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Chemistry, Zonation and Distribution Coefficients of Elements in Eclogitic Minerals from the Eastern Sesia Unit, Italian Western Alps

By *Jacqueline Desmons**) and *Edward D. Ghent***)

Abstract

Rocks and minerals have been analyzed from the eastern Sesia unit. This unit consists of continental crust formed prior to the Alpine orogeny, but eclogitic, jadeite and glaucophane-bearing assemblages developed during Late Cretaceous (Eo-Alpine) times.

The eclogitic rocks, derived from igneous protoliths, show a calc-alkaline trend. Garnet is pyrospite and plots in the field of Group C eclogitic garnets of COLEMAN et al. (1965). Pre-Alpine garnets, richer in almandine, may co-exist with Eo-Alpine garnets. The common zonation pattern is bell-shaped for both Mn and Ca. Na-pyroxene is omphacite in eclogite, schist and marble, but jadeite in meta-pegmatite, metagranitoid and "kinzigite". The jadeite content characteristically shows a slight increase towards the rim of the grains. Na-amphibole is glaucophane. White micas of both phengitic and paragonitic composition have been analyzed.

The values of the distribution coefficient $K_D^{\text{Fe}^{2+}}_{\text{Mg}} - \text{gr}_{\text{pyx}}$, when compared to experimental data (Fe-Mg partition, and plagioclase breakdown curves), suggest a temperature of formation of $505 \text{ to } 525 \pm 30^\circ\text{C}$ with $P > 11\text{--}12.5 \text{ kb}$, values which are in good agreement with stable isotope and other petrological data.

INTRODUCTION

Chemical data have been collected on rocks and minerals from the easternmost, eclogite-bearing unit of the Western Alps, the Sesia unit. The aim of this investigation is: (1) to characterize the chemistry of the mineral phases, (2) to interpret the crystallization history, and (3) from the partition of elements between mineral pairs, to determine the presence or lack of equilibrium, and the P-T conditions attending the eclogitic metamorphism.

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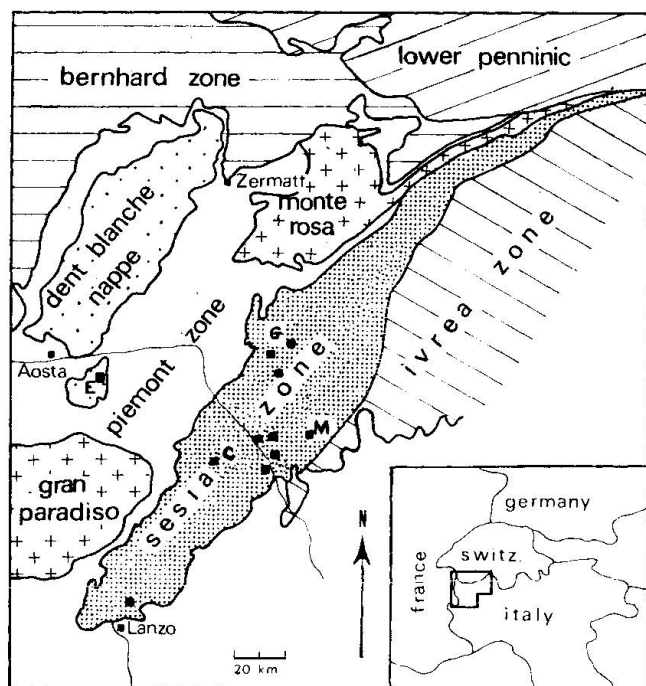


Fig. 1. Map showing the Sesia unit and the surrounding units. Samples have been collected from the lower Aosta Valley, Val Gressoney (G), Mt. Mucrone area (M), Delpizzen in Val Chiusella (C), Monastero di Lanzo (near Lanzo), and the Mt. Emilia klippen (E).

The Sesia unit (Fig. 1) is a basement, crystalline unit, which, like the Ivrea unit, is considered as a part of the South-Alpine plate (one of the subplates forming the leading edge of Africa, before its collision with Europe). It is largely composed of metamorphosed basic and pelitic rocks, with minor amounts of carbonate and siliceous rocks. Amphibolite to granulite facies metamorphism affected rocks of both Sesia and Ivrea units in pre-Alpine times. Granitoidic rocks intruded the Sesia unit in Late Hercynian time. During the Alpine orogeny the Sesia unit was detached from the South-Alpine block and, unlike the Ivrea unit, was involved in the Alpine metamorphism and tectonization. The Dent Blanche nappe, and a few klippen, in particular the Mt. Emilia klippen, represent outliers of Austro-Alpine material.

