MAGNESIOCARPHOLITE AND MAGNESIOCHLORITOID: TWO INDEX MINERALS OF PELITIC BLUESCHISTS AND THEIR PRELIMINARY PHASE RELATIONS IN THE MODEL SYSTEM MgO–Al₂O₃–SiO₂–H₂O

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ABSTRACT. Metapelitic rocks from blueschist-facies terranes, hitherto considered to be devoid of critical mineral assemblages, are in fact not. Recently described rocks from the Alps and the Mediterranean contain two index minerals for blueschist metamorphism: carpholite, \((\text{Mg,Fe}^{2+})\text{Al}[\text{Si}_2\text{O}_5](\text{OH})_2\)\(^\text{a}\), with compositions varying from the Fe to the Mg endmember, and Mg-rich chloritoid, \((\text{Mg,Fe}^{2+})\text{Al}_2\text{O}[\text{Si}_2\text{O}_5](\text{OH})_2\)\(^\text{a}\), containing up to 74 mol percent Mg endmember. On the basis of their assemblages, four different grades of blueschist metamorphism can be distinguished in simple AFM-plots (in the order of increasing grade): (1) only Fe-rich carpholite present; (2) Mg-rich carpholite coexisting with Fe-rich chloritoid; (3) intermediate Fe–Mg chloritoid with talc and chlorite; (4) Mg-rich chloritoid with talc and kyanite.

High-pressure experimentation in the system MgO–Al₂O₃–SiO₂–H₂O in the range 15 to 35 kb water pressure and 400° to 800°C led to the synthesis of both magnesiocarpholite and magnesiochloritoid. The preliminary petrologic grid derived from a limited number of bracketing runs shows both minerals to be typical high-pressure phases with stability fields limited by minimum pressures of about 7 kb for Mg–carpholite and 18 kb for Mg–chloritoid. The less hydrous Mg–chloritoid is stable at higher temperatures, but its stability range overlies that of the carpholite phase.

As a result of the relative locations of the stability fields of the Fe and Mg endmembers of both the carpholite and the chloritoid series, FeMg–carpholites and Mg-rich chloritoids can form under metamorphic conditions characterized by low geothermal gradients (about 8°-15°C/km). The four consecutive metamorphic grades of blueschist metapelites outlined above can be rationalized by mineral reactions occurring in the petrologic grid of the Fe-free model system, although for Mg–chloritoid its metastable phase relations with quartz have to be taken into account. The two metapelitic index minerals and their varying parageneses and Mg/Fe ratios may become useful geobarometers and thermometers for different types and grades of blueschist metamorphism in complex areas of subduction.

INTRODUCTION

Until very recently, petrologic studies in blueschist metamorphic terranes concentrated strongly on basic igneous rocks and graywackes, which — due to their bulk chemistry — may develop characteristic blueschist in-

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dex minerals such as glaucophane, jadeite, lawsonite, and aragonite, all being Na- or Ca-bearing phases. Indeed, a set of new hydrous calcium silicates was detected through such studies: they are rosenhahnite (Pabst, Gross, and Alfors, 1967; Pabst, 1977), vuagnatiite (Sarp, Bertrand, and McNear, 1976), and chantalite (Sarp, Deferne, and Liebich, 1977), among which at least rosenhahnite may be confined in its pressure temperature stability to the blueschist environment (Leistner and Chatterjee, 1978). Mineralogical work on iron-rich metasediments within blueschists had revealed the existence of three new hydrous iron silicate minerals: deerite, howieite, and zussmanite (Agrell, Brown, and McKie, 1965), which later on turned out to represent additional index minerals for this metamorphic facies (Muir Wood, 1979a,b, 1980; Lattard and Schreyer, 1981).

On the other hand, rocks of pelitic compositions appeared to be free from minerals or mineral assemblages diagnostic for blueschist metamorphism (compare Miyashiro, 1973; Turner, 1981; Winkler, 1979), if one ignores the common but not spectacular occurrence of Si-rich phengites instead of muscovite (Ernst, 1968). The surprising discovery of phengite coexisting with talc (Abraham and Schreyer, 1976) initiated more detailed studies of the blueschist phyllosilicate assemblages, especially after it was shown experimentally that the assemblage phengite—talc does indeed form at high pressures (Schreyer and Baller, 1977). Recently Chopin (1981) demonstrated that this pair is of widespread occurrence in high-grade pelitic blueschists of the Western Alps. Independently, it was shown by several authors who will be quoted in the next section that pelitic blueschists carry Mn-poor, (Mg,Fe)-rich carpholites which have never been found in metapelites of low- and medium-pressure metamorphism. In the latter environments carpholite is predominantly a manganese mineral with the formula \((\text{Mn}^{2+},\text{Mg,Fe}^{2+})(\text{Al,Fe}^{3+})_2[\text{Si}_2\text{O}_5](\text{OH})_4\) (Mottana and Schreyer, 1977). Finally and significantly, Mg-rich chloritoids (“sissomdines”), \((\text{Mg,Fe}^{2+})(\text{Al,Fe}^{3+})_2\text{O}[\text{Si}_3\text{O}_8](\text{OH})_2\), have thus far been found only in areas where glaucophane occurs (Bearth, 1963). Thus it would seem that, despite classical prejudice, metapelites in blueschist environments are not necessarily devoid of critical mineral assemblages.

In the present paper we attempt to approach the problem of the behavior of metapelitic rocks under blueschist facies conditions from two different ends:

First, the mineral assemblages as described in the petrographic literature on relevant natural rocks are reviewed, and a subdivision relating to different metamorphic grades within the blueschist facies is proposed, also trying to define the interconnecting mineral reactions.

Second, new experimental results in the simplest model system for metapelites, that is MgO–Al₂O₃–SiO₂–H₂O, are presented that define, in a preliminary fashion, phase relations at high water pressures and low temperatures thus extending the work of Schreyer and Seifert (1969a,b) toward lower temperatures, where previously no reactions had been achieved. The incentive for this study was the surprising success of Chopin and Goffé (1981) to synthesize pure magnesiocarpholite, MgAl₂[Si₂O₇](OH)₄, and more recently, also pure magnesiochloritoid (Chopin, in preparation).
Table 1
Mineralogy of high-pressure, low-temperature metapelites
(Fe-carpholite: < 50 mol% Mg endmember; Mg-carpholite: > 50 mol% Mg endmember; Fe-chloritoid: < 25 mol% Mg endmember; Fe-Mg-chloritoid: 25-50 mol% Mg endmember; Mg-chloritoid: > 50 mol% endmember)

