	6.85			
Ti	0.00	0.00	0.00	0.00	0.00	Ti	0.00	0.00			
Al <sup>IV</sup>	0.02	0.02	0.00	0.01	0.01	Al <sup>IV</sup>	1.10	1.16			
Al <sup>VI</sup>	0.00	0.00	0.04	0.01	0.08	Al <sup>VI</sup>	3.37	3.36			
Cr	0.00	0.00	0.00	0.00	0.00	Cr	0.00	0.00			
Fe <sup>3+</sup>	0.08	0.14	0.00	0.02	0.01	Fe <sup>2+</sup>	0.17	0.19			
Fe <sup>2+</sup>	0.39	0.34	0.46	0.46	0.31	Mn	0.00	0.00			
Mn	0.02	0.01	0.01	0.01	0.01	Mg	0.51	0.51			
Mg	0.53	0.56	0.48	0.48	0.60	Ca	0.02	0.04			
Ca	1.00	0.98	0.95	0.98	0.93	Na	0.01	0.00			
Na	0.01	0.02	0.04	0.03	0.08	K	1.51	1.61			
K	0.00	0.00	0.00	0.00	0.00	Total	13.60	13.72			
Total	4.00	4.00	3.99	3.99	4.02						

\* Formulae calculated on the basis of 6 O. Fe<sup>3+</sup> by charge balance. † Formulae calculated on the basis of 22 O. ‡ Formulae calculated on the basis of 10 O. All Fe was calculated as Fe<sup>3+</sup>.

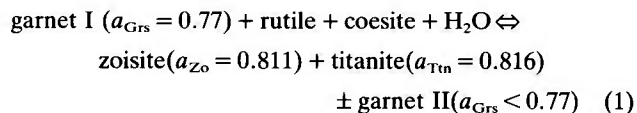


**Fig. 7.** Rutile relics (arrowhead) in titanite enclosed in zoisite (sample 755I, depth: 165.15 m; scale bar = 0.01 mm; plane polarized light).

and Berman (1990) does not significantly differ from these activity values. Ideal mixing-on-sites models were used for clinzoisite/zoisite (Powell, 1978) and titanite (Manning & Bohlen, 1991). The activity of CaFeSi<sub>2</sub>O<sub>6</sub> in clinopyroxene was calculated as  $X_{\text{Fe}}$  assuming ideal mixing (e.g. Harley & Buick, 1992). Activities for rutile and quartz are

assumed to be 1. Mineral abbreviations used, if not otherwise stated, were taken from Kretz (1983).

The porphyroblastic garnet is pseudomorphed by zoisite, which also contains inclusions of titanite replacing rutile (Fig. 7). This reaction texture suggests the reaction

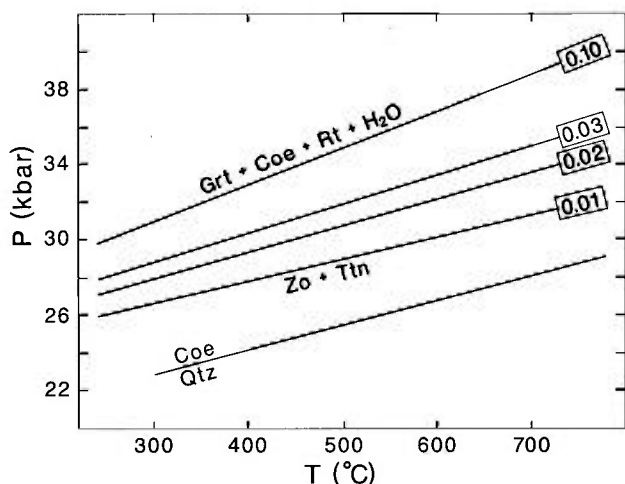


in the CaO–TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O–CO<sub>2</sub> (CTASV-system) (Fig. 8). This reaction has a positive slope in  $P$ – $T$  space (see also Chopin *et al.*, 1991). Thus, rutile would have reacted with garnet I to form titanite, zoisite and less grossular-rich garnet II, indicating decompression during this reaction. This implies that the composition of the garnets is a function of  $P$  and  $T$ ; with decreasing pressure the composition of garnet I will become depleted in Ca. Garnets I and II both are porphyroblastic and cannot be distinguished optically. Garnet with a grossular activity > 0.7 can only coexist with rutile within the coesite stability field (Holland & Powell, 1990). Using the GEOCALC software (Berman *et al.*, 1987) and the data base of Berman (1988), Chopin *et al.* (1991) verified these results for fine-grained, high-pressure gneisses of the Dora Maira massif.

