

**Zeitschrift:** Schweizerische mineralogische und petrographische Mitteilungen =  
Bulletin suisse de minéralogie et pétrographie

**Band:** 54 (1974)

**Heft:** 2-3: Alpidische Metamorphosen in den Alpen

**Artikel:** Blue amphiboles of the Western Alps : chemistry and physical  
characters

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**DOI:** <https://doi.org/10.5169/seals-42203>

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# Blue Amphiboles of the Western Alps

## Chemistry and Physical Characters

By *Jacqueline Bocquet* (Grenoble)\*)

With 10 figures and 2 tables in the text

### Abstract

Twenty-one new analyses of blue amphiboles (glaucophane, ferroglaucophane, crossite, magnésioriebeckite, and riebeckite) from the Western Alps are presented, and compared to earlier chemical data. Their chemical composition shows a strong correlation with the host-rock composition. Some of the samples contain up to about 24% of the actinolite-tremolite molecule. Under the microprobe the zonation appears to be due to an irregular, step-by-step decrease of the iron content toward the rims, with concomitant increase of Mg and Al. The X-ray data (310 and 110 reflections, and cell parameters) are related to the Fe<sup>III</sup> content, and, for the  $c_0$  parameter, to the Fe<sup>II</sup> content.

The possibility of the zoneographic control of blue amphibole composition in the Western Alps is investigated.

### Résumé

Vingt-et-une nouvelles analyses d'amphiboles bleues (glaucophane, ferro-glaucophane, crossite, magnésioriebeckite et riebeckite) provenant des Alpes occidentales, sont présentées et comparées à quelques données antérieures de même origine. Leur composition chimique est en nette corrélation avec celle de la roche hôte. Certains échantillons comportent jusqu'à 24% de molécule actinote-trémolite. La microsonde montre que la zonation est due à une diminution irrégulière de la teneur en fer du centre vers les bords des cristaux, compensée par une augmentation de Mg et Al dans la même direction. Les caractères radiocristallographiques (position des raies 310 et 110, et constantes réticulaires) sont en relation avec la teneur en Fe<sup>III</sup>, sauf  $c_0$  qui varie avec Fe<sup>II</sup>.

La question de savoir s'il existe une variation zonéographique du chimisme de l'amphibole bleue dans les Alpes occidentales, est examinée.

### Zusammenfassung

21 neue Analysen von blauen Amphibolen (Glaukophan, Ferroglaukophan, Crossit, Magnésioriebeckit und Riebeckit) werden verglichen mit früheren Analysen aus den

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Westalpen. Die chemische Zusammensetzung der blauen Amphibole zeigt eine starke Abhängigkeit vom Pauschalchemismus des Gesteins. Einige Amphibole enthalten bis zu 24% Aktinolith-Tremolit-Molekül. Mikrosondeanalysen zeigen, dass die Zonierung mit einer stufenweisen Abnahme des Eisengehaltes gegen den Rand verknüpft ist. Hand in Hand mit dieser Eisenabnahme geht eine Zunahme von Mg und Al. Die Röntgendaten (310- und 110-Reflektionen und Gitterkonstanten) hängen vom Fe<sup>III</sup>-Gehalt ab, und für den c<sub>0</sub>-Parameter vom Fe<sup>II</sup>-Gehalt.

Die Möglichkeit eines Zusammenhanges der chemischen Zusammensetzung der blauen Amphibole mit der Zoneographie in den Westalpen wird untersucht.

### Riassunto

Sono stati analizzati 21 anfiboli blu (glaucofane, ferroglaucofane, crossite, magnesioriebeckite e riebeckite) delle Alpi occidentali ed i risultati sono confrontati con analisi preesistenti. La loro composizione chimica è in netta relazione con quella della roccia. Alcuni campioni contengono fino ad 24% di molecola tremolite-attinoto. Lo studio alla microsonda delle zonature indica che esse sono dovute ad una irregolare diminuzione del contenuto in Fe dal centro alla periferia dell'anfibolo, compensata da un aumento, nello stesso senso, di Mg e Al. Le caratteristiche cristallografiche (posizione di 310 e 110 e costanti reticolari) sono in relazione con il tenore in Fe<sup>3+</sup>, ad eccezione di c<sub>0</sub> che varia con Fe<sup>2+</sup>.

Si esamina infine il problema se esista una variazione zoneografica del chimismo dell'anfibolo blu nelle Alpi occidentali.

### Legend to Fig. 1

Symbols: Piemont zone and Versoyen:	a: meta-ophiolites.
	b: calc- and quartz-schists.
	c: quartz-ironstones.
Briançon-Bernhard zone:	d: mica- and glaucophane-schists.
	e: limestones and marbles.

### Structure:

1. Dauphiné-Helvetic cover, Ultra-dauphiné zone, molasse and quaternary basins.
2. Prealps.
3. Dauphiné-Helvetic crystalline massifs with their Permo-Carboniferous cover.
4. Embrunais-Ubaye and Ligurian flysch (notably Helminthoid flysch), with associated tectonic slices.
5. Subbriançon, Versoyen, Ferret, and Sion-Courmayeur zones.
6. Briançon-Bernhard zone: outer part, with cover (for the northern half: «zone houillère»); Moncucco and Orselina zones.
7. Briançon-Bernhard zone, undifferentiated (Savona region).
8. Briançon-Bernhard zone: inner part, with cover.
9. Piemont zone: «Schistes lustrés» (= calcschists), and ophiolites; Lanzo peridotite massif.
10. Piemont zone: crystalline massifs (from north to south: Mte Rosa, Gran Paradiso, Dora-Maira).
11. Arolla series of the Dent Blanche nappe, Sesia zone.
12. Tessin nappes.
13. Valpelline series of the Dent Blanche nappe, "2nd Diorito-kinzigitic zone", Canavese, and Ivrea-Verbanò zone.

Sources of structural data: unpublished structural sketch of the Western Alps, scale 1 : 500 000 (Uselle 1966); tektonische Karte der Schweiz, scale 1 : 500 000; Italian geological maps, scale 1 : 100 000.

