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Michel Ballevre, J.L Pinardon, Jean Robert Kienast, Jean-Paul Vuichard. Reversal of Fe-Mg partitioning between garnet and staurolite in eclogite-facies metapelites from the Champtoceaux nappe (Brittany, France). Journal of Petrology, 1989, 30 (6), pp.1321-1349. 10.1093/petrology/30.6.1321. insu-01493270

# HAL Id: insu-01493270 https://insu.hal.science/insu-01493270

Submitted on 31 Mar 2017  $\,$ 

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# Reversal of Fe-Mg Partitioning Between Garnet and Staurolite in Eclogite-facies Metapelites from the Champtoceaux Nappe (Brittany, France)

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(Received 29 June 1988; revised typescript accepted 24 January 1989)

#### ABSTRACT

This paper concentrates on the petrology of eclogite-facies metapelites and, particularly, the significance of staurolite in these rocks.

A natural example of staurolite-bearing eclogitic micaschists from the Champtoceaux nappe (Brittany, France) is first described. The Champtoceaux metapelites present, in addition to quartz, phengite, and rutile, two successive parageneses: (1) chloritoid+staurolite+garnet cores, and (2) garnet rims+kyanite $\pm$ chloritoid.

Detailed microprobe analyses show that garnet and chloritoid evolve towards more magnesian compositions and that staurolite is more Fe-rich than coexisting garnet. A comparison of the studied rocks with other known occurrences of eclogitic metapelites shows that whereas staurolite is always more Fe-rich than garnet in high-pressure eclogites, the reverse is true in low- to medium-pressure micaschists.

Phase relations between garnet, staurolite, chloritoid, biotite, and chlorite are analysed in the KFMASH system (with excess quartz, phengite, rutile, and  $H_2O$ ). The topology of univariant reactions is depicted for a normal and a reverse Fe–Mg partitioning between garnet and staurolite. Mineral compositional changes are also predicted for varying bulk-rock chemistries.

In the studied micaschists, the zonal arrangement of garnet inclusions and the progressive compositional changes of ferromagnesian phases record part of the prograde P-T path, before the attainment of 'peak' metamorphic conditions (at about 650–700 °C, 18–20 kb). The retrograde path, which records the uplift of the Champtoceaux nappe, occurs under decreasing temperatures.

# INTRODUCTION

Recent discoveries show that mineral assemblages in eclogitic metapelites are powerful tools for evaluating P-T conditions (Chopin & Schreyer, 1983; Koons & Thompson, 1985; Goffé & Chopin, 1986; Vuichard & Ballèvre, 1988). Their use requires a theoretical knowledge of phase relations in the KFMASH multisystem and experimental data on the limiting KFASH or KMASH systems. In addition, careful examination of natural samples is necessary to depict actual phase relations.

Previous works (Harte & Hudson, 1979; Koons & Thompson, 1985; Vuichard & Ballèvre, 1988) show that stable associations at relatively low temperatures (i.e., lower than about 600 °C) are garnet-chloritoid-chlorite and garnet-chloritoid-kyanite, and that garnetchloritoid-talc does not occur in pelitic rocks of 'normal' aluminous composition, i.e., intermediate to high Fe/(Fe + Mg) ratio (Vuichard & Ballèvre, 1988). At temperatures higher than about 600 °C, critical assemblages are garnet-chlorite-kyanite and garnet-talc-kyanite (Vuichard & Ballèvre, 1988). Staurolite was not considered in detail in these previous studies.

The purpose of this paper is to discuss phase relations between garnet, chloritoid, staurolite, and kyanite in high-pressure metapelites. Staurolite-bearing eclogitic metapelites are known in Kazakhstan (Udovkina *et al.*, 1980), the Dora-Maira nappe in the Western Alps (Chopin, 1985), the Fairbanks district of Alaska (Brown & Forbes, 1986), the Hohe Tauern in the Eastern Alps (Spear & Franz, 1986), the Najac klippe in the Massif Central, France (Delor *et al.*, 1987), and the Champtoceaux nappe in Brittany, France (Ballèvre *et al.*, 1987). Our discussion does not take into account the Hohe Tauern example because staurolite is stabilized there by high amounts of ZnO (Leupolt & Franz, 1986; Spear & Franz, 1986). In the five other occurrences, staurolite is a matrix phase in the Fairbanks and Najac micaschists and is observed only as inclusions within garnet in the Kazakhstan, Dora-Maira and Champtoceaux micaschists.

In this paper, we will first describe the petrology of the Champtoceaux metapelites and compare them with other occurrences of eclogite-facies micaschists. We will show that a reversal of Fe-Mg partitioning between garnet and staurolite occurs in high-pressure metapelites as previously suggested by Chopin (1985) and Vuichard & Ballèvre (1988), and then explore the major consequences of this reversal for phase relations in the KFMASH multisystem.

# **GEOLOGICAL SETTING**

The Champtoceaux nappe (Brittany, France) is located in the South Armorican domain between two major crustal faults: the Nort-sur-Erdre Fault to the north and the southern

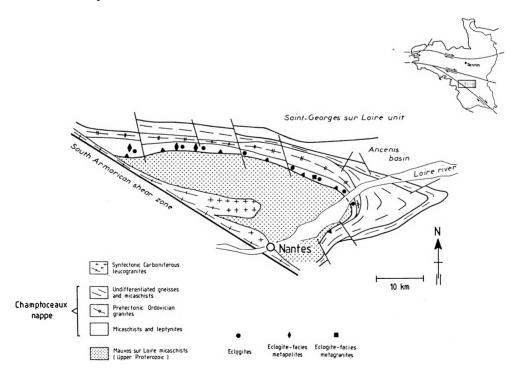


FIG. 1. Schematic structural map of the Champtoceaux nappe. Inset shows the location of the study area in Brittany (France). It should be noted that eclogite-facies metapelites are known only in the lower unit.

branch of the South Armorican Shear Zone to the south (Fig. 1). The Champtoceaux nappe is thrust over low-grade metasediments of presumed Upper Proterozoic age. It consists of several superimposed units (Marchand, 1981), which underwent distinctive P-T histories during the Variscan collisional event.

The lower unit of the Champtoceaux nappe consists essentially of leucocratic gneisses (i.e., leptynites) and micaschists which enclose numerous metabasic lenses. In general, the exact age of the protoliths is unknown, although some leptynites result from the intense deformation of granites (Lasnier *et al.*, 1973; Lagarde, 1978) of probable Lower Paleozoic age (Vidal *et al.*, 1980). The granites intruded sediments which locally preserve evidence of contact metamorphism (Marchand, 1983). The metabasites have basaltic whole-rock compositions and MORB-type REE patterns (Paquette, 1987). Relicts of primary igneous textures or minerals are lacking in the metabasites.

The lower unit of the Champtoceaux nappe suffered an eclogitic metamorphism at an early stage of the Variscan orogeny (Paquette *et al.*, 1984, 1985; Paquette, 1987). Eclogitic parageneses are well known in the metabasic lenses (Lacroix, 1891; Brière, 1920; Velde, 1966, 1970; Godard *et al.*, 1981; Paquette *et al.*, 1985) but have been only recently discovered in the quartzites (Ballèvre *et al.*, 1987). Garnet-kyanite assemblages in micaschists were first described by Lacroix (1891) but were attributed to the eclogitic episode much later (Ballèvre *et al.*, 1987). In addition, coronitic transformations in undeformed volumes of granitic rocks (Lasnier *et al.*, 1973) could also be attributed to eclogite-facies rather than to granulite-facies metamorphism. Garnet-omphacite  $\pm$  kyanite associations from quartzites will be described fully elsewhere (Ballèvre and Kiénast, in preparation), and this paper concentrates on the petrology of the micaschists.

Abbreviations	Mineral names
Ab	Albite
Adr	Andradite
Alm	Almandine
An	Anorthite
And	Andalusite
Bt	Biotite
Chl	Chlorite
Cld	Chloritoid
Gr	Graphite
Gro	Grossular
Grt	Garnet
H <sub>2</sub> O	Vapour
Ilm	Ilmenite
Jd	Jadeite
Ку	Kyanite
Phg	Phengite
Pg	Paragonite
Pyr	Pyrope
Qtz	Quartz
Rt	Rutile
Sil	Sillimanite
Spe	Spessartine
St	Staurolite
Tlc	Talc
WM	White micas

TABLE 1

List of mineral abbreviations used in text, figures, and table	List of	<sup>c</sup> mineral	abbreviations	used i	n	text.	fiaures.	and	tables
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#### PETROGRAPHY

Observed mineral parageneses in the Champtoceaux micaschists are listed in Table 2. All micaschists contain quartz, white mica, garnet, and rutile. In addition, kyanite is observed in some samples. Particular attention has been paid to garnet inclusions, notably chloritoid and staurolite, to define mineral assemblages during garnet growth (Table 2).

