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-Al2O3-SiO2-CO2-H2O 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 $X_{H_2O} \leq 0.03$. Small volumes of a CO2-N2-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. $X_{CO_2}$ of the H2O-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 northwestern margin of the Bohemian Massif in SE Germany (Fig. 1). It is considered to be a nappe pile resting on the autochthonous, archi-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
'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 ± 50°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.
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, clinzoisite, 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 clinzoisite, 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 TiO₂ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Grt</th>
<th>Cpx</th>
<th>Zo</th>
<th>Czo</th>
<th>Cal</th>
<th>Ttn</th>
<th>Rt</th>
<th>Phen</th>
<th>Otz</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>754U</td>
<td>165.40</td>
<td>+, R</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>R</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>755</td>
<td>165.16</td>
<td>+, R</td>
<td>+</td>
<td>R</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>R</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>761</td>
<td>166.20</td>
<td>+ , R</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>R</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>166.02</td>
<td>166.02</td>
<td>+, R</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>R</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>785</td>
<td>172.0</td>
<td>+, R</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>R</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

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

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.%) and 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 clinzoisite 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 ± magnetite (Fig. 6). The composition is salitic to ferrosalitic (Table 3) with \( X_{Mg} \) 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 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.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample</th>
<th>755II/5 rim</th>
<th>755II/7 core</th>
<th>755II/9 rim</th>
<th>755II/6 core</th>
<th>755II/8</th>
<th>755II/10 rim</th>
<th>166.02/1 core</th>
<th>166.02/1 core</th>
<th>166.02/1 core</th>
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</thead>
<tbody>
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<td>SiO₂</td>
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<td>38.01</td>
<td>38.96</td>
<td>38.36</td>
<td>38.59</td>
<td>38.14</td>
<td>38.78</td>
<td>38.67</td>
<td>38.75</td>
<td>37.91</td>
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<tr>
<td>TiO₂</td>
<td>0.37</td>
<td>0.42</td>
<td>0.15</td>
<td>0.20</td>
<td>0.24</td>
<td>0.15</td>
<td>0.22</td>
<td>0.41</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>CrO₃</td>
<td>0.03</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.81</td>
<td>0.82</td>
<td>1.60</td>
<td>3.10</td>
<td>2.07</td>
<td>2.17</td>
<td>2.02</td>
<td>2.64</td>
<td>2.48</td>
<td>4.10</td>
</tr>
<tr>
<td>FeO</td>
<td>2.13</td>
<td>2.13</td>
<td>1.44</td>
<td>4.21</td>
<td>3.36</td>
<td>21.27</td>
<td>6.85</td>
<td>5.05</td>
<td>5.47</td>
<td>5.31</td>
</tr>
<tr>
<td>MnO</td>
<td>0.26</td>
<td>0.32</td>
<td>0.36</td>
<td>1.58</td>
<td>0.58</td>
<td>2.77</td>
<td>1.44</td>
<td>1.21</td>
<td>1.27</td>
<td>7.22</td>
</tr>
<tr>
<td>MgO</td>
<td>0.04</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>1.35</td>
<td>0.16</td>
<td>0.02</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>CaO</td>
<td>35.57</td>
<td>35.17</td>
<td>35.58</td>
<td>32.58</td>
<td>34.19</td>
<td>14.84</td>
<td>29.52</td>
<td>31.36</td>
<td>30.81</td>
<td>25.86</td>
</tr>
<tr>
<td>Total</td>
<td>99.79</td>
<td>98.13</td>
<td>99.19</td>
<td>100.01</td>
<td>99.82</td>
<td>100.12</td>
<td>99.49</td>
<td>99.54</td>
<td>99.35</td>
<td>98.68</td>
</tr>
</tbody>
</table>

Fig. 6. Replacement of diopside (large light grain) by calcite, quartz and magnetite (sample 755I, depth 163.15 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.

<table>
<thead>
<tr>
<th>Grain Sample</th>
<th>CPX 1</th>
<th>CPX 2</th>
<th>CPX 3</th>
<th>CPX 4</th>
<th>CPX 5</th>
<th>CPX 6</th>
</tr>
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<tbody>
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<td>754H</td>
<td>754B1</td>
<td>754B1</td>
<td>754B1</td>
<td></td>
</tr>
<tr>
<td>9/18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>50.25</td>
<td>49.92</td>
<td>51.82</td>
<td>51.05</td>
<td>52.86</td>
<td>52.95</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.05</td>
<td>0.09</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>0.38</td>
<td>0.90</td>
<td>0.50</td>
<td>1.98</td>
<td>1.56</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.04</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>1.56</td>
</tr>
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<td>4.67</td>
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<td>0.00</td>
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<tr>
<td>Fe₂O₃</td>
<td>11.98</td>
<td>10.50</td>
<td>14.34</td>
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<td>10.10</td>
<td>9.68</td>
</tr>
<tr>
<td>FeO</td>
<td>0.65</td>
<td>0.40</td>
<td>0.31</td>
<td>0.23</td>
<td>0.23</td>
<td>2.64</td>
</tr>
<tr>
<td>MnO</td>
<td>9.12</td>
<td>9.68</td>
<td>8.34</td>
<td>8.31</td>
<td>10.71</td>
<td>1.71</td>
</tr>
<tr>
<td>MgO</td>
<td>23.94</td>
<td>23.61</td>
<td>22.91</td>
<td>23.40</td>
<td>23.40</td>
<td>9.08</td>
</tr>
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<td>CaO</td>
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<td>0.29</td>
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<td>1.04</td>
<td>9.59</td>
</tr>
<tr>
<td>Na₂O</td>
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<td>0.01</td>
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<td>Total</td>
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<tr>
<td>K₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95.59</td>
</tr>
</tbody>
</table>