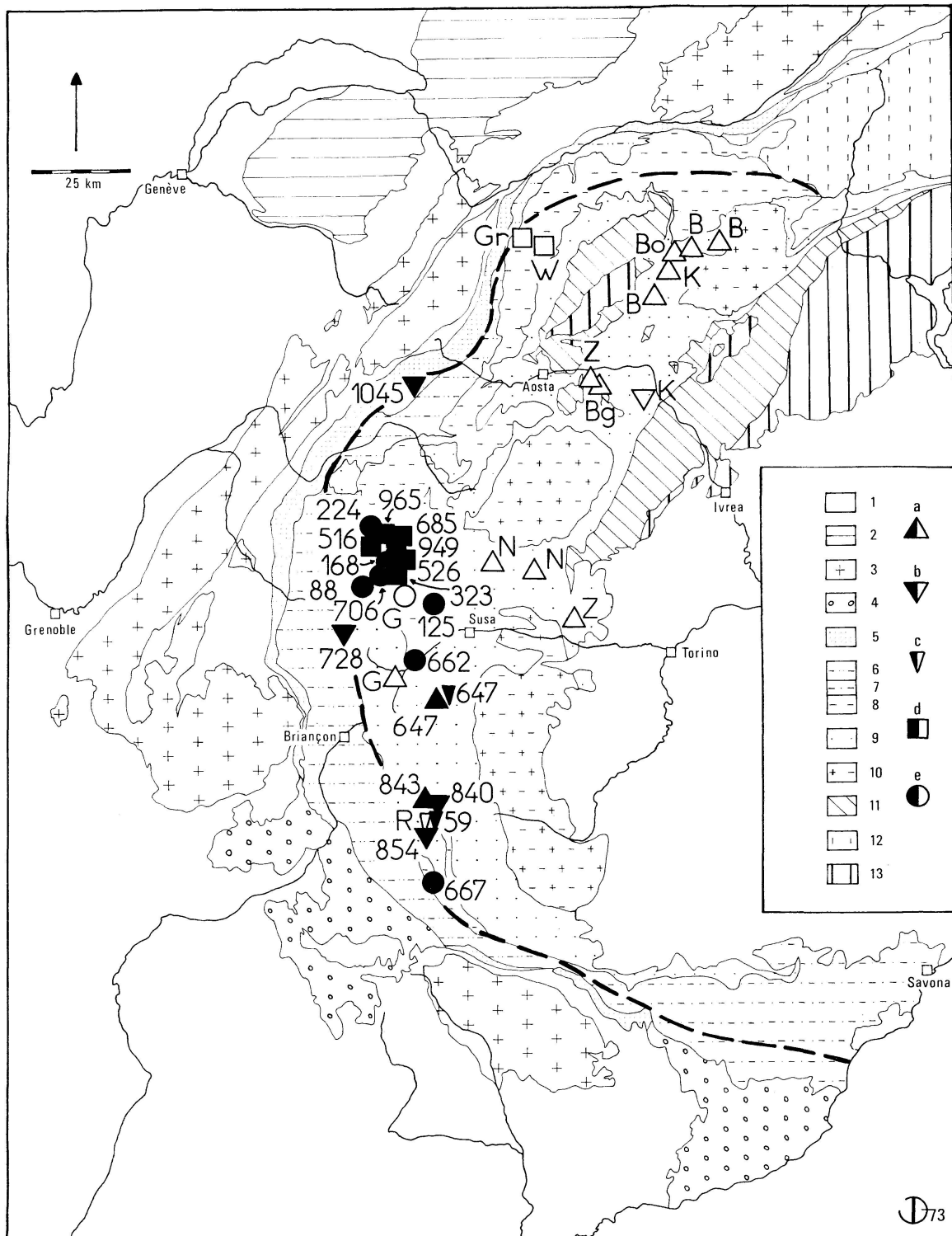


Fig. 1. Structural map of the Western Alps showing location of samples. The dashed line is the outer limit of the occurrence area of sodic amphiboles. Solid symbols refer to author's samples, open symbols to literature samples: B: BEARTH (1967); Bg: BORG (1967); Bo: BODEWIG (1876; G: GAY (1972); Gr: GRUBENMANN (1906); K: KUNITZ (1930); N: NICOLAS (1966); R: ROUTHIER (1946); W: WOYNO (1912); Z: ZAMBONINI (1906). One sample of KUNITZ (Salève), and the samples of CHATTERJEE do not appear on the map, as their exact location is not known.

Table 1. *Location of author's samples, with Lambert coordinates and sheet number, structural unit, stratigraphic age of the host-rock, nature of the host-rock, and mineralogical association*  
 Second numbers refer to BOCQUET'S (1971) numbering

59 (7.01.9):	Saint-Véran, Cu mine. Aiguilles n° 5: x = 963.0; y = 274.5; z = 2380. Piemont zone. Mesozoic. Amphibole and pyroxene metachert. Quartz - riebeckite - aegyrine - ore minerals ± chlorite ± apatite.
88 (5.06.5):	Roc du Bourget. Modane n° 7: x = 942.3; y = 333.1; z = 1280. Briançon zone. Upper Jurassic. Amphibole limestone. Calcite - albite - crossite - quartz - chlorite - green biotite - white mica - ore minerals.
125 (6.04.5):	Mont Cenis, near marble quarry. Lanslebourg n° 6: x = 962.1; y = 334.7; z ≈ 1900. Briançon zone. Upper Jurassic. Amphibole marble. Calcite - crossite - white mica - quartz - albite - chlorite - epidote - ore minerals.
168 (5.08.5):	Termignon, scree from Col de Belle Place. Modane n° 4: x = 948.6; y = 341.0; z = 2700. Briançon zone. Lias. Amphibole limestone. Calcite - riebeckite - Fe chlorite - albite - magnetite ± deerite ± aegyrine.
224 (5.03.5):	Pralognan, Mont Bochor. Moutiers n° 7: x = 943.8; y = 351.9; z ≈ 1780. Briançon zone. Upper Jurassic. Amphibole limestone. Calcite - magnesio-riebeckite - chlorite - green biotite - ore minerals.
323 (5.12.3):	Termignon, ravin du Pisset. Modane n° 4: x = 949.4; y = 342.0; z = 2200. Briançon zone. Pre-Westphalian basement. Amphibole micaschist. Quartz - white mica - ferroglaucophane - chlorite - epidote - apatite - calcite - hematite.
516 (5.32.3):	Pralognan, scree in ravin des Nants. Modane n° 3: x = 941.5; y = 347.7; z = 1750. Briançon zone. Pre-Westphalian basement. Amphibole micaschist. Quartz - white mica - ferroglaucophane - chlorite - titanite - apatite - calcite - hematite.
526 (5.11.3):	Termignon, near Bellecombe lake. Modane n° 4: x = 951.7; y = 346.6; z = 2380. Briançon zone. Pre-Westphalian basement. Amphibole micaschist. Quartz - muscovite - paragonite - crossite - chlorite - albite - garnet - epidote - tourmaline - hematite.
642 (8.02.9):	Troncea, miniere del Beth-Ghinivert. Col-Saint-Martin: x = 966.5; y = 305.5; z = 2800. Piedmont zone. Mesozoic. Amphibole chert. Quartz - crossite - stilpnomelane - deerite - chlorite - calcite - ore minerals ± apatite.
647 (8.25.8):	Troncea, Punta del Beth. Col-Saint-Martin: x = 966.2; y = 305.9; z = 2900. Piedmont zone. Mesozoic. Meta-ophiolite. Crossite - chlorite - albite - ilmenite - leucoxene - titanite ± calcite.
662 (6.03.5):	Ulzio, molino della Beaume. Névache: x = 954.2; y = 314.8; z ≈ 1055. Briançon zone. Trias. Amphibole marble. Calcite - crossite - albite - white mica - chlorite - green biotite - hematite.
667 (9.01.5):	Acceglio, colle del Val Fissela. Aiguille de Chambeyron: x = 965.4; y = 258.3; z = 2650. Briançon zone. Upper Jurassic. Amphibole calcschist. Calcite - white mica - riebeckite - quartz - ore minerals.
685 (5.33.3):	Termignon, near the lakes of the ruisseau des Gorges. Modane n° 4: x = 949.1; y = 346.4; z = 2690. Briançon zone. Pre-Westphalian basement. Amphibole vein in amphibole micaschist. Crossite - quartz - chlorite - hematite ± white mica.
706 (5.11.5):	Aussois, Lozes quarry. Modane n° 8: x = 946.7; y = 334.4; z = 1475. Briançon zone. Upper Cretaceous. Amphibole-chlorite marble. Calcite - crossite - chlorite - white mica - quartz - albite - hematite ± epidote.
718 (6.01.5):	Bramans, between Bellecombe and Arella passes. Lanslebourg n° 5: x = 954.7; y = 335.2; z = 2530. Briançon zone. Upper Jurassic (?). Amphibole-magnetite brecciated marble. Calcite - blue amphibole - albite - quartz - chlorite - green biotite - ore minerals ± dolomite. (Microprobe profiles here presented; analysis in GAY 1972.)
728 (5.09.7):	Charmaix, W side of the Petit Argentier. Névache n° 2: x = 938.3; y = 323.9; z ≈ 2200. Piedmont zone. Mesozoic. Amphibole quartzschist. Quartz - ferroglaucophane - aegyrine - white mica - chlorite - calcite - titanite - hematite.