Most samples show evidence for ductile deformation during the growth of primary parageneses. In particular, garnet, kyanite, and sometimes white mica display numerous tiny inclusions of rutile  $\pm$  graphite, whose shape fabric defines an internal schistosity  $S_i$  (Spry, 1969). Staurolite and/or chloritoid inclusions within garnets are parallel to the  $S_i$  (Figs. 2 and 3). The matrix foliation (i.e., external schistosity  $S_e$ ) is generally deformed by small-scale folds. Garnet and kyanite porphyroblasts have been submitted to rotations after their growth ceased. In consequence,  $S_i$  and  $S_e$  are no longer continuous. Kyanite and white mica also show evidence of intracrystalline deformation (undulose extinctions and kink-bands) (Lacroix, 1891).

A retrogressive overprint is generally present. In some samples, secondary phases grew in the absence of ductile deformation. For example, garnet is sometimes pseudomorphed by chlorite aggregates which preserve its shape and the alignment of rutile inclusions. Most samples suffered a ductile deformation during the retrograde history. In these cases, the overprint is generally more extensive. Shear bands nucleate on garnet or kyanite grains and a new foliation may develop; garnet, kyanite, and white mica act as porphyroclasts.

### Primary assemblages

Primary metamorphic assemblages contain quartz, white mica, garnet, kyanite, and rutile. Microprobe analyses of white mica reveal that only phengite is present, except in samples CH13 and FAY26 where primary paragonite is also present. Talc was not observed. A detailed investigation of garnet-kyanite assemblages is presented in this study.

Garnet porphyroblasts commonly present inclusion-rich cores and inclusion-poor rims (Figs. 2 and 3). Garnet cores include quartz, phengite, rutile, and/or graphite. Garnet cores also include aluminous and ferromagnesian phases: chloritoid, staurolite or chloritoid + staurolite. Chloritoid shows a pale blue colour, a faint pleochroism, and sometimes polysynthetic twinning. Staurolite is colourless or pleochroic from pale yellow to yellow. Garnet rims contain kyanite, phengite, paragonite, and sometimes chloritoid, but never staurolite.

Kyanite porphyroblasts contain quartz, rutile  $\pm$  graphite, and white mica inclusions. Microprobe analyses reveal that most micas are phengites but paragonite was detected in sample CH13.

Chloritoid is observed in the matrix in samples FAY24, FAY26, and CH13 (Fig. 3). It is never in contact with quartz, garnet or kyanite and has irregular shapes. Matrix chloritoids have been partly 'dissolved' and are now observed as corroded relicts within white mica  $\pm$  chlorite aggregates.

To summarize, textural relations suggest the following successive parageneses (Figs. 2 and 3). During a first stage, garnet + chloritoid + staurolite assemblages crystallized. The second stage is related to the disappearance of chloritoid + staurolite and the growth of kyanite, leading to garnet-kyanite or garnet-chloritoid-kyanite assemblages. Garnet-staurolite-kyanite assemblages have never been observed. In garnet-chloritoid-kyanite assemblages, chloritoid also has been removed from the matrix assemblage, but is locally preserved within phengite  $\pm$  chlorite aggregates.

	Cx12	<b>FAY3</b>	FAY6A, FAY6C	FAY6B	FAY9	FAY20	FAY21	FAY22	FAY23	FAY24	FAY25	FAY26	BOUI	BOU4	BOU5	CH10	CH11	CH12	CH13	CH14	CH18	CH19	CH20	CH21
Qtz WM	٠	٠	•	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	•
	•	٠	٠	•	٠	•	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	•	•	•	٠	٠	•	٠
Grt	٠	•		٠	٠	٠	٠	٠	٠	٠	٠	٠	•	٠	٠	٠	٠	٠	•	٠	•	•	٠	٠
Кy	•	•		٠		٠	•			٠	٠	•				٠	۲	٠	•		2			
Cld		0						0		00	0	00				0	0		00					
St I		0		0								ο				0								
St II																								
Ch 1										?		?							?					
Ru	•	•	•	•	•	•	•	•	٠	٠	•	•	٠	•	•	٠	•	٠	•	٠	٠	•	٠	٠
Gr						ō	ō			0	ō	0												

TABLE 2Observed primary parageneses in the Champtoceaux micaschists

Mineral abbreviations are described in Table 1. •=matrix phases; o=inclusions with garnet cores; = retrograde phases.

1325

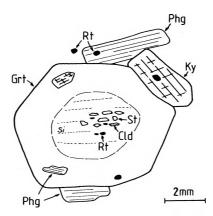


FIG. 2. Schematic textural relations between primary phases in the Champtoceaux micaschists (sample FAY3). Noteworthy features are the inclusion-rich core with internal schistosity  $S_i$  defined by minute graphite and rutile grains, and the progressive grain coarsening recorded by inclusions within garnet as compared with matrix grains. Mineral abbreviations are described in Table 1.

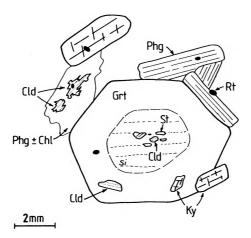


FIG. 3. Schematic textural relations between primary phases in the Champtoceaux micaschists (sample FAY26). Same remarks as for Fig. 2.

#### Secondary assemblages

Secondary phases are only locally developed and have the following features:

(1) Staurolite and chloritoid inclusions are frequently replaced by fine-grained aggregates containing chlorite, paragonite, margarite, kyanite, and ilmenite. Chlorite, paragonite, and margarite are intergrown.

(2) Garnet is sometimes pseudomorphed by chlorite aggregates containing zircon grains with pleochroic aureoles (Lacroix, 1891).

(3) Kyanite inclusions and porphyroblasts are rimmed by fine-grained micaceous aggregates.

(4) Large primary phengites are locally destabilized into finer-grained secondary phengites.

(5) In samples FAY26 and FAY24, rare plagioclase grains have grown in the matrix or in garnet cracks.

(6) In rare instances (sample FAY25), staurolite II + chlorite has grown at the expense of garnet + kyanite. Staurolite II grains are euhedral or subhedral, whereas staurolite grains included in garnets are anhedral.

#### MINERALOGY

Garnet- and kyanite-bearing micaschists were selected with no or little retrograde overprint. Mineral analyses were performed on five samples (FAY3, FAY24, FAY25, FAY26, and CH10) with a Camebax microprobe analyser (Paris VI University). Operating conditions were: 15 kV accelerating voltage, 10 nA probe current and 10 s counting-time. Standards were: albite (Na), orthoclase (K, Al), diopside (Ca, Mg, Si), MnTiO<sub>3</sub> (Mn, Ti), Fe<sub>2</sub>O<sub>3</sub> (Fe) and ZnS (Zn). Zn was detected with the  $L_{\alpha}$  ray, and all others using the  $K_{\alpha}$  ray. Micas and plagioclases were analysed with an enlarged beam to avoid alkali loss. Additional information on mineral compositions has been obtained with the 'Microsonde Ouest' (Brest) on samples Cx12 and CH13.

# Garnet (Table 3)

In all the analysed micaschists, garnets have low CaO and MnO contents and are zoned. From core to rim, they display a decrease in MnO and CaO content, an increasing MgO content and the FeO content remains approximately constant. In consequence, the Mg/(Fe + Mg) ratio  $(X_{Mg})$  increases from 0.10 to 0.25 (Fig. 4). Small chemical differences between garnet rims from different samples are observed.

(1) The grossular content of garnet rims is negligible in sample FAY26 (2 mol.%) but attains up to 9 mol.% in sample FAY3 (Table 2).

(2) The  $X_{Mg}$  ratio is higher in samples FAY24 and FAY26 (0.25–0.27) than in samples FAY3 and CH10 (0.22–0.25).

Chemical gradients within garnet grains are smoother in staurolite + chloritoid-bearing garnet cores than in staurolite-free rims. Moreover, in samples FAY26 and CH13, where chloritoid occurs in garnet rims and in the matrix, the magnesium enrichment in garnet is stronger than in samples FAY3 and CH10, where only kyanite is observed in garnet rims (Fig. 4).

# Chloritoid (Table 4)

Chloritoid grains show trace amounts of TiO<sub>2</sub> and ZnO, very low MnO content, and no  $Al_2O_3$  variation. Calculated  $Fe_2O_3$  content is generally very low (1 wt.% or less). The main chemical variation is due to the  $FeMg_{-1}$  substitution.

In staurolite-chloritoid garnet cores, chloritoid grains are less magnesian in the inner zone ( $X_{Mg} = 0.20$ ) than in the outer zone ( $X_{Mg} = 0.25$ ).

In samples FAY24, FAY26, and CH13, chloritoid inclusions in the garnet rim and matrix chloritoids have similar  $X_{Mg}$  (near 0-3). As for garnet, the magnesium enrichment is stronger in samples FAY26 and CH13 than in samples FAY3 and CH10. These observations show that the disappearance of the staurolite + chloritoid assemblage is accompanied by a strong  $X_{Mg}$  increase in the remaining ferromagnesian phases, i.e., garnet and chloritoid.