<table>
<thead>
<tr>
<th>Localities</th>
<th>Mineral contents in metapelitic rocks</th>
<th>Type of occurrence</th>
<th>Index minerals or parageneses in neighboring rocks; additional remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern Central Sulawesi (Celebes, Indonesia)</td>
<td>Fe-carpholite, quartz, white mica, chlorite, hematite</td>
<td>Quartz veins, metaconglomerate nesosital, blastocaminitic quartzite</td>
<td>Lawsonite, jadeite-quartz, crossite, Mg-riebeckite, aragonite. No chloritoid</td>
<td>W. P. de Roever, 1947, 1951; W. P. de Roever and Beunk, 1978</td>
</tr>
<tr>
<td>Haute Ubaye (Piemont zone, Western Alps, France)</td>
<td>Fe-carpholite, quartz, calcite</td>
<td>Vein in calc-schist</td>
<td>Lawsonite, jadeite-quartz, glauconphane. No chloritoid, no garnet</td>
<td>Scaini, Mottana, and Abraham, 1976</td>
</tr>
<tr>
<td>Amorgos island (Greece)</td>
<td>Fe-carpholite</td>
<td>Vein in metabauxite</td>
<td>Blue amphibole? Probably no chloritoid, no garnet</td>
<td>Minoux, Bonneau, and Kienast, 1981</td>
</tr>
<tr>
<td>Eastern Crete (Greece)</td>
<td>Fe-carpholite, quartz, calcite, pyrophyllite, chlorite</td>
<td>Pyrophyllite schist, segregations in sheared zones of quartzites and phyllites</td>
<td>Riebeckite/crossite, aegyrite-augite, lawsonite. No garnet, no chloritoid</td>
<td>Seidel, 1978; Viswanathan and Seidel, 1979</td>
</tr>
<tr>
<td>Central Crete</td>
<td>Fe-carpholite, Fe-chloritoid, pyrophyllite or chlorite, white micas, hematite, quartz</td>
<td>Phyllites, vein fillings</td>
<td>Remnants of blue amphiboles (glauconphane, crossite)</td>
<td>Seidel, 1978; Viswanathan and Seidel, 1979</td>
</tr>
<tr>
<td></td>
<td>Mg-carpholite, pyrophyllite, diaspore, (Fe-chloritoid)</td>
<td>Metabauxites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southern Briançon zone (Western Alps, Italy)</td>
<td>Fe-carpholite, Fe-chloritoid, chlorite, white micas, lawsonite, quartz</td>
<td>Schists</td>
<td>Lawsonite, jadeite-quartz, glauconphane — No garnet</td>
<td>Chopin and Goffé, unpub. data</td>
</tr>
<tr>
<td></td>
<td>Mg-carpholite, quartz</td>
<td>Vein filling in phengite-chlorite schists</td>
<td></td>
<td></td>
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<tr>
<td>Peloponnnesus (Greece)</td>
<td>Mg-carpholite, Fe-chloritoid, quartz, chlorite</td>
<td>Schists, vein fillings</td>
<td>Glaucophane, lawsonite, garnet</td>
<td>Skarpelis and Seidel, in preparation</td>
</tr>
<tr>
<td>Northern Calabria (Italy)</td>
<td>Fe-carpholite</td>
<td>Veins in phyllite</td>
<td>Lawsonite, albite, pumpellyte, chlorite</td>
<td>E. W. F. de Roever and Beunk, 1971</td>
</tr>
<tr>
<td>Location</td>
<td>Metamorphic Assemblage</td>
<td>Minerals</td>
<td>References</td>
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<tr>
<td>Central Calabria</td>
<td>Mg-carpholite, Fe-chloritoid, quartz, calcite, white micas, chlorite</td>
<td>Quartzite</td>
<td>Greenschist parageneses but remnants of lawsonite, blue amphibole, and green sodic pyroxene. No Fe-carpholite</td>
<td>Dubois, 1976; Dubois and Kienast, 1975; E. W. F. de Roever and Beunk, 1971</td>
</tr>
<tr>
<td>Vanoise and Liguria (Western Alps, France and Italy, respectively)</td>
<td>Mg-carpholite, Fe-chloritoid, quartz, pyrophyllite, diasporite, chlorite, white micas, cookeite</td>
<td>Aluminous metapelites, metapexite, quartz veins</td>
<td>Lawsonite No garnet?</td>
<td>Goffé and Saliot, 1973; Goffé and Saliot, 1977; Goffé, 1979, 1980, 1982</td>
</tr>
<tr>
<td>Samos island (Greece)</td>
<td>Mg-carpholite, Fe-Mg-chloritoid, chlorite, quartz, pyrophyllite, white micas</td>
<td>Phyllite</td>
<td>Albite, epidote, chlorite, glaucophane, diasporite, garnet</td>
<td>Okrusch, 1981</td>
</tr>
<tr>
<td>Gran Paradiso area and Aosta valley (Western Alps, France and Italy)</td>
<td>Fe-Mg-chloritoid, quartz, garnet, talc, Mg-chlorite, glaucophane, white micas, epidote</td>
<td>Quartzite, schist</td>
<td>Omphacite-garnet, jadeite-quartz, margarite, zoisite. No carpholite</td>
<td>Chopin, 1979, 1981</td>
</tr>
<tr>
<td>Zermatt area (Western Alps, Switzerland)</td>
<td>Fe-Mg-chloritoid, talc, garnet, glaucophane, quartz, epidote</td>
<td>Metabasite, schist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mont Rosa area (Western Alps, Italy)</td>
<td>Mg-chloritoid, talc, Mg-chlorite, quartz, kyanite, phengite</td>
<td>Mafic microsystem within unfoliated metagabbro</td>
<td>Omphacite-garnet, zoisite, No carpholite</td>
<td>Bearth, 1963, 1967; Chinner and Dixon, 1973</td>
</tr>
<tr>
<td>Hohe Tauern (Eastern Alps, Austria)</td>
<td>Mg-chloritoid, talc, kyanite, either quartz or Mg-chlorite</td>
<td>Pelitic pods within eclogite</td>
<td>Omphacite-garnet, glaucophane, zoisite, margarite. No carpholite</td>
<td>Miller, 1974, 1977</td>
</tr>
</tbody>
</table>
While the detailed experimental data will be published elsewhere, we wish to emphasize, in this homage to the late P. M. Orville, the application of our results to a kind of progressive metamorphism that seems to be typical of subduction zones along Alpine-type plate boundaries. We hope that Phil, who had developed a keen interest in the metamorphism of the Alps as well as of other Alpidic Mediterranean areas, would have appreciated this contribution.

MINERALS AND MINERAL ASSEMBLAGES OF HIGH-PRESSURE, LOW-TEMPERATURE METAPELITES

The main results of recent petrographic work on metapelites and related rocks from blueschist terranes, largely of the Alps and the Mediterranean, are summarized in table 1. Only assemblages of regional significance are mentioned. This compilation shows that, indeed, FeMg-carpholite and chloritoid are common mineral constituents which may coexist with quartz, pyrophyllite, diaspore, chlorite, and, possibly, garnet, talc, and/or kyanite, as far as alkali- and Ca-free phases are concerned. A brief survey of the chemical variations of both carpholite and chloritoid (fig. 1) confirms that in the blueschist facies these minerals are virtually confined to ferromagnesian compositions. Low-pressure metamorphic environments carry only Mn-dominant carpholites; Fe-rich chloritoids may appear both in blueschist and low-pressure regimes.