The present rock sequence in the eastern Sesia unit consists of eclogites and glaucophanites (former pre-Alpine amphibolites), glaucophane-garnet-mica \pm chloritoid schists (former pre-Alpine biotite-sillimanite-garnet gneisses), marbles which may contain Na-pyroxene and zoisite, quartzites, and Na-pyroxene-garnet-bearing metagranitoids. Some blue-green amphiboles, albite and chlorite locally indicate a slight alteration of the high-pressure associations to greenschist facies. The Alpine tectonization generated tight folds in all rocks, and strong boudinage of the basic layers.

The age of the eclogitic metamorphism has been radiometrically dated as Late Cretaceous (DAL PIAZ *et al.*, 1972; HUNZIKER, 1974). This first phase of the Alpine metamorphism is called Eo-Alpine, in contrast with the Meso-Alpine (also called Lepontine), greenschist to amphibolite, metamorphic phase

of Late Eocene-Early Oligocene, which according to geochronological results has not affected the eastern part of the Sesia unit.

The Eo-Alpine high-pressure metamorphism was generated during a subduction event (DAL PIAZ et al., 1972; ERNST, 1973) involving the Sesia unit, the ophiolitic unit (called Zermatt-Saas unit), which represents the former intervening oceanic basin, and some of the Penninic units (part of the European plate).

Available mineralogical, chemical and petrologic data concerning the Sesia unit are summarized by COMPAGNONI et al. (1975), who also present an interpretation of the evolution of the entire unit. Stable isotope analyses on some of the rocks described here have been obtained by DESMONS and O'NEIL (in prep.).

SAMPLING AND METHODS

Samples have been collected in the Sesia unit from the Mt. Mucrone area, the lower Aosta Valley and adjacent valleys, the Val Chiusella, the Corio-Monastero region to the southwest of the unit near Lanzo, and from Mt. Emilius klippen (Fig. 1). Rock types studied are eclogite, glaucophanite, amphibolite, gneiss, schist, metagranitoid, metapegmatite, and metagabbro. Twenty-three bulk rock analyses have been made. Garnets from 29 different rocks, clinopyroxenes from 23 rocks, amphiboles from 13 rocks, and white micas from 6 rocks have been analyzed either by electron microprobe or, after separation, by classical procedures.

Bulk rocks have been analyzed in Grenoble (Institut Dolomieu) by flame spectrometry (alkalies) and "wet" methods (other elements). Analyses of separated minerals have been performed in Nancy (Laboratoire de Pétrologie) by flame spectrometry (alkalies), atomic absorption and X-ray fluorescence (other elements). Microprobe analyses have been made on the ARL-EMX electron probe microanalyzer at the University of Calgary. Analytical conditions are described by GHENT (1970).

Both methods have given similar results on several garnet, pyroxene, and amphibole samples¹).

CHEMICAL CHARACTERS OF HOST ROCKS

Bulk rock chemistry of Sesia rocks are plotted on an ACF-diagram (Fig. 2a), where they are compared with other rock analyses. Points representative of glaucophanite and amphibolite are somewhat closer to the F-apex than

¹) Analytical results are available on request, from J. Desmons or E. Ghent.

