# **Alpine metamorphic evolution of Ligurian Alps (North-West Italy): chemography and petrological constraints inferred from metamorphic climax assemblages**

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**Abstract.** The up-to-date petrological and microtextural information on the Ligurian Alps indicates that the metamorphic rocks from the oceanic lithosphere and the paleo-European continental margin underwent an alpine-type metamorphic evolution characterized by low *dT/dP* gradients. In particular, rocks from the Ligurian-Piedmontese oceanic lithosphere underwent an alpine metamorphism typical of alpine-type blueschist rocks. The distribution of the alpine metamorphic facies in paleo-European continental margin is closely related to the structural position of the different tectonic units. The prograde evolution frequently preserves paragenetic and textural relics of the earlier parageneses. If relics of the earlier parageneses are preserved, the rock exhibits continuous prograde reactions confirmed by strong compositional zoning of the metamorphic minerals. Therefore, these reactions lead to chemical and microtextural equilibrium relations, between the minerals, in limited domains of the rocks (microtextural sites). The main compositional aspect of coronitic textures is the mineral zoning, particularly when the minerals of the coronas are the consequence of a wide range of solid solutions. In such cases, the reacting minerals are armored and the kinetics are lowered. The prograde metamorphic evolution, which involved the rocks from the oceanic lithosphere and the paleo-European continental margin, is quite consistent with a subduction-type geodynamic process in different ages during alpine times.

## **Introduction**

Geological and petrological studies carried out systematically on the Ligurian Alps in the last few years (from the Sestri-Voltaggio Zone to the Ellero River) have been devoted mainly to understanding the different characteristics of the polyphase alpine metamorphic evolution of this sector of the Western Alps (Fig. 1 A). Such polyphase metamorphism, characterized by low *dT/dP* gradients, affected ancient metamorphic rocks (i.e. pre-Namurian polymetamorphic basement), Mesozoic ophiolites, which underwent an oceanic-type metamorphism, and unmetamorphosed sequences (i.e. volcanic and volcanoclastic rocks and post-Namurian sedimentary sequences) (Dal Piaz et al. 1972; Dal Piaz 1974; Messiga and Piccardo 1974; Chiesa et al. 1975; Compagnoni 1976).

As already pointed out by Vanossi et al. (1985), terrains belonging to the Ligurian Alps can be referred to three main paleogeographic domains: the Ligurian-Briangonnais Domain; the Piedmontese Domain; and the Ligurian-Piedmontese Domain (Fig. 1 B).

Previous papers give geological and petrological data on: (1) the lithological and structural arrangement; (2) the primary lithologies; and (3) the metamorphic evolution of the different units (Mottana and Bocchio 1975; Ernst 1976; Cortesogno etal. 1977; Messiga etal. 1977, 1982, 1983; Cimmino et al. 1979, 1980; Piccardo et al. 1979; Cimmino and Messiga 1979; Beccaluva et al. 1979; Ernst et al. 1983; Cimmino and Messiga 1983; Vanossi 1984; Messiga 1985).

As already described and discussed elsewhere (see references), the characteristics of the alpine metamorphism in the Ligurian Alps indicate either a very low grade or a low grade metamorphism (Winkler 1974) at a range of pressures. The upper temperature is limited by the glaucophane stability in mafic rocks and by the stability of chloritoid plus quartz relative to staurolite plus almandine plus  $H<sub>2</sub>O$ in metapelites (according to Maresch 1977; Rao and Johannes 1979).

The regional distribution of different metamorphic facies is given in Fig. 1 C. In this paper parageneses characterizing the climax metamorphic conditions only will be discussed. A forthcoming paper (Messiga, in preparation) will deal with the whole picture of the metamorphic evolution of this sector of the Western Alps.

The present work is a synthesis of detailed microtextural and mineral chemistry investigations and mainly concerns rocks which did not suffer penetrative deformation, when they underwent alpine metamorphic re-equilibration.

# **Metamorphic facies and parageneses**

The mineral assemblages characterizing the different chemistries of the different rocks and the different metamorphic facies are shown in Table 1.1

*<sup>1</sup> Mineral abbreviations: Ab* albite; *Acm* acmite; *Alm* almandine; *Amp* amphibole; *Ant* antigorite; *Act* actinolite; *Bt* biotite; *Ced*  celadonite; *Chl* chlorite; *Chlrm* chloromelanite; *Chltd* chloritoide; *Cpx* clinopyroxene; *Di* diopside; *Ep* epidote; *Fo* forsterite; *Gl* glaucophane; *Gnt* garnet; *Gro* grossular; *Hed* hedenbergite; *Hor* hornblende; Jdjadeite; *Kfld* K-feldspar; *Lau* laumontite; *Lw* lawsonite; *Ma* margarite; *Mu* muscovite; *Omp* omphacite; *Pa* paragonite; *Ph* phengite; *Pl* plagioclase; *Py* pyrope; *Pyr* pirophyllite; *Prh* prehnite; *Pump* pumpellyite; *Qz* quartz; *Rieb* riebeckite; *Rut* rutile; *Tchu* titanclinohumite; *Te* talc; *Tr* tremolite; *Zeo* zeolites; *Zo* zoisite; *Wm* white mica



