Garnet-chloritoid-kyanite metapelites from the Raspas Complex (SW Ecuador): a key eclogite-facies assemblage

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Abstract: The Raspas Complex (Ecuador) contains one of the few eclogitic bodies in the northern Andes. It consists of metaperidotites, eclogites, and metapelites. The latter display three assemblages: (i) garnet + chloritoid + kyanite, (ii) garnet + chloritoid and (iii) garnet + chlorite, in all cases with quartz and muscovite in addition. The growth of these assemblages was coeval with the main ductile deformation, and was followed by minor reequilibration (chlorite growth in garnet + chloritoid samples and chloritoid + quartz aggregates replacing garnet and kyanite in garnet + chloritoid + kyanite samples). Detailed microprobe analyses show increasing magnesian compositions for garnet (from core to rim) and chloritoid (inclusions within garnet compared to matrix grains) in kyanite-bearing samples. The above data are interpreted in the framework of the KFMASH system. Reaction progress along the divariant reaction Cld = Grt + Ky explains the change in chemistry of coexisting phases. The divariant Grt-Cld-Ky assemblage has a narrow stability field, and the P-T conditions are estimated at about 20 kbar, 550-600°C. Decompression, recorded by chloritoid-quartz pseudomorphs of garnet, probably occurred as temperature decreased.

Key words: eclogite-facies metamorphism; Ecuador; metapelite; Raspas Complex.

Mineral abbreviations are from Kretz (1983).

Introduction

Since the advent of plate tectonics, high-pressure metamorphic rocks have been recognised as an essential characteristic of convergent plate boundaries. Most blueschists and eclogites are derived from subduction of oceanic lithosphere, but relics of high-pressure to ultra-high-pressure parageneses in continentally-derived material have also proven the existence of continental subduction (e.g. Compagnoni et al., 1977; Chopin, 1984; Maruyama et al., 1996). The link between high-pressure metamorphism and lithospheric subduction results from the thermal structure of subduction zones, where low geothermal gradients prevail during convergence (e.g. Ernst, 1973; Peacock, 1996).

The Andean Range along the western side of South America is a typical example of an active margin, where the oceanic crust from the Pacific and Nazca plates is currently being subducted under the South American continent. A thickened crust has developed above the subduction zone as a result of magmatic underplating and/or accretion at various times of magmatic arcs and oceanic plateaux (Gansser, 1973; Feininger & Bristow, 1980; Aspden &

McCourt, 1986; Mégard, 1987; Litherland *et al.*, 1994). High-pressure rocks developed at some stage during the long-standing subduction history are sparsely represented along the Andean Range (see review in Maruyama *et al.*, 1996). In the northern Andes three occurrences of high-pressure rocks have been found in Colombia (Orrego *et al.*, 1980; Feininger, 1982a; de Souza *et al.*, 1984) and one in Ecuador (Feininger, 1980).

This study aims at clarifying the P-T evolution of one of these occurrences, namely the Raspas Complex in southern Ecuador (Feininger, 1980). In particular, the purpose of this study is to document the reaction history and P-T conditions of well-preserved occurrences of garnet-chloritoid-kyanite metapelites. Because this paragenesis is a rare eclogite-facies assemblage, it can be considered as a key for the determination of high-pressure conditions in pelitic systems.

Geological setting

Ecuador can be divided into two main domains separated by a major suture zone striking N/NE-S/SW and

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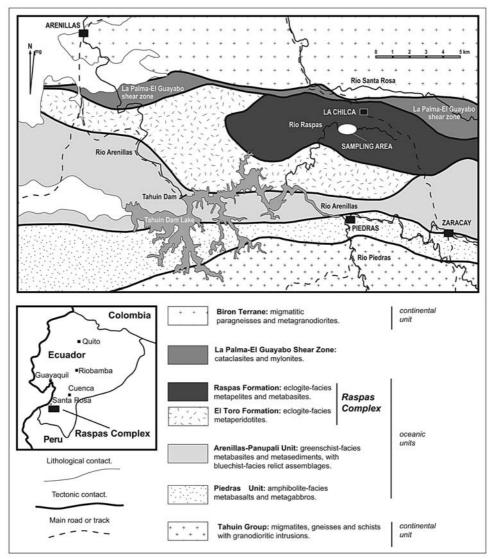


Fig. 1. Simplified tectonic map of the studied area, El Oro Province, southwestern Ecuador (Gabriele, 2002).

located between the eastern margin of the inter-Andean valley and the western foot of the Cordillera Real.

The eastern domain, of continental derivation, is composed of the Precambrian Amazon craton, covered by the Tertiary-Quaternary deposits of the Oriente Basin, and of a variety of metamorphic and magmatic rocks, Palaeozoic to Jurassic in age, forming the Cordillera Real. This domain was the active continental margin facing the subduction zone until the end of the Jurassic (*ca.* 140 Ma) (Aspden *et al.*, 1987; 1995; Jaillard *et al.*, 1990).

In the western domain, between 1°N and 3°S, most of the geological units of the Western Cordillera and Coastal Domain are magmatic bodies with an oceanic affinity, associated with different subduction-accretion events occurring since Early Cretaceous times (Gansser, 1973; Feininger & Bristow, 1980; Litherland *et al.*, 1994; Jaillard *et al.*, 1997; Reynaud *et al.*, 1999; Spikings *et al.*, 2001; Hughes & Pilatasig, 2002).

In the El Oro province of south-western Ecuador (between 3°S and 4°S; 79°30'W and 80°50'W), the

Cordillera de Tahuin, a foothills range west of the Andes, forms the western shoulder of the South American continent. In this region, various metamorphic terranes (Feininger, 1982b) have been grouped together as the "El Oro Metamorphic Complex" (about 2,700 km²) (Aspden et al., 1995). These terranes can be interpreted (i) as independent allochtonous or parautochtonous bodies (Feininger, 1987), (ii) as large displaced blocks (Amotape-Tahuin block of Mourier et al., 1988), (iii) as a late Jurassic - early Cretaceous tectonic mélange representing part of an accretionary prism (Aspden et al., 1995). The El Oro Metamorphic Complex is characterised by varied lithologies and assemblages, the metamorphic ages of which range from the Palaeozoic to the Cretaceous (Aspden et al., 1995). According to Aspden et al. (1995), this area is crosscut by several E-W-trending strike-slip faults that subdivide the El Oro Metamorphic Complex into smaller units.