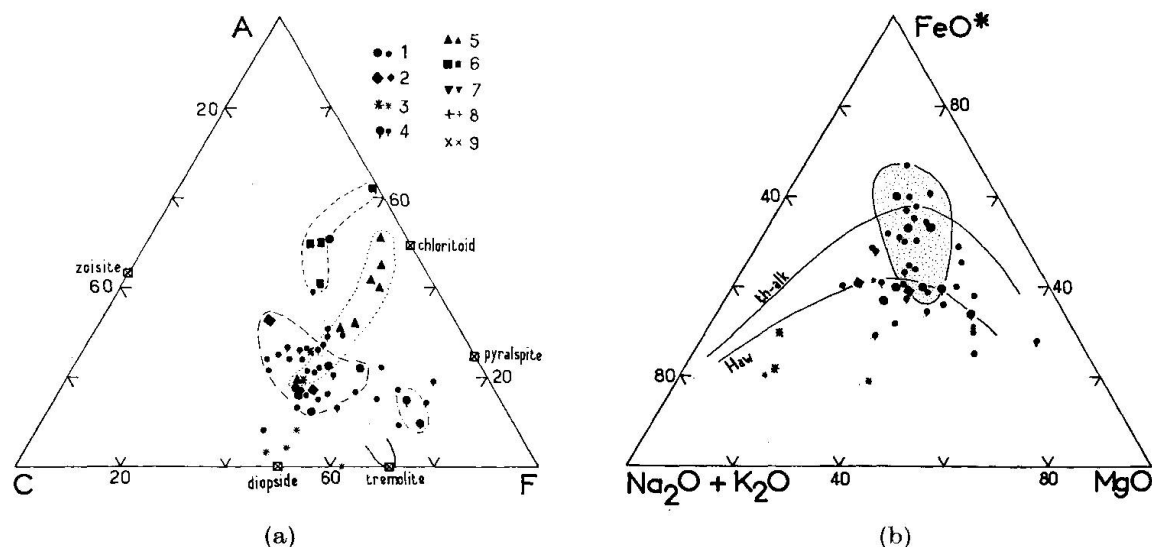


Fig. 2. Chemical composition of host rocks. (a) ACF diagram; the composition fields refer only to the new data. (b) Alk-F-M diagram (in weight %); the stippled area contains the group C eclogites according to COLEMAN et al. (1965, but calculated by simply adding FeO to Fe₃O₂). th-alk: boundary between tholeiitic and calc-alkalic trends. Haw: composition field of Hawaiian lavas (from COLEMAN et al., 1965). Large symbols: new data; small symbols: literature data (CALLEGARI and VITERBO, 1966; VITERBO-BASSANI and BLACKBURN, 1968; LIEBEAUX, 1975).

Key to symbols for Fig. 2, 3, 5 and 7: 1, eclogite; 2, eclogite in marble; 3, clinopyroxenite; 4, glaucophanite and amphibolite; 5, micaschists; 6, meta-pegmatite; 7, metagranitoid; 8, metagabbro; 9, "kinzigite".

eclogite. However, as shown in the AFM diagram (Fig. 2b), they contain as much Fe as eclogites, but are enriched in Mg. Nevertheless, some analyses from the literature referred to as glaucophanite or amphibolite also plot together with eclogites.

High Ti-content (up to 1.30 wt. %) seems to indicate that all analyzed eclogitic rocks, including those enclosed as layers or boudins in marbles, have a mafic igneous protolith. This conclusion is also supported by the igneous trend shown by the eclogites in an *al-alk* versus *c* diagram (LEAKE, 1970), in contrast to the sedimentary trend of the schists.

Eclogites range from just saturated to slightly under-saturated in silica: in STRECKEISEN's (1976) Q-A-P-F diagram the compositions plot from Q = 7 down to F = 25% (if calculated in wt. % normative minerals), and from P = 28 to 51%. They thus contain more normative alkali-feldspar (A) than plagioclase (P).

The Alk, Fe and Mg proportions are shown in the AFM diagram (Fig. 2b). The analyzed metabasites appear to be relatively Fe-poor ($F \leq 37\%$), and show a calc-alkaline trend. The Alk-F-M proportions define a field which is slightly enlarged relative to the Group C eclogite field as proposed by COLEMAN et al. (1965). In two specimens of clinopyroxenite or clinopyroxene-rich eclogite the alkali content is especially high, reflecting high Na-pyroxene

concentration. It is not clear whether the high alkali concentration of these and other specimens mentioned by previous authors is due to Eo-Alpine metasomatism, or to some particular composition of the rock already acquired before Alpine times (either a magmatic or a pre-Alpine metamorphic feature) (e.g., see GHENT and COLEMAN, 1973).

CHEMICAL CHARACTERS OF MINERALS

1. Garnet

Compositions of garnets determined from separates are shown in Fig. 3a, where the andradite end member has been added to grossularite. Microprobe analyses (total Fe calculated as FeO) are plotted in Fig. 3b and c. Comparison of two electron microprobe analyses with analyses on mineral separates suggests the presence of little ferric iron in eclogitic garnets. The comparison of diagrams Fig. 3a to c shows that oxidized iron is most pro-