Fig. 1. A Index map:  $a$  the pennidic front and  $b$  the internal realm of the orogenic alpine metamorphism. B Tectonic map of the Ligurian Alps. Paleogeographic domains: *A1* external Briangonnais Domain; *A 2* internal Brianconnais Domain; *B1* external Piedmontese Domain; B2 internal Piedmontese Domain, Tectonic units: 10rmea; 2 Pamparato-Murialdo; 3 Calizzano-Savona; 4 Bagnaschino; 5 Montaldo; 6 Cravasco-Voltaggio-Montenotte; 7 Voltri Massif. Uninvestigated areas and Tertiary molasses are unornamented in the map. C Areal distribution of metamorphic facies in the Ligurian Alps. D Inferred PT conditions for the different alpine metamorphic facies: 1 eclogites; 2 blueschists; 3 glaucophane-bearing greenschists; 4 chl + ab; 5 anchimetamorphism. Also shown are experimentally determined stabilities for: (1)  $lw +$  $id = pa + zo + qz$  (Heinrich and Althaus 1980); (2)  $lw + gl = tr +$  $chl + ab$  (Perchuk and Aranovich 1980; (3)  $ab = jd + qz$  (Holland 1980); (4)  $lw + jd = ab + zo + pa$  (Heinrich and Althaus 1980); (5)  $prh + chl = pump + act + qz$  (Nitsch 1971); (6) natural glaucophane stability field (Maresch 1977); (7) Chltd + qz = st + alm +  $H_2O$  (Rao and Johannes 1979). *Dashed* and *dotted lines* represent the alpine metamorphic gradients for units of oceanic and continental lithosphere, respectively. The main geographic localities: *AL* Alassio; *CA* Calizzano; *FI* Firenze; *GE* Genova; *LU* Lurisia; *SV* Savona; *TO* Torino ; *VG* Voltaggio

## *The eclogites*

In mafic rocks the eclogitic parageneses, for different whole rock compositions, may be summarized as follows: Napyroxene (chloromelanite) and almandine-rich garnet in Feand Ti-gabbros; omphacitic pyroxene, pyrope-rich garnet and zoisite in Mg-gabbros (Ernst 1976; Messiga et al. 1983). A minimum pressure value of 10 kb has been deduced from the jadeite content of ompacites coexisting with quartz (Holland 1980).

Employing garnet clinopyroxene geothermometry (Ellis and Green 1979) a temperature range between  $480^{\circ}$  C and 550~ has been calculated for the eclogitic assemblages

(Ernst 1976; Messiga et al. 1983) at 10 kb (Fig. 1D). The pelitic rocks exhibit an eclogitic paragenesis comprising the following minerals: phengite, paragonite, almandine-rich garnet and/or zoisite (Cimmino and Messiga 1979). The ultramafic rocks are characterized by forsterite, antigorite, and diopside, with or without titanclinohumite (Piccardo et al. 1980).

The above parageneses are mainly recorded in the internal Ligurian-Piedmontese Domain (Gruppo di Voltri)  $(Fig. 1C)$ .

## *The blueschists*

The blueschists are characterized by the minerals glaucophane and lawsonite with or without an Na-pyroxene and albite in Fe-rich mafic rocks. According to the reaction: albite equals jadeite plus quartz (Holland 1980), these rocks are formed at pressures lower than the jadeite plus quartz stability field and at temperatures not exceeding the stability boundary of the assemblage lawsonite plus glaucophane (Perchuck and Aranovich 1980). This indicates pressures lower than 8 kb for temperatures not exceeding  $400^{\circ}$  C (Fig. I D) (Beccaluva et al. 1979).

These parageneses characterize the ophiolitic rocks of the Cravasco-Voltaggio-Montenotte Unit (internal Ligurian-Piedmontese Domain) and the mafic rocks of the Bagnaschino Unit (internal Briangonnais Domain) (Fig. 1 C).

#### *The glaucophane-bearing greenschists*

The main parageneses in mafic rocks consist of Na-amphibole, chlorite, pumpellyite + actinolite + epidote  $\pm$  quartz, whereas mineral assemblages such as Na-amphibole, Napyroxene, pumpellyite, phengite and quartz; Na-amphibole, phengite, Na-pyroxene $\pm$  quartz; or phengite, chloritoid and quartz occur, respectively, in quartz porphyrites, marbles, and Carboniferous phyllites (Messiga et al. 1982).