| Si            | 1.95  | 1.93  | 2.01  | 1.99  | 1.99  | 6.90  |
| Ti            | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Al³⁺          | 0.02  | 0.00  | 0.00  | 0.00  | 0.00  | 1.00  |
| Cr            | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 3.37  |
| Fe⁺⁺          | 0.08  | 0.14  | 0.00  | 0.02  | 0.00  | 0.17  |
| Fe³⁺          | 0.39  | 0.34  | 0.46  | 0.46  | 0.31  | 0.17  |
| Mn            | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Mg            | 0.02  | 0.01  | 0.01  | 0.01  | 0.00  | 0.00  |
| Ca            | 0.53  | 0.56  | 0.48  | 0.48  | 0.60  | 0.02  |
| Na            | 0.01  | 0.00  | 0.01  | 0.03  | 0.08  | 0.00  |
| K             | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 1.51  |
| Total         | 4.00  | 4.00  | 3.99  | 3.99  | 4.02  | 13.60 |

* Formulae calculated on the basis of 6 O. Fe³⁺ by charge balance. † Formulae calculated on the basis of 22 O. ‡ Formulae calculated on the basis of 11 O. All Fe was calculated as Fe³⁺.

Fig. 7. Rutile relics (arrowhead) in titanite enclosed in zoisite (sample 7551, 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 clinopyroxene, phengite and titanite (Manning & Bohlen, 1991). The activity of CaFeSiO₄ in clinopyroxene was calculated as $X_{Fe}$ 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

$$\text{garnet I} (a_{\text{Grs}} = 0.77) + \text{rutile} + \text{coesite} + H_2O \Leftrightarrow \text{zoisite} (a_{\text{Zns}} = 0.811) + \text{titanite} (a_{\text{Tit}} = 0.816)$$

$$+ \text{garnet II} (a_{\text{Grs}} < 0.77) \quad (1)$$

in the CaO-TiO₂-Al₂O₃-SiO₂-H₂O-CO₂ (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 GECALC 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 Moira massif.
The minimum pressures with acceptable standard deviations (1σ) recorded in the Weissenstein calc-silicates are 33 kbar (1σ = 2.9 kbar) at 578°C (1σ = 178°C) and aH2O = 0.03 and 30 kbar (1σ = 3.6 kbar) at 595°C (1σ = 178°C) and aH2O = 0.01 (Fig. 8). The T-XCO2 diagram in the CTASV-system constrains XH2O at 33 kbar in the coexisting fluid to be ±0.03 between 578 and 880°C (Fig. 9). This XH2O estimate is in excellent agreement with fluid inclusion studies in the calc-silicates, which suggest a high CO2-N2 and a low H2O activity during high-pressure metamorphism (Klemd et al., 1992a, b). However, if the H2O 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 \( P-T-X_0-C0_2 \) 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

\[
2 \text{zoisite} + 3 \text{quartz} + 5 \text{calcite} \rightleftharpoons 3 \text{garnet \text{III} + 5 \text{CO}_2 + \text{H}_2\text{O}}. \quad (2)
\]

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):

\[
garnet \text{I, II} + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{clinozoisite} + \text{quartz} + \text{calcite} \pm \text{garnet \text{IV}}. \quad (3)
\]

\[
garnet \text{III} + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{clinozoisite} + \text{quartz} + \text{calcite} \pm \text{garnet \text{V}}. \quad (4)
\]

Another important reaction

\[
\text{zoisite} \rightleftharpoons \text{clinozoisite} \quad (5)
\]

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 \( T-X_0 \) 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 breakdown reaction

\[
diopside + \text{CO}_2 + 2H^+ \rightleftharpoons \text{2 quartz} + \text{calcite} + \text{Mg}^{2+} + \text{H}_2\text{O}; \quad (6)
\]

the \( Mg^{2+} \) may be consumed during formation of garnets IV and V. A minimum temperature of 523°C (1σ = 7°C) at 10 kbar (1σ = 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 (≥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 \( T-X_0 \) 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).
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 (\( 1\sigma = 8^\circ \) 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 (\( X_{\text{CO}_2} = 0.1 \Rightarrow T > 700^\circ \) 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 Fe\textsubscript{2}O\textsubscript{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 \( \approx 31 \) 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$_2$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$_2$O activities is in agreement with fluid inclusion studies in high-pressure metamorphic veins in some mafic eclogites, which exclusively contain H$_2$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$_2$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$_2$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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