On the basis of the mineral contents given in table 1, both of metapelites and of neighboring rocks with different chemistry, all the blueschist environments listed can readily be subdivided into two groups:

![Diagram of chemical composition of natural carpholite and chloritoid](image)

Fig. 1. Chemical composition of natural carpholite and chloritoid. The ruled areas represent the compositional ranges in the low- to intermediate-pressure metamorphic areas. Blueschist-facies carpholite and chloritoid are shown individually, indicating their parageneses by different symbols. Data for carpholite were taken from Goffé (ms), Kramm (1980), Viswanathan and Seidel (1979) and from the compilation of Mottana and Schreyer (1977); for chloritoid from Bearth (1963), Chopin (ms, and unpub. data), Fransolet (1978), Goffé (ms), Halfferdahl (1961), Kramm (1980), and Miller (1977).
1. Those exhibiting a relatively low grade of metamorphism indicated by the occurrence of pyrophyllite, diaspor, and lawsonite. Typical mafic phases of the metapelites are here carpholite and chlorite. This group includes about the first dozen localities of table I.

2. Other environments which, due to the appearance of kyanite, margarite, and zoisite, represent a higher grade of metamorphism. They carry Mg-rich chloritoid, talc, and garnet as mafic phases.

The phyllite from Samos, in which Okrusch (1981) found coexisting magnesiocarpholite, Mg-rich chloritoid, and kyanite may be taken as a transitional type between the two groups. The above grouping can be further refined, if the mineral chemistry of the mafic metapelite phases is taken into account. Ferrocarrpholite occurs largely in regions where neither chloritoid nor garnet is known. Eastern Crete, Haute Ubay, Northern Calabria, and the Celebes occurrence are examples of what is considered here to represent the lowest grade of metamorphism amongst the

Fig. 2. Four characteristic stages in the mineralogical evolution of blueschist facies metapelites, as represented by AFM-type plots with excess quartz. The sequence A to D indicates principally increasing metamorphic grade. For further discussion see text. Abbreviations: Car = carpholite, Chl = chlorite, Ctd = chloritoid, Gt = garnet, Ky = kyanite, Pyroph = pyrophyllite, Tc = talc.
PLATE 1

Microphotographs of some important assemblages in blueschist metapelites (abbreviations as in figure 2; q = quartz).


B. Talc-chloritoid-chlorite-quartz assemblage in "silvery micaschist" from the Gran Paradiso area, France. Crossed nichols.
C. Reaction zone consisting of kyanite (small grains with high relief) and a fine-grained chlorite groundmass (white) between magnesiochloritoid (upper portion) and talc (lower portion). Chloritoid quartzite from the Monte Rosa area, Italy. Plane polarized light.

localities of table 1. The AFM-type plot of figure 2A depicts schematically the characteristic phase relations, which involve the coexistence of chlorite and pyrophyllite (Seidel, 1978, p. 112).

As a next step toward higher grade, iron-rich chloritoid appears and may coexist with a more Mg-rich ferrocarpholite (Central Crete, southern Briançon zone) and, subsequently, even with magnesiocarpholite (Western Crete; Vanoise, see pl. 1-A; Liguria; Southern Calabria; Peloponnesus). In 1977 E. W. F. de Roever recognized the significance of carpholite-chloritoid coexistence, in which both phases become increasingly rich in Mg with rising grade. Seidel (1981) and Goffé (ms) confirmed this to be one of the key features of the low grades in the high-pressure metamorphic evolution of pelitic rocks. It should be emphasized, however, that the Mg contents of the chloritoids are still relatively low and fall into the same range as for chloritoids of “normal,” low-pressure metamorphic terranes (fig. 1). Figure 2B illustrates the paragenetic relationships indicating that, in the presence of quartz, the carpholite–chloritoid assemblage prohibits the coexistence of chlorite and pyrophyllite, which form a typical pair in lower-pressure metamorphic terranes (for example, Tobschall, 1969; Frey, 1978), but probably also in the lowest grades of the high-pressure evolution (compare fig. 2A). In the higher-grade assemblages with Mg-rich chloritoid, but without carpholite, the common characteristic is the appearance of the pairs FeMg garnet–talc and chloritoid–talc which are due to a progressive restriction of the stability of chlorite in the presence of quartz.
First, talc, chloritoid, and quartz may still coexist with Mg-rich chlorite as in the Gran Paradiso area (pl. 1-B; fig. 2C). At a still more advanced stage chlorite disappears from the assemblage in favor of the pair talc–kyanite (Zermatt area; Hohe Tauern; fig. 2D), leading to kyanite–talc whiteschists in highly magnesian rocks, as described by Schreyer (1977).

Obviously, the evolutionary sequence presented in figure 2, A to D, is by no means complete, and it may indeed be questioned as to whether or not the different stages recognized from different areas do belong to a single trend of increasing metamorphic grade. However, this sequence appears reasonable, if one emphasizes the stepwise dehydration of the mineral assemblages that is so characteristic in progressive metamorphism. Thus the following general conclusions about mineral stabilities seem justified and should be compared with the results of the experimental work to be reported later:

1. The long-standing question of the relative stabilities of chloritoid and carpholite, first posed for the Mn-rich members carpholite sensu stricto and ottrelite (Mügge, 1918), finds a clear answer from figure 2 with chloritoid being the high-temperature mineral. For any given intermediate Mg/Fe ratio carpholite breaks down with rising temperature into the less hydrous alternative assemblage according to the reaction:

   \[ \text{MgFe carpholite} \rightarrow \text{MgFe chloritoid} + \text{quartz} + \text{H}_2\text{O} \]  

2. Since, in the above divariant breakdown reaction, Mg is preferentially incorporated in carpholite, magnesiocarpholite must be stable, for a given water pressure, toward higher temperatures than ferrocarpholite.

3. The relative stabilities are similar in the MgFe–chlorite series, in the presence of quartz, with the following breakdown reactions taking place at increasing grade:

   \[ \text{Fe-rich chlorite} + \text{quartz} \rightarrow \text{garnet} + \text{talc} + \text{H}_2\text{O} \]  

   \[ \text{FeMg–chlorite} + \text{quartz} \rightarrow \text{FeMg chloritoid} + \text{talc} + \text{H}_2\text{O} \]  

   \[ \text{Mg–chloritoid} + \text{quartz} \rightarrow \text{kyanite} + \text{talc} + \text{H}_2\text{O} \]  

4. The formation of very Mg-rich chloritoid, in the presence of quartz, does not seem to be due to the breakdown of preexisting Mg-rich carpholites but rather follows the reactions

   \[ \text{chlorite} + \text{kyanite} + \text{H}_2\text{O} \rightarrow \text{chloritoid} + \text{quartz} \]  

   \[ \text{talc} + \text{kyanite} + \text{H}_2\text{O} \rightarrow \text{chloritoid} + \text{quartz} \]  

both of which require the addition of water. This seems anomalous for progressive metamorphism, and the PT slope of the requisite reaction curves will be of particular interest.