The P-T boundary of the above parageneses is defined by the breakdown of the join lawsonite and glaucophane, although these minerals separately can still be stable in different chemical systems. Glaucophane-bearing assemblages occur in mafic rocks, with low A1 content, whereas parageneses containing lawsonite characterize chemical systems in which the  $AI/Fe + Mg$  ratio is higher than in chlorites: in fact, lawsonite + pirophyllite + chloritoid parageneses characterize Al-rich meta-sediments  $(A1/Fe + Mg_{rock} > Al/Fe +$ Mg<sub>chltd</sub>) (Goffé 1979). All the above parageneses indicate pressures ranging from 4 to 6 kb and temperatures not exceeding  $400^{\circ}$  C (Fig. 1D) and are widespread in the internal Briangonnais Domain (Calizzano-Savona, Mallare and Pamparato-Murialdo Units) and in the external Piedmontese Domain (Montaldo Unit) (Fig. 1 C).

## *The chlorite + albite facies*

The metamorphic assemblages, mainly developed in the crystalline basement and in its Permo-Carboniferous cover, can be summarized as follows: chlorite, albite, pumpellyite + Fe-epidote and quartz (ortho- and paragneiss); chlorite, albite, prehnite, actinolite  $+$  Fe-epidote (amphibolites); chlorite, albite, phengite, pumpellyite, green biotite and quartz (qz-porphyrites); chlorite, albite, prehnite, actinolite  $\pm$  Fe-epidote (mafic volcanics).

Accordingly,  $P$  less than 4 kb and  $T$  not exceeding  $300^{\circ}$  C (Fig. 1D) can be inferred. Such parageneses charac-





<sup>a</sup> Carboniferous and Permian volcanics and volcanoclastics (qz-porphyrites); <sup>b</sup> Pre-Namurian amphibolites; <sup>c</sup> Carboniferous and Permian volcanics; <sup>4</sup> Pre-Namurian orthogneiss; <sup>e</sup> Carboniferous and Permian volcanics (qz-porphyrites); <sup>f</sup> Pre-Namurian paragneiss; Carboniferous and Permian volcanics and pre-Namurian amphibolites; <sup>h</sup> Carboniferous and Permian qz-porphyrites; <sup>1</sup> Mesozoic limestones and marbles; <sup>J</sup> Carboniferous phyllites; <sup>k</sup> Mesozoic Al-rich metasediments (Goffé 1979); <sup>1</sup> Pre-Namurian amphibolites; <sup>m</sup> Mesozoic ophiolite-type breccia; " Mesozoic ophiolitic Mg-gabbros; ° Mesozoic ophiolitic Fe- and Ti-gabbros; <sup>p</sup> Ophiolitic serpentinites; <sup>q</sup> Mesozoic ophiolitic sedimentary cover (calcschists)

Table 2. Composition of mineral phases involved in mass balance equations



terize the external border of crystalline basement of Savona, the intermediate Brianqonnais Domain (Ormea Unit, pro parte) (Fig.  $1<sub>C</sub>$ ).

## *The anchimetamorphic facies*

The volcanic and volcanoclastic rocks are characterized by kaolinization of feldspars and chlorite and zeolite blastesis. This facies is widespread in the external Briançonnais Domain (Ormea Unit, pro parte) (Figs. 1 C, D).

## **Mineral composition and chemography**

Compositions of minerals were obtained by using electron microprobe analysis. (2) The chemography will be discussed

 $2$  Mineral chemistry data was performed with: (1) ARL SEMQ Microprobe in the Istituto di Mineralogia e Petrologia, Università di Modena (Fig. 2A, B pro parte; 3C, 3D; 4A, B; 5A, B, D; 7); (2) ARL SEMQ Microprobe in the Dipartimento di Scienze della Terra, Università di Milano (Figs. 2F; 5C; 6B); (3) CAME-BAX MICROBEAM, Laboratoire de Petrologie, Université P et M Curie, Paris (Fig. 2A, B. pro parte, D, E)

in the relevant simplified systems and will concern only prograde metamorphic reactions leading to the peak of metamorphism in the rocks. Chemography and metamorphic reactions were computed by using the LINEQU computer program proposed by Spear et al. (1982), using real mineral compositions (Table 2).

# *The eclogite facies*

The following data concern the main intrusive lithologies of the meta-ophiolites : plagioclase peridotites, Mg-gabbros and Fe- and Ti-gabbros as representative compositions of different steps of fractional crystallization of primary tholeiitic basaltic magmas (cf. Piccardo 1985 and Serri 1979). In this section mineral chemistry data on eclogitic metaplagioclase peridotites from Monviso meta-ophiolites will also be used as reference (data from Kienast and Messiga 1987, and unpublished).