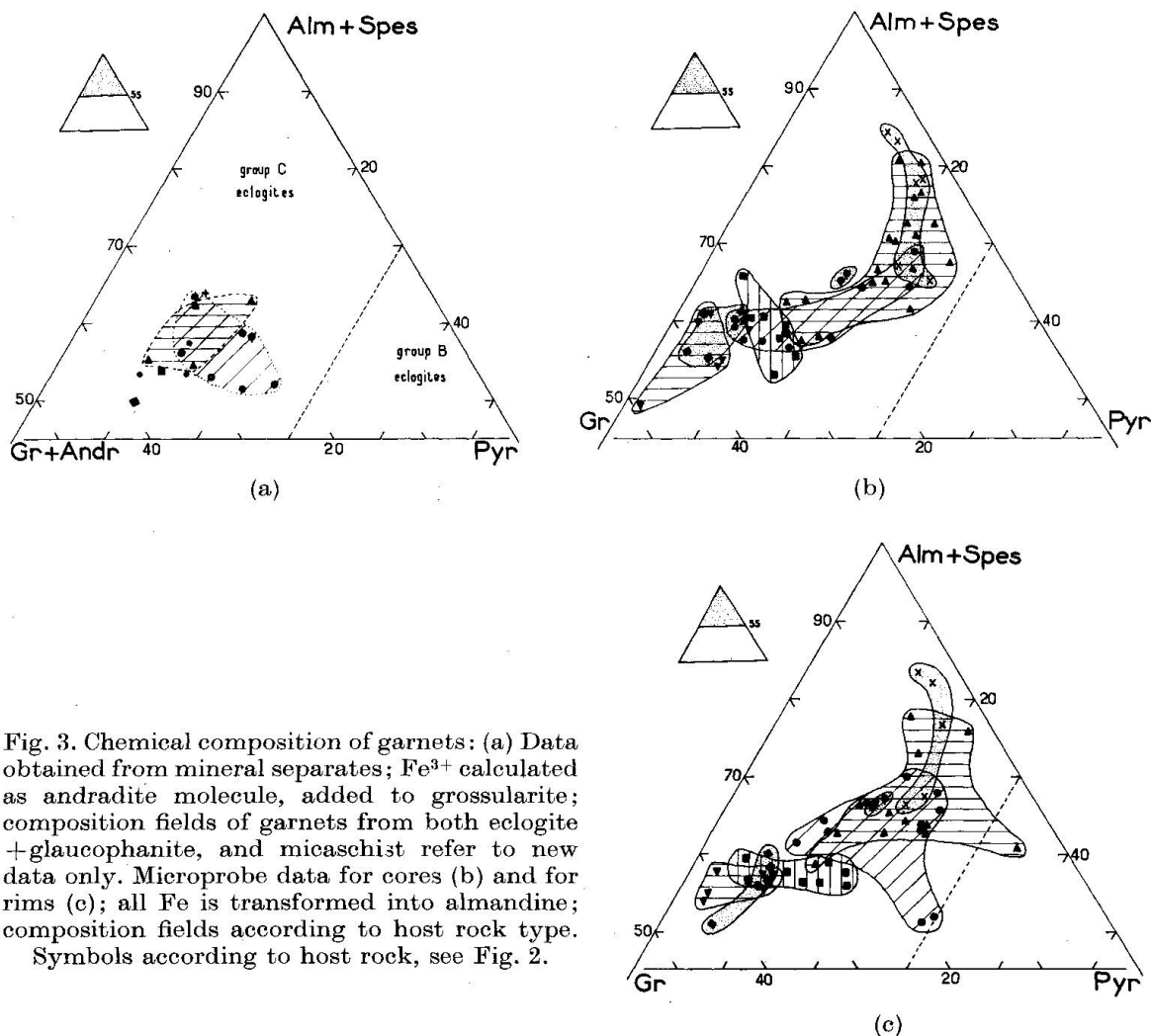


Fig. 3. Chemical composition of garnets; (a) Data obtained from mineral separates; Fe^{3+} calculated as andradite molecule, added to grossularite; composition fields of garnets from both eclogite + glaucophanite, and micaschist refer to new data only. Microprobe data for cores (b) and for rims (c); all Fe is transformed into almandine; composition fields according to host rock type. Symbols according to host rock, see Fig. 2.

minant in garnets from schists, secondarily from eclogites, but is almost absent in garnets from meta-pegmatitic rocks.

The overall compositions are pyrope-rich and, owing to the relatively low pyrope contents, plot in the field of garnets from group C eclogites according to COLEMAN et al. (1965), or would plot with garnets from SMULIKOWSKI's (1972) "ophiolitic" eclogites, i.e., the lowest grade eclogites. However, most garnets from Sesia eclogites are richer in pyrope and show a wider range of grossularite content than garnets from California and Oregon eclogites (GHENT and COLEMAN, 1973).

Garnets from eclogitic layers or boudins enclosed in marbles, and garnets from metagranitoids are richest in grossularite. In granitoids this might be due to the fact that garnet is the only Ca-rich phase.

Kinzigite (i.e. biotite-garnet \pm sillimanite gneiss of pre-Alpine age, but more or less altered to jadeite \pm kyanite-bearing schist in Alpine times), and chloritoid-mica-schist (which probably has been derived from kinzigite) contain garnets that are especially rich in almandine (Fig. 3b). Likewise, the points representing garnets from an unaltered hornblende amphibolite, the inferred parent-rock of eclogites, are shifted towards the almandine end-member with respect to the garnets from eclogites.