# Staurolite (Table 5)

Following Pigage & Greenwood (1982), we adopted the formula  $Fe_2Al_9Si_{3.75}O_{22}(OH)_2$  for staurolite and calculated the structural formulae on a basis of 23 oxygens.

	1	2	3	4	5	6	7
			San	nple FAY3			
SiO <sub>2</sub>	37.36(0.37)	37.36(0.26)	36.75(0.04)	37.48 (0.08)	37.61 (0.04)	37.73 (0.03)	37.77 (0.04)
TiO <sub>2</sub>	0.07(0.01)	0.05 (0.02)	0.05 (0.04)	0.10(0.01)	0.05 (0.02)	0.05 (0.04)	0.05 (0.02)
Al <sub>2</sub> O <sub>3</sub>	20.93 (0.06)	20.39 (0.22)	20.48 (0.40)	21.10(0.04)	21.22(0.04)	21.34 (0.07)	21.08 (0.04)
$Cr_2O_3$	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Fe <sub>2</sub> O <sub>3</sub>	0.15(0.22)	0.61 (0.28)	0.45(0.12)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
FeO	30.64 (0.34)	30.27 (0.39)	30.34 (0.34)	30.56 (0.03)	30.42 (0.18)	30.17 (0.17)	30.41 (0.11)
MnO	3.08 (0.60)	2.91 (0.34)	2.02(0.14)	1.65 (0.23)	1.21 (0.04)	1.22(0.06)	1.13 (0.02)
MgO	2.36(0.17)	2.49 (0.15)	2.64 (0.15)	2.72(0.05)	3.96(0.11)	4.74 (0.15)	5.07 (0.08)
CaO	5.00 (0.28)	5.03 (0.32)	5.29 (0.27)	5.44 (0.04)	4.57 (0.11)	3.76(0.16)	3.37 (0.11)
Eoxides	99.59 (0.29)	99.07 (0.04)	97.96(0.57)	99.03 (0.15)	99.04 (0.12)	99.00 (0.12)	98.85(0.21)
Si	3.006	3-020	3.001	3.014	3.007	3.006	3.013
Al <sup>iv</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
EIV	3.006	3.020	3.001	3.014	3.007	3.006	3.013
VI VI	1.986	1.944	1.971	2.000	2.000	2.005	1.982
Гі	0.004	0-003	0.003	0.006	0.003	0.003	0.003
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>3+</sup>	0.009	0.037	0.027	0.000	0.000	0.000	0.000
2VI	2.000	1.984	2.002	2.006	2.003	2.007	1.985
$e^{2+}$	2.062	2.047	2.072	2.055	2.034	2.011	2.029
vîn 🛛	0.210	0.200	0.140	0.112	0.082	0.082	0.076
Иg	0.283	0.300	0.321	0.325	0.472	0.562	0.602
Ca	0.431	0.436	0.463	0.468	0.392	0.321	0.288
$\Sigma^{2+}$	2.986	2.982	2.995	2.961	2.980	2.976	2.995
Mg/(Mg + Fe)	0.12	0.13	0.13	0.14	0.19	0.22	0.23
Alm	69.07	68.64	69.17	69.41	68·27	67.56	67.74
<b>`</b> yr	9.48	10.06	10.71	10.99	15.84	18.90	20 1 1
pe	7.02	6.69	4.68	3.78	2.75	2.77	2.54
Gro	13.74	12.38	13.93	15.52	13.00	10.64	8.89
Adr	0.46	1.34	1.01	0.19	0.09	0.09	0.09

TABLE 3Representative garnet analyses and structural formulae on a basis of 12 oxygens

			Sai	mple CH10			
SiO <sub>2</sub>	35.77 (0.46)	36.30 (0.25)	36.67 (0.06)	37.26(0.27)	37.56(0.03)	37.15(0.27)	36.94 (0.17)
TiO <sub>2</sub>	0.06 (0.04)	0.02 (0.02)	0.15(0.16)	0.07 (0.07)	0.12(0.01)	0.03 (0.05)	0.07 (0.01)
$Al_2O_3$	21.25 (0.17)	21.34 (0.05)	21.62(0.05)	21.60 (0.18)	21.85 (0.06)	21.71 (0.26)	21.76(0.21)
$Cr_2O_3$	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
$Fe_2O_3$	1.34 (0.18)	0.65(0.07)	1.01 (0.40)	0.40(0.19)	0.40 (0.56)	0.81 (0.56)	0.86(0.57)
FeO	30.90(0.39)	32.28 (0.70)	32.15(0.28)	31.99 (0.26)	30.93 (0.41)	30.90 (1.00)	30.65 (0.22)
MnO	4.16(0.48)	2.03 (0.13)	1.01 (0.05)	0.89 (0.08)	0.99 (0.06)	1.13 (0.09)	0.97 (0.07)
MgO	2.30(0.15)	2.75 (0.08)	3.53 (0.57)	3.69 (0.31)	4.98 (0.36)	5.01 (0.18)	5.83 (0.48)
CaO	4.19 (0.88)	4.17 (0.68)	4.61 (0.46)	4.57 (0.27)	3.95(0.01)	3.60 (0.83)	2.75(0.08)
$\Sigma$ oxides	99·96 (0·79)	99.55(0.21)	100.72 (0.10)	100.45 (0.46)	100.76 (0.58)	100.34 (0.70)	99.83 (1.23)
Si	2.900	2.935	2.917	2.958	2.951	2.937	3.013
Al <sup>IV</sup>	0.100	0.065	0.083	0.042	0.049	0.063	0.000
$\Sigma^{IV}$	3.000	3.000	3.000	3.000	3.000	3.000	3.013
Al <sup>VI</sup>	1.931	1.969	1.944	1.979	1.975	1.961	1.982
Ti	0.003	0.003	0.009	0.004	0.007	0.002	0.003
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>3+</sup>	0.082	0.040	0.060	0.024	0.023	0.048	0.000
$\Sigma^{VI}$	2.017	2.011	2.013	2.007	2.005	2.011	1.985
Fe <sup>2+</sup>	2.096	2.183	2.139	2.124	2.033	2.043	2.029
Mn	0.286	0.139	0.068	0.060	0.066	0.076	0.076
Mg	0.278	0.331	0.419	0.436	0.583	0.590	0.602
Ca	0.364	0.361	0.393	0.389	0.333	0.305	0.288
$\Sigma^{2+}$	3.023	3.014	3.018	3.009	3.014	3.015	2.995
Mg/(Mg + Fe)	0.12	0.13	0.13	0.14	0.19	0.22	0.23
Alm	69.33	72.42	70.88	70.60	67.44	67.78	67.74
Pyr	9.18	10.98	13.87	14.50	19.33	19.58	20.11
Spe	9.46	4·61	2.24	1.98	2.19	2.51	2.54
Gro	7.81	9.88	9.58	11.54	9.32	7.64	8.89
Adr	2.82	1.40	2.29	0.92	1.00	1.66	0.09

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	Sample	FAY26	Sample FAY25
	Core	Rim	Rim
SiO <sub>2</sub>	36.43 (0.43)	37.88 (0.26)	38.10 (0.30)
TiO <sub>2</sub>	0.06(0.03)	0.03 (0.03)	0.03 (0.04)
$Al_2\bar{O}_3$	21.33 (0.25)	21.60 (0.17)	21.51 (0.09)
$Cr_2O_3$	0.00 (0.00)	0.00 (0.00)	0.05 (0.05)
$Fe_2O_3$	0.73 (0.47)	0.26(0.15)	0.20(0.07)
FeO	31.14 (0.04)	33-18(0-37)	30.09 (0.29)
MnO	3.33 (0.13)	0.54(0.13)	0.73 (0.04)
ИgO	2.22 (0.09)	5.84 (0.42)	6.79 (0.17)
CaO	4.88 (0.20)	1.17(0.10)	2.11 (0.45)
oxides	100-11 (0-69)	100.51 (0.54)	99.55 (0.18)
i	2.936	2.981	2.994
1 <sup>IV</sup>	0.064	0.019	0.006
IV	3.000	3 000	3.000
JVI	1.963	1.986	1.987
ï	0-003	0.002	0-001
r	0-000	0.000	0-001
e <sup>3+</sup>	0.045	0.016	0.012
VI	2.011	2.003	2.002
e <sup>2 +</sup>	2.099	2.184	1.978
⁄In	0.228	0.036	0.048
Лg	0.267	0.685	0.796
Ca	0.421	0.099	0.178
2 +	3.014	3.004	3.000
$\frac{1}{2}(Mg + Fe)$	0.11	0.24	0.29
lm	69.63	72.70	65.94
Pyr	8.85	22.81	26.52
Spe	7.55	1.19	1.61
Gro	11.58	2.43	5.21
Adr	1.59	0.57	0.44

TABLE 3 (Continued)

Fe<sup>3+</sup> is estimated by stoichiometry. Each analysis is an average of three to four spot analyses clustered within a small area. Values in parentheses are standard deviations. Increasing numbers denote locations of clusters within garnets from core to rim.