As shown in Figs. 2A and B a sharp compositional variation exists both in Na-clinopyroxenes and garnets crystallized in the different mafic rocks. Going from Fe- and Tigabbros to plagioclase peridotite bulk composition, garnets show a CMFe-I substitution, Na-pyroxenes show a decrease of the sodic component.

This fact is indicative of a close relationship between chemical compositions of minerals and the bulk chemistry of the rock. Moreover, the garnets from eclogitic plagioclase peridotites show the highest pyrope content (up to 40%), and this value seems to be the maximum for the alpine garnets of the Voltri Massif (and Monviso) meta-ophiolites. The inferred values of the intensive paramters  $\overline{P}$  and  $T$ of the alpine metamorphism prevent the crystallization of more pyrope-rich garnet; in fact, Mg-Al-silicates (such as chlorite and chloritoid) crystallize instead of garnets in rocks with high MgO/MgO + FeO ratio (i.e. chloritoid, talc, omphacite assemblages of plagioclase peridotites and chlorite+ omphacite parageneses from Monviso meta-ophiolites; Lombardo et al. 1978; Kienast and Messiga 1987).

The correlation between the  $id + \text{acm}/di + \text{hed}$  values in metamorphic clinopyroxenes and whole host rock compositions is indicated by the A1NaCa-1 FM-1 complex substitution in sodic clinopyroxenes, In fact, the metamorphic clinopyroxenes from meta plagioclase peridotites are lowest in sodic end-members according to the low  $Na<sub>2</sub>O$  and

**Fig.** 2A-F. Voltri Massif (and Monviso) eclogitic Ophiolites. Compositional variations of Na-pyroxenes (A) and garnets (B) in the Voltri Massif (Messiga et al. 1983; Messiga and Cimmino, 1983) and Monviso (only plagioclase peridotites; Kienast and Messiga, unpublished data). 1 plagioclase peridotites; 2 Mg-gabbros; 3 intermediate gabbros; 4 Fe-Ti-gabbros. *OTHERS* (Ca-, Ca-Ti-, Ca-Crtschermak; enstatite; ferrosiljte; wollastonite). After to the endmembers calculation scheme proposed by Cawthorn and Collerson (1974). C Simplified ACF-type projection (Thompson 1981) from Qz-fluid phase  $(H_2O, CO_2, etc.)$  and along the AlFe<sup>3+</sup>-1, MgFe-1 vectors of the eclogitic parageneses in Mg- and Fe-Ti-gabbros from the Voltri Massif. The compositional range for garnets and Napyroxenes is indicated by *heavy solid lines* and the mean value by *dots (1* Mg-gabbros; 2 Fe-Ti-gabbros). *Dotted* and *solid enclosures* show compositional range for Mg- and Fe-Ti-gabbros, respectively. *Open cirele* and *triangle* refer to mean values for bulk rock compositions for Mg- and Fe-Ti-gabbros, respectively. Compositional data are from Cortesogno et al. (1977), Cimmino and Messiga (1983), Messiga et al. (1983) and unpublished sources. Cr



distribution in minerals grown as coronas around pseudomorphs after Cr-spinel *(dashed* areas): D omphacite; E chloritoid (Monviso eclogites; Kienast and Messiga 1987); F garnet (Voltri Massif metarodingites; R. Basso, F. Cimmino and B. Messiga, unpublished data). Bars represent 1 mm

 $\text{Al}_2\text{O}_3$  content of the host rock; the jadeite content increases in Na-clinopyroxenes from meta-Mg-gabbros, and this is related to the high plagioclase content of the host rock. Moreover, the high acmite content in the Na-pyroxenes from meta-Fe-Ti-gabbros is related to the involvement of magnetite in the reaction.

The chemography is shown on an ACF-type projection (Thompson 1981) of the CMASH chemical system where both the compositional ranges for garnets and Na-pyroxenes and the compositional field of whole rock compositions is projected (Fig. 2C). The projection is simplified and indicative only for eclogitic paragenesis of the Voltri Massif meta-ophiolites; it indicates that only Al-poor gabbros can produce the ideal bimineralic eclogite assemblage; these parageneses can be found only in almost equilibrated blastomylonitic rocks. Undeformed Fe- and Ti-gabbros are characterized by more complex mineral associations due to the development of corona textures (Cimmino and Messiga 1983). Such textures record microtextural sites, inherited from primary minerals, in which different mineralogical assemblages crystallize during eclogitic metamorphism (i.e. : augite-rich chloromelanite in pseudomorphs after primary clinopyroxene; omphacite-rich chloromelanite + garnet in pseudomorphs after plagioclase; Na-amphibole + rutile in pseudomorphs after primary intergrowth of hornblende and Fe and Ti ores).