**Table 4.** Selected microprobe analyses of coexisting zoisite–clinozoisite pairs and clinozoisite in contact with garnet.

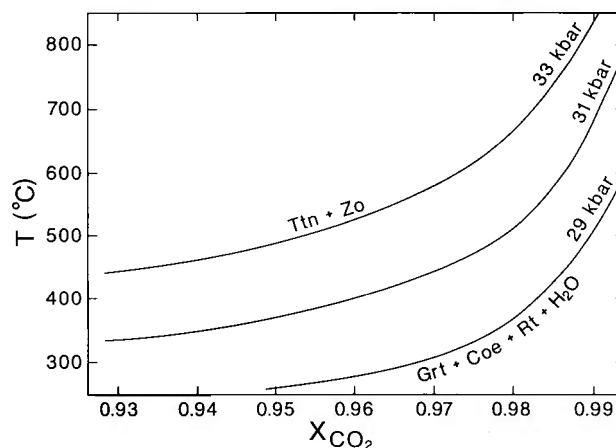
Grain Sample Mineral	15/6 755 Zo	6 755 Czo	ZO 2 166-1B Zo	CZO 2 166-1B Czo	B2 ZO3 166.02/1 Zo	B2 CZO3 166.02/1 Czo	B1 ZO2 761 Zo	B1 CZO1 761 Czo	BZ CZO1 166.02/1 Czo/Grt	B3 CZO2 785-B3 Czo/Grt
SiO <sub>2</sub>	38.21	38.76	39.28	37.60	38.78	37.44	39.85	38.30	36.70	36.53
TiO <sub>2</sub>	0.00	0.21	0.05	0.10	0.02	0.00	0.08	0.26	0.00	0.06
Al <sub>2</sub> O <sub>3</sub>	32.64	20.96	32.14	25.66	32.65	25.06	32.82	27.74	22.20	25.03
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.00	0.00	0.00	0.00	0.03	0.02	0.01	0.05	0.01
Fe <sub>2</sub> O <sub>3</sub>	0.67	5.44	1.40	10.18	0.56	10.71	1.12	6.82	14.26	9.97
MnO	0.00	0.55	0.03	0.13	0.00	0.09	0.00	0.09	0.54	0.00
MgO	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
CaO	24.06	33.83	24.72	23.54	25.05	24.08	24.70	24.06	23.32	23.61
BaO	0.06	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.01
Na <sub>2</sub> O	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.03
K <sub>2</sub> O	0.01	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Total	95.67	99.82	97.63	97.23	97.06	97.41	98.61	97.30	97.09	95.27
Si	5.94	6.14	6.00	5.97	5.96	5.96	6.02	6.00	5.95	5.95
Ti	0.00	0.03	0.00	0.01	0.00	0.00	0.01	0.03	0.00	0.00
Al	5.99	3.91	5.79	4.80	5.91	4.70	5.84	5.12	4.24	4.24
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Fe <sup>tot</sup>	0.08	0.68	0.16	1.22	0.07	1.28	0.13	0.80	1.74	1.74
Mn	0.09	0.07	0.00	0.02	0.00	0.01	0.00	0.01	0.07	0.07
Mg	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	4.01	5.74	4.05	4.00	4.12	4.10	4.00	4.04	4.05	4.05
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	16.02	16.58	16.00	16.02	16.06	16.05	16.00	16.00	16.06	16.06

Formulae were calculated on the basis of 25 O. All Fe was calculated as Fe<sup>3+</sup>.



**Fig. 8.** The position of the reaction  $\text{Grt} + \text{Coe} + \text{Rt} + \text{H}_2\text{O} \rightleftharpoons \text{Zo} + \text{Ttn}$  with varying  $X_{\text{H}_2\text{O}}$  values using calculated solid phase activities and the thermodynamic dataset of Holland & Powell (1990). Coe = coesite.