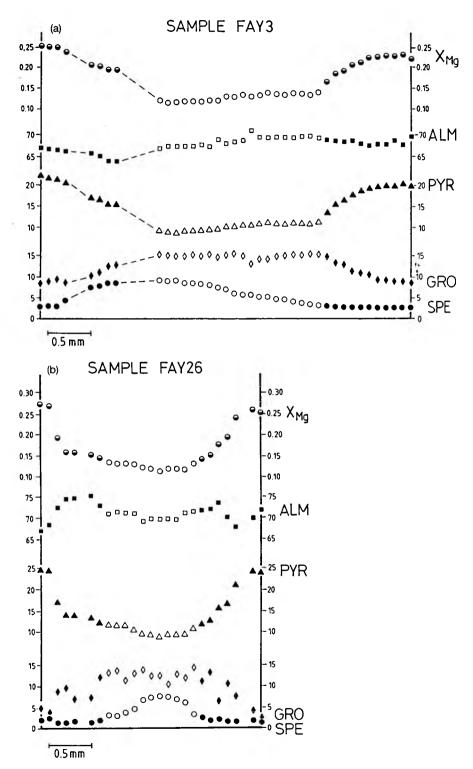


FIG. 4. Compositional zoning in garnets from samples FAY3 (a) and FAY26 (b). Open symbols represent analyses from Cld + St inclusion-rich cores. Full symbols represent analyses from Ky-bearing rims (FAY3) and Ky + Cldbearing rims (FAY26).

TABLE 4
Representative chloritoid analyses and structural formulae on a basis of 11 oxygens

		Sample FA	Y3		Sample CH	10		Sample FAY2	6
	1	2	3	1	2	3	In Grt core	In Grt rim	In matrix
SiO2	25.09 (0.33)	24.89 (0.15)	25.02 (0.39)	23.46 (0.18)	23.83 (0.13)	23.58 (0.05)	23.90 (0.29)	24.61 (0.08)	24.44 (0.32)
ΓiO <sub>2</sub>	0.02 (0.02)	0.00 (0.00)	0.05 (0.04)	0.02 (0.02)	0.03 (0.01)	0.06 (0.04)	0.01 (0.01)	0.05(0.02)	0.01 (0.02)
M₂Ō₃	42.16(0.05)	42.12(0.33)	42.26 (0.34)	40.94 (0.43)	41.22 (0.20)	41.36 (0.06)	41.57 (0.21)	41.97 (0.02)	41.43 (0.30)
$Fe_2O_3$	0.00 0.00)	0.00 (0.00)	0.00 (0.00)	0.57 (0.14)	0.22(0.31)	0.62 (0.37)	0.00 (0.00)	0.24 (0.34)	0.34 (0.22)
<b>FeO</b>	21.94 (0.08)	21.75(0.25)	20.91 (0.35)	22.81 (0.26)	22.69 (0.01)	22.15(0.37)	22.88 (0.04)	20.21 (0.23)	20.23 (0.20)
MnO	0.51 (0.16)	0.35(0.01)	0.30(0.15)	0.56(0.12)	0.25(0.02)	0.14(0.05)	0.45(0.04)	0.18(0.01)	0.29 (0.05)
ИgO	3.13 (0.32)	3.58 (0.30)	4.06 (0.16)	3.07 (0.10)	3.38 (0.14)	3.87 (0.13)	3.13 (0.18)	5.01 (0.46)	4.94 (0.05)
ZnO	0.00 (0.00)	0.04 (0.06)	0.08 (0.05)	0.09 (0.07)	0.08 (0.00)	0.03 (0.04)	0.06 (0.03)	0.02 (0.03)	0.02 (0.02)
E oxides	92.83 (0.43)	92.71 (0.30)	92.66 (0.40)	91.50 (0.74)	91-68 (0-81)	91-80 (0-61)	91-99 (0-78)	92.28 (0.56)	91.71 (0.76)
Si	2.031	2.016	2.019	1.952	1.970	1.944	1.9.70	1.991	1.994
Al <sup>iv</sup>	0.000	0.000	0.000	0.048	0.030	0.056	0.030	0.009	0.006
EIV	2.031	2.016	2.019	2.000	2.000	2.000	2.000	2.000	2.000
Al <sup>vi</sup>	4.025	4.024	4.021	3.970	3.989	3.965	4.011	3.995	3.979
Гi	0.001	0.000	0.003	0.001	0.002	0-004	0-001	0.003	0.001
Fe <sup>3+</sup>	0.000	0.000	0.000	0.036	0.013	0.039	0.000	0.015	0.021
<u>v</u> i	4.026	4.024	4.024	4.007	4 004	4 008	4.012	4.012	4.000
$Fe^{2+}$	1.486	1.474	1.411	1.588	1.569	1.528	1.578	1.368	1.380
Мn	0.035	0.024	0.020	0.039	0.017	0.010	0.031	0.012	0.020
Иg	0.377	0.432	0.488	0.380	0.417	0.475	0.385	0.604	0.601
Zn	0.000	0.002	0.002	0.002	0.002	0.002	0.004	0.001	0.001
$\Sigma^{2+}$	1.898	1.932	1.925	2.013	2.008	2.010	1.997	1.985	2.003
Mg/(Mg + Fe)	0.20	0.23	0.26	0-19	0.21	0.24	0.20	0.31	0.30

 $Fe^{3+}$  is estimated by stoichiometry. Each analysis is an average of three to four spot analyses clustered in a small area denoted by the same number as the enclosing garnet. Values in parentheses are standard deviations.

		Sample FAY3			Sample CH10		Sample FAY26	Sample FAY25
	1	2	3	1	2	3	In Grt core	Std II
SiO <sub>2</sub>	28.40(1.13)	28.46(0.95)	28.07 (0.23)	26.94 (0.24)	27.66 (0.23)	27.62 (0.45)	28-31 (0-13)	27.88 (0.53)
TiO <sub>2</sub>	0.30(0.10)	0.36(0.10)	0.29(0.11)	0.43 (0.07)	0.43 (0.05)	0.45(0.07)	0.46(0.03)	0.13(0.08)
$Al_2O_3$	54.08 (3.24)	56.09 (0.85)	55.71 (1.24)	55.76(0.44)	54.65 (0.29)	55.14(0.25)	54.76(0.01)	54.93 (0.33)
FeO	11·79 (0·17)	11.11(1.03)	10.20 (0.53)	12.04 (0.79)	11.45(0.09)	10.69 (0.44)	10.73 (0.11)	8.24 (0.14)
MnO	0.41 (0.05)	0.44(0.16)	0.51 (0.17)	0.39(0.04)	0.28 (0.03)	0.39(0.00)	0.43 (0.04)	0.49(0.09)
MgO	0.77(0.12)	0.59 (0.16)	0.54 (0.08)	0.76(0.05)	1.04(0.11)	0.75(0.08)	0.53 (0.06)	1.06(0.07)
ZnO	1.01 (0.07)	1.33(0.63)	1.67 (0.11)	1.41 (0.18)	2.51 (0.13)	2.70(0.23)	3.24(0.13)	4.16(0.22)
$\Sigma$ oxides	96.75(2.04)	98·36(0·61)	96·96(1·44)	97.74 (0.41)	98.02 (0.51)	97.72 (0.34)	98.44 (0.08)	96.88 (0.69)
Si	3.959	3.892	3.887	3.739	3.836	3.831	3.906	3.885
Al <sup>iv</sup>	0.041	0.108	0.113	0.261	0.164	0.169	0.094	0.115
$\Sigma^{IV}$	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Al <sup>VI</sup>	8.848	8.937	8.984	8.863	8.773	8.849	8·816	8.910
Ti	0.031	0.037	0.030	0.045	0.045	0.047	0.048	0.014
Fe <sup>3+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$\Sigma^{VI}$	8.880	8.974	9.013	8.909	8-818	8.896	8.864	8.923
Fe <sup>2+</sup>	1.375	1.271	1.181	1.398	1.328	1.241	1.238	0.960
Mn	0.048	0.020	0.060	0.046	0.033	0.046	0.020	0.057
Mg	0.159	0.119	0.110	0.157	0.214	0.154	0.109	0.221
Zn	0.104	0.134	0.170	0.145	0.257	0.276	0.330	0.428
$\Sigma^{2+}$	1.686	1.574	1.522	1.745	1.833	1.717	1.727	1.666
Mg/(Mg + Fe)	0.10	0.09	0.09	0.10	0.14	0-11	0.08	0.19

Representative staurolite analyses and structural formulae on a basis of 23 oxygens

TABLE 5

All Fe is calculated as Fe<sup>2+</sup>. Each analysis is an average of three to four spot analyses clustered in a small area denoted by the same number as the enclosing garnet. Values in parentheses are standard deviations.