For Mg-gabbroic rocks too, the chemographic relations indicate a Na-pyroxene, garnet, zoisite  $(+quartz+H<sub>2</sub>O)$ eclogitic paragenesis; the undeformed Mg-gabbros, with corona textures, show different mineralogical associations linked to different microtextural sites, i.e. diopside-rich omphacite and talc in pseudomorphs after exsolved primary clinopyroxenes; jadeite-rich omphacite + garnet + zoisite  $\pm$ quartz as pseudomorphs after primary plagioclases; omphacite + talc + Na-amphibole as pseudomorphs after primary olivine.

Both lithotypes show garnet coronas between pseudomorphs after mafic minerals and plagioclases, and the compositional zoning of the coronitic garnet is very marked.

The presence of mineral associations more complex than the ideal ones must be related to the pre-alpine textural arrangement characterized, in the undeformed rocks, by microtextural sites in which different mineral associations grow. Such features, when deformation is lacking, prevent the attainment of chemical equilibrium in the rocks during alpine metamorphism. In fact, the compositional zoning of minerals can be related to disequilibrium relations during metamorphic recrystallization. Chemical equilibrium conditions can be reached only along Na-clinopyroxene-garnet grain boundaries, where FeMg-I and MgCa-1 exchange reactions occur during peak metamorphic conditions. Equilibrium conditions can be inferred from the constant values of  $K_{\text{D}}$  (Fe/Mg gnt/cpx) calculated both in corona rocks, along such grain boundaries, and in blastomylonitic eclogites, where the two minerals are recrystallized during a syn-eclogitic deformation.

Strong compositional asymmetry is very frequently shown by the coronitic minerals. Some examples of Cr distribution in eclogitic minerals, such as omphacite, chloritoid and garnet growing as coronas in meta-plagioclase peridotites, are shown in Fig. 2D-F. The data pertinent to omphacite and chloritoid are from the Monviso meta-ophiolites (Kienast and Messiga 1987), whereas garnet is from a Voltri Massif meta-rodingite.

## *Blueschist facies*

As discussed by Borgogni and Messiga (1985), taking into account the progressive decrease of the  $FeO/FeO + MgO$ ratio in the host rocks, the following parageneses can appear: (1) lawsonite, Na-pyroxene, glaucophane and albite; (2) lawsonite, glaucophane, pumpellyite and albite; (3) pumpellyite, glaucophane, chlorite and albite; (4) pumpellyite, chlorite, tremolite and albite (Fig. 3 A). Assemblages (3) and (4) pertain to rocks with a low  $FeO/FeO + MgO$ ratio (Mg-gabbros); (1) characterizes Fe- and Ti-gabbros; and (2) is present exclusively within amphibolites from the Bagnaschino Unit.

*Mafic rocks from the Montenotte Nappe.* Microtextural characters of these rocks show that the alpine paragenesis (Na-pyroxene, lawsonite, Na-amphibole and albite) overprint an older oceanic-type metamorphism (Beccaluva et al. 1979). On the Na<sub>2</sub>O-CaO-(Fe, Al)<sub>2</sub>O<sub>3</sub>-(Fe, Mg)O triangle (Fig. 3 B) the reaction between the above metamorphic facies is illustrated (see also reaction 1, Table 3). Na-pyroxene and Na-amphibole compositions are shown in Fig. 3 C, D.

Although the mineral compositions show significant dependency on the bulk rock composition of the primary lithologies, sharp compositional variations of minerals in a single rock sample are related to the microtextural sites in which they crystallize. For example, Na-pyroxene compositions from Ti- and Fe-grabbros vary widely: chloromelanite to aegirine-augites characterize the pseudomorphs after primary clinopyroxenes; aegirine-augite to aegirine-rich pyroxenes grow as coronas between pseudomorphs after ores or primary clinopyroxenes and pseudomorphs after plagioclases; jadeite-rich clinopyroxenes crystallize in pseudomorphs after plagioclase.

Detailed spot microprobe analyses through zoned Naamphiboles and Na-pyroxenes show that the asymmetric zoning is linked to the different chemical compositions of the pre-metamorphic microtextural sites which react during metamorphism (i.e., going from cores of mafic minerals towards pseudomorphs after plagioclases). The growth of successive rims with different compositions, shown also by compositional gaps, stresses that the composition of solid solutions is governed by net-transfer (continuous) reactions, as shown in Fig. 4A and B and Table 3 (reactions 2, 3, 4, 5).

*Amphibolites from the Bagnaschino unit.* The compositions of pyroxenes and amphiboles from amphibolites, together with the chemistry of minerals from metavolcanites and meta-sediments of the Briangonnais Units are reported in Fig.  $5A-D$ .