All these mineral reactions derived from petrologic observation would obviously require experimental investigations in the system MgO–FeO–Al₂O₃–SiO₂–H₂O. The results to be discussed in the following section
Magnesiocarpholite and magnesiochloritoid

from the system MgO–Al₂O₃–SiO₂–H₂O can, therefore, only represent a limiting case, which may, or may not, be a model for the phase relations deduced from natural blueschist metapelites.

**EXPERIMENTAL RESULTS IN THE SYSTEM MgO–Al₂O₃–SiO₂–H₂O**

A systematic study of phase relations in the system MgO–Al₂O₃–SiO₂–H₂O at water pressures in excess of 10 kb has thus far not been undertaken. However, the reconnaissance study of Schreyer (1968) had revealed a fascinating set of new high-pressure phases like yoderite, Mg-staurolite, and kornerupine that were characterized in more detail by Schreyer and Seifert (1969a). Although a few experiments had also been performed at relatively low temperatures, the phase magnesiocarpholite was not encountered, and the appearance of small amounts of magnesiochloritoid could only be suspected (Schreyer, 1968). In the present study experiments were conducted at water pressures between 15 and 35 kb and in the temperature range from 400° to 800°C. Figure 3 depicts all the crystalline phases encountered or considered relevant for the phase relations to be discussed in this PT-range.

**Synthesis of magnesiocarpholite and magnesiochloritoid.**—The first synthesis of a phase with a carpholite structure of the endmember composition MgAl₂[Si₂O₆](OH)₄ was recently reported by Chopin and Goffé (1981). Synthesis conditions were 25 kb water pressure and temperatures between 415° and 600°C. Like natural carpholite the synthetic phase is orthorhombic, space group Ccca, and the cell parameters are a = 13.706; b = 20.075; c = 5.107 Å.

![Figure 3](image)

Fig. 3. Selected crystalline phases of the system MgO–Al₂O₃–SiO₂–H₂O projected onto the water-free plane.
Table 2
Stable and metastable reactions investigated in the system
MgO–Al₂O₃–SiO₂–H₂O

A. Stable reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpholite ⇌ chlorite + kyanite + quartz + H₂O</td>
<td>(8)</td>
<td></td>
</tr>
<tr>
<td>Carpholite ⇌ chlorite + kyanite + talc + H₂O</td>
<td>(7)</td>
<td></td>
</tr>
<tr>
<td>Carpholite + quartz ⇌ kyanite + talc + H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carpholite + diaspore ⇌ chlorite + kyanite + H₂O</td>
<td>(10)</td>
<td></td>
</tr>
<tr>
<td>Chloritoid ⇌ chlorite + kyanite + corundum + H₂O</td>
<td>(6)</td>
<td></td>
</tr>
<tr>
<td>Chloritoid ⇌ pyrope + corundum + H₂O</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>Chloritoid + talc ⇌ chlorite + kyanite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Metastable reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpholite ⇌ chloritoid + quartz + H₂O</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>Chloritoid + quartz ⇌ talc + kyanite + H₂O</td>
<td>(6)</td>
<td></td>
</tr>
</tbody>
</table>

Numbers refer to reactions discussed in the text.

Magnesiochloritoid, MgAl₂O₃[SiO₄](OH)₂, could be synthesized from the anhydrous composition MgO·Al₂O₃·SiO₂ (fig. 3) only at water pressures in excess of 30 kb and at temperatures between 600° and 750°C. Powder X-ray diffraction patterns of the synthetic products indicate that both the monoclinic and the triclinic chloritoid polytypes are present, with the triclinic one dominating and increasing in amount at rising tem-

Fig. 4. Results of bracketing runs conducted to define the location of the invariant point IP involving the phases magnesio-carpholite (Car), chlorite (Chl), talc (Tc), kyanite (Ky), quartz (Q), and fluid (V) near 18 kb, 540°C. Filled symbols show reaction proceeding to left or right as indicated, half-filled symbols no reaction. Bars represent brackets obtained by Massonne, Mirwald, and Schreyer (1981) on the reaction as given in the inset leading to the pairs shown by large letters in the lower and upper right portion. The large field of the assemblage Car–Q is indicated crudely on the left.
perature, as one would expect from entropy considerations. The cell parameters of the triclinic form are $a = 9.43; \, b = 5.44; \, c = 9.13 \, \text{Å};$ and $\alpha = 96.4^\circ; \, \beta = 101.1^\circ; \, \gamma = 90.0^\circ;$ space group $\text{C} \, 2/c$.

Preliminary phase relations.—A limited number of reactions that were considered appropriate to constrain the topology of the system have been investigated experimentally thus far (table 2). For each reaction a mixture of presynthesized, crystalline reactants and products in nearly stoichiometric proportions was used as starting material. The curves of those reactions which turned out to be stable were determined reversibly in the range 15 to 30 kb, some of them also along their metastable extensions.

For the present purpose, the experimental results were used in combination with a chemographic analysis of the system to construct a preliminary petrogenetic grid that encompasses primarily the phase relations of the synthetic phases magnesioactinolite and magnesiochloritoid. The detailed experimental results will be published elsewhere (Chopin, in

![Fig. 5. Selected stable phase relations in the system MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O at high water pressure and low to moderate temperature. The position of the heavy curves is based upon experimental equilibrium determinations (see table 2). The light curves are either calculated (in the system Al$_2$O$_3$–SiO$_2$–H$_2$O; Halbach and Chatterjee, 1982b), extrapolated, or estimated. The data concerning the stability of Mg-staurolite and pyrope are adapted from Schreyer and Seifert (1969a), and, for clarity, the stability field of pyrope has been chosen to lie entirely within that of Mg-staurolite. The quartz–coesite transition is ignored in this representation. Numbers 1 to 4 refer to the reactions which for clarity reasons are given in the lower right hand corner of the figure but do not correspond to the reaction numbers used in the text.](image-url)
preparation), but some critical run data bearing on carpholite stability above 15 kb are given in figure 4 and table 3. Figure 4 also shows brackets reported by Massonne, Mirwald, and Schreyer (1981). For pressures below 15 kb the phase relations shown in the grid of figure 5 have been deduced by extrapolating the curves of the reactions

\[
\text{carpholite} + \text{diaspore} = \text{kyanite} + \text{chlorite} + \text{H}_2\text{O} \quad (7)
\]

and

\[
\text{carpholite} = \text{kyanite} + \text{chlorite} + \text{quartz} + \text{H}_2\text{O} \quad (8)
\]

established at higher pressures and considering their intersections with the reaction curves of the system Al$_2$O$_3$–SiO$_2$–H$_2$O as calculated by Halbach and Chatterjee (1982b). This extrapolation is loosely constrained by unreversed experimental data at 6.5 kb for reaction (8) and at 14 kb for the reaction (see table 3)

\[
\text{carpholite} = \text{chlorite} + \text{pyrophyllite} + \text{diaspore} + \text{H}_2\text{O}. \quad (9)
\]