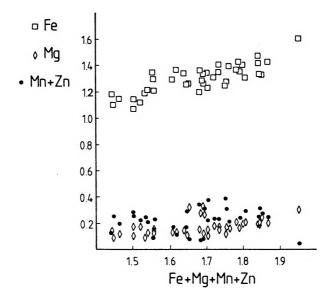


FIG. 5. Fe, Mg, and Mn+Zn content against sum of divalent cations in staurolite inclusions from the Champtoceaux micaschists. Numbers represent cations per formula unit.

The most important feature of these staurolites is their low  $X_{Mg}$  value. All staurolites have lower  $X_{Mg}$  than coexisting garnets (see later). A comparison of our staurolite analyses with those from the Dora-Maira micaschists (Chopin, 1985) shows that the Champtoceaux staurolites have higher Mn + Zn contents.

The analyses performed in the present study suggest the following remarks:

(1) The sum of divalent cations  $(R^{2+})$  is variable and always significantly smaller than 2. In contrast, the staurolite analyses of Holdaway *et al.* (1986*a*) have  $R^{2+}$  always equal to or greater than 2. The same is true for staurolite from Rangely Quadrangle (Guidotti, 1974) or Picuris Range (Holdaway, 1978). According to Holdaway *et al.* (1986*b*, fig. 1), low  $R^{2+}$  suggests a high (H + F) content. For a mean value of  $R^{2+}$  equal to 1.70, the suggested (H + F) value would be 2.35. The MnO content of analysed staurolites is always very small (less than 0.5 wt.%, i.e., 0.06 cation per formula unit).

(2) Neither Mg nor Mn + Zn shows sympathetic variation with  $R^{2+}$ , whereas Fe does. Thus,  $R^{2+}$  variations seem to be related to  $Fe^{2+}$  variations (Fig. 5). These observations are consistent with previous studies, suggesting an incomplete Fe–Mg exchange in the staurolite structure (Grambling, 1983; Holdaway *et al.*, 1986b).

(3) As shown by Griffen *et al.* (1982),  $Al^{vi}$  and  $R^{2+}$  are strongly correlated but this is probably a consequence of the fixed H<sup>+</sup> content assumed in the calculation of structural formulae (Holdaway *et al.*, 1986a). The latter authors suggested that H<sup>+</sup> content in staurolite is variable and they proposed a method for its estimation. This method (assuming Al + Si = 25.53) has been tested, but unlikely high H<sup>+</sup> values (> 2.5) have been calculated as a result.

#### White micas (Table 6)

The maximum celadonite content of primary phengite lies around Si = 3.3, with high  $X_{Mg}$  values ranging from 0.75 to 0.80. Na/(Na + K) is generally low, smaller than 0.15 (Fig. 6).

•		•		5		5
-	Phg I 13	Phg I 14	Phg II 15	Phg II 16	Phg I 32	Pg 33
SiO <sub>2</sub>	48.81	48.90	46.22	46.52	49.53	46.99
TiO <sub>2</sub>	0.56	0.69	0.50	0.23	0.44	0.07
Al <sub>2</sub> O <sub>3</sub>	31.05	31.09	36.70	37.66	30.21	39.08
$Cr_2O_3$	0.00	0.06	0.00	0.06	0-00	0-00
FeO	1.43	1.43	0.80	0.46	2.06	0.58
MnO	0.00	0.00	0.00	0.06	0-00	0.01
MgO	2.62	2.40	0.85	0.28	2.47	0.22
CaO	0.00	0.00	0.00	0.00	0.00	0.24
Na <sub>2</sub> O	0.72	0.80	1.47	1.75	0.72	6.54
K <sub>2</sub> O	8∙76	8.98	8.39	8.17	10.25	1.22
$\Sigma$ oxides	<u>93</u> .95	94·35	94.63	95·19	<b>95</b> ∙68	94.95
Si	3.259	3.257	3.056	3-049	3.286	3.016
Al <sup>IV</sup>	0.741	0.743	0.944	0.951	0.714	0.984
$\Sigma^{IV}$	4.000	4-000	4.000	4-000	4.000	4.000
Al <sup>vi</sup>	1.703	1.698	1.917	1.960	1.649	1.973
Ti	0.028	0.035	0.010	0.011	0.022	0-003
Cr	0.000	0-003	0-000	0-003	0.000	0.000
Fe <sup>2+</sup>	0.080	0.080	0-044	0.025	0.114	0.031
Mn	0.000	0-000	0-000	0.003	0-000	0-001
Mg	0.261	0.238	0.084	0.027	0.244	0.021
$\Sigma^{VI}$	2.072	2.054	2.055	2.029	2.029	2.029
Ca	0.000	0.000	0-000	0-000	0.000	0.017
Na	0.093	0.103	0.188	0.222	0.093	0.814
К	0.746	0.763	0.708	0.683	0.868	0.100
Σint	0.839	0.866	0.896	0.905	0.961	0.931

TABLE 6

Representative white mica analyses and structural formulae on a basis of 11 oxygens

All Fe is calculated as Fe<sup>2+</sup>.

1

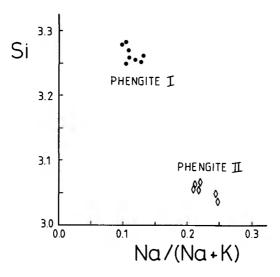


FIG. 6. Si content against Na/(Na + K) ratio in phengites from the Champtoceaux micaschists (sample Cx12).

Secondary phengites have a lower celadonite content (Si = 3.05-3.10) than primary phengites, but a higher Na/(Na + K) ratio (0.2-0.25) (Fig. 6).

Paragonite has a low Ca content [Ca/(Na + K + Ca) = 0.08] and can have a K/(Na + K + Ca) ratio ranging up to 0.10.

# Kyanite

Kyanite is always nearly pure, with only trace amounts of metallic cations.

### Chlorite

Chlorite compositions are relatively heterogeneous ( $X_{Mg}$  values range from 0.4 to 0.6). Variations occur in each sample and between adjacent grains. It has not been possible to distinguish primary and secondary chlorites.

# **Plagioclase**

Plagioclase composition varies with the textural position of the grains; for example, plagioclases from sample FAY26 are purely albitic in the matrix but unzoned grains occurring in cracks in garnet contain around 15 mol.% An.

# PHASE RELATIONS OF STAUROLITE IN ECLOGITIC METAPELITES

#### Phase relations in the Champtoceaux micaschists

The Champtoceaux micaschists can be studied in the KFMASH system. MnO and CaO are considered as negligible components because they are strongly partitioned into garnets. Assuming that  $H_2O$  is in excess, and taking into account the presence of quartz and

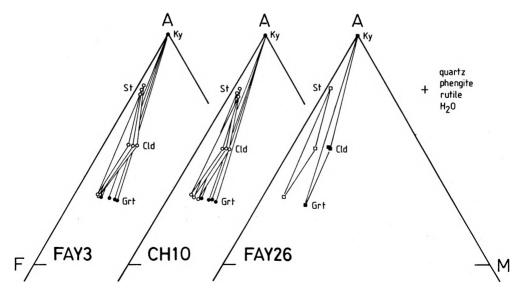


FIG. 7. Al<sub>2</sub>O<sub>3</sub>-FeO-MgO projection from quartz, rutile and H<sub>2</sub>O of coexisting minerals in the Champtoceaux micaschists. Open symbols represent garnet inclusions and coexisting garnets. Filled symbols represent garnet rims and matrix phases. Projected mineral compositions are reported in Tables 3-5.

phengite, the AFM projection can be used to show phase relations in the Champtoceaux micaschists (Fig. 7). Textural observations and chemical analyses show that the primary assemblage represents a state of partial equilibrium (Loomis, 1983): chloritoid and staurolite are in equilibrium with garnet cores, but are not in equilibrium with garnet rims and matrix phases. The local development and chemical heterogeneity of secondary phases suggests that only local equilibrium was achieved during the retrograde history. Thus, their use for reconstructing the P-T path of the Champtoceaux micaschists will be more uncertain than the use of relict prograde phases included within garnet cores.

# Primary assemblages

In the studied samples, the matrix equilibrium assemblage is garnet rim + kyanite (+ phengite + quartz + rutile). Inclusions of staurolite  $\pm$  chloritoid in garnet cores are used to define prograde assemblages.

All samples show a striking evolution from a garnet-chloritoid-staurolite assemblage (garnet cores) towards a garnet-kyanite association (garnet rims + matrix phases) (Fig. 7). Coexisting garnet-staurolite-kyanite was never observed, but garnet-chloritoid-kyanite was stable in sample FAY26, where chloritoid grains are present in the matrix. During the final stages of the metamorphic history, matrix chloritoid reacts with matrix phases and is now enclosed in a phengitic aggregate (Fig. 3), or separated from garnet and kyanite by chlorite sheaves.

Staurolite is always more Fe-rich and chloritoid more Mg-rich than the coexisting garnet (Fig. 7). In other words, the Fe-Mg partitioning between AFM phases is, according to an increasing  $X_{Mg}$  ratio: St <Grt <Cld.