The amphibolites with pre-Westphalian metamorphic overprint (hornblende + plagioclase  $\pm$  garnet  $\pm$  clinopyroxene assemblages) reacted during the blueschists facies metamorphic evolution and developed an Na-amphibole  $\pm$  pumpellyite+lawsonite paragenesis. The chemographic relationships between the main pre-alpine parageneses (plagioclase + clinopyroxene + hornblende; plagioclase + hornblende + garnet), still preserved as relics, and the new alpine parageneses are shown by the  $Na<sub>2</sub>O$ -CaO-(Fe, Al)<sub>2</sub>O<sub>3</sub>-(Fe, Mg)O projection: the presence of pre-alpine clinopyroxenes or garnets in the reacting system favors the blastesis of pumpellyite or lawsonite, respectively (according to reactions 6 and 7, Table 3 and Fig. 6A).



Fig. 3. A Projection from AB, PYR, QZ, H<sub>2</sub>O on a CMF diagram of the parageneses (real compositions) to the blueschist facies. Napyroxene and Na-amphibole compositional variations are also shown *(heavy lines),* as are bulk rock composition of the blueschists Fe-Ti-gabbros *(open circles)* and Mg-gabbros *(open squares)* (Beccaluva et al. 1979). B Metamorphic reactions between oceanic offridge *(dashed triangle)* and blueschist facies *(ruled triangle)* assemblage in meta-ophiolites from the Montenotte Nappe. C, D Compositional variations of Na-pyroxenes (C) and Na-amphiboles (D) from Montenotte Nappe meta-ophiolites. *Solid circles* meta-Fe-Tigabbros; *open circles* meta-radiolarian cherts; *open squares* metadiorites; *solid triangle* ophiolitic sands; *open triangles* meta-basalts. *OTHERS* as in Fig. 3A. Data from Beccaluva et al. (1979)



Fig. 4A, B. Compositional profiles on amphiboles and pyroxenes from meta-Fe-Ti-gabbroic rocks from Montenotte Nappe. A Naamphiboles: coronas between pseudomorphs after primary amphiboles and plagioclases. B Coronas between pseudomorphs after primary clinopyroxene and plagioclase. The rims grow according to reactions 2, 3, 4, 5 (Table 3). Bars represent 1 mm

**Table** 3. Mass balance equations

- 1)  $Ab + Prh + Chl$  .... > Na-cpx +  $Gl + Lw + H_2O + Qz$ 2) Amp  $(16) + Ab + H_2O + Qz$  .... > Amp  $(13) + Lw$ <br>3) Amp  $(13) + Ab + H_2O$  .... > Amp  $(14) + Lw + Oz$ Amp  $(13) + Ab + H_2O$  .... > Amp  $(14) + Lw + Qz$ 4) Na-cpx (1) + Ab +  $H_2O$  ---- > Na-cpx (3) + Lw + Qz 5) Na-cpx  $(3) + Ab + H_2O$  ----> Na-cpx  $(4) + Lw + Qz$ 6) Hor + Pl + Di + H<sub>2</sub>O  $\cdots$  > Gl + Pump + Oz 7) Hor + Gnt  $(1)$  + Pl + H<sub>2</sub>O .... > Gl + Lw + Qz
- 8) Bt + Kfld + Wm (I) + Qz + H<sub>2</sub>O ---- > Wm (II)
- 9) GI + Lw + Ep ---- > Omp + Gnt  $(2)$  + Oz + H<sub>2</sub>O
- 10) Gl+Lw ----> Omp + Gnt  $(2)$  + Par + Qz + H<sub>2</sub>O



Fig. 5A-D. Metamorphic rocks from the Briangonnais Domain. Composition of pyroxenes (A) and amphiboles (B) *open circles*  amphiboles from the Bagnaschino Unit; *solid circles*, meta-qz-porphyrites; *solid squares* mafic metavolcanics; *open squares* metasediments; *OTHERS* as in Fig. 3C. C CED-PA-MU plot of the white micas composition from internal Briangonnais meta-sediments (i.e., pelites and verrucane). *Solid squares* detrital pre-alpine muscovites; *open circles* alpine phengites crystallized along fold axial plane foliation; *open squares* rims around pre-alpine muscovites. D CED-PA-MU plot of white micas compositions from qzporphyrites of internal Briangonnais Domain. The white micas crystallized during alpine metamorphism and exhibit homogeneous compositions

## *The glaucophanitic greenschist facies*

Meta-volcanics both mafic (andesites) and acidic (qz-porphyrites) are characterized by Na-amphibole and Na-pyroxene crystallization, whereas Na-amphiboles + white mica associations are present in meta-sediments (meta-graywackes). Figure  $5\overline{A}$  and B exhibits the chemical compositions of Na-amphiboles and Na-pyroxenes, and in Fig. 5D white mica compositions are projected. The microtextural characters indicate that the white micas crystallized during alpine metamorphism and their chemical compositions are