One of these, the Raspas Complex, is bounded to the North by the La Palma - El Guayabo shear zone and to the South by a major tectonic contact (Fig. 1). The Raspas

Assemblage Sample	Grt+Cld+Ky			Grt+Cld			Grt+Chl				
	98RR11	97Ce5	97Ce6	98RR2	98RR12	97Ce4	98RR7	98RR10	97Ce2	97Ce3	
Qtz	x	х	×	×	х	x	х	x	×	×	
W.M.	x	×	x	×	x	x	×	×	X	×	
Grt	(x)	(x)-x	(x)-x	(x)	(x)	(x)	×	×	X	×	
Cld	II-IIIa-IIIb	I-II-IIIa-IIIb	II-IIIa-IIIb	II-IIIa-IIIb	II-IIIa-IIIb	II-IIIa-IIIb					
Chl				Ш	III		Ш	11	11	П	
Ку	x	×	×								
Rt	x	×	x	×	x	×	×	×	×	×	
Ttn								10			
Gr	X	X	x	×	x	×	X		×	x	
Tur				×							
Ap								×			
Sulphides		×	x	x		x	×		×		
Microprobe analyses	+	+		+	+			+		+	
Whole-rock chem. anal.	+	+	+	+	+				+	+	

Table 1. Mineral assemblages of the analysed samples. Abbreviations follow Kretz (1983), except W.M. (white mica).

Abbreviations are after Kretz (1983); in addition W.M., white mica; (x), pseudomorphosed; I, inclusion in Grt; II, synkinematic;

III, post-kinematic (IIIa: pseudomorph of Grt; IIIb: porphyroblasts randomly oriented across the main schistosity).

Complex comprises two formations, namely the El Toro Formation, made of eclogite-facies metaperidotites, and the Raspas Formation, consisting of eclogites, garnet-amphibolites, blueschists and garnet-chloritoid micaschists (Feininger, 1978, 1980; Gabriele, 2002). Geochemical data show that the Raspas Complex is a composite fragment of oceanic lithosphere, the eclogite-facies mafic rocks presenting OPB-type affinities (Arculus et al., 1999; Bosch et al., 2002). To the south of the Raspas Complex, the mafic rocks from the Arenillas-Panupali and Piedras Units show MORB-type affinities (Aspden et al., 1995; Bosch et al., 2002; Gabriele, 2002). The Raspas Complex, in association with the Arenillas-Panupali and Piedras Units, represents a piece of oceanic lithosphere sandwiched between continentally-derived units, i.e. the Biron Terrane to the North, and the Tahuin Group to the South (Feininger, 1978 and 1987; Gabriele, 2002) (Fig. 1). K-Ar data on phengite (132 ± 5 Ma, Feininger, 1980) suggest a lowermost Cretaceous age for cooling of the high-pressure metamorphism.

Petrography

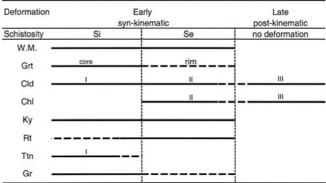
The studied pelitic schists have been sampled in the northern part of the Raspas Complex. The best outcrops are located in the Rio Raspas, where the trail from La Chilca village crosses the brook (Fig. 1, UTM-WGS84: 17 / 620500E-9602100N).

The metapelites (Table 1) are medium- to coarse-grained graphite-bearing schists, with conspicuous crystals of garnet up to 1 cm in diameter. Most garnet grains are blackish rather than reddish, either because they contain abundant graphite inclusions or because they are partially to wholly replaced by a fine-grained aggregate consisting of chloritoid and quartz.

Textural observations show an early, synkinematic, stage of mineral growth, followed by post-kinematic growth (Fig. 2). While syn-kinematic phengite clearly defines the main schistosity, the relation between graphite

growth and deformation is more ambiguous. The graphite occurs mainly as an internal schistosity in garnet porphyroblasts (Fig. 3a) or as rootless isoclinal folds (in microlithons) having an axial plane sub-parallel to the main schistosity. This observation is consistent with the existence of several generations of structures (e.g. the graphite-bearing schistosity preserved within garnet or microlithons) developed before the main schistosity (i.e. the schistosity defined by shape-preferred orientation of phengite).

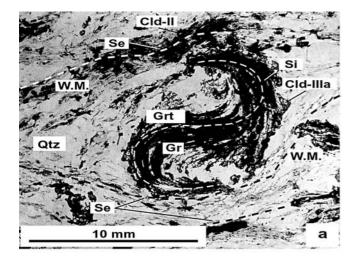
The white mica defines the main schistosity (*i.e.* the external schistosity) which corresponds in the field to the regional schistosity (Fig. 3). Idioblastic or sub-idioblastic phengite is usually concentrated in millimetre-thick layers alternating with quartz-rich, granoblastic layers. Some white mica aggregates are oblique to the main schistosity, and define microlithons which include rootless isoclinal folds defined by graphite-rich layers.



Abbreviations are after Kretz (1983), except W.M.: white mica. I, inclusion in Grt; II, synkinematic; III, post-kinematic. Si and Se refer to the internal (i.e. in Grt porphyroblasts) and external (i.e. in the matrix) schistosity.

Ttn has been observed only in sample 98RR10.

Fig. 2. Timing of mineral growth and ductile deformation in the metapelites from the Raspas Complex.



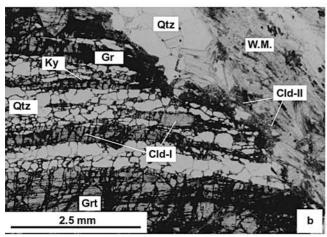


Fig. 3. Photomicrographs (plane-polarised light) showing the main textural features of the Raspas metapelites. (a): Garnet porphyroblast with aligned inclusions defining an internal schistosity (Si) (sample 98RR2) and showing rotation with respect to the external schistosity (Se). (b) Garnet poikiloblast showing alternating quartz-rich and quartz-poor layers, and inclusions of kyanite, chloritoid (Cld I) and graphite (sample 97Ce5).