Reaction (1) was crossed during decompression and the reaction curve thus only gives *minimum* pressures (Fig. 8). The minimum pressures with acceptable standard deviations ( $1\sigma$ ) recorded in the Weissenstein calc-silicates are 33 kbar ( $1\sigma = 2.9$  kbar) at 578° C ( $1\sigma = 178^\circ$  C) and  $a_{\text{H}_2\text{O}} = 0.03$  and 30 kbar ( $1\sigma = 3.6$  kbar) at 595° C ( $1\sigma = 178^\circ$  C) and  $a_{\text{H}_2\text{O}} = 0.01$  (Fig. 8). The  $T$ - $X_{\text{CO}_2}$  diagram in

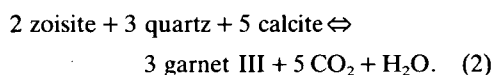


**Fig. 9.** Isobaric  $T$ - $X_{\text{CO}_2}$  diagram illustrating the reaction curve  $\text{Grt} + \text{Coe} + \text{Rt} + \text{H}_2\text{O} \rightleftharpoons \text{Zo} + \text{Ttn}$  at varying pressures using calculated solid phase activities and the thermodynamic dataset of Holland & Powell (1990).

the CTASV-system constrains  $X_{\text{H}_2\text{O}}$  at 33 kbar in the coexisting fluid to be  $\leq 0.03$  between 578 and 880° C (Fig. 9). This  $X_{\text{H}_2\text{O}}$  estimate is in excellent agreement with fluid inclusion studies in the calc-silicates, which suggest a high  $\text{CO}_2$ - $\text{N}_2$  and a low  $\text{H}_2\text{O}$  activity during high-pressure metamorphism (Klemd *et al.*, 1992a, b). However, if the  $\text{H}_2\text{O}$  activities were to be higher, the minimum pressures would also be higher (Figs 8 & 9). In contrast to the

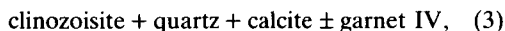
calc-silicates, high  $H_2O$  activities are estimated for the adjacent mafic eclogites (Klemd, 1989; Massonne, 1991). This indicates local fluid gradients and/or local buffering during *very* high-pressure metamorphism. An  $H_2O$ -independent minimum pressure estimate of about 14 kbar at 630°C is given by the maximum Si content of 3.45 p.f.u., using phengite barometry of Massonne & Schreyer (1987).

The amphibolite facies overprint can be modelled in the  $CaO-Al_2O_3-SiO_2-CO_2-H_2O$  (CASV) system (Holland & Powell, 1990). However, the construction of the  $P-T-X$  diagram is hampered by the absence of critical mineral phases such as plagioclase, Ca-bearing mica, amphibole, or Al-silicate. Important evidence for a period of isothermal decompression is provided by the grossular-rich garnet coronas, separating zoisite from quartz and calcite, with zoisite, quartz and calcite being alteration products of the older porphyroblastic garnet (Fig. 3). The formation of the garnet coronas is attributed to the net transfer reaction

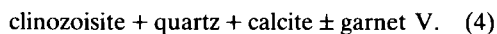


The decomposition of the garnet coronas (garnet III) and relics of the porphyroblastic garnet I, II is reflected only by a change in the grossular component of the garnets (garnets IV and V have lower grossular components, Table 2), reflecting a pressure and temperature decrease during the reactions (3) and (4):

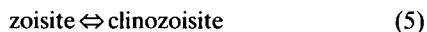
garnet I, II +  $H_2O$  +  $CO_2$   $\Leftrightarrow$



garnet III +  $H_2O$  +  $CO_2$   $\Leftrightarrow$



Another important reaction



shows textural disequilibrium features such as sutured grain boundaries and, when these minerals occur in mutual contact, also a large range in clinozoisite (40–65 mol.%  $Al_2Fe$ ) and zoisite (3–11 mol.%  $Al_2Fe$ ) composition. Clinozoisite replacing garnet consumes additional  $Fe^{3+}$  (up to 87 mol.%  $Al_2Fe$ ) liberated during garnet alteration. The large compositional variation of the  $Al_2Fe$  contents of coexisting zoisite/clinozoisite pairs is in excellent agreement with the observations of Franz & Selverstone (1992), that large compositional variations between these minerals occur in high-pressure rocks. Furthermore, our data clearly support their hypothesis of a transformation loop between zoisite and clinozoisite at 400–600°C. When using the  $T-X$  diagram for zoisite and clinozoisite of Prunier & Hewitt (1985), disequilibrium conditions are implied: 8 pairs of mutually coexisting zoisite and clinozoisite show a large temperature range from 400 to 700°C and crossing tie lines (Fig. 10).