Na<sub>2</sub>0  $+07.$ H<sub>20</sub> Α (Fe,Al)<sub>2</sub>0 Ğ  $\mathsf{W}_0$ **PUMP** GN1 CaO DI (Fe,Mg)O  $\mathsf{KFLD}:\mathbb{R}^{3}\rightarrow\mathbb{R}^{3.5}$  **Si** WM(II)  $20, 32$ <br>wM(I)  $20, 32$ <br> $\uparrow$   $\uparrow$   $\uparrow$  **B**  $\sim$  ,  $\sim$   $\frac{1}{2}$   $\sim$  3  $\approx$   $\approx$   $\sim$   $\sim$   $\sim$ +QZ.H20  $0.6$  $\mathsf{WM}(\mathsf{I})$ **KFLD**  $WM(n)$  $R_{20}$  BT (Fe,Mg)O

Fig. 6. A Metamorphic reactions between pre-alpine amphibolite and alpine blueschists facies parageneses in amphibolites from the Bagnaschino Unit: *solid circles* pre-alpine parageneses; *open circles*  alpine parageneses. See text for details. B Compositional profile through a reacting zone between pre-alpine white micas (wmI) and K-feldspar: the alpine white mica (wmII) grows according to reaction 8 (Table 3) Bar represents I mm

characterized by high phengitic contents. In the metasediments, however, relics of pre-alpine muscovite flakes, strongly deformed during alpine metamorphism, are associated with alpine phengites which crystallize parallel to the axial plane of the folds; white micas, with intermediate compositions, occur between the pre-alpine muscovites and the later muscovites (Fig. 5C). The alpine phengites grew, in the orthogneisses from the Savona Crystalline Massif, according to the mass-balance reaction (8) (see Table 3; Fig. 6B); this reaction, which involves biotites in orthogneiss occurs at the boundaries between muscovite (I) (prealpine) and K-feldspar but not between muscovite (I) and quartz.

When coexisting phengites and Na-amphiboles exhibit microtextural equilibrium, they show both a constant value of Fe/Mg<sub>amp</sub>/Fe/Mg<sub>wm</sub> (K<sub>D</sub>=2) and a significant parallelism of the tie lines in the  $Al^{VI}$ -Fe<sup>2+</sup>-Mg triangle (Fig. 7).

### **Metamorphic reactions and kinetics constraints**

In the rocks investigated discontinuous and continuous reactions occur between the minerals. In continuous reactions, the reaction development is stressed by the concomitant increase of the products at the expense of the reactants. According to Thompson and Thompson (1976), both the discontinuous and the continuous reactions can be defined as net-transfer reactions, since they alter the relative molar proportions of the phases.



Fig. 7. Chemical equilibrium relationships between coexisting phengites (wm) and Na-amphiboles from internal Briançonnais rocks. *Symbols* as in Fig. 5 B

Generally the development of discontinuous reactions is seen, in thin section, by the complete recrystallization of the rock and the complete disappearance of mineral relics: the type of reacting minerals can be inferred only from the occurrence of pseudomorphs.

The discontinuous reactions can be considered as representatives of transitions of facies: reaction (1) indicates, for the meta-ophiolites of the Montenotte Nappe, the transition between low grade oceanic metamorphism and blueschist facies metamorphism; reactions (6) and (7), related to the amphibolitic rocks of the crystalline basements, are indicative of the transition between pre-alpine amphibolitic parageneses and alpine blueschist facies parageneses; reactions (9) and (10) describe the transition, occurring in meta-ophiolitic rocks, from blueschist parageneses towards eclogitic facies parageneses during prograde metamorphism.

The continuous reactions are indicated in thin section by the presence of compositional zoning of minerals and of corona textures, preserving reacting mineral relics adjacent to the newly produced minerals.

The blueschist facies overprint recorded by the Fe- and Ti-gabbros of the Cravasco-Voltaggio-Montenotte Unit shows examples of a relationship between continuous and discontinuous reactions. In fact, the Na-pyroxenes and Naamphiboles grow by means of continuous reactions between primary clinopyroxenes or amphiboles and the albite component of primary plagioclase. The progress of the reaction is indicated by an increase in the glaucophane and jadeite contents in amphiboles and clinopyroxenes, respectively, and by a concomitant increase in the amount of lawsonite within the pseudomorphs after plagioclase. The above reactions, as a whole, can be considered continuous reactions, since they advance by means of a sequence of discontinuous reactions recorded, in the rock, by sharp compositional changes in Na-amphiboles and Na-pyroxenes. Such compositional jumps can be ascribed either both to miscibility gaps in the mineral solid solutions or to low reaction kinetics due to the absolute values of the intensive parameters and/or limited solid diffusion. As for the miscibility gaps, it should be noted that a continuous reaction yields compositional variations within a stable mineral structure; when a composition incompatible with a given mineral structure is reached a discontinuous reaction produces the sharp compositional change required by the mineral structure.