- 840 (7.09.7): Molines-en-Queyras, vallon du Longet. Aiguilles n° 5: x = 962.9; y = 276.9; z = 2480. Piedmont zone. Mesozoic. Amphibole marble. Calcite – ferroglaucophane – chlorite – albite – quartz – white mica – rutile – ore minerals.
- 843 (7.27.8): Molines-en-Queyras, vallon du Longet. Aiguilles n° 5: x = 962.7; y = 276.9; z = 2420. Piedmont zone. Mesozoic. Metagabbro. Glaucophane – lawsonite – chlorite – relictual pyroxene – albite – epidote – white mica – ilmenite – leucoxene.
- 854 (7.04.6): Ceillac, ravin des Prés Bergers. Aiguilles n° 5: x = 958.5; y = 271.9; z = 2370. Piedmont zone. Mesozoic. Amphibole schist. Quartz – crossite – white mica – ore minerals.
- 949 (5.38.3): Termignon, N side of the Arpont glacier. Modane n° 4: x = 947.8; y = 345.1; z = 2850. Briançon zone. Pre-Westphalian basement. Amphibole micaschist. Quartz – white mica – ferroglaucophane – chlorite – albite – hematite ± zircon.
- 965 (5.32.3-b): Pralognan, cirque du Dard. Moutiers n° 7: x = 946.0; y = 350.8; z = 2300. Briançon zone. Pre-Westphalian basement. Amphibole micaschist. Quartz – phengite – ferroglaucophane – chlorite – albite – tourmaline – rutile – zircon – hematite.
- 1045 (2.09.6): Bourg-Saint-Maurice, Pointe du Clapey. Bourg-Saint-Maurice n° 4: x = 949.5; y = 383.1; z = 2560. Versoyen zone. Mesozoic. Amphibole schist. Ferroglaucophane – white mica – albite – chloritoid – jadeite – chlorite – calcite – rutile – titanite – ore minerals.

## INTRODUCTION

During mineralogical and petrological investigations of Alpine metamorphic rocks from the French Alps, particular attention has been devoted to those characteristic blue minerals, the amphiboles of the glaucophane-riebeckite series.

Their field distribution in the inner Western Alps is known through the studies of VAN DER PLAS (1959), BEARTH (1962), NIGGLI and NIGGLI (1965), and BOCQUET (1971), and is shown on the map fig. 1, where the previously known distribution area has been completed by new data collected by the present author.

Blue amphiboles are characteristic of a first, Eoalpine event of the Alpine metamorphism. They are late Cretaceous in age (HUNZIKER 1971, DAL PIAZ et al. 1972), and are roughly coeval with – or slightly post-dated – eclogitic assemblages (BEARTH 1967, 1973; BOCQUET et al., in press), but formed still later. This is evident from the work of RAGUIN (1925) who showed that late Cretaceous fossils were enclosed in blue amphibole crystals. Under greenschist facies conditions, the sodic amphiboles later transformed into chlorite + albite, blue green amphibole, green biotite, etc. Moreover, late rock-forming and vein-filling riebeckite is known to occur within unmetamorphosed associations, anchizone and beginning greenschist zone in eastern Switzerland (FREY et al. 1973).

Chemical analyses of Western Alpine blue amphiboles have been carried out as far back as 1875 (COSSA in Strüver), but, to the author's knowledge, none from the French Alps before 1946 (ROUTHIER). Occurrences have been

reported in many regional studies, a number of which will be mentioned in the text. Other references are found in the above mentioned papers on the distribution of Alpine metamorphic minerals and Alpine metamorphism in general.

The geographic and structural location of the samples is shown on Fig. 1 (for structural outlines the non-Alpine reader is referred to TRÜMPY 1960 and 1973, and to DEBELMAS and LEMOINE 1970), and listed in Table 1, together with the mineral assemblages of the host-rocks.

Blue amphiboles occur in metamorphosed basic volcanic rocks (metaphiolites), amphibolites, eclogites, mica- and quartz-schists, limestones and marbles. All these associations are represented in the batch of investigated samples; the most common blue amphibole-bearing associations are thus found in the parageneses of the host-rocks as listed in Table 1.

Twenty-one of the analyses shown are new data contributed by the present author; the others were taken from the literature. Some ancient analyses of dubious value have not been made use of, the calculated atomic proportions being too far from the normal formula of sodic amphiboles. These are:

- COSSA (in Strüver 1875): no distinction made between Fe<sup>''</sup> and Fe<sup>'''</sup>; probably too much Al;
- COLOMBA (1894): too much Ca, Al; cf. author's analysis n° 662, of the same occurrence;
- ZAMBONINI (1902): too much Ca, no distinction made between Fe<sup>''</sup> and Fe<sup>'''</sup>;
- COSSA (in Zambonini 1906): too much Ca, Al; cf. Zambonini, 1906, quoted below;
- GRILL (1922): too much Na;
- TSCHOPP (1923): too much Al and Si.

### Experimental

*Separation:* Carried out by means of a Frantz electromagnetic separator and heavy liquids.