The question arises as to what extent the garnets are pre-Alpine, or Alpine, or some mixture of both. A few schists contain large, older garnet grains together with smaller, younger ones which are clustered around the larger ones, and are also scattered throughout the rock. In two samples, garnets of the first generation contain less Mg and less Ca than the second generation garnets. In another sample the Ca content is distinctly higher in the later-formed grains. The composition of the first generation garnets plots in the "kinzigite" field. As only one metamorphic phase of Alpine age is known in this part of the Sesia unit (the Eo-Alpine phase), and owing to the compositional similarity of these large grains with bona fide pre-Alpine garnets, the larger grains in these rocks are considered to have been generated during a pre-Alpine phase of metamorphism, while the small ones are ascribed to Eo-Alpine crystallization. No such difference in size, aspect, and composition of grains has been found among the other rock types investigated. In these rocks all analyzed garnets are thus regarded as generated in Eo-Alpine times. Where two garnet generations are distinguishable partial homogenization by diffusion (ANDERSON and BUCKLEY, 1973) is inferred not to have taken place. Recent work (WOODSWORTH, 1977) suggests that homogenization by diffusion may not take place except under sillimanite zone temperatures. Moreover, only very short-distance diffusion associated with retrogression has been found to occur as a post-crystallization process in garnets from other Western Alpine units (DE BÉTHUNE et al., 1975).

Eclogitic garnets from blueschist terranes are commonly found to be zoned

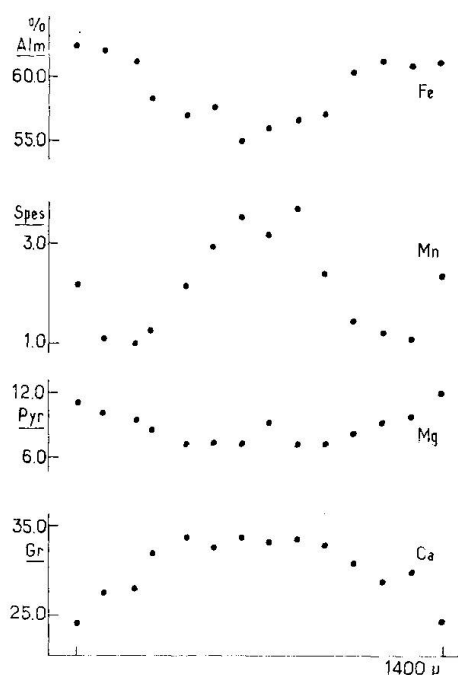


Fig. 4. Example of microprobe profile of garnet, obtained from individual analyses. Eclogite, Ivery, Nr. M. 143-B.

and the amount of compositional variation in the investigated garnet grains is highly variable between each rock specimen. Many grains considered to form relics of pre-Alpine crystallization only show a slight zonation. In some rock types Eo-Alpine garnets, low in Mn content, also show a slight zonation.

Examples of zonation patterns are shown in Fig. 4. A common zonation pattern is bell-shaped for Mn and Ca, bowl-shaped for both Fe and Mg.

A complex pattern is that of triple domes for Mn, Fe and Mg, one at the core and one at each rim, compensated by reverse pattern for Ca. This has been found in idioblastic grains showing no sign of two separate crystallization phases. Such a pattern could be explained by two pulses in the garnet growth during a single metamorphic phase, but this hypothesis is not supported by other observations.

At the edge of some garnet grains Mn sharply increases (Fig. 4). In this case Ca varies antithetically with Mn. Continuous profiles, or profiles obtained from very closely spaced analytical points, are needed here in order to establish whether this constitutes another case of limited diffusion during resorption as described by DE BÉTHUNE et al. (1975) in other units of the Western Alps.

2. Pyroxene

Pyroxene end-members have been calculated according to the method of CAWTHORN and COLLERSON (1974), which leads to higher values for jadeite content than BANNO's (1959) method.

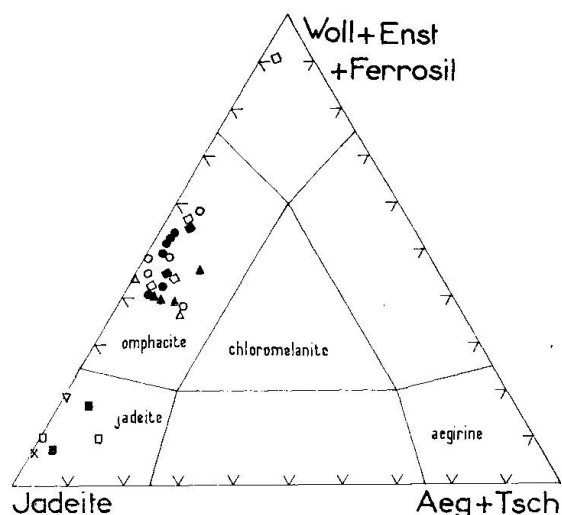


Fig. 5. Chemical composition of clinopyroxene. End-members calculated according to CAWTHORN and COLLERSON (1974). Key to symbols: see Fig. 2. Solid symbols: data from mineral separates. Open symbols: microprobe data.