Garnet poikiloblasts contain inclusions of quartz, kyanite, chloritoid, graphite and rutile (Table 1). The poikiloblasts can show an internal schistosity (Si) mainly defined by minute graphite inclusions and small chloritoids (Fig. 3). The presence of sigmoidal structures in porphyroblasts and the continuity of internal (Si) and external (Se) schistosity (*i.e.* the main schistosity) (Zwart, 1960) indicate that garnet growth was pre-to-synkinematic with respect to the main schistosity (*i.e.* Se) (Fig. 2 and 3). Garnet microstructures are strikingly similar to those described by Stöckhert *et al.* (1997).

Three different generations of chloritoid are identified, namely (1) relict xenoblastic crystals included in the garnet; (2) xenoblastic to sub-idioblastic crystals dispersed in the matrix and aligned along the main schistosity; and (3) idioblastic chloritoid randomly oriented across the schistosity or pseudomorphing garnet. In most samples of

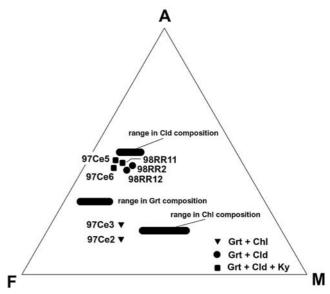


Fig. 4. AFM whole-rock chemistry projected from quartz, muscovite, paragonite and H₂O.

kyanite-bearing schists, garnet is replaced by very finegrained aggregates of randomly-oriented chloritoid associated with minute quartz grains. In kyanite-free samples, garnet is replaced by chlorite-chloritoid aggregates. Chlorite is present as idioblastic synkinematic crystals or as secondary minerals in pseudomorphic aggregates after garnet and/or chloritoid (Table 1, Fig. 2). Kyanite is observed as inclusions defining the internal schistosity (Si) in the garnet and in the matrix (Table 1, Fig. 2 and 3b). It often shows a reaction rim consisting of chlorite and white mica (phengite), and also a pseudomorphic replacement by chloritoid and white mica. Graphite is mainly found in the grains whose growth began before the development of the main schistosity (Table1 and Fig. 2). Therefore, graphite may have been exhausted during the prograde metamorphic history, before or close to the peak P-T conditions. Rutile is present in all studied samples. Titanite is only found in sample 98RR10 as inclusions in garnet cores and is substituted by rutile in garnet rims and in the matrix.

To sum up, all the metapelites from the Raspas Complex contain quartz + white mica + rutile. Three synkinematic parageneses are distinguished, namely Grt+Cld+Ky, Grt+Cld and Grt+Chl. Late-kinematic phases include replacement of garnet and kyanite by chloritoid-quartz aggregates in the kyanite-bearing samples, and garnet replacement by chloritoid-chlorite aggregates in the kyanite-free samples.

Whole-rock chemistry

Whole-rock chemical analyses (Table 2) show that the metapelites have aluminium-rich and iron-rich compositions. In an AFM projection (Fig. 4), the analysed samples define three groups according to their parageneses.

Assemblage	(Grt+Cld+Ky		Grt+Cld			Chl
Sample	98RR11	97Ce5	97Ce6	98RR2	98RR12	97Ce2	97Ce3
SiO ₂	77.80	76.03	76.86	81.86	67.93	72.14	74.30
TiO ₂	0.75	0.82	0.88	0.64	1.02	0.46	0.52
Al ₂ O ₃	12.24	13.05	12.45	9.99	17.65	12.90	11.87
Fe ₂ O ₃ *	3.68	4.15	4.68	2.70	4.38	5.26	5.71
FeOcal	3.31	3.74	4.21	2.43	3.95	4.73	5.14
MnO	0.03	tr.	0.03	0.02	0.04	0.14	0.07
MgO	0.57	0.45	0.54	0.52	0.86	1.26	1.28
CaO	0.13	0.18	0.28	0.13	0.20	0.51	0.69
Na ₂ O	0.60	0.68	0.58	0.61	1.18	0.84	0.63
K ₂ O	1.33	1.31	1.27	1.06	1.91	2.22	1.88
P ₂ O ₅	0.07	0.08	0.10	0.08	0.11	0.18	0.09
LOI	2.59	3.11	-	2.14	4.04		2.84

Table 2. Whole-rock chemistry of metapelites from the Raspas Complex.

99.86

Grt+Chl samples are aluminium-poor compared to Grt+Cld+Ky and Grt+Cld samples. The latter are distinguished by their magnesium content, the Grt+Cld samples being more magnesium-rich than the Grt+Cld+Ky ones. The main variations in composition are due to the aluminium content, whereas a minor impact is related to the iron-magnesium ratio. This variation in the bulk rock chemistry suggests that the three different parageneses characterising the Raspas Complex metapelites are due to differences in the protolith composition rather than metamorphic conditions. Rare-earth element patterns of the garnet-chloritoid metapelites are similar to those of average pelites, indicating a continental source for the detrital material (Arculus et al., 1999; Bosch et al., 2002).

total*

Mineral chemistry

99.32

95.91

99.88

99.75

The chemical composition of white mica, garnet, chloritoid and chlorite were determined at the University of Lausanne, Switzerland, using the wavelength dispersive electron microprobe (CAMECA SX50). Complementary analyses have been performed with the Microsonde Ouest (Brest, France). In both cases, operating conditions were: 15 kV accelerating voltage and 15 nA sample current, after a calibration on natural mineral standards. Both simple point determinations and/or zoning profiles were obtained.

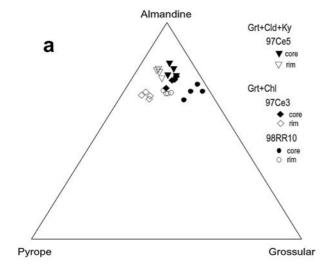
Garnet is characterised by a high almandine endmember content, averaging around 65 mol% (Table 3, Fig. 5). The zoning profile (Fig. 5b) shows a decreasing

Table 3. Representative electron microprobe analyses and structural formulae of garnet. Estimation of the Fe³⁺ content in garnet has been done on the basis of 24 oxygens and 16 cations (e.g. Spear, 1993). End-members have been calculated according to Deer et al. (1992).