*Chemical analyses:* Carried out by wet methods (K and Na by flame spectrophotometry) in the chemical laboratory of the Dolomieu Institute, Grenoble, in the Centre de Recherches Pétrographiques et Géochimiques of Nancy, and in the Laboratoire d'Analyses Physiques in Pau.

Weight % corrected, when needed, for unseparated impurities, according to optical and X-ray checks.

*Microprobe profiles:* Performed with CAMECA MS 46 equipment in the Metallurgy Dept of the Centre d'Etudes Nucléaires of Grenoble. Carbon-coating through vacuum evaporation.

*X-rays:* Powder diagrams obtained with Ni-filtered CuK<sub>α</sub> radiation, on a Philips diffractometer with C.G.R. amplifier and counter. Positioning of 310- and 110-reflections through step-by-step counting, with silicon external standard.

*Cell parameters:* Computed from 11 to 21 peaks graphically positioned on the powder





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diagrams. Peaks indexed according to the ASTM cards n° 19-1061, 20-376 and 20-453 (Borg's data), and three full computed reflections patterns made by B. NUBER in Heidelberg with personal program (BERDESINSKI and NUBER 1966). Least squares refinement program carried out on the IBM 160 computer of the University of Grenoble.

*Refractive indices:* Measured with Cargille liquids. Accuracy considered to be  $\pm 0.004$  (the error including correction for white light, temperature, and precision of the measurement itself).

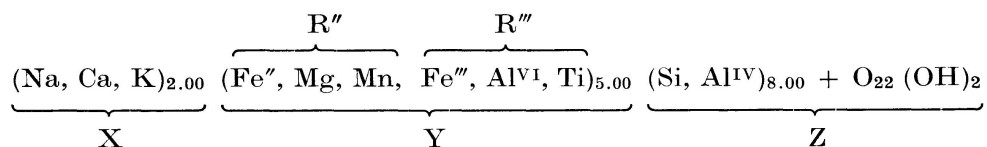
*Density:* Measured by centrifugation in heavy liquids. Mean accuracy:  $\pm 0.05$ .

## CHEMISTRY

Results of the new chemical analyses are given in Table 2. Author's calculation of atomic proportions of elements from other analyses carried out before 1950 are also given.

The atomic proportions were calculated on an anhydrous basis of 23 oxygens per half unit cell, as the  $H_2O^+$  content of amphiboles often fails to escape completely at  $1000^\circ$ , and its weight percent is therefore unreliable.

They are all close to the ideal formula:



with  $R''' \cong 2/3 R''$ .

PHILLIP'S (1963) and LEAKE'S (1968) criteria for good calcic-subcalcic amphibole analyses, adjusted for sodic amphiboles with  $1.75 < X < 2.25$ , are fulfilled.

The chief source of possible unrepresentativeness of the analyses would lie in the often strong internal zonation of the crystals, and in the differentiation between them, where glaucophane to crossite, or crossite to riebeckite compositions may be present in one single crystal or in one single thin section. For instance, partial analyses on two fractions, A and B, of the same sample – A being lighter in colour and less magnetic than B – gave the following results (sample n° 536, same origin as n° 168, see Table 1):

	A	B
Fe <sub>total</sub> as Fe <sub>2</sub> O <sub>3</sub>	18.03 weight %	27.43
MgO	7.08	3.78

These proportions would respectively agree with crossite (A), and with riebeckite (B), and besides the grains analyzed were internally zoned. Of course during the separation processes, those relatively few grains whose properties lie further from the average, tend to be discarded, and it has always been tried to keep only grains with intermediate electromagnetic and density properties.

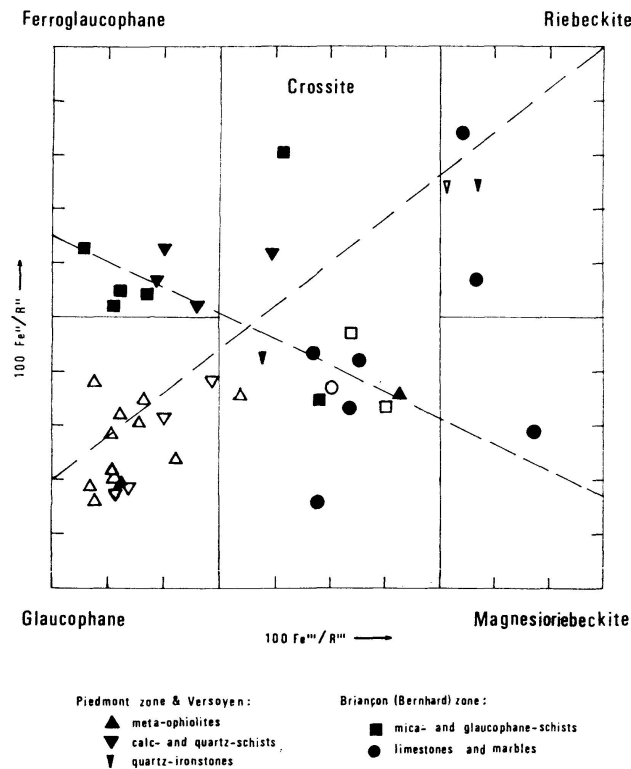


Fig. 2. Variation in chemical composition of blue amphiboles in Miyashiro's diagram. Solid symbols refer to author's data, open symbols to literature data. Dashed lines are the proposed solid solution tie-lines.

The analyses have been plotted on MIYASHIRO'S (1957) diagram, with the name crossite replacing subglaucophane, as suggested by DEER et al. (1962) and now generally accepted (Fig. 2). The five fields of the diagram are all occupied. More particularly, seven amphiboles plot as ferroglaucophane, which was not long ago said to be very rare or even non-existent in nature. However, a blue amphibole from the Bagnes valley (Valais, Switzerland), reported by TSCHOPP (1923; analysis not quoted here owing to probable micaceous and siliceous impurities), and KUNITZ' (1930) amphibole from Greece (quoted by MIYASHIRO 1957), are ferroglaucophanes. More recently ferroglaucophane has been reported in Japan (IWASAKI 1963), New Caledonia where it is said to be common in the Ouegoa district (BLACK 1970, 1973), and Ile de Groix, France (MAKANJUOLA and HOWIE 1972). The location of the ferroglaucophanes on the diagram obviously precludes the possibility of the analyzed samples being zoned mixtures of Mg- and Fe<sup>III</sup>-richer terms (glaucophane + crossite).