Reactions (3) and (4) consume the  $H_2O$  and  $CO_2$  which were liberated by corona formation during reaction (2). The local consumption of  $CO_2$  is also indicated by the

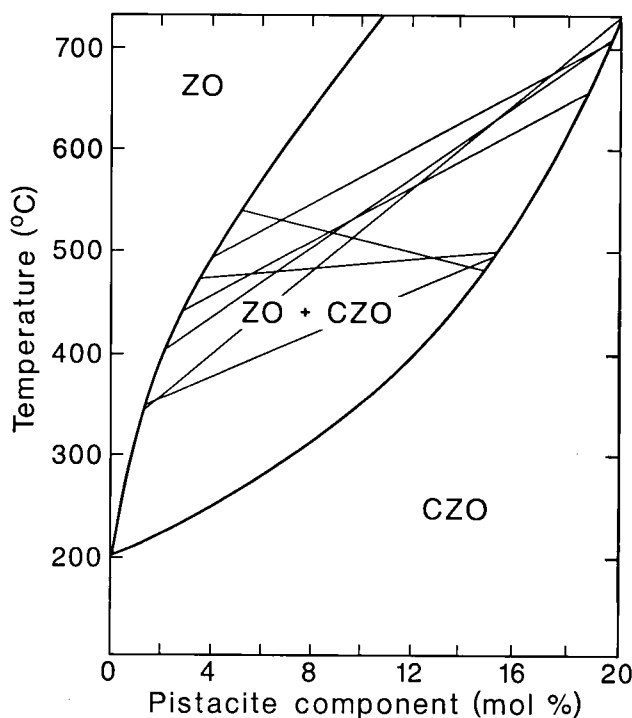
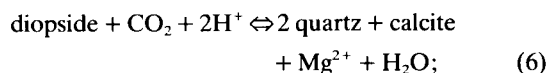


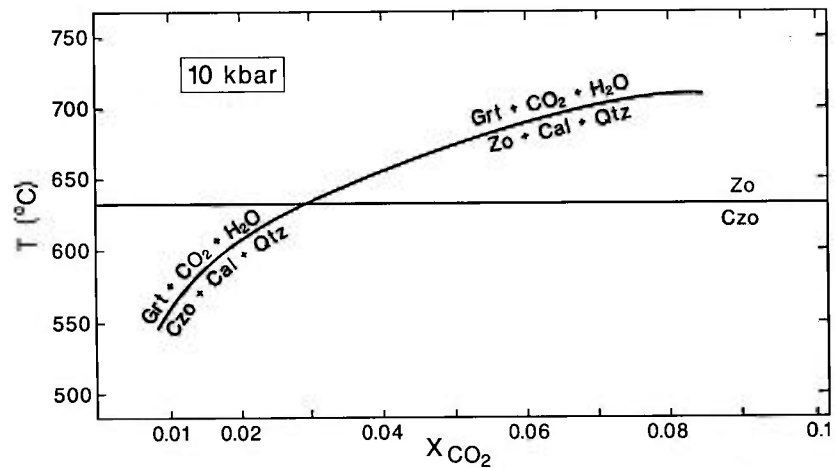
Fig. 10. Composition of coexisting zoisite and clinozoisite. The two-phase field is taken from Prunier & Hewitt (1985). Pistacite component =  $Fe^{3+}/(Fe^{3+} + Al)$ .