Sample	97Ce	5 (Grt+Cld+K)	()	98RR10 (G	rt+Chl)	97Ce3 (Grt+Chl)		
manananinin in	core	core	rim	core	rim	core	rim	
Analysis	14	8	23	251	225	16	2	
SiO ₂	37.14	37.41	37.05	37.29	37.79	36.74	37.74	
TiO ₂	0.01	0.00	0.00	0.21	0.16	0.12	0.08	
Al ₂ O ₃	21.03	21.46	21.16	20.37	21.05	20.74	21.30	
FeO*	35.44	34.37	34.31	29.38	30.08	32.65	29.75	
MnO	0.42	0.44	0.35	2.73	0.14	0.62	0.49	
MgO	1.98	3.53	3.31	0.61	3.00	2.52	5.43	
CaO	4.86	3.76	3.79	9.96	8.45	6.77	5.75	
Total	100.88	100.97	99.97	100.55	100.67	100.15	100.55	
Numbers of ion	ns on the basis	of 16 cations	and 24 oxygens	s				
Si	5.94	5.92	5.93	5.97	5.95	5.87	5.89	
Al ^{VI}	3.96	4.00	3.99	3.84	3.91	3.91	3.93	
Fe ³⁺	0.16	0.16	0.15	0.16	0.14	0.32	0.27	
Ti	0.00	0.00	0.00	0.03	0.02	0.02	0.01	
Mg	0.47	0.83	0.79	0.15	0.70	0.60	1.26	
Fe ²⁺	4.58	4.39	4.44	3.77	3.82	4.04	3.61	
Mn	0.06	0.06	0.05	0.37	0.02	0.08	0.07	
Ca	0.83	0.64	0.65	1.71	1.43	1.16	0.96	
Total	16.00	16.00	16.00	16.00	16.00	16.00	16.00	
Mol per cent e	nd-members							
Almandine	77.1	74.2	74.9	62.9	64.0	68.7	61.2	
Spessartine	1.0	1.0	0.8	6.2	0.3	1.4	1.1	
Pyrope	7.9	14.1	13.3	2.4	11.8	10.2	21.4	
Grossular	10.1	6.9	7.3	24.4	20.4	11.9	9.6	
Andradite	4.0	3.9	3.7	4.1	3.5	7.8	6.7	
X _{Mg}	0.09	0.16	0.15	0.04	0.16	0.13	0.26	

^{*:} all iron as Fe²⁺; X_{Mg}=Mg/(Mg+Fe²⁺)

^{97.67} *: all iron as Fe3+; cal: calculated (FeO=Fe2O3/1.111); **: calculated using all iron as Fe3+.



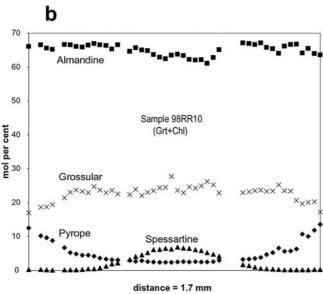


Fig. 5. (a) Garnet composition in terms of almandine, pyrope and grossular end-members. (b) Garnet zoning in sample RR 10 shows a smooth profile, with decreasing spessartine and grossular and increasing pyrope from core to rim. This profile is typical of growth zoning.

spessartine content and an increasing pyrope content from core to rim. The spessartine content decreases down to values less than 1 mol per cent in the outer part of the garnet porphyroblasts. Average variations in core and rim compositions are Alm60-76, Sps1-6, Prp2-9, Grs13-27 and Alm60-73, Sps0.3-1 Prp8-20, Grs15-23, respectively. All samples show a decreasing grossular content from core to rim, but garnet from sample 98RR10 shows a larger variation in grossular content compared to the other samples (Fig. 5a). This behaviour is consistent with the occurrence of titanite inclusions (instead of rutile) in garnet cores from sample 98RR10. The Mg/(Fe+Mg) ratio is higher in the samples 98RR10 and 97Ce3 compared to the sample 97Ce5, *i.e.* in the Grt+Chl paragenesis compared to the Grt+Cld+Ky paragenesis.

Chloritoid compositions change depending upon their microstructural site of growth (Table 4). Chloritoid inclusions (*i.e.* Cld-I) in garnet cores show a lower $X_{\rm Mg}$ with respect to chloritoid inclusions close to garnet rims ($X_{\rm Mg}$ varies from 0.11 to 0.18). Matrix chloritoid (*i.e.* Cld-II) is slightly more magnesian ($X_{\rm Mg} = 0.21\text{-}0.23$) than the most magnesian inclusions in the garnet grains, while the randomly-oriented grains (*i.e.* Cld-IIIb) in the matrix and the chloritoid grains pseudomorphing garnet (*i.e.* Cld-IIIa) are less magnesian ($X_{\rm Mg} = 0.15\text{-}0.21$). Synkinematic chlorites (*i.e.* Chl-III) are richer in Si and Mg ($X_{\rm Mg} = 0.43\text{-}0.58$) than post-kinematic chlorites (*i.e.* Chl-III) ($X_{\rm Mg} = 0.33\text{-}0.36$) growing at the expense of garnet or chloritoid (Table 5).

White mica is phengitic muscovite, except in sample 97Ce3 where paragonite has also been found. Phengite displays a relatively high Si content (from 6.30 to 6.72 atoms p.f.u on the basis of 22 oxygen) and the Mg+Fe(tot) content varies between 0.35 and 1.08 atoms p.f.u. (Table 6 and Fig. 6). All the studied samples, except 98RR10, are graphite-bearing metapelites, suggesting that relatively low fO₂ conditions prevailed during most of the prograde history. Accordingly we assume that all iron is divalent (Guidotti, 1984). In addition, analyses of phengite from graphite-bearing samples plot close to the ideal Tschermak substitution, suggesting that a negligible amount of ferric iron is present (Guidotti, 1984; Spear, 1993). If graphite is lacking (sample 98RR10), the analyses plot significantly above the ideal substitution (Fig. 6), indicating that a significant amount of ferric iron is present. The Si content is higher in chloritoid-free samples (Si = 6.45-6.60 pfu) than in chloritoid-bearing samples (Si = 6.35-6.45 pfu). Phengite grains are locally slightly zoned, with decreasing Si-content from core to rim.