Solid solution lines may be drawn for the glaucophane-riebeckite series between  $Gl_{80}Fegl_{20}$  and  $Rb_{100}$ , as also proposed by MAKANJUOLA and HOWIE (1972), and for the ferroglaucophane-magnesianriebeckite series between  $Fegl_{65}Gl_{35}$  and  $Mgrb_{83}Rb_{17}$  (also passing through the point  $100 Fe'' : R'' = 50 / 100 Fe''' : R''' = 30$ ). Of the diagonals  $Gl_{100}-Rb_{100}$ , and  $Fegl_{100}-Mgrb_{100}$  considered by BORG, the first shows an increase of total iron content at the expense of both Mg and Al<sup>VI</sup>; the second shows the oxidation state of the iron. The here

suggested tie-lines depart from these in order to fit the data, and point to the fact that pure end-members (except riebeckite) are not common in nature.

An  $Al^{VI}$ - $Fe_{total}$ -Mg triangular diagram (BLACK 1973) is useful for plotting microprobe analyses where the oxidation state of iron is not known. However, it does not sharply separate each member from another. Anyway the  $Fe'''/Fe''$  determination is essential for a precise blue amphibole classification, otherwise it is only situated on a line parallel to  $G1_{100}$ - $Rb_{100}$ .

The data have been plotted in Fig. 2 as a function of the lithostructural relationships of the host-rocks. One thus finds:

— Piemont zone:

- in meta-ophiolites: mostly glaucophane, some crossite
- in calc- and quartz-schists: glaucophane, ferroglaucophane and crossite with  $Fe''' : R''' < 50\%$
- in quartz-ironstones: riebeckite and crossite

— Briançon-Bernhard zone:

- in mica- and glaucophane-schists: ferroglaucophane and crossite
- in limestones and marbles: crossite, magnesioriebeckite and riebeckite

Somes limestones and marbles from the Briançon zone locally exhibit associations of blue amphibole with abundant magnetite, and so they may be regarded as ironstones.

In order to possibly separate the chemical from the zoneographic control of composition, two diagrams (Fig. 3a and b) have been drawn, which show

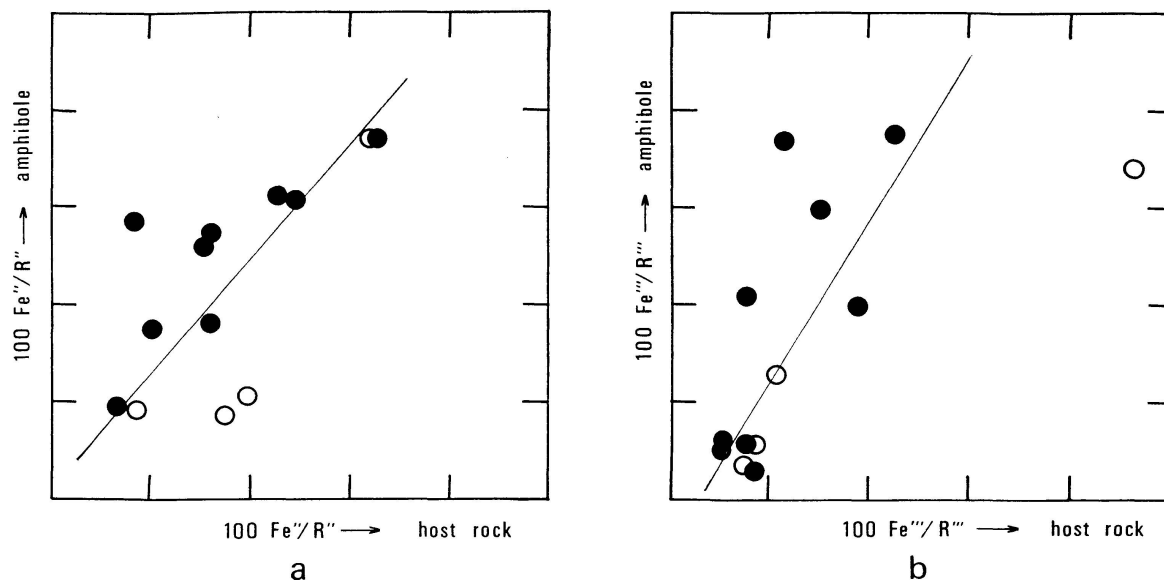


Fig. 3. Relation between blue amphibole and host-rock  $Fe''$  (a), and  $Fe'''$  (b) contents (in atomic proportions). Solid circles: author's data; open circles: literature data (ROUTHIER 1946, BEARTH 1967, and CHATTERJEE 1971).

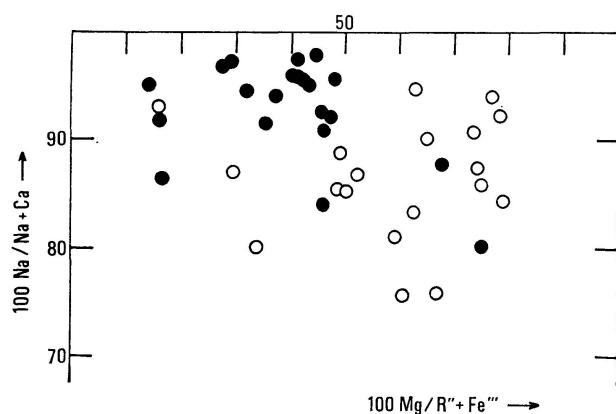


Fig. 4. Ca content of blue amphiboles as a function of the Mg content (in atomic proportions). Solid circles are author's data, open circles literature data.

strong correlations between host-rock and guest-amphibole  $\text{Fe}''$  and  $\text{Fe}'''$  contents. Host-rock compositions are taken from BOCQUET (in prep.).

Many samples, mainly glaucophanes, contain Ca in their formula. Plotted as a function of  $\text{Mg} : \text{Fe}_{\text{total}} + \text{Mg} + \text{Mn}$  (Fig. 4), the Ca content shows an increase towards the higher Mg content (BLACK, 1973, reported the same relationship). The question of the extent of actinolite-glaucophane s. l. solid solution has been debated. KUNITZ (1930) felt that there existed a continuous series, and 17 amphiboles plotted in his diagram indicate only narrow miscibility gap between  $\text{Gl}_{63}\text{Ac}_{37}$  and  $\text{Gl}_{40}\text{Ac}_{60}$ . SUNDIUS (1946) and MIYASHIRO (1957) claimed the existence of such a miscibility gap that would extend, according to IWASAKI (1963), and COLEMAN and PAPIKE (1968), from  $\text{Gl}_{80}\text{Ac}_{20}$  to  $\text{Gl}_{50}\text{Ac}_{50}$ .

Molecular proportions have been calculated from all analyses in the following sequence:

- a) If there is enough Na and  $\text{R}''$ ,  $\text{Al}^{\text{VI}}$  is assigned to glaucophane-ferroglaucophane.
- b) Any  $\text{Al}^{\text{VI}}$  left is allotted for a theoretical Al-tschermakite end-member.
- c) What is left of Na is calculated as riebeckite-magnesianriebeckite; the remaining  $\text{Fe}'''$  is added to  $\text{Fe}''$ , thus admitting a possible error in the  $\text{Fe}_2\text{O}_3/\text{FeO}$  determination or a post-crystallization oxidation.
- d) Either Ca or  $\text{Fe}''$  are calculated as actinolite-tremolite.
- e) Finally any  $\text{Fe}''$  left is calculated as cummingtonite-grunerite.