breakdown reaction

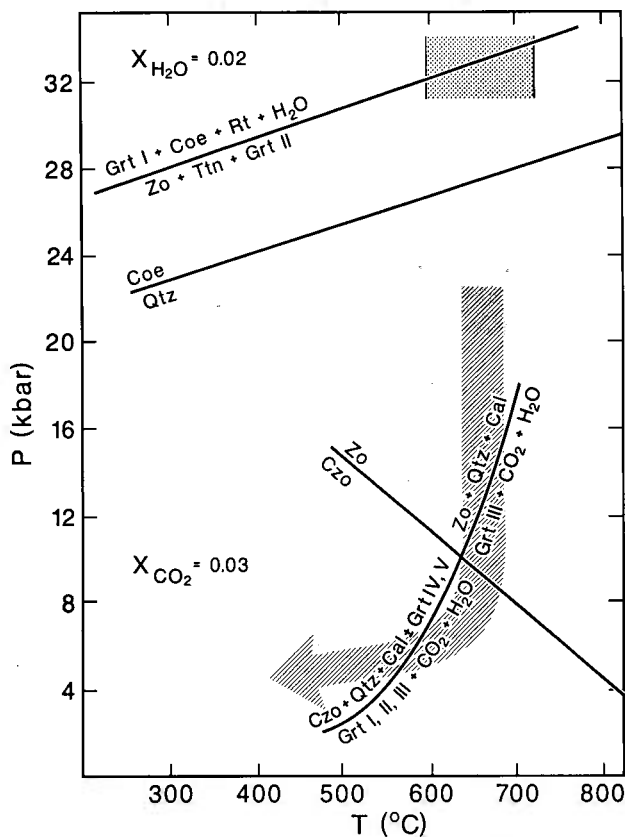


the  $Mg^{2+}$  may be consumed during formation of garnets IV and V. A minimum temperature of 523°C ( $1\sigma = 7^\circ C$ ) at 10 kbar ( $1\sigma = 0.4$  kbar) is provided by the absence of dolomite and the presence of diopside (Holland & Powell, 1990). Therefore, reaction textures (2), (3), (4) and (6) are associated with local fluid buffering by the mineral phases. Most probably, a period of fluid absence in the calc-silicate layers prevailed during the uplift from *very* high-pressure conditions ( $\geq 30$  kbar) until the beginning of the amphibolite facies metamorphism, since no observable mineral reactions occurred within this  $P-T$  range. However, it is likely that for at least parts of the amphibolite facies overprint the fluid composition was buffered externally by fluid introduction due to the dehydration of adjacent metasediments and, subsequently, removal of this fluid by means of the hydration of the adjacent mafic eclogites. The  $T-X_{CO_2}$  diagram for the CASV system at 10 kbar using pure end-member compositions shows an invariant point at  $X_{CO_2} = 0.03$  and 634°C (Fig. 11), indicating that the  $CO_2$  activity, buffered by the solid phases, was low during the amphibolite facies conditions. This activity estimate corresponds well with the fluid inclusion studies which suggest high  $H_2O$  and low  $CO_2$  activities at these conditions (Klemd *et al.*, 1992b).





**Fig. 11.** Isobaric ( $P = 10$  kbar)  $T$ - $X_{\text{CO}_2}$  diagram illustrating the reaction curves in the CASV system using unit activities and the thermodynamic dataset of Holland & Powell (1990).



**Fig. 12.**  $P$ - $T$  diagram displaying the evolution of the high-pressure rocks of the Münchberg gneiss complex using reaction textures preserved in calc-silicates. The very high-pressure reaction curve ( $X_{\text{H}_2\text{O}} = 0.02$ ) was constructed using the thermodynamic dataset of Holland & Powell (1988) and calculated solid phase activities. The estimated  $P$ - $T$  conditions for the high-pressure metamorphism is shown by the shaded area. The invariant point at 10 kbar and 634°C and  $X_{\text{CO}_2} = 0.03$  displays amphibolite facies conditions and was constructed using pure end-member compositions. A generalized exhumation path followed by the calc-silicates is shown by a solid arrow for the amphibolite facies conditions. For details see text.

The  $P$ - $T$  conditions for reactions (2)–(5) at  $X_{\text{CO}_2} = 0.03$  are displayed on a  $P$ - $T$  diagram (Fig. 12) showing the position of an invariant point at 10 kbar ( $1\sigma = 0.3$  kbar) and 634°C ( $1\sigma = 8^\circ\text{C}$ ) using unit activities. The equilibria of the end-member phases are consistent with the formation of garnets with decreasing grossular component during decompression. At  $X_{\text{CO}_2} > 0.03$  calculated pressures decrease and temperatures increase to unrealistically high values ( $X_{\text{CO}_2} = 0.1 \Rightarrow T > 700^\circ\text{C}$ ). Furthermore, the position of the invariant points also strongly depends on the chosen activity models and chemical equilibrium conditions. When using calculated solid phase activities it is impossible to calculate an invariant point for the CFASV system (Figs 11 & 12). This is due to the change in variance when incorporating  $\text{Fe}_2\text{O}_3$ . However, Figs 11 & 12 are useful to illustrate the position of the reaction curves, thereby constraining the lower part of the unroofing path followed by the calc-silicates and, probably, of the adjacent metasediments and mafic eclogites.