Discontinuous reactions can yield compositional zoning when the reaction kinetics and diffusion are low; they are characteristic features of the coronitic textures, mainly when the coronitic mineral allows a wide range of solid solution. In such cases the net-transfer reaction progress is strongly inhibited by the discontinuous reactions.

The microstructure proves that substantial amounts of fluids are involved during both prograde and retrograde metamorphism: generally the maximum dehydration is reached during the peak of metamorphism.

During the prograde evolution, which produces the blueschist facies assemblages, the growth of glaucophane and lawsonite requires hydration of the starting material (even if the rocks were already composed of hydrated mineral assemblages). Reactions  $(2)$ ,  $(3)$ ,  $(4)$ ,  $(5)$ ,  $(6)$  and  $(7)$ (Table 3) describe the prograde metamorphism in the metaophiolites from the Montenotte Nappe and in the amphibolites from the Bagnaschino Unit, and all lead to a greater degree of hydration.

On the other hand, reactions (9) and (10) (Table 3), which appear to be relevant for the transition from blueschist to eclogite facies conditions, produce a significant dehydration of mineral assemblage.

As a rule, the microtextural characteristics of the undeformed rocks, where the corona textures are widespread and the metastable relics together with the previous microtextures are preserved, indicate a limited mass transfer during metamorphism. In contrast, the deformed rocks, characterized by a lack of paragenetic and textural relics, by mineral size shortening and more compositional homogeneity in the metamorphic phases, indicate that penetrative deformations allowed a great element migration during the textural arrangement and, consequently, a more pervasive chemical equilibration.

Temperature and total pressure are the main kinetic factors governing the blastesis of paragenesis. All the metamorphic facies characterizing the different tectonic units of the Ligurian Alps define relatively low  $dT/dP$  gradients for units both of oceanic (dashed line in Fig. 1 D) and of continental lithosphere (dotted line in Fig. 1 D).

For low T values the reaction kinetics are very slow, as indicated by the presence of relics of older paragenesis and compositional zoning of the new metamorphic minerals, i.e. the white micas from continental rocks and the Na-amphiboles and Na-pyroxenes from meta-ophiolites of the Montenotte Nappe (Figs. 4, 5C, 6B).

Few comments can be made on the role of fluids during alpine metamorphism, since detailed studies on fluid inclusions and fluid compositions are lacking.

As already emphasized (Messiga 1984), the ophiolitic rocks, before the prograde alpine metamorphism, underwent metamorphic transformations during oceanic metamorphism. Such transformations were characterized by hydrous mineral crystallization (i.e., chlorite, prehnite, pumpellyite, actinolite).

During prograde metamorphism water was retained by the hydrous minerals, and only during the eclogite peak did the water became an independent phase when dehydration reactions took place. The eclogite peak represents the P-T conditions in which anhydrous  $\pm$  hydrous phases coexist with water-rich fluid [fluid-present metamorphic conditions as defined by Thompson (1983)]. The absence of veins or vugs filled by high-pressure minerals and the early crystallization, during retrograde metamorphism, of Na-amphiboles along grain boundaries between Na-pyroxenes and garnets indicate that the  $H<sub>2</sub>O$  phase may have been confined in these microtextural sites during eclogite metamorphism.

In the eclogite facies rocks the lack of paragenetic relics can be explained by the concomitance of dehydration reaction and fast temperature increases. The rocks, during prograde evolution, probably suffered a fast rate of temperature increase only when the deeper levels were reached without equilibration at intermediate temperatures. As discussed by Thompson (1983), dehydration reactions and fluid present metamorphism are characteristic of rapid temperature increases during non-progressive prograde metamorphism.

## **Conclusions**

The metamorphic peak conditions for the Ligurian Alps are achieved, for different structural domains, in various metamorphic environments according to different  $P$  and T values. But the metamorphic facies series are only ascribed to a low *dT/dP* gradient. As shown in Fig. 1 D, the metamorphic overprints of the oceanic lithosphere and internal parts of the paleo-European Domain indicate equilibrium under conditions compatible with a low *dT/dP* gradient, and the alpine metamorphism of the Ligurian Alps falls into the glaucophane stability field [as defined by Maresch (1977)]. Thus, they are consistent with a compressional geodynamic environment characterized by underthrusting of lithospheric sections (both oceanic and continental) along diachronic subduction zones (Messiga et al. 1982; Vanossi et al. 1985).

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