The molecular proportions are shown in the triangular diagrams of Fig. 5; in the first triangle (a), the actinolite-tremolite content is added to cummingtonite-grunerite and to Al-tschermakite; in the second (b), all blue amphibole molecules appear on the same apex.

Two analyses (one from BEARTH and one from KUNITZ) contain somewhat more than 20% of the actinolite-tremolite component (resp. 23 actinolite-tremolite + 1.5% Al-tschermakite, and 24% actinolite-tremolite), and thus plot inside the above mentioned miscibility gap.

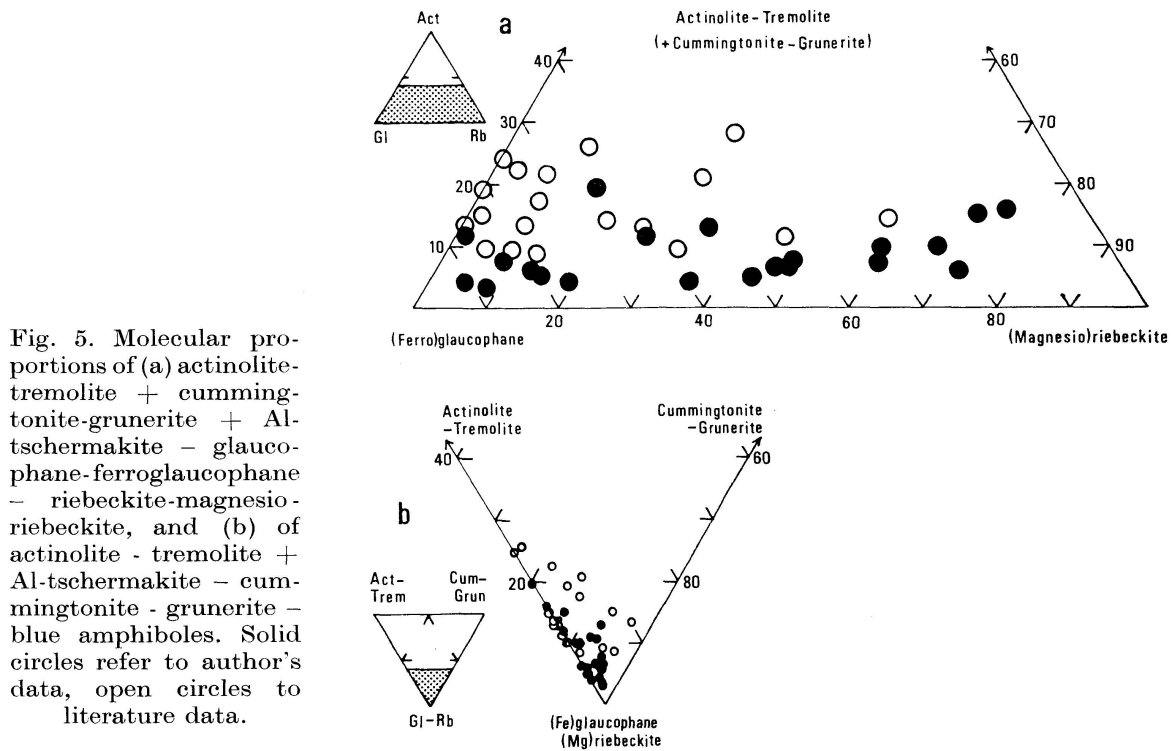


Fig. 5. Molecular proportions of (a) actinolite-tremolite + cummingtonite-grunerite + Al-tschermakite - glaucophane-ferroglaucophane - riebeckite-magnesio-riebeckite, and (b) of actinolite - tremolite + Al-tschermakite - cummingtonite - grunerite - blue amphiboles. Solid circles refer to author's data, open circles to literature data.

Other blue amphibole analyses of the French Alps, one from a metaophiolite (Piemont zone), calculated as having 21% cummingtonite-grunerite end-member, and one from a garnet-bearing glaucophanite (pre-Westphalian basement of the Vanoise massif, Briançon zone) with the A site partly filled up, have not been quoted here, as it is not yet clear whether they are solid solutions, juxtapositions of different amphiboles, one being replaced by the other, or mixtures of an amphibole with some submicroscopic replacing mineral (such as talc).

#### MICROPROBE STUDIES OF THE ZONATION

Two sets of profiles (Fe, Mg, Al, Ca, Na), obtained from basal and elongated sections of blue amphibole from a marble (n° 718) (photos Fig. 6), are shown in Fig. 7a and c. Bulk composition of a sample from the same occurrence belongs to a Mg-rich crossite (GAY 1972, analysis n° 2). In these sections the intensity of the absorption colours increases towards the margins. The inner part of the rhombic section consists of a lighter-coloured material contiguous to a quartz inclusion. In the elongated section, the b crystallographic axis lies close to Z in the core, then close to Y, and again close to Z in the outermost rim. The profiles show:

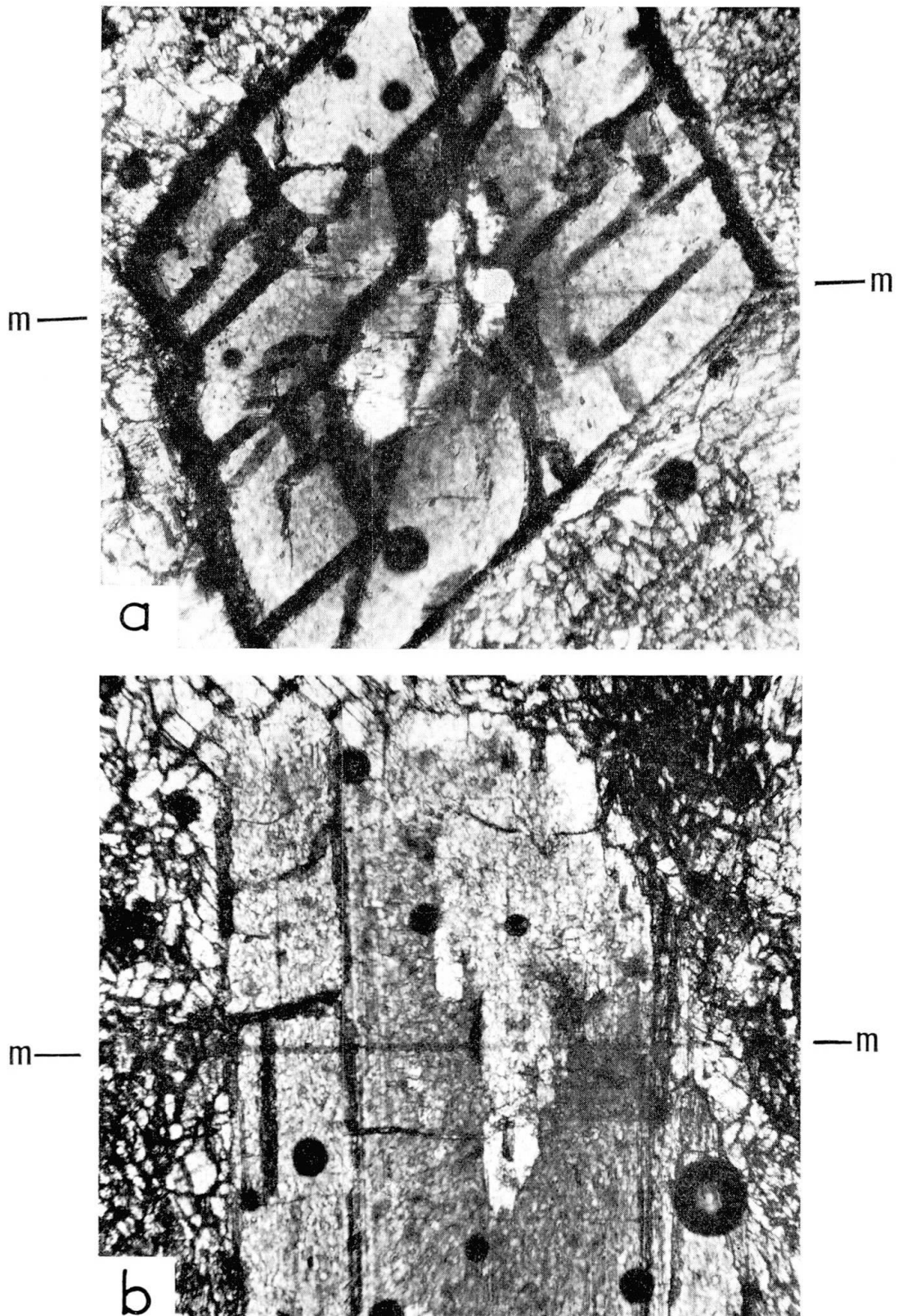


Fig. 6. Basal (a), and elongated (b) sections of blue amphibole in limestone, Mesozoic cover of the Ambin massif, Briançon zone (sample n° 718). Microprobe tracks visible between m-m. Carbon coated section. The dark circles are bubbles in the coating. Width of the crystals:  $300 \mu$  for the rhombic section, and  $500 \mu$  for the elongated section.

- A core which is richer in glaucophane molecule (comparatively more Al and Mg, and less Fe), sharply separated from the other part of the crystal; this core is slightly zoned.
- A progressive impoverishment in iron with concomitant enrichment in Al and Mg, indicating a general decrease from the riebeckite towards the glaucophane pole. In the elongated section this decrease occurs first through mainly Fe-Al substitutions (i. e. toward ferroglaucophane), then through Fe-Mg substitutions (i. e. towards glaucophane). Moreover, these variations are irregular, and do not plot as smooth curves, the cleavage planes forming break between each step.
- The outermost rim of the section is Fe-poor, Mg- and Al-rich, but less than the core.
- The cleavages of the elongated section are filled up with a Ca-rich material (calcite?); those of the basal section, with a Mg-rich unidentified material.

The approximate zoning paths are tentatively outlined in MIYASHIRO'S composition diagram (Fig. 7 a and b).

Other blue amphiboles from limestones (Briançon zone) gave analogous bell-

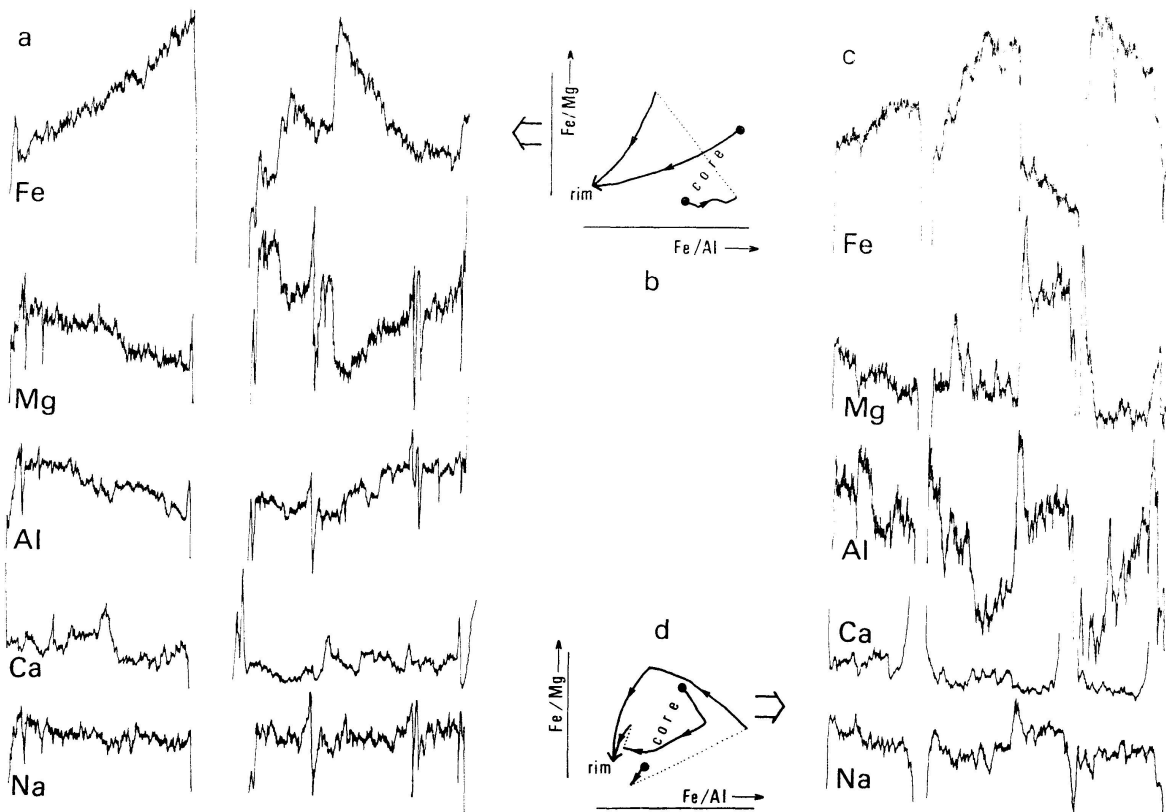


Fig. 7. Microprobe profiles and rough sketches of zonation paths: basal section (a, b), and elongated section (c, d) (sample n° 718).



shaped Fe-profiles, and bowl-shaped Mg-profiles, with zoned steps delimited by the cleavage planes. Cores are iron-poor in one sample, iron-rich in another.