Clinopyroxene from eclogite, schist and marble is omphacite (Fig. 5). Omphacite from schist is slightly richer in aegirine component, and thus would plot as chloromelanite according to MAKANJUOLA and HOWIE (1972). In meta-pegmatite, metagranitoid, and biotite-garnet gneiss ("kinzigite"), where Na-pyroxene grows at the expense of feldspar, the pyroxene is jadeite. Diopside occurs in one marble sample.

Compositional profiles across Na pyroxene grains generally show irregular zoning. However, in those specimens where a regular variation has been found, Al and Na slightly increase, whereas both Mg and Ca decrease towards the rims. Fe varies sympathetically with either Na and Al (suggesting solid solution of aegirine in jadeite), or more commonly with Mg and Ca (suggesting diopside-hedenbergite solid solution in jadeite).

3. Na-amphibole

All Na-amphibole separates analyzed, when plotted in Miyashiro's diagram, prove to be true glaucophanes. Some of the microprobe analyses have been recalculated according to the method described by STOUT (1972) in order to estimate the $\text{Fe}^{2+}/\text{Fe}^{3+}$ content. These recalculated analyses also plot in the glaucophane field. Glaucophane analytical data are summarized in Fig. 6 where

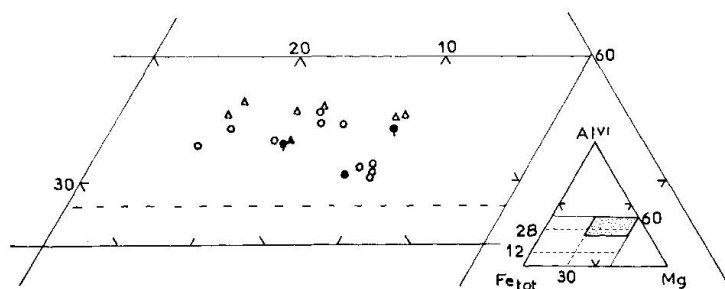


Fig. 6. Chemical composition of Na-amphibole in the Al^{VI} - Fe_{tot} -Mg triangle. Key to symbols: see Fig. 2. Solid symbols: data from mineral separates; open symbols: microprobe data.

both Fe^{2+} and Fe^{3+} are plotted as total Fe. Na-amphibole from schist appears to be slightly more aluminous than Na-amphibole from eclogite and glaucophanite, but in both rock types glaucophane shows the same range of variation in Fe and Mg.

Microscopic study shows that some glaucophane grains vary in color and birefringence, indicating chemical zoning. Microprobe analyses show that the darker colored rims are enriched in Fe and depleted in Mg and Al; the composition, however, remains in the field of glaucophane. In some cases the Ca-content is slightly higher at the rim.

4. White mica

Both phengite and paragonite have been analyzed, the former from schists and the latter from metamorphic pegmatites. In the AKF diagram (Fig. 7) the white K-micas plot in the blueschist facies field delineated by COLEMAN (1967).

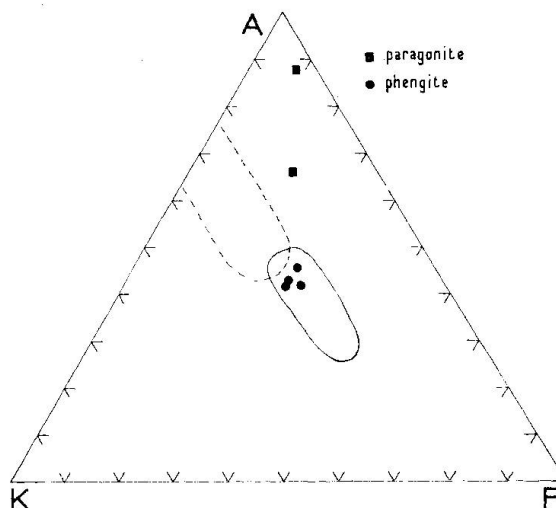


Fig. 7. Chemical composition of white micas in the ACF diagram. All data obtained on separates. Solid line: composition field of white K-micas from blueschist facies; dashed line composition field of white K-micas from greenschist and amphibolite facies (according to COLEMAN, 1967).

DISTRIBUTION COEFFICIENTS (K_D)

The distribution of ferrous iron and magnesium between coexisting garnet and clinopyroxene in eclogitic rocks has been shown to be both temperature and pressure dependent (BANNO, 1970), and can be used to indicate approach to equilibrium. Experimental values relating the distribution coefficient K_D of Fe^{2+} and Mg to temperature and pressure have been obtained for the mineral pair garnet-clinopyroxene by RÅHEIM and GREEN (1974), and applied by the same authors (1975, modified by RYBURN et al., 1976) to natural eclogites.