Garnet shows, from core to rim, an increasing  $X_{Mg}$  ratio. Chemical gradients are relatively smooth in the chloritoid + staurolite inclusion-rich cores but strongly increase in garnet rims. Chloritoid inclusions evolve towards more Mg-rich compositions from the inner to the outer zone of garnet cores. In addition, chloritoid inclusions in staurolite-free garnet rims and matrix chloritoid grains have similar compositions, which are much more magnesian than the last chloritoid inclusions coexisting with staurolite (Fig. 7). The chemical evolution of staurolite could not be precisely constrained, because of the narrow Fe–Mg substitution range and chemical heterogeneities within single grains.

# Secondary assemblages

Secondary chlorite-staurolite associations are observed only in sample FAY25: staurolite II presents a higher  $X_{Mg}$  (of about 0.19) than staurolite I, but chlorite compositions are variable ( $X_{Mg} = 0.40-0.60$ ). The chemical heterogeneity of plagioclase grains depends on local equilibria. Biotite is not observed.

#### Fe-Mg partitioning between garnet and staurolite

A literature survey shows that staurolites have a higher  $X_{Mg}$  than coexisting garnets in low- to medium-pressure metapelites, but that the reverse is true in high-pressure metapelites. Numerous studies are available in low- to medium-pressure metapelites (e.g., Albee, 1972; Guidotti, 1974; Holdaway, 1978; Yardley *et al.*, 1980; Pigage & Greenwood, 1982; Grambling, 1983; Lang & Rice, 1985; Gibson & Speer, 1986; Klaper & Bucher-Nurminen, 1987; Holdaway *et al.*, 1988). In contrast, only five occurrences are reported in high-pressure metapelites (see Introduction).

Figure 8 presents a compilation of Fe/Mg values for coexisting garnet and staurolite. From the numerous papers on low- to medium-pressure micaschists, we extract analyses

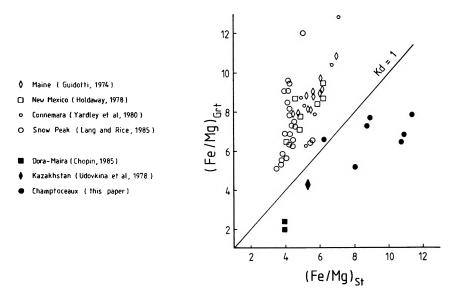


FIG. 8. (Fe/Mg) in staurolite vs. (Fe/Mg) in coexisting garnet. Data for the Champtoceaux micaschists are taken from Tables 3 and 5.

from coexisting garnets and staurolites which have crystallized at almost fixed P-T (Holdaway, 1978; Lang & Rice, 1985) or along a P-T 'gradient' (Guidotti, 1974; Yardley *et al.*, 1980). All available data for high-pressure metapelites have been reported (i.e., from Kazakhstan and Dora-Maira), but only mean analyses were used for the Champtoceaux micaschists. Figure 8 clearly shows that  $K_d$  values are greater than 1 in medium-pressure metapelites but less than 1 in high-pressure metapelites. It thus demonstrates that a reversal of Fe-Mg partitioning occurs between garnet and staurolite.

Such a reversal has already been described between chloritoid and staurolite by Grambling (1983). He paid particular attention to possible misinterpretations of chemical data. According to him, apparent Fe-Mg reversal could result from (1) disequilibrium relations between garnet and staurolite, or (2) perturbations of the Fe-Mg exchange caused by minor elements, notably  $Fe^{3+}$ , Mn, or Zn. The presence of graphite + rutile and the lack

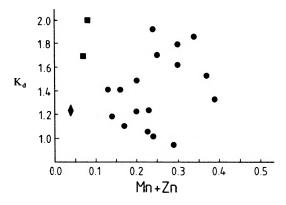


FIG. 9. Plot of  $K_d$  vs. minor elements in staurolites. Same symbols as for Fig. 8. We used all available garnet-staurolite pairs from the Champtoceaux micaschists for sake of complete representation.

of ilmenite, magnetite, or haematite (Table 2) suggest a low oxygen fugacity. Very low  $Fe^{3+}$  estimates in garnet and chloritoid are consistent with the preceding statement. MnO, which essentially enters into garnet, is negligible in staurolite. ZnO is preferentially partitioned into staurolite, but there is no correlation between  $K_d$  value and Zn + Mn content (Fig. 9). Disequilibrium between garnet and staurolite cannot be totally excluded but no evidence for it could be found.

In conclusion, available data strongly favour the existence of an inverse Fe-Mg partitioning between garnet and staurolite in high-pressure metapelites, possibly as a result of the non-ideal behaviour of the Fe-Mg solid solution in staurolite suggested by Holdaway *et al.* (1988). Preliminary experimental investigations of Fe-Mg partitioning between garnet and staurolite (Rice, 1985) also show the occurrence of such a reversal.

# Topological consequences of the Fe-Mg reversal

Most authors have analysed phase relations in metapelites using the KFMASH multisystem (e.g., Albee, 1972; Harte & Hudson, 1979; Koons & Thompson, 1985; Vuichard & Ballèvre, 1988). In fact, most metapelites can be rigorously described using the AFM projection (e.g., Thompson, 1957; Greenwood, 1975).

This paper focuses on phase relations between garnet, staurolite, chloritoid, chlorite, and kyanite (with excess quartz, muscovite, and  $H_2O$ ) in high-pressure metapelites. We are thus concerned only with reactions around the [Crd, Bt] KFMASH invariant point of Harte & Hudson (1979), which is equivalent to the [Bt, Tlc] invariant point of Vuichard & Ballèvre (1988). These authors assumed a normal Fe-Mg partitioning between AFM phases. If a reversal of Fe-Mg partitioning between garnet and staurolite occurs the three terminal staurolite-out reactions:

$$St = Grt + Cld + Ky$$
(1)

$$St = Grt + Chl + Ky$$
(2)

$$St = Grt + Bt + Ky$$
(3)

are replaced by the non-terminal reactions:

$$St + Cld = Grt + Ky$$
<sup>(4)</sup>

$$St + Chl = Grt + Ky$$
(5)

$$St + Bt = Grt + Ky.$$
(6)

Therefore, the staurolite stability field is extended toward higher pressures and temperatures than in the case of a normal partitioning.

We will now consider in some detail what occurs around the KFMASH invariant point [Bt, Tlc] which is critical for the understanding of phase relations in high-pressure metapelites. Figure 10 shows the topology of univariant KFMASH reactions around the [Bt, Tlc] invariant point with normal Fe-Mg partitioning (Fig. 10a) and with inverse partitioning (Fig. 10b). If  $X_{Mg}^{St} = X_{Mg}^{Grt}$ , the degenerate reaction

$$St = Grt + Ky$$
(7)

will be coincident with

$$Fe_St = Alm + Ky$$
(8)

eliminating the (Bt, Chl, Tlc) and (Bt, Cld, Tlc) KFMASH reactions by degeneracy. Thus

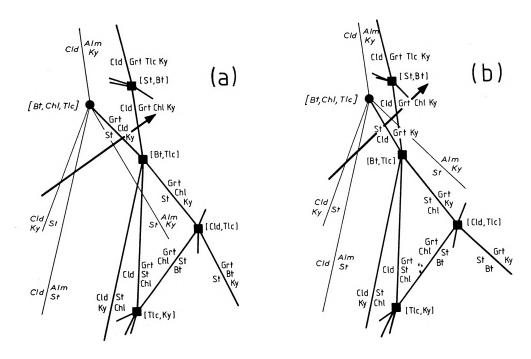


FIG. 10. Phase relations of garnet, chloritoid, staurolite, biotite, and chlorite in the KFMASH multisystem for normal, i.e., Barrovian (a) and reverse (b) Fe-Mg partitioning between garnet and staurolite. Squares and heavy lines refer to invariant points and univariant reactions in the KFMASH system. Full circles and light lines refer to invariant points and univariant reactions in the FASH system, respectively.

Fig. 10a will change to Fig. 10b at least in part of the P-T field, by Fe\_Mg changes along the (Bt, Chl, Tlc) or (Bt, Cld, Tlc) reactions. The inversion may occur at pressures between the invariant points [Bt, Tlc] and [Bt, Chl, Tlc] or [Bt, Tlc] and [Cld, Tlc]. Another way to relate Fig. 10a and Fig. 10b is to consider that each Schreinemakers net represents a projection in the P-T plane of univariant reaction surfaces in a three-dimensional space. The third intensive parameter is not identified at present but could be the oxygen fugacity (see, for example, Hensen, 1986) or the hydrogen content of staurolite.

Figure 11 shows the predicted Fe-Mg evolution of AFM phases along a particular P-T path (arrows on Fig. 10) for aluminous bulk-rock compositions. We also represent the two types of Fe-Mg partitioning. Two main consequences are to be stressed:

(1) An Fe-Mg reversal does not enable a strong Mg-enrichment in staurolite, contrary to the assessment of Vuichard & Ballèvre (1988). In fact, magnesian staurolites coexisting with garnet have been reported only from quartz-free metabasites (Smith, 1984; Ward, 1984; Enami & Zang, 1988) or silica-deficient peraluminous rocks (Grew & Sandiford, 1984; Schreyer *et al.*, 1984). The last two studies are concerned with non-metapelitic rocks where  $SiO_2$  is not in excess. In consequence, the hypotheses required for AFM projection are not fulfilled. Moreover, Schreyer *et al.* (1984) stated that such magnesian staurolites cannot be stable with quartz, as with pure Mg-staurolite (Schreyer, 1968).