The petrogenetic grid of figure 5 also takes into account that, according to the experimental results of Goffé (ms), natural magnesiocarpholite (66 mole percent Mg endmember) is unstable at and below 4 kb water pressure at all temperatures. The resulting low-pressure topology, provided no additional phase is considered (see below), represents a unique solution, although the exact locations and slopes of the different curves (for example 1, 2, 3 in fig. 5) are still unknown. Their overall uncertainty on the low-pressure stability limit of magnesiocarpholite is thought to be

### Table 3

Results of critical runs bearing on the stability of magnesiocarpholite.

Symbols for reaction rate are: + weak reaction, ++ strong reaction, +++ complete or nearly complete reaction. Abbreviations as in figure 5.

<table>
<thead>
<tr>
<th>$P_{\text{H}_2\text{O}}$ (kbar)</th>
<th>$T$ (°C)</th>
<th>Duration (hours)</th>
<th>Solid phases</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.9</td>
<td>539</td>
<td>97</td>
<td>Car +, Chl Ky Q –</td>
<td>+</td>
</tr>
<tr>
<td>19.0</td>
<td>564</td>
<td>87</td>
<td>Car –, Chl Ky Y +</td>
<td>++</td>
</tr>
<tr>
<td>17.7</td>
<td>517</td>
<td>182</td>
<td>Car +, Chl Ky Q –</td>
<td>++</td>
</tr>
<tr>
<td>17.5</td>
<td>549</td>
<td>126</td>
<td>Car –, Chl Ky Q +</td>
<td>+++</td>
</tr>
<tr>
<td>15.0</td>
<td>508</td>
<td>236</td>
<td>Car –, Chl Ky Q +</td>
<td>+</td>
</tr>
<tr>
<td>6.5</td>
<td>430</td>
<td>2260</td>
<td>Car –, Chl Ky Q +</td>
<td>+</td>
</tr>
<tr>
<td>14.0</td>
<td>550</td>
<td>120</td>
<td>Car +, Chl Py Dia –</td>
<td>++</td>
</tr>
<tr>
<td>19.0</td>
<td>535</td>
<td>137</td>
<td>Car +, Chl Ky Tc –</td>
<td>+</td>
</tr>
<tr>
<td>19.1</td>
<td>557</td>
<td>119</td>
<td>Car –, Chl Ky Tc +</td>
<td>+</td>
</tr>
<tr>
<td>30.0</td>
<td>569</td>
<td>115</td>
<td>Car +, Chl Ky Tc +</td>
<td>+</td>
</tr>
<tr>
<td>29.9</td>
<td>587</td>
<td>85</td>
<td>Car –, Chl Ky Tc +</td>
<td>+++</td>
</tr>
<tr>
<td>20.0</td>
<td>543</td>
<td>94</td>
<td>Car Q +, Tc Ky –</td>
<td>+</td>
</tr>
<tr>
<td>20.0</td>
<td>561</td>
<td>120</td>
<td>Car Q –, Tc Ky +</td>
<td>+</td>
</tr>
<tr>
<td>30.1</td>
<td>560</td>
<td>83</td>
<td>Car Q +, Tc Ky –</td>
<td>+</td>
</tr>
<tr>
<td>30.1</td>
<td>580</td>
<td>46</td>
<td>Car Q –, Tc Ky +</td>
<td>+</td>
</tr>
</tbody>
</table>
± 2 kb. In its high-temperature portion the grid utilizes earlier data of Schreier and Seifert (1969a).

The salient features of the new grid (fig. 5) may be enumerated as follows:

1. Magnesio-carpholite and magnesio-chloritoid are indeed high-pressure phases with stability fields limited by minimum pressures of about 7 and 18 kb, respectively. Compared with magnesio-carpholite, the pressure uncertainty for the magnesio-chloritoid stability is smaller (± 1 kb).

2. Magnesiocarpholite is, relatively speaking, the low-temperature phase. Its stability field lies entirely within the diaspore field, with an upper temperature stability near 580°C for 30 kb water pressure.

3. Both magnesiocarpholite and magnesiochloritoid also exhibit low-temperature stability limits, along which they break down into more hydrous assemblages.

4. Mg–chloritoid displays phase relations with Mg–carpholite in the low-temperature part of its stability field and with Mg–staurolite as well as pyrope near its high-temperature end at about 750°C and high water pressures.

5. This indicates that, at pressures of 20 kb and more, the entire sub-solidus range of the system MgO–Al₂O₃–SiO₂–H₂O is continuously covered by overlapping stability fields of high-pressure MgAl silicates. The Fe analogues of most of these phases are well-known minerals stable at low pressures.

6. Mg–chloritoid does not seem to display stable phase relations with boron-free kornurupine, because this phase forms only at higher temperatures (Seifert, 1975). The same appears to hold for yoderite, especially as this phase may show an upper pressure limit near 25 kb (Schreier and Seifert, 1969a, p. 423).

7. Mg–chloritoid cannot coexist with quartz over the entire area of the stability range investigated, alternative assemblages like talc–kyanite or just carpholite alone being stable up to the quartz–coesite transition. However, Mg–chloritoid might well coexist with coesite at still higher pressures.

8. Mg–carpholite, on the other hand, may appear in the presence of quartz over most of its stability field except probably for a small area near the low-pressure end.

9. The invariant point located near 18 kb, 540°C and involving the solid phases chlorite, quartz, talc, kyanite, and Mg–carpholite terminates the reaction curve

\[
\text{chlorite + quartz} \rightarrow \text{talc + kyanite + H}_2\text{O}
\]

which is considered to represent the lower temperature stability limit of whiteschists (Schreier, 1977) and, equally, the upper thermal stability of the chlorite–quartz pair (fig. 4). At pressures higher and at temperatures lower than that of the invariant point the chlorite–quartz stability is even more restricted due to its
breakdown into the assemblage talc + Mg-carpholite. Moreover, at pressures above that of the invariant point, the whiteschist assemblage talc–kyanite is limited, toward lower temperatures, by a reaction to form carpholite + quartz. The temperature of the invariant point (540°C) thus represents the absolute temperature minimum for the appearance of talc + kyanite in the presence of excess water vapor.