Reaction history of the Raspas metapelites

Mineral assemblages and compositions from the Raspas micaschists are shown in an Al₂O₃-FeO-MgO (AFM) projection assuming excess quartz, muscovite and water (Thompson, 1957) (Fig. 7 and 8). Phase relations between observed phases are best illustrated in the SiO₂-Al₂O₃-FeO-MgO-K₂O-H₂O (KFMASH) system (Fig. 9). Few topologies are possible in this multisystem, due to numerous experimental data in the limiting FASH system (Rao & Johannes, 1979). Theoretical and calculated grids show two alternatives, whether staurolite is more magnesian than coexisting garnet (Harte & Hudson, 1979; Spear, 1999) or vice-versa (Chopin, 1984; Ballèvre et al., 1989; Powell & Holland, 1990). Empirical (e.g. Harte & Hudson, 1979; Vuichard & Ballèvre, 1988; Ballèvre et al., 1989) as well as calculated KFMASH (e.g. Powell & Holland, 1990; Powell et al., 1998; Spear, 1999) grids show that the assemblage garnet-chloritoid-kyanite is stable within a narrow temperature range at high pressure.

Possible P-T paths in the KFMASH system

Possible P-T paths for the Raspas metapelites will be discussed first in the model KFMASH system (Fig. 9).

Table 4. Representative electron microprobe analyses and structural formulae of chloritoid. Estimation of the Fe³⁺ content in chloritoid has been done assuming stoichiometry, *i.e.* Fe³⁺ = 4-(Ti⁴⁺+Al³⁺) (Deer *et al.*, 1992).

Sample Generation	98RR11 (Grt+Cld+Ky)			97Ce5 (Grt+	Cld+Ky)		98RR2 (Grt+Cld)			98RR12 (Grt+Cld)		
	11	IIIb		1	11	IIIb	- 11	Illa	IIIb	- 11	Illa	IIIb
Analysis	36	35	11	7	32	57	11	23	10	45	15	40
SiO ₂	24.44	24.23	24.23	24.48	25.00	24.30	24.09	24.10	24.39	23.91	24.13	23.91
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00
Al ₂ O ₃	41.27	41.06	40.07	40.69	41.04	40.24	41.01	40.70	41.11	40.78	41.04	40.76
FeO*	23.54	24.30	26.31	24.40	22.83	24.63	23.17	25.16	23.08	24.33	24.63	24.23
MnO	0.08	0.25	0.12	0.06	0.03	0.21	0.18	0.23	0.34	0.22	0.34	0.34
MgO	3.45	3.07	1.76	2.98	3.66	2.55	3.87	2.49	3.39	3.05	2.57	2.85
Total	92.79	92.93	92.54	92.62	92.58	91.94	92.33	92.72	92.37	92.33	92.84	92.13
Numbers of	ions on the bas	sis of 12 O										
Si	2.00	1.99	2.01	2.01	2.03	2.02	1.98	1.99	2.00	1.98	1.99	1.98
Al	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Al	0.98	0.97	0.93	0.95	0.95	0.94	0.97	0.97	0.98	0.98	0.98	0.98
Ti	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 ³⁺	0.02	0.03	0.07	0.05	0.05	0.06	0.03	0.03	0.02	0.02	0.02	0.02
Fe ²⁺	1.58	1.64	1.76	1.62	1.50	1.65	1.56	1.71	1.56	1.66	1.69	1.67
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.02	0.02
Mg	0.42	0.37	0.22	0.36	0.44	0.31	0.47	0.31	0.42	0.37	0.31	0.35
Total	8.00	8.01	7.99	7.99	7.98	7.98	8.03	8.02	8.01	8.02	8.01	8.02
X _{Fe}	0.79	0.81	0.89	0.82	0.77	0.83	0.76	0.84	0.78	0.81	0.83	0.82
X _{Mn}	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01
X _{Mg}	0.21	0.18	0.11	0.18	0.23	0.16	0.23	0.15	0.21	0.18	0.16	0.17

^{*:} all iron as Fe^{2+} ; $X_{Fe}=Fe^{2+}/(Mg+Mn+Fe^{2+})$; $X_{Mn}=Mn/(Mg+Mn+Fe^{2+})$; $X_{Mg}=Mg/(Mg+Mn+Fe^{2+})$

According to the KFMASH grids calculated by Powell & Holland (1990) and Powell *et al.* (1998), the assemblage Grt-Cld-Ky is stable at higher pressures than the KFMASH invariant point (*i.e.* at about 12 kbar), in a narrow temperature interval (560-600°C). Specifically, the lower temperature limit of the Grt-Cld-Ky assemblage is defined by the incoming of almandine + kyanite at the expense of Fe-chlo-

ritoid + quartz, and the upper temperature limit by the breakdown of chloritoid through the KFMASH univariant reaction Cld = Grt + Chl + Ky +V.

The P-T evolution of the Raspas metapelites can be described in this simplified model by path A (continuous line on fig. 9). Garnet and chloritoid coexisting with kyanite in sample 97Ce5 (Figs. 7 and 8) show increasing

Table 5. Representative electron microprobe analyses and structural formulae of chlorite. All iron is assumed to be divalent.