(2) Garnet-kyanite is a critical assemblage in eclogitic metapelites: its occurrence extends towards more magnesian compositions with increasing P-T conditions. Thus, most high-pressure metapelites would appear as monotonous garnet-kyanite micaschists.

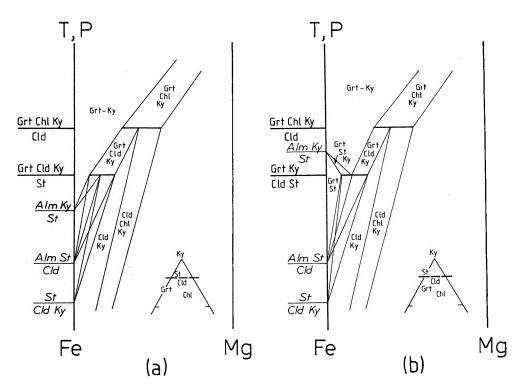


FIG. 11. Schematic pseudo-binary loops for aluminous, ferrous to intermediate bulk-rock compositions. The diagrams depict the evolution of mineral compositions and assemblages along a P-T gradient (arrows on Fig. 10) for a normal (a) and a reverse (b) Fe-Mg partitioning between garnet and staurolite.

The main limitation of the above approach is that pseudo-binary loops do not take into account substitutions other than Fe-Mg and non-ideal mixing behaviour in AFM phases.

# A model reaction history for the Champtoceaux micaschists

# Prograde reaction history

As a whole, the observed parageneses in the Champtoceaux micaschists and their predicted evolution in the KFMASH system are consistent. Some points deserve further comment.

(1) Reaction (4) describes the actual reaction path in the studied micaschists. The garnet-chloritoid-staurolite assemblage is present in the garnet cores of all studied samples (Fig. 7). Garnet-staurolite-kyanite and garnet-chloritoid-kyanite assemblages are stable on the high-pressure side of reaction (4) but only garnet-chloritoid-kyanite is known at present in the Champtoceaux micaschists.

(2) Chlorite could result from the reaction

$$Cld = Grt + Chl + Ky$$
(9)

but textural evidence in favour of this is not conclusive. If this reaction actually occurred, chlorite was probably re-equilibrated during the retrograde history.

(3) Pseudo-binary loops (Fig. 11b) are compatible with the observed chemical evolution of garnet and chloritoid, in particular with the strong Mg-enrichment after reaction (4)

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occurred. The chemical evolution of staurolite inclusions within garnet cores would tend to a slight Mg-enrichment (Fig. 11b). This is not detectable in our analyses, possibly because of (a) analytical uncertainties and (b) complex solid solution behaviour of staurolite. It should be noted that the evolution from chloritoid-staurolite-garnet to garnet-chloritoid-kyanite assemblages can occur in both Fe-Mg partitioning schemes. Only the evolution from chloritoid-staurolite-garnet assemblages would be diagnostic of an inverse partitioning.

In summary, the Champtoceaux micaschists preserve part of a prograde P-T path in garnet inclusion-rich cores, whereas matrix phases (kyanite and phengite) and garnet rims represent the 'peak' metamorphic conditions.

#### Retrograde reaction history

Reaction (5) could be used to describe the retrograde growth of chlorite + staurolite II assemblage in sample FAY25 if we assume that staurolite II, chlorite, and garnet are in equilibrium. In addition, the lack of biotite in garnet-bearing micaschists suggests that the reaction

$$Grt + Chl = St + Bt \tag{10}$$

never takes place.

# **P-T CONDITIONS OF THE ECLOGITE-FACIES METAMORPHISM**

Even if observed phase relations in the Champtoceaux micaschists clearly show that they are true eclogite-facies parageneses, it would be highly desirable to determine the P-T conditions of this metamorphism. Few geothermobarometers are available for high-pressure metapelites, but independent estimates in eclogite-facies metabasites and quartzites can be used for reference. Quantitative evaluation of the P-T history of the studied rocks is very difficult, but the shape of the prograde P-T path can be qualitatively constrained.

### Geothermobarometry

Classical geobarometers are lacking in the studied micaschists, for example, garnet-plagioclase-kyanite-quartz (Newton & Haselton, 1981). The observed associations can only be used to infer minimum or maximum pressures. In the absence of biotite and K-feldspar, the Si<sup>4+</sup> content of primary phengites (Massone & Schreyer, 1987) gives minimum pressures of the order of 10 kb at temperatures ranging from 600 to 700 °C. In the absence of ilmenite, the GRAIL equilibrium (Bohlen *et al.*, 1983) gives minimum pressures around 8 kb. This equilibrium unfortunately cannot be applied to garnet cores where an aluminosilicate phase is generally lacking and coexisting rutile and ilmenite are not found (see below). In the absence of sodic pyroxene, the paragonite + kyanite assemblage gives a maximum pressure at around 25 kb at 700 °C [assuming  $a(H_2O) = 1$ ] (Holland, 1979).

Most geothermometers are based on Fe-Mg exchange reactions between coexisting ferromagnesian minerals, notably garnet-biotite (Ferry & Spear, 1978) and garnet-phengite (Green & Hellman, 1982). Given that biotite is lacking, temperatures can only be calculated using the garnet-phengite geothermometer. The use of phengite analyses with all Fe as Fe<sup>2+</sup> yields unreasonably high temperature estimates ranging from 800 to 850 °C at 20 kb pressure. In consequence, the Fe<sup>3+</sup> content of phengites has been calculated assuming that Mg + Fe<sup>2+</sup> = Si - 3. In some cases, this leads to recalculation of all Fe as Fe<sup>3+</sup>. Such analyses have been rejected from further calculations. Using the calibration of Green &

		Sample	FAY3		Sa	mple FAY	26
Grt							
Ca	0.295	0	272	0.282	0-099	0.274	0.176
Fe	2.025	2	·038	2.026	2.207	2.049	2.099
Mg	0.596	0	-594	0.609	0.654	0.705	0.710
Fe/Mg	3.40	3	·43	3.33	3.37	2.91	2.96
Phg							
Fe	0.071	0	·071	0.071	0.072	0.067	0.064
Mg	0.210	0	210	0.210	0.254	0.254	0.224
Fe/Mg	0.34	0	·34	0.34	0.28	0.26	0.29
K <sub>d</sub>	10-05	10	·15	<b>9</b> ∙84	11.90	11.02	10.35
			Temperati	ıres (°C)			
P = 15  kb	643	642		646	621	631	639
P = 20  kb	670	669		673	647	657	666
			Sample I	AIOB			
Grt	5	11	13	29	31	33	39
Ca	0.441	0.309	0.304	0.311	0.353	0.329	0.448
Fe	1.784	1.839	1.871	1.869	1.834	1.880	1.83
Mg	0.683	0.754	0.741	0.752	0.760	0.748	0.498
Fe/Mg		~			2.41	2.51	3.69
10/116	2.61	2.44	2.52	2.49	2.41	2.21	507
	2·61 4	2·44 10	2·52 12	2·49 28	30	32	37
Phg	4 0-044	10 0-058	12 0·060	28 0·077	30 0·109	32 0·055	37 0·102
Phg Fe Mg	4 0-044 0·210	10 0-058 0-236	12 0.060 0.273	28 0·077 0·243	30 0·109 0·263	32 0·055 0·249	37 0·102 0·288
Phg Fe	4 0-044	10 0-058	12 0·060	28 0·077	30 0·109	32 0·055	37 0·102
Phg Fe Mg	4 0-044 0·210	10 0-058 0-236	12 0.060 0.273	28 0·077 0·243	30 0·109 0·263	32 0·055 0·249	37 0·102 0·288
Phg Fe Mg Fe/Mg	4 0-044 0·210 0·21	10 0-058 0-236 0-25 9-92	12 0.060 0.273 0.22	28 0·077 0·243 0·32 7·84	30 0·109 0·263 0·41	32 0·055 0·249 0·22	37 0·102 0·288 0·35
Phg Fe Mg Fe/Mg	4 0-044 0·210 0·21	10 0-058 0-236 0-25 9-92	12 0·060 0·273 0·22 11·49	28 0·077 0·243 0·32 7·84	30 0·109 0·263 0·41	32 0·055 0·249 0·22	37 0·102 0·288 0·35

 TABLE 7

 Garnet-phenaite thermometry in the Champtoceaux micaschists

Hellman (1982) (for low Ca and low Mg systems) with garnet rims and primary phengite compositions, temperatures ranging from 650 to 680 °C have been calculated for a pressure of 20 kb (Table 7).