10. The assemblage chlorite + kyanite, which was found unstable in nearly all experiments conducted by Schreyer (1968) thus leading to a drastic rearrangement of tie lines (for example, talc–corundum, talc–Mg staurolite) at higher temperatures, can be seen in figure 5 to be limited toward higher pressures by a sequence of breakdown reactions. They cause the appearance of the following alternative pairs, beginning at high temperatures and pressures: Mg–chloritoid + talc: Mg–chloritoid + Mg–carpholite; and Mg–carpholite + diaspore. All these pairs have Mg–Fe-bearing analogues in blueschist metapelites (see table 1). The reaction

\[
\text{chlorite + kyanite} = \text{talc + Mg–chloritoid}
\]

(10)

releases no, or only very little, water, depending on the exact compositions of the chlorite and talc phases participating, thus resulting in a rather flat PT slope (see fig. 5). Therefore, the high-pressure pair chloritoid–talc is restricted, in the purely magnesian system, to astonishingly high water pressures of at least 25 kb.

Finally, it should be noted that the phase relations near the low-pressure end of the magnesiocarpholite stability field may yet have to be modified drastically upon further experimentation. Fransolet and Schreyer (ms in preparation) have found that the di/trioctahedral chlorite sudoite (fig. 3), \(\text{Mg}_2\text{Al}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_8\) (see also Fransolet and Bourguignon, 1978), has a low-pressure, low-temperature stability field extending at least to some 7 kb water pressure and 350°C. Therefore a reaction relationship

\[
\text{sudoite + quartz} = \text{magnesiocarpholite}
\]

(11)

may exist which, importantly, does not involve loss or gain of water and shows a strong volume decrease (> 6 percent) toward the formation of Mg–carpholite. Thus the requisite reaction curve must be strongly pressure-dependent. It would lead to still another low-pressure equivalent of magnesiocarpholite (see also Chopin and Goffé, 1981). If the sudoite/Mg–carpholite reaction is indeed stable, the lower pressure limit of magnesiocarpholite would be raised against that shown in figure 5 thus making this mineral an even more pronounced high-pressure phase.

**APPLICATION AND DISCUSSION**

As indicated before, the phase relations depicted in figure 5 for the pure magnesian system can only be considered as a limiting case for the metapelite reactions deduced from natural assemblages. Perhaps the most severe deviation of the synthetic system from the natural one is the incom-
patibility of Mg–chloritoid with quartz. Thus two of the outstanding
natural reactions, namely

\[
\text{carpholite} = \text{chloritoid} + \text{quartz} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{chlorite} + \text{quartz} = \text{chloritoid} + \text{talc} + \text{H}_2\text{O} \quad (2)
\]
do not appear in the petrogenetic grid of figure 5. For due comparison,
therefore, the metastable locations of these reaction curves in the pure
magnesian system will have to be employed.

As a first approach figure 6 summarizes the known and estimated sta-
bility limits of the Mg- and Fe-endmembers of the carpholite, chlori-
toid, and staurolite mineral series. The stability limits of ferrocrapholite,
FeAl_2[Si_6O_{18}](OH)_6, which thus far could not be synthesized despite
considerable efforts by Beunk and Maresch (personal commun., 1978),
were estimated in accordance with the data of table 1 and figure 2A and B.
The result turns out to be basically consistent with the pressure-temperature
behavior of Fe–chloritoid and Fe–staurolite relative to their Mg endmem-
bers. However, both the ferrocrapholite stability and the low-temperature
end of the Fe–chloritoid field might actually lie as much as 100°C lower
than drawn in figures 6 and 7.

Fig. 6. Pressure-temperature plot showing the relative position of the stability
fields of the Mg and Fe endmembers of carpholite, chloritoid, and staurolite as com-
pared with possible metamorphic P,T trajectories (I–III). See text for discussion. The
Mg– and Fe–staurolite fields are after Schreyer (1968) and Ganguly (1972), respectively;
the Fe–chloritoid upper stability (for NNO-QFM buffer) is taken from Ganguly (1969),
its lower stability limit is hypothetical, just as the field of ferrocrapholite. Aluminum
silicates phase relations are after Holdaway (1971).
It can be appreciated immediately from figure 6 that along "normal" low- to intermediate-pressure, metamorphic gradients such as from green-schist to granulite approximated by arrow I Fe–Mg carpholites cannot appear, and chloritoid, limited to low and medium grades, must be very iron-rich. Similar relations hold for staurolite which makes its appearance at medium grades. Increasing Mg-contents in staurolite could be expected in rocks formed at high temperatures ($700^\circ$-$800^\circ$C), provided that pressures typical for the lower continental crust are prevailing and that there is no quartz present which is known to limit staurolite stability (Richardson, 1968; Schreyer, 1968; Ganguly, 1972). However, Mg-rich staurolites are not known thus far, possibly due to the chemical restriction.

Turning to the other end of the terrestrial pressure-temperature scale with low geothermal gradients near 10°C/km (fig. 6) as typical for many blueschist environments, it is also obvious why Fe–Mg carpholites must appear as the first index minerals in metapelitic compositions (arrow III). Following such gradient toward higher metamorphic grades it is understandable that carpholites give way gradually to chloritoid, and that the latter will show a tendency toward Mg–chloritoid (compare fig. 2, A and B). If the stability range of Mg-rich chloritoid is to be attained without previously entering the field of Mg–Fe carpholite, as might possibly have been the case for rocks characterized by the assemblages of figure 2, C and

![Diagram](image)

Fig. 7. Approximate location of the most important metastable reaction curves (heavy lines) involving the phases carpholite, chlorite, chloritoid, kyanite, quartz, talc and vapor, in the system MgO–Al₂O₃–SiO₂–H₂O. For comparison with figure 5, the upper stability limit of Mg–carpholite is indicated by a dotted line, and the two stable reactions (4) and (10) by light lines. Solid circles are stable, open circles are metastable invariant points defined by Roman numbers. The heavy dashed line is the hypothetical upper stability limit of Fe–carpholite as shown in figure 6. Abbreviations as in figure 5. Reactions are numbered as in the text.
Magnesiocarpholite and magnesiochloritoid

D, PT paths such as that indicated by arrow II must be assumed. A geologic model for verifying such PT trajectory will be discussed in the final section.

After this rather general picture an attempt is made in the following to elaborate in greater detail on the reaction relations leading to the appearance, or disappearance, of the two index minerals of blueschist metamorphism discussed here. Wherever the univariant reaction curves are not known from experiment, their approximate slopes were estimated using known volume data for the solid phases and, for H₂O, the new PVT data of Halbach and Chatterjee (1982a).