Only grains from the Eo-Alpine crystallization phase have been used to calculate the distribution coefficients. Although garnet and clinopyroxene

grains were not in all cases contiguous, the K_D values are regarded as good approximations, as there is no wide scattering of composition for rims and cores in a given rock section.

Here, the Fe^{3+} content of garnet and pyroxene has been calculated according to the formulas:

$$\text{in garnet} \quad \text{Fe}^{3+} = 16 - 2\text{Si} - \text{Al}^{\text{IV}} - \text{Al}^{\text{VI}}$$

$$\text{in clinopyroxene} \quad \text{Fe}^{3+} = 4 - 2\text{Si} - \text{Al}^{\text{IV}} - \text{Al}^{\text{VI}} + \text{Na}$$

(RYBURN et al., 1976).

(Ti, K and Cr have not been determined under the microprobe, but these are likely to be negligible: e.g., ESSENE and FYFE, 1967; GHENT and COLEMAN, 1973.)

Three groups of values have been obtained for the eclogitic rocks of the Sesia unit: from chemical data obtained on mineral separates (10 values), from microprobe data for cores of both garnet and clinopyroxene (7 values), and from microprobe data for rims of the same grains. The average K_D values for these three groups respectively are (Fig. 8): 16.8 (separates), 21.1 (cores), and 15.3 (rims). In metabasites of the same Sesia unit LIEBEAUX (1975) obtained K_D values ranging from 10 to 45.

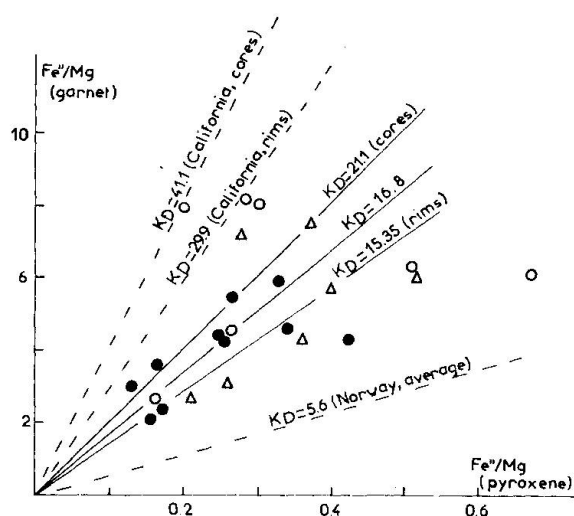


Fig. 8. Distribution of Fe^{2+} to Mg between coexisting garnet and Na-pyroxene. Symbols: solid circles, data obtained on separates; open circles, microprobe data obtained on cores; triangles, microprobe data obtained on rims. K_D values obtained for eclogites from California by RYBURN et al. (1975), and Norway by RÅHEIM and GREEN (1974).

Compared with other $K_D \frac{\text{Fe}^{2+}}{\text{Mg}} - \text{gr}_{\text{pyx}}$ values for group C eclogites, the present values appear to be lower than most. For example, in California RYBURN et al. (1976) quote K_D values ranging from 30 (rims) to 41 (cores). In Liguria, ERNST (1976) reports K_D values near 30. On the other hand, the Sesia values are definitely higher than those shown by eclogites from Norway which belong to group B eclogites (i.e., from gneissic terrane: $K_D = 5.6$, RÅHEIM and GREEN, 1975).

In California, as well as in other eclogites from glaucophanitic terranes (New Guinea, Colombia, Liguria), the K_D values for the cores of the pair garnet-pyroxene are higher than for the rims, whereas the opposite is found in the average K_D value obtained for the Sesia samples. As mentioned above, the garnet rims are found to be enriched in both Fe^{2+} and Mg, with respect to the cores. At the same time, the ratio Fe^{2+}/Mg slightly increases when the sum $\text{Fe}^{2+} + \text{Mg}$ is increasing. On the other hand, Fe^{2+} and Mg do not show a large variation between cores and rims of pyroxene. Consequently, the variation of the ratio Fe^{2+}/Mg in garnet controls for K_D value range, and, on the average, the calculated K_D values have thus been found to be higher for the cores than for the rims.

Scattering of the points in the diagram may be due to three factors. (1) Either complete equilibrium was lacking between the minerals (oxygen isotope data on the same rocks are interpreted as giving evidence of a not entirely pervasive fluid (DESMONS and O'NEIL, in prep.)). (2) In the case of mineral separates, the scattering could originate in the mixing of chemically different parts of each mineral species. (3) In the case of chemical data obtained through the microprobe, the K_D values might have been calculated from portions of the grains which have not equilibrated.