Sample	98RR2 (G	98RR2 (Grt+Cld)		R12 (Grt+0	Cld)	98RF	98RR10 (Grt+Chl)			97Ce3 (Grt+Chl)		
	core	rim	core	rim	max. Mg	core	rim	min. Mg	core	rim	min. Mg	
Analysis	27	26	16	17	12	30	27	33	59	54	64	
SiO ₂	23.43	23.74	23.44	23.31	24.07	26.70	26.48	29.40	26.20	25.76	26.27	
TiO ₂	0.07	0.05	0.08	0.11	0.05	0.07	0.07	0.11	0.05	0.03	0.07	
Al ₂ O ₃	21.62	21.41	21.07	21.63	20.90	20.01	19.93	19.38	21.49	21.23	21.17	
Cr ₂ O ₃	0.01	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.05	0.04	0.03	
FeO*	31.97	32.62	33.21	33.67	32.62	23.68	24.18	23.64	23.09	24.71	28.65	
MnO	0.17	0.13	0.17	0.15	0.16	0.00	0.02	0.04	0.05	0.03	0.17	
MgO	10.16	10.39	9.05	9.41	9.99	18.08	16.91	14.49	17.40	15.95	11.94	
CaO	0.00	0.03	0.00	0.07	0.04	0.02	0.03	0.15	0.01	0.00	0.10	
Na ₂ O	0.00	0.01	0.03	0.02	0.00	0.03	0.02	0.03	0.02	0.01	0.01	
K₂O	0.00	0.02	0.01	0.00	0.01	0.02	0.02	0.35	0.03	0.01	0.01	
Total	87.42	88.45	87.08	88.42	87.84	88.64	87.67	87.61	88.38	87.77	88.43	
Numbers of	ions on the b	asis of 28 O					9					
Si	5.16	5.18	5.22	5.12	5.28	5.51	5.54	6.09	5.40	5.40	5.57	
Al ^{IV}	2.84	2.82	2.78	2.88	2.72	2.49	2.46	1.91	2.60	2.60	2.43	
Al ^{VI}	2.77	2.68	2.75	2.72	2.69	2.37	2.46	2.83	2.62	2.64	2.85	
Ti	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	
Cr	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.00	
Fe*	5.89	5.95	6.19	6.18	5.99	4.08	4.23	4.10	3.98	4.33	5.08	
Mn	0.03	0.02	0.03	0.03	0.03	0.00	0.00	0.01	0.01	0.01	0.03	
Mg	3.33	3.38	3.00	3.08	3.27	5.56	5.27	4.48	5.34	4.98	3.77	
Ca	0.00	0.01	0.00	0.02	0.01	0.01	0.01	0.03	0.00	0.00	0.02	
Na	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	
K	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.09	0.01	0.00	0.00	
Total	20.03	20.06	20.01	20.06	20.00	20.05	20.00	19.57	19.99	19.98	19.78	
X _{Mg}	0.36	0.36	0.33	0.33	0.35	0.58	0.55	0.52	0.57	0.53	0.43	

^{*:} all iron as Fe2+; X_{Mg}=Mg/(Mg+Fe*)

	Grt+C	ld+Ky		Grt+Cld		Grt+Chl				
Sample	98RR11	97Ce5	98RR2	98R	R12	98RR10	97Ce3			
	phengite	phengite	phengite	phengite	paragonite	phengite	phengite	paragonite		
Analysis	27	43	6	30	5	44	5	8		
SiO ₂	48.21	48.52	48.00	47.60	46.63	48.58	49.08	46.34		
TiO ₂	0.47	0.44	0.45	0.48	0.11	0.94	0.43	0.11		
Al ₂ O ₃	33.12	32.45	33.16	33.16	38.79	26.51	30.97	39.45		
Cr ₂ O ₃	0.00	0.06	0.04	0.02	0.08	0.14	0.03	0.05		
FeO*	1.44	1.34	1.35	1.27	0.49	2.65	1.30	0.26		
MnO	0.00	0.01	0.03	0.03	0.01	0.04	0.02	0.00		
MgO	1.61	1.62	1.69	1.65	0.13	3.72	2.51	0.17		
CaO	0.02	0.00	0.02	0.00	0.31	0.00	0.00	0.33		
Na ₂ O	1.10	1.21	1.37	1.31	6.79	0.53	1.06	7.08		
K₂O	8.54	8.94	8.73	8.68	1.26	9.99	8.83	0.95		
Total	94.52	94.60	94.84	94.20	94.60	93.10	94.22	94.74		
Numbers o	f ions on the bas	is of 22 O								
Si	6.40	6.45	6.36	6.35	6.02	6.67	6.54	5.96		
Al ^{IV}	1.60	1.55	1.64	1.65	1.98	1.33	1.46	2.04		
Al ^{VI}	3.57	3.53	3.55	3.56	3.92	2.96	3.41	3.95		
Ti	0.05	0.04	0.05	0.05	0.01	0.10	0.04	0.01		
Cr	0.00	0.01	0.00	0.00	0.01	0.02	0.00	0.01		
Fe*	0.16	0.15	0.15	0.14	0.05	0.30	0.15	0.03		
Mn	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00		
Mg	0.32	0.32	0.33	0.33	0.03	0.76	0.50	0.03		
Ca	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.05		
Na	0.28	0.31	0.35	0.34	1.70	0.14	0.27	1.77		
K	1.44	1.52	1.48	1.48	0.21	1.75	1.50	0.16		
Total	13.83	13.88	13.91	13.90	13.97	14.03	13.87	13.99		

Table 6. Representative electron microprobe analyses and structural formulae of white micas. All iron is assumed to be divalent.

 $X_{\rm Mg}$, indicating increasing temperature during garnet growth. This records part of the prograde P-T path, ideally taking place over a short temperature interval, of the order of 20°C. The other peak parageneses observed (Table 1 and Fig. 7 and 8), namely garnet + chloritoid and garnet + chlorite are trivariant in the KFMASH system. Peak P-T conditions are located within the shaded area in Fig. 9.

Retrograde phases include chloritoid + quartz in kyanitebearing rocks and chloritoid + chlorite in kyanite-absent samples. These two retrograde assemblages document backreaction along the two divariant reactions, Grt+Ky = Cld+Qtz and Grt = Cld+Chl, respectively (Fig. 9). In both reactions, the amount of retrograde products will depend upon the amount of available H_2O . Two cases are to be considered. First, if $a(H_2O) = 1$ throughout decompression, the P-T path during decompression should cross the bounding FASH reaction above the KFASH invariant point, *i.e.* above 15 kbar. This places severe constraints on the shape of the P-T path, indicating decreasing temperatures during the earliest stage of the decompression. Second, the

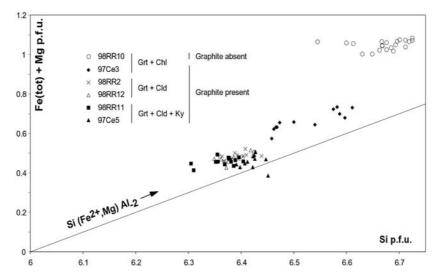


Fig. 6. Phengite chemistry in terms of Si content (on the basis of 22 oxygens) and Fe(total)+Mg content. The line represents the ideal inverse Tschermak substitution.