## DISCUSSION

The calc-silicate interlayers provide excellent constraints on the  $P$ - $T$  conditions and synmetamorphic fluid composition. The high-pressure conditions have been estimated at about 630°C and  $\geq 31$  kbar with  $X_{\text{H}_2\text{O}} \leq 0.03$  (Fig. 12), which supports the possible former presence of coesite in the adjacent mafic eclogites (e.g. Smith, 1984; Okrusch *et al.*, 1991). The low  $X_{\text{H}_2\text{O}}$  values are in agreement with fluid inclusion studies, which revealed the presence of a high-density  $\text{CO}_2$ - $\text{N}_2$ -rich fluid phase in the calc-silicate rocks during high-pressure metamorphism (Klemd *et al.*, 1992b). The complete absence of such a fluid in the mafic eclogites argues against a pervasive infiltration of a  $\text{CO}_2$ - $\text{N}_2$ -rich fluid, but instead for the presence of small amounts of fluids, the composition of which was buffered at a local scale. The high-pressure relics may not represent the original peak-metamorphic conditions. Incomplete replacement of high-pressure minerals is characteristic of kinetic barriers to polymorphic

inversion in response to decompression (Rubie & Thompson, 1984). Thus, they may only display another stage of the unroofing path. This is indicated by the possible former presence of coesite in the mafic eclogites (for discussion see Smith, 1984; Okrusch *et al.*, 1991).

In contrast to the calc-silicate rocks, the H<sub>2</sub>O activity in the mafic eclogites was estimated at between 0.64 and 0.9 (see Klemd, 1989; Massonne, 1991; O'Brien, 1993). The estimation of the high H<sub>2</sub>O activities is in agreement with fluid inclusion studies in high-pressure metamorphic veins in some mafic eclogites, which exclusively contain H<sub>2</sub>O-rich inclusions (Klemd, 1989, 1993a, b). This suggests that large fluid composition gradients existed during high-pressure metamorphism, a feature that appears to occur at great depths associated with subduction zones (Selverstone *et al.*, 1992). Furthermore, the absence of mineral reactions between metamorphic peak conditions and the beginning of amphibolite facies metamorphism in the calc-silicates, gneisses and almost all eclogites precludes external buffering of the peak-metamorphic fluid composition by means of pervasive, large-scale fluid infiltration, because there had to be some means of removing this fluid before the onset of retrograde reactions (for discussion see Fitzsimons & Thost, 1992).

The *P-T* conditions of the amphibolite facies overprint are difficult to constrain due to disequilibrium conditions. However, from the reactions involving grossular-rich garnet it can be deduced that the very high-pressure metamorphism was followed by an isothermal pressure decrease, which is also exhibited by mineral reactions in the adjacent mafic eclogites and gneisses (Klemd *et al.*, 1991; O'Brien, 1993). The various reaction textures show evidence for multiple recrystallization phases during exhumation. *P-T* conditions for the onset of the amphibolite facies overprint are ≈10 kbar at 630°C (Fig. 12). Amphibolite facies *P-T* conditions in the adjacent mafic eclogites and gneisses span a wide pressure range, between 6 and 12 kbar at about 630°C (Matthes *et al.*, 1974; Franz *et al.*, 1986; Klemd *et al.*, 1991; O'Brien, 1993) and, furthermore, are characterized by abundant disequilibrium conditions (Klemd, 1993a, b). Thus, the amphibolite facies *P-T* estimate for the calc-silicates is probably just one stage of recrystallization of the uplift history.  $X_{\text{CO}_2}$  during amphibolite facies conditions is relatively low (<0.03) which also is applicable to the mafic eclogites and adjacent gneisses (Klemd, 1989; Klemd *et al.*, 1991; Massonne, 1991; O'Brien, 1993). This calculated  $X_{\text{CO}_2}$  value is supported by fluid inclusion studies in the mafic eclogites and gneisses, which revealed predominantly water-rich inclusions with densities appropriate to amphibolite facies conditions supporting the presence of a free, H<sub>2</sub>O-rich fluid phase during these conditions (Klemd, 1989; Klemd *et al.*, 1992b). In view of the small size of the calc-silicate layers and the dehydration reactions in the gneisses present under amphibolite facies conditions, a sequential influx of H<sub>2</sub>O released from adjacent gneisses may have played a role in lowering  $X_{\text{CO}_2}$  during amphibolite facies conditions. This led to the formation of reaction textures and a heterogeneous composition of

garnet coronas. However, the presence of multiple generations of minerals in individual thin sections precludes a pervasive post-peak metamorphic fluid flow promoting re-equilibration within the calc-silicates. The preservation of very high-pressure relics and compositional differences of the same mineral phases in individual thin sections, combined with the fact that no major temperature increase occurred after high-pressure metamorphism, is in excellent agreement with a fast, tectonically driven uplift of the high-pressure rocks (Klemd *et al.*, 1991; Klemd, 1993a, b; O'Brien, 1993).

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