Using RÅHEIM and GREEN's experimental data, the albite = jadeite + quartz boundary of JOHANNES et al. (1971) and HAYS and BELL (1973), and the $\text{Jd}_{50}\text{Di}_{50}$ boundary extrapolated from KUSHIRO (1969), the above-mentioned K_D values would correspond to minimum temperatures of crystallization of, respectively, 510 (separates), 475 (cores), and 530°C (rims), with the minimum pressure being equal to 11 to 12.5 kb (if a composition of $\text{Jd}_{50}\text{Di}_{50}$ is considered). As Na-pyroxene up to Jd_{90} formed in rocks of suitable composition in the same area, higher values of P and T are likely to have existed (approximately 20°C and 2.5 kb higher). In the cases where the jadeite content of Na-pyroxene is higher in the rims than in the cores of the grains, an increasing pressure (or a slightly decreasing temperature) may be inferred during the crystallization. The decrease in $K_D^{\text{Fe}^{2+}} - \frac{\text{gr}}{\text{pyx}}$ from cores to rims suggests, however, an increasing temperature during crystallization.

Distribution coefficients between other mineral pairs (garnet-glaucophane, glaucophane-pyroxene, garnet-white mica, pyroxene-white mica) are based on too few values to be conclusive as to the lack or attainment of equilibrium.

CONCLUSIONS

The rock sequence of the eastern Sesia unit is made up of both sedimentary and igneous rocks which have been metamorphosed during pre-Alpine, probably Hercynian times, then in Eo-Alpine time. Some of the paraschists still

contain pre-Alpine garnets together with the garnet grains generated in Eo-Alpine times.

The composition of the garnets of the eclogitic assemblages plot in the field of group C eclogites, i.e. eclogites associated with glaucophane metamorphism as delineated by COLEMAN et al. (1965). Their zonation patterns are varied, but most commonly show a bell-shaped profile for Mn and Ca.

The composition of Na-pyroxene is strongly controlled by the nature of the host rock, in particular, the Fe^{2+} content of the host rock. Thus one should not attempt to use jadeite contents of pyroxenes as regional indicators of pressure, unless rocks of similar chemistry are compared (see also GHENT and COLEMAN, 1973).

The temperature range (505 to $525 \pm 30^\circ\text{C}$) inferred from the distribution coefficient of Fe^{2+}/Mg in garnet and Na-pyroxene is in good agreement with the data obtained through stable isotope measurements: $545 \pm 30^\circ\text{C}$ for quartz-rutile and $535 \pm 40^\circ\text{C}$ for quartz-phengite (DESMONS and O'NEIL, in prep.).

These temperatures are also consistent with the fact that the stable Ca-silicate is zoisite or clinozoisite, not lawsonite. The temperature must have been higher than approximately 425°C for $P_{\text{H}_2\text{O}} = P_{\text{tot}} \approx 10$ kb (NITSCH, 1974). On the other hand, chloritoid, not staurolite, is the stable phase in the high-pressure mineral assemblage. This sets a maximum limit on T of about 550 to 610°C (GANGULY, 1969) for pressure from 5 to 15 kb.

There is another, less precise, petrologic argument in favor of temperature lower than 550 to 600°C (BOCQUET [DESMONS] et al., in press; HUNZIKER, 1974). A slight alteration of the eclogitic assemblages led to the formation of greenschist, not amphibolite facies minerals (blue-green amphibole, albite, chlorite). This alteration is dated as Eo-Alpine, thus it took place very shortly after the development of the high-pressure event. Had the temperature during the high-pressure metamorphism been higher than 600°C , the formation of greenschist minerals would imply a drastic temperature drop in a very short time-span, which is unlikely on a regional scale. KIENAST and VELDE (1970), and VELDE and KIENAST (1973) used the Si-content of phengite to estimate $T = 600\text{--}650^\circ\text{C}$ and $P = 11\text{--}12$ kb attending the Sesia eclogitic metamorphism. These estimates at best can be only maximum values since they are based on solid solution in a single mineral (see discussion by BROWN, [1968]).

Slightly lower values ($480\text{--}500^\circ\text{C}$) have been proposed through the same K_D method for eclogites of the adjoining Zermatt-Saas unit of the Western Alps (DAL PIAZ and ERNST, 1976), which underwent a similar Eo-Alpine metamorphic history (DAL PIAZ, 1974). On the other hand, K_D values shown by BANNO (1970, Fig. 7), calculated from literature crystallochemical data concerning the same Zermatt-Saas unit, are a bit higher than those obtained

for the Sesia unit; the inferred temperature and pressure would thus be slightly higher.

Finally, eclogites from the Tauern Window (Austrian Alps) show similar distribution coefficients and, accordingly, identical values for the temperature of their formation (MILLER, 1976). A coherent P-T pattern thus arises for the highest pressure mineral associations in the Alps.

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