^{*:} all iron as Fe2+

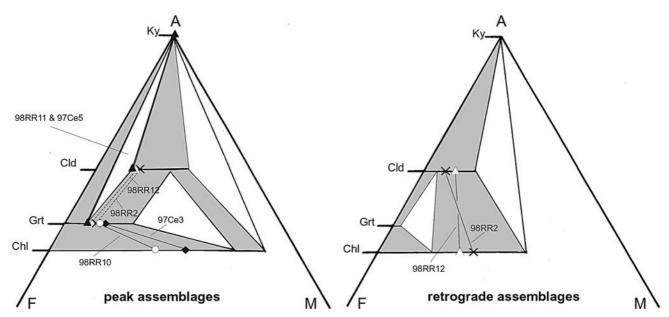


Fig. 7. AFM projection of coexisting minerals in the Raspas metapelites. Peak assemblages are depicted using measured compositions (full lines), and assumed compositions when garnet is totally pseudomorphed (dashed lines). Crossing tie-lines for retrograde assemblages indicate disequilibrium or growth at different P-T conditions in the two investigated samples. The grey fields indicate the extent of trivariant assemblages in the AFM diagram.

assumption of a unit activity for H_2O during decompression is unlikely. Decreasing the $a(H_2O)$ displaces the divariant equilibria towards lower temperatures. Consequently, the garnet breakdown reaction could have taken place at a lower pressure than the KFASH invariant point, but still at higher pressures than the location of the Alm-St-Cld-Ky invariant point for the corresponding $a(H_2O)$ (open circle in Fig. 9). This would also indicate decreasing temperature at an early stage of the decompression.

Possible P-T paths in the KFMnMASH system

The model KFMASH system needs some refinement, for two main reasons. First, because of the presence of graphite, the activity of H₂O in the fluid phase is expected to be slightly lower than 1, resulting in all fluid-bearing equilibria being displaced towards lower temperatures. Second, the incorporation of MnO into garnet displaces the KFASH invariant point towards lower P-T, ideally along the Grt-absent reaction if MnO only enters garnet or if X_{Mn} (Cld) = X_{Mn} (St), neither of these limiting assumptions being strictly true (Droop & Harte, 1995). Moreover, MnO will stabilise the KFMnMASH reaction Cld+Ky = Grt+St+Chl+V (Fig. 9), and the corresponding KFMASH reactions will become divariant. Accordingly, the equilibrium curves bounding the garnet-chloritoid-kyanite stability field will be displaced towards lower temperatures, potentially greatly extending the stability field of the assemblage Grt-Cld-Ky (Fig. 9).

The main consequence for the possible P-T paths of the Raspas metapelites is that peak temperatures could potentially be at lower temperature than the KFASH equilibria Cld+Qtz = Alm+Ky+V (dashed line on Fig. 9). The change

in chemistry during garnet growth is interpreted in the same manner than discussed above in the pure KFMASH system, indicating increasing temperature during garnet growth but at lower absolute values. As also discussed above, the retrograde reactions could indicate two types of

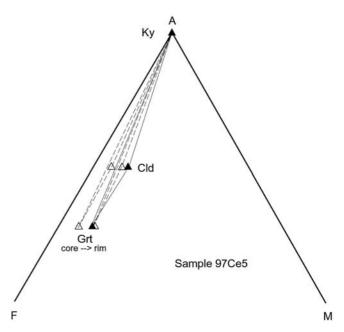


Fig. 8. AFM projection showing the prograde evolution of the Grt-Cld-Ky assemblage. The displacement of the three-phase field towards higher magnesian compositions is recorded by chloritoid (and kyanite) inclusions within garnet (open symbols), then matrix chloritoid coexisting with garnet rims (filled symbols).

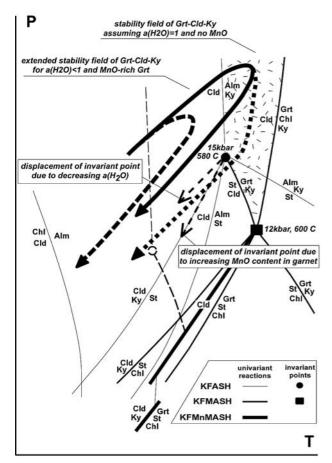


Fig. 9. Possible P-T path for the Raspas metapelites. The topology of the KFMASH grid is taken from Powell & Holland (1990). Note the narrow stability field of the Grt-Cld-Ky assemblage, provided that garnet does not contain a significant amount of spessartine and assuming a unit H₂O activity. The continuous line describes the simplest P-T path. Increasing the spessartine content in garnet and/or decreasing the H₂O activity displace the KFASH invariant point (filled circle) towards lower P-T. Accordingly, the stability field of the trivariant assemblage Grt-Cld-Ky is extended towards lower P-T conditions. Taking these additional complexities into account, two other P-T paths (short- and long-dashed lines) are possible (see text for further discussion). Note that conventional thermometry, indicating high temperatures of equilibration, would favour the simplest P-T path.

P-T paths, both requiring a temperature decrease at an early stage of the decompression.

Although potentially significant, the effect of MnO is considered minor in the Raspas metapelites because of the observed mineral compositions: the spessartine content in garnet rims does not exceed 1.1 mole per cent (Table 3 and Fig. 5b), and the $X_{\rm Mn}$ in chloritoid is equal or lower to 0.01 (Table 4).

Estimation of peak P-T conditions

Few geothermobarometers can be applied in the Raspas metapelites (Table 7). The FeMg_1 exchange between

garnet and phengite is an experimentally-calibrated thermometer (Green & Hellman, 1982). Application of this thermometer in rocks is limited by the problem of determination of the ferric iron in phengite. In the studied samples, this is not considered as a serious limitation, because the presence of graphite suggests low oxidation conditions. Results of calculations in three samples (Table 7) indicate temperatures for the peak metamorphism of the order of 620-650°C at a nominal pressure of 15 kbar. Because of the assumption that all the iron is divalent, the calculated temperatures represent maximum values. Assuming 10 % of the iron is ferric, the estimated temperatures decrease by 5-10°C, an amount smaller than the uncertainty associated to the calibration itself. The empirically-calibrated Fe-Mg₋₁ exchange between garnet and chlorite (Dickenson & Hewitt, 1986, modified in Laird, 1988; Grambling, 1990; Perchuk, 1991) give temperatures of 580-620°C for samples 98RR10 and 97Ce3 (Table 7). On the whole, the garnet-phengite thermometer gives temperatures 0-50°C higher than the garnet-chlorite thermometer. The chloritoid-chlorite geothermometer (Vidal et al., 1999) can be used for the retrograde assemblages in the kyanite-absent samples. The temperatures calculated are much higher than expected, possibly because of disequilibrium.