Magnesiocarpholite.—The reactions limiting the field of Mg-carpholite (fig. 5) are most likely to occur in highly magnesian and/or highly oxidized metapelitic rocks. The direct formation of magnesiocarpholite in quartz-free rocks such as metabauxites might occur according to the reaction

\[ \text{kaolinite + chlorite} \rightarrow \text{Mg-carpholite + H₂O} \]  \hspace{1cm} (12)

In this reaction the chlorite phase is assumed to be sufficiently aluminous to be colinear with kaolinite–carpholite and thus allow the degeneracy shown in figure 5. If this is not the case, diaspore should participate on the low-temperature side of the reaction that is shifted toward slightly lower pressures.

At higher temperature, that is within the pyrophyllite field, the carpholite-forming reaction, in the presence of quartz, becomes

\[ \text{chlorite + pyrophyllite + H₂O} \rightarrow \text{Mg-carpholite + quartz} \]  \hspace{1cm} (13)

Due to small amounts of water participating in this reaction and because of a negative volume change of about 3 to 4 percent the slope must be relatively flat (see 3 in fig. 5). This represents a useful pressure indication and defines the common chlorite–pyrophyllite pair as a low-pressure assemblage (see also Dubois and Kienast, 1975; Viswanathan and Seidel, 1979). Alternatively, with retrograde pressure decrease, or isobaric temperature increase, reaction (13) may also proceed in the opposite direction causing the breakdown of Mg–carpholite. This very relationship was recently observed by Goffé (ms) in rocks from the Vanoise area, where in quartz-bearing assemblages magnesiocarpholite (80 percent Mg endmember) is partly or totally replaced by chlorite with pyrophyllite and/or cookeite, whereas it remained stable in the quartz-free, diaspore-bearing parageneses.

Despite this apparently satisfactory applicability of the low-pressure reactions of figure 5 the reader should be reminded once again of the unknown role of the di/trioctahedral chlorite sudoite on the low-pressure phase relations of Mg–carpholite (see p. 86), which may lead to another strongly pressure-dependent low-pressure limit of magnesiocarpholite following the reaction

\[ \text{sudoite + quartz} \rightleftharpoons \text{magnesiocarpholite}. \]  \hspace{1cm} (11)

For more information from natural systems a careful search for sudoite,
which is difficult to distinguish from normal Mg-rich chlorite, in pelitic rocks of very low grade is highly desirable.

In more iron-rich pelitic rocks of the low-grade blueschist facies ferrocarpholite develops as the first carpholite phase, and its formation follows principally similar reaction relations as those shown in figure 5 for the magnesian system. Therefore, in these rocks, the formation of magnesiocarpholite is different from that in Mg-rich rocks, because—as outlined in a previous section (see p. 80)—ferrocarpholite reacts, with rising grade, continuously toward more magnesian carpholites while the ferrous component breaks down in favor of Fe-rich chloritoid (E. W. F. de Roever, 1977).

Regarding the final disappearance of magnesiocarpholite with increasing metamorphic grade the situation in nature is not clear as yet. In principle, it should be possible that the well-known greenschist-facies assemblage chlorite + kyanite + quartz represents the breakdown product of magnesiocarpholite at pressures as high as 18 kb (fig. 5) according to the reaction

\[
magnesiocarpholite \rightarrow \text{chlorite} + \text{kyanite} + \text{quartz} + \text{H}_2\text{O}. \quad (8)
\]

In iron-bearing rocks, the prerequisite for reaction (8) to take place is the previous disappearance of the chloritoid-carpholite assemblage (see fig. 2B) according to the reaction

\[
\text{ferrochloritoid} + \text{magnesiocarpholite} \rightarrow \text{chlorite} + \text{kyanite} + \text{H}_2\text{O}. \quad (14)
\]

This will limit the range of bulk compositions in which reaction (8) occurs to high Mg/Fe ratios. Because of the rather "normal" nature of the chlorite–kyanite–quartz assemblage to most petrologists, its significance in blueschist metamorphic terranes may have been overlooked thus far. The unique association of magnesiocarpholite with kyanite, chlorite, quartz, and chloritoid from Samos (Okrusch, 1981; and table 1) may be considered as the relevant assemblage corresponding to reaction (14), the presence of quartz making it univariant.

**Magnesiochloritoid.**—The second index mineral magnesiochloritoid, containing up to 74 mol percent Mg endmember as known thus far, is of particular significance for blueschist metamorphism inasmuch as its appearance is possible over a rather wide range of rock compositions. While the common Fe-rich chloritoid of low-pressure metamorphism, and also of low-temperature blueschist metamorphism (see preceding section), is confined to strongly Al-rich rocks (see also fig. 2B), the magnesiochloritoid of higher-grade blueschist terranes may also appear in much Al-poorer environments because of its characteristic association with the virtually Al-free mineral talc. The role that magnesiochloritoid plays in high-temperature blueschist facies is best demonstrated by figure 2C to D.

The following attempts to decipher reaction relationships in the development of Mg-dominant chloritoids cannot be based on the grid of figure 5, because the natural Mg-rich chloritoid–talc parageneses are com-
monly stable in the presence of quartz, a feature that is not verified in figure 5. Therefore, figure 7 presents a simplified grid of the type of figure 5 but with the important metastable reactions indicated as deduced chemographically. All these reactions are the pure magnesium equivalents of divariant assemblages occurring in nature.

The metastable reaction

\[ \text{Mg carpholite} \rightarrow \text{Mg chloritoid} + \text{quartz} + \text{H}_2\text{O} \]  

(1)

has a steep slope as is to be expected for a strong dehydration reaction. Using a similar slope the equivalent reaction for the breakdown of pure ferrocargarpholite,

\[ \text{Fe–carpholite} \rightarrow \text{Fe–chloritoid} + \text{quartz} + \text{H}_2\text{O} \]  

(1a)

is also shown in figure 7. Thus the continuous breakdown of Fe–Mg carpholites into more and more Mg-rich chloritoids as described before must essentially be a temperature-dependent process. However, due to the vastly different pressure locations of the stability fields of the endmember chloritoids relative to those of the carpholites (see fig. 6), a pressure influence on the Fe/Mg partitioning between the two minerals can be expected as it was also predicted by Seidel (1981) from volume considerations for the exchange reaction.

On the other hand, the initial reaction allowing the coexistence of chloritoid and talc, that is in the pure magnesian system

\[ \text{chlorite} + \text{quartz} \rightarrow \text{magnesiochloritoid} + \text{talc} + \text{H}_2\text{O} \]  

(3)

has, again as a metastable curve, a much flatter and negative slope (fig. 7) that lies intermediate between the slopes of the chlorite + quartz breakdown curves into kyanite + talc and into magnesiocargarpholite + talc (see fig. 5). There is a negative volume change toward chloritoid and talc of about 3 to 4 percent. This metastable curve and its expected more iron-rich and, thus, lower-pressure equivalents in the Fe–Mg system lie more or less at right angles to the PT-trajectories of increasing metamorphism. Therefore, the progressive gliding of the 3-phase field talc–chloritoid–chlorite of figure 2C (in the presence of quartz) toward the Mg-side is both a pressure and temperature dependent process. Such reaction relationships are typical for the Gran Paradiso area (see pl. 1-B and Chopin, ms and 1981).