Previous authors have estimated the P-T conditions of the eclogite-facies metamorphism in the Champtoceaux nappe using assemblages from eclogites (Godard *et al.*, 1981; Paquette *et al.*, 1985) and quartzites (Ballèvre *et al.*, 1987). Temperatures of the order of 700 °C have been calculated using Fe-Mg partitioning between garnet and omphacite (Ellis & Green, 1979). Pressures were found to be in the range 16-20 kb (Godard *et al.*, 1981) or 18-20 kb (Ballèvre *et al.*, 1987). Garnet-phengite thermometry in the studied micaschists gives slightly lower temperatures than these previous estimates. This discrepancy probably results from uncertainties in the Fe<sup>3+</sup> content.

In conclusion, estimated P-T conditions for the eclogitic metamorphism are 650-700 °C at pressures ranging from 10 to 20 kb.

# P-T evolution of the Champtoceaux micaschists

As shown previously, the Champtoceaux micaschists preserve part of their prograde P-T path. A first step towards quantitative estimates is shown in Fig. 12, where phase relations

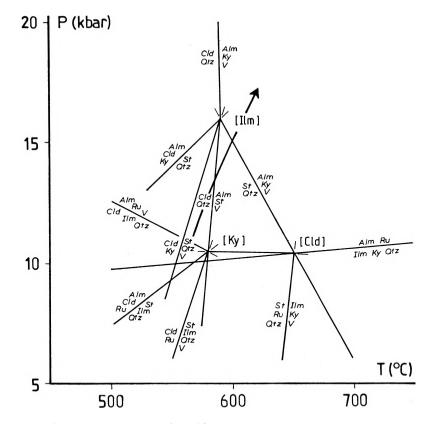


FIG. 12. Phase relations in the FeO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system. Mineral abbreviations are listed in Table 1. Only quartz-bearing reactions are represented. The St + IIm + Qtz (Ky, Cld) Alm + Rt + H<sub>2</sub>O is not labelled. The arrow shows the prograde P-T path as recorded by mineral assemblages during garnet growth.

between almandine, chloritoid, staurolite, kyanite, rutile, and ilmenite with excess quartz and vapour are depicted in the  $FeO-Al_2O_3-TiO_2-SiO_2-H_2O$  system. Experimental data allow the location of some reaction curves:

(1) According to Rao & Johannes (1979), the [Ilm] invariant point is located at around 590°C and 16 kb. Three of the five curves emanating from this invariant point have been experimentally studied (Richardson, 1968; Ganguly, 1972; Rao & Johannes, 1979):

$$4Fe_Cld + 5Ky = 2Fe_St + 1.5 Qtz + 2H_2O$$
(11)

$$23Fe_{Cld} + 7Qtz = 4Fe_{St} + 5Alm + 19H_{2}O$$
 (12)

$$6Fe_{-}St + 12.5Qtz = 4Alm + 23Ky + 6H_{2}O$$
 (8)

(2) Bohlen et al. (1983) studied the P-T location of the reaction:

$$Alm + 3Rt = 3Ilm + Ky + 2Qtz$$
(13)

and showed that the [Cld] invariant point is situated at around 11 kb, 650 °C.

Without an internally consistent set of thermodynamic data on end-member phases, we have been unable to calculate the exact position of the univariant reaction curves. Moreover, observed phases in the Champtoceaux micaschists are not purely ferrous. Consequently,

univariant reactions of the model system are divariant equilibria in the FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system. Despite these uncertainties, the model system provides useful constraints on the prograde P-T path.

Indeed, the lack of ilmenite and kyanite and the presence of chloritoid and staurolite within garnet cores show that the prograde P-T path took place along curve (12), at pressures between the [Ky] and [Ilm] invariant points. Equilibrium (8) was exceeded when staurolite broke down and kyanite grew (garnet rims). This shows that garnet growth occurred during a strong pressure increase while temperature rose slightly, and suggests that the matrix assemblages equilibrated at pressures higher than 16 kb.

# Geological significance of the P-T history

Figure 13 shows a part of the P-T history of the lower unit of the Champtoceaux nappe. A detailed discussion of the entire P-T history is clearly beyond the scope of this paper, because the last stages of the uplift path are not well constrained and other units within the Champtoceaux nappe (Fig. 1) have suffered different P-T histories during the Variscan orogeny. It thus seems premature to discuss only a particular P-T history—that of the

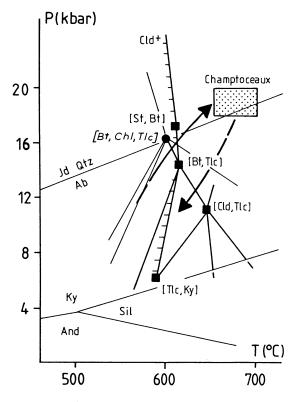


FIG. 13. Pressure-temperature history of the Champtoceaux metapelites. Alumino-silicate phase relations after Holdaway (1971). Ab = Jd + Qtz after Holland (1980). The KFMASH multisystem of Fig. 10b is approximately located on the P-T diagram after Rao & Johannes (1979), Koons & Thompson (1985) and Vuichard & Ballèvre (1988). Upper limit of the chloritoid stability field is indicated (Cld<sup>+</sup>). Shaded area represents peak metamorphic conditions for the Champtoceaux nappe. Arrows show P-T path for the Champtoceaux.

studied unit—without reference to lower and higher structural levels of the same nappe pile. Some comments on the P-T history are nevertheless useful:

(1) In the unit studied, eclogite-facies metamorphism is recorded not only in the metabasites but also in pelitic and quartzitic sediments (Ballèvre *et al.*, 1987). Incomplete coronitic transformations observed within low-strained granitic areas (Lasnier *et al.*, 1973) can also be attributed to the eclogite-facies metamorphism. Thus the studied unit should no longer be considered as a 'tectonic melange' (e.g., Marchand, 1981; Godard, 1983).

(2) The lack of relict parageneses from a previous metamorphic event suggests that the studied unit was most probably submitted to a single metamorphic cycle. For example, such relicts are frequently observed in the Western Alps, where a Paleozoic continental basement was submitted to an eclogite-facies metamorphism during the Cretaceous Eoalpine events (e.g., Compagnoni, 1977; Dal Piaz & Lombardo, 1986). In the present example, however, the breakdown of the graphitic material observed in the metapelites during the prograde history (Figs. 2 and 3) argues for a single-phase metamorphic history and therefore for pelitic sediments of Lower Paleozoic age.

(3) Consequently, the lower unit of the Champtoceaux nappe is a fragment of the upper levels of the continental crust, which was buried to depths of *ca*. 60 km at an early stage of the Variscan events. This shows that crustal thickening was a major process during the Variscan orogeny, which is consistent with present models of the tectonic evolution of the whole belt (e.g., Matte, 1986).

(4) The P-T path of the studied unit is mainly characterized by the fact that the maximum temperature is achieved at a depth equal to the maximum amount of burial (Fig. 13). This is the only known example of such a P-T path in the Variscan belt. This kind of P-T path is not consistent with most simple one-dimensional thermal models (England & Richardson, 1977; England & Thompson, 1984), except those obtained with high uplift rates, e.g., in the case where extension followed thickening (Thompson & Ridley, 1987), or those calculated with normal uplift rates but where thermal re-equilibration is cancelled by screen effects (Rubie, 1984; Davy & Gillet, 1986). Clearly, more data on the P-T evolution of the whole Champtoceaux nappe are needed to constrain possible thermal-tectonic models.

### CONCLUSIONS

The main conclusions of this study are as follows:

(1) A reversal of Fe-Mg partitioning occurs in high-pressure metapelites, where staurolite is more Fe-rich than coexisting garnet (Fig. 7). Only three natural occurrences are known at present (in Kazakhstan in the USSR, the Dora-Maira nappe in the Western Alps, and the Champtoceaux nappe in Brittany) but careful examination of garnetkyanite-phengite-rutile micaschists world-wide may reveal further examples.

(2) Taking into account the Fe-Mg reversal between garnet and staurolite, we analyse the phase relations between garnet, chloritoid, staurolite, and kyanite in eclogitic metapelites. The resulting topology of univariant reactions in the KFMASH multisystem is depicted in Fig. 10b, and compositional changes are predicted by Fig. 11b.

(3) The Champtoceaux micaschists record a trend of increasing pressures and temperatures towards 'peak' metamorphic conditions which have been estimated at around 18–20 kb, 650–700 °C. During this prograde evolution, mineralogical and compositional changes are controlled by the KFMASH univariant reaction:

$$St + Cld = Grt + Ky.$$

(4) The lower unit of the Champtoceaux nappe (Brittany, France) records burial of continental basement to depths of *ca*. 60 km during the early stages of the Variscan orogeny.

# **ACKNOWLEDGEMENTS**

Many thanks are due to Philippe Bertrand for his helpful suggestions during the course of this work. Critical reviews by S. L. Harley and N. B. W. Harris were greatly appreciated. M. S. N. Carpenter helped us to improve the English text.

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