Although pressure estimates are difficult, maximum values are indicated by the stability of paragonite, which is defined by the reaction Pg = Jd + Ky at approximately 25 kbar (Holland, 1979a). Experimental data on the assemblage Alm-Ky-Phe in the KFASH system (Massonne & Szpurka, 1997) indicates pressures of the order of 20 kbar (at 600°C). The uncertainty associated with this estimation is probably quite large, because a minor variation along the $SiMgAl_{-2}$ exchange is accompanied by a significant change in pressure.

A phase diagram approach has been used for garnet-chloritoid-kyanite parageneses by Konopasek (2001), who has calculated the topology of the KFMASH system using the Vertex software (Connolly, 1990). According to his calculations, peak P-T conditions in sample 97Ce5 would be at about 15 kbar, 580°C.

On the whole, conventional and multiequilibrium thermobarometry suggest P-T conditions of the order of 20 \pm 5 kbar, 550 \pm 50°C. The temperature value is far better constrained than the pressure value. The temperatures obtained using the H₂O-independent exchange reactions are not significantly lower than those predicted by the KFMASH grid, showing that the uncertainties associated with the minor components are negligible or, at best, smaller than the uncertainties associated to the calculation procedures used for P-T estimations. The P-T values reported in this study for the Raspas Complex are not very different from those calculated by Feininger (1980), i.e. 13 \pm 3 kbar at 580 \pm 20°C but are significantly higher than those proposed by Duque (1993), i.e. 9 ± 0.5 kbar and 460 ± 30°C. Duque (1993) used the equilibrium garnet-plagioclase-kyanite-quartz in the metapelites and plagioclaseomphacite-quartz in the metabasites for estimating peak pressures, assuming that plagioclase was in equilibrium with the other minerals. Because plagioclase is lacking in both the metapelites and the eclogites, and because plagio-

Conv	ventional thermometry	98RR10 (°C)	97Ce3 (°C)	97Ce5 (°C)	98RR2 (°C)	98RR12 (°C)
Grt-Phe	Green & Hellman (1982)	617	646	617		
	Laird (1988)	617	600			
Grt-Chl	Grambling (1990)	585	573			
	Perchuk (1991)	584	576			
Cld-Chl	Vidal et al. (1999)				649*	668*

Table 7. Summary of geothermometric calculations at a nominal pressure of 15 kbar.

clase is a late, retrograde phase, in the blueschists (Feininger, 1980), Duque's estimations should be considered as minimum pressures for the eclogite-facies event.

Discussion

Metapelitic rocks are sensitive recorders of P-T paths in high-pressure terranes. To a first approximation, the KFMASH grid as calculated by Powell & Holland (1990) is a primary tool for describing the P-T paths (Fig. 9). Although minor departures from the KFMASH grid can be expected due to incorporation of MnO and CaO into garnet and the effect of variable water and oxygen fugacities, three main types of assemblages are recorded, briefly described below in order of increasing peak temperature.

At relatively low temperatures, the Grt-Cld-Chl assemblage is stable. As recorded in numerous blueschist-facies terranes, for example in the Seward Peninsula, Alaska (Thurston, 1985; Patrick & Evans, 1989), New Caledonia (Ghent *et al.*, 1987), the western Alps (Vuichard & Ballèvre, 1988) and the Variscan belt (Guiraud *et al.*, 1987; Bosse *et al.*, 2002). Garnet-chloritoid metapelites are generally associated with garnet-bearing blueschists and low-temperature, glaucophane-bearing, eclogites. Because the divariant reaction Cld = Grt + Ky has not been attained, kyanite is lacking in the garnet-chloritoid metapelites.

At slightly higher temperatures, the divariant reaction Cld = Grt + Ky allows kyanite to develop in the most ironrich bulk-rock compositions. Four occurrences of Grt-Cld-Ky micaschists are known to the authors, namely the Raspas Complex (Feininger, 1980; this study), the Sesia zone, western Alps (Pognante et al., 1980; Vuichard & Ballèvre, 1988; Zucali et al., 2002), the Tauern window, eastern Alps (Holland, 1979b; Miller, 1986; Spear & Franz, 1986; Stöckhert et al., 1997) and the Bohemian Massif (Konopasek, 2001). In these four occurrences, garnet-chloritoid-kyanite micaschists are associated with garnetomphacite-amphibole eclogites, the amphibole being a glaucophane and/or a barroisite, or a barroisite rimmed by glaucophane (Raspas Complex: Gabriele, 2002; Sesia Zone: Koons, 1982; Tropper & Essene, 2002). The P-T estimates in these areas are at about 17-21 kbar, 550-650 °C in the Sesia Zone (e.g. Tropper et al., 1999; Tropper & Essene, 2002), 20 kbar, 600 ± 20 °C in the Tauern Window (Holland, 1979b). In this latter locality, chloritoid growth at the expense of garnet has been described (Holland, 1979b). Chloritoid-quartz aggregates replacing garnet and kyanite have been reported in the Sesia Zone, western Alps (Vuichard & Ballèvre, 1989), and the Raspas Complex (see above). These textures basically indicate decreasing temperatures during decompression, and are consistent with glaucophane overgrowths on barroisite (Koons, 1982; Tropper & Essene, 2002; Gabriele, 2002).

At still higher temperatures, Grt-Cld-Ky was a stable assemblage during part of the prograde, up-temperature, history, but the chloritoid stability was exceeded resulting in Grt-Ky, Grt-Chl-Ky or Grt-Tlc-Ky assemblages. Chloritoid is thus found only as inclusions in garnet cores. Examples include the ultra-high pressure Dora-Maira massif in the western Alps (Chopin, 1984; Compagnoni *et al.*, 1995; Simon *et al.*, 1997; Compagnoni & Hirajima, 2001), the high-pressure Champtoceaux Complex in the Variscan belt (Ballèvre *et al.*, 1989; Ballèvre & Marchand, 1991; Bosse *et al.*, 2000) and the Adula Nappe in the central Alps (Meyre *et al.*, 1999). Associated eclogites are characterized by barroisitic amphiboles, glaucophane being restricted to highly sodic and magnesian bulk-rock compositions (Kiénast *et al.*, 1991).

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Abbreviations are after Kretz (1983); in addition Phe, phengite;

^{*} Cld and Chl are post-kinematic (generation III).

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