Likewise, the progressive Mg-enrichment of chloritoid coexisting with chlorite and kyanite, in the presence of quartz (fig. 2C) with increasing grade, is a result of the reaction

\[ \text{chlorite} + \text{kyanite} + \text{H}_2\text{O} \rightarrow \text{magnesiochloritoid} + \text{quartz} \]  

(5)

which is linked with a volume decrease of about 3 percent. Once again, this reaction is metastable in the model system, but its location is shown in figure 7, where it exhibits a flat, but positive slope. Thus, any progressive metamorphism leading to Mg-rich chloritoid according to reaction (5) must be characterized by very low geothermal gradients. At still higher
grades, in the absence of chlorite (fig. 2D), further Mg-enrichment in chloritoid would imply the reaction relationship

\[ \text{talc + kyanite + H}_2\text{O} \rightarrow \text{magnesiochloritoid + quartz}. \] (6)

In the model system this reaction involving hardly any volume change is also metastable with a fairly steep, positive slope (fig. 7). It seems doubtful that any progressive metamorphic PT path would intersect such reaction curve in the direction toward the more hydrated assemblage. This may account for a limit in the Mg-contents of chloritoid with rising grade in quartz-bearing assemblages. The highest percentage of Mg endmember chloritoid (up to 74 mol percent) known thus far was recently found (Chopin, unpub. data) in a chlorite-talc-kyanite-chloritoid-quartz-phengite rock from the Monte Rosa area (table 1). The apparently higher-grade, chlorite-free assemblage from Hohe Tauern (table 1) carries a Mg-chloritoid with only 65 percent endmember (Miller, 1977).

In quartz-free environments the important reaction relationship becomes

\[ \text{chlorite + kyanite} \rightarrow \text{magnesiochloritoid + talc}. \] (10)

This reaction involving also a 3 to 4 percent volume decrease is a stable one in the pure system MgO-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O, and its curve is located, with a rather flat slope (see p. 86), at very high water pressures of at least 25 kb (figs. 5 and 7). The four coexisting phases were recorded previously (table 1) from rocks of the Zermatt area (Chinner and Dixon, 1973) and the chloritoid contains about 65 mol percent of the Mg endmember. As reaction (10) does not involve practically any change in water content (see p. 86), it will be rather insensitive to water activity and could thus provide a very useful geobarometer for high-grade blueschist terranes. Direct textural evidence for reaction (10) is presented in plate 1-C from the Monte Rosa rock, where secondary chlorite and kyanite appear as retrograde products in a local quartz-free environment.

Considering the primary bulk mineralogy of the Monte Rosa rock which includes quartz (table 1), this assemblage must be univariant. An attempt was made to estimate pressures for this rock from reaction (10); using an ideal ionic solution model. For a temperature of about 500°C this led to pressures between 15 and 18 kb (Chopin, unpub. data).

**Whiteschists of different pressure regimes.**—As reactions (6) and (10) involve both talc and kyanite the rocks discussed in the preceding paragraph might be called whiteschists in the sense of Schreyer (1977). Clearly, for the Zermatt and Hohe Tauern rocks the assemblage Mg-chlorite + quartz is no longer stable. However, as can be seen from figure 5 the assemblage talc-kyanite covers a wide pressure range beginning at some 6 kb (Massonne, Mirwald, and Schreyer, 1981) and extending to at least 35 kb above a minimum temperature of about 540°C. For the pure model system a subdivision of this range is only possible when additional, less siliceous mineral phases such as Mg-carpholite, chlorite, or Mg-chloritoid are coexisting. Whereas rocks of such extreme MgAl-rich compositions are
not known as yet, a subdivision of the more siliceous natural occurrences seems feasible when a coexisting iron-bearing mafic phase is considered.

In this respect the index mineral magnesiochloritoid coexisting with talc and kyanite is of prime interest (fig. 2D). As discussed previously this assemblage indicates pressures of considerable magnitude (15-20 kb), while the talc–kyanite pair alone requires at least 540°C for water pressure equaling total pressure. Thus this high-temperature blueschist facies assemblage is, at the same time, a high-pressure whiteschist.

On the other hand, the more common whiteschists appearing in amphibolite-facies terranes as layers of highly magnesian, meta-evaporitic rocks must have formed at much lower pressures (Schreyer, 1977). PT trajectories near gradients of about 20°C/km may lead to these whiteschists that, upon further increase in grade, can develop yoderite at temperatures near 700°C. Such whiteschists should thus be termed low-pressure whiteschists.

The one and only occurrence recorded thus far, in which the talc–kyanite pair coexists with a Mg-rich garnet may be of an intermediate nature. This whiteschist occurs in an eclogite terrane in Tasmania (Räheim and Green, 1974). The talc–kyanite–garnet assemblage clearly precludes the coexistence of Mg-rich chloritoid with talc and kyanite as found in the blueschist terranes (see fig. 2D) and must, therefore, belong to a different PT-regime. More experimental and theoretical work, especially on garnet activity/composition relations, is necessary to define this environment more closely.

**GEOLOGIC ASPECTS**

It is now commonly accepted that the realm of blueschist metamorphism characterized by high confining pressures and low temperatures is best explained geologically as a result of subduction of lithospheric plates, or platelets, in collision zones. Nevertheless, many different kinds of subduction processes seem possible. Thus the subducted, “down-going” slab may not always be of oceanic origin; indeed, in continent/continent collisions clearly continental crust may be subducted as well.

In the orogenic region of the Alpine and Mediterranean System a great many different events of local collisions and subductions have occurred, which may have led to different types of subduction-zone, blueschist metamorphism, with variable PT-trajectories. Even if the PT-gradients during the subduction process were alike or similar (see arrows II and III of fig. 6), this complicated collision system between the European and African continents may have provided a series of platelets with different initial temperatures that would, during subduction, create different series of progressive blueschist metamorphism. In this picture, arrow II of figure 6 could simply be due to a higher heat content of the plate prior to subduction relative to arrow III that may be valid for initial near-surface conditions. Indeed higher initial temperatures may prevail in slabs of lower or middle continental crust or even in freshly produced slabs of oceanic crust.

The results presented in this paper can only be considered as a first step, and much more experimental work aimed at calibrating mineral re-
actions and the resulting Mg/Fe partitioning will be necessary. However, it seems that, for an important and hitherto in blueschist terranes rather neglected group of rocks, the metapelites, new avenues for geobarometry and -thermometry can be opened. This is particularly important, because future views on the geodynamics of subduction processes in zones of plate collision will depend largely on the success of depth/temperature analyses as a function of geologic time.

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