These isolated cores could be interpreted as being evidence of a first, different stage of crystallization, which is as yet highly hypothetical in the concerned region. As to the step zoning, it will require more extensive investigations before inferences can be drawn in favour of either primary chemical variations during crystallization, likely due to P and/or T changes (which seem to be inconsistent with the step zonation), or secondary variations caused, for instance, by leaching fluids penetrating along the cleavage planes.

### X-RAY DATA

The general pattern of the powder diagrams is in good agreement with BORG'S lists of reflections (ASTM cards n° 19-1061, 20-376 and 20-453). Ferroglaucophane reflections do not essentially differ from those of either glaucophane or crossite.

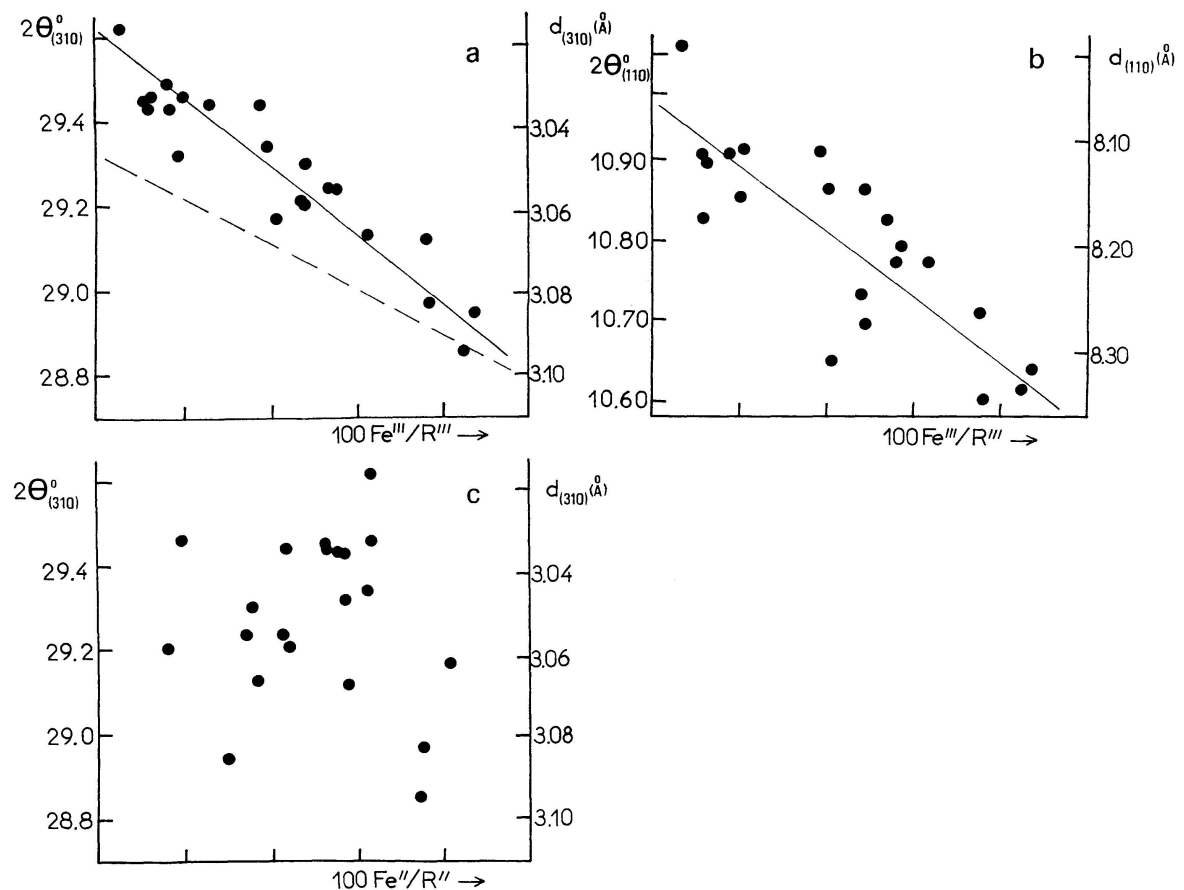


Fig. 8. Variation of the values of (a) 310, and (b) 110 reflections with  $\text{Fe}'''$  content, and (c) of 310 with  $\text{Fe}''$  content (in atomic proportion). Full lines in (a) and (b) are regression lines graphically drawn from the present data. Dashed line in (a) is from COLEMAN and PAPIKE (1968). All author's data.

As the  $\text{Fe}^{III}$  ionic radius (0.64) is larger than the Al ionic radius (0.51), the  $\text{Fe}^{III}$  content is likely to affect the  $a_0$  and  $b_0$  cell parameters, and thus the  $hk0$  reflections. Out of these, the  $d$  values of the 310 and 110 reflections have been plotted against the  $\text{Fe}^{III}$  content in  $\text{Y}^{III}$  position (Fig. 8a and b): the  $2\theta^\circ$  values decrease, or  $d(\text{\AA})$  values increase with increasing  $\text{Fe}^{III}$ . The correlation is better with 310 than with 110.

The dashed line in Fig. 8a is the regression line of COLEMAN and PAPIKE (1968) for the Cazadero (California) sodic amphiboles. It lies somewhat beneath the regression line drawn from the Western Alps data (due to differences in operating conditions?). A correlation between the 310 reflection values and  $\text{Fe}^{II}$ -Mg in addition to  $\text{Fe}^{III}$ - $\text{Al}^{VI}$  substitutions, as suggested by the diagram of ERNST et al. (1970) – a plot in MIYASHIRO'S composition diagram, where the lines connecting equal 310 values are oblique, not parallel to the  $\text{Fe}^{II}/\text{R}^{II}$  ordinate – is not apparent from the present data: the 310 position is not significantly affected by the Mg- $\text{Fe}^{II}$  substitution (Fig. 8c), although the cell parameters are (see below). Thus the position of the 310 reflection with respect to measured standardized material, may be used as an  $\text{Fe}^{III}$  indicator, within error limits of about  $\pm 15\%$ .

#### CELL PARAMETERS

The values of the cell parameters are plotted against the  $\text{Fe}^{III}$  content in Fig. 9a, and against the  $\text{Fe}^{II}$  content in Fig. 9b, the regression lines proposed by BORG (1967), and by COLEMAN and PAPIKE (1968) being also shown.

There exists a correlation between  $\text{Fe}^{III}$  and  $a_0$  and  $b_0$ , especially for amphiboles plotting near the Gl-Rb line in Miyashiro's diagram: discrepancies occur for those amphiboles which, in this diagram, fit better with a  $\text{Fe}^{II}$ -Mg tie-line. This can be explained by the Fe-Mg substitution. Although the difference between the ionic radii of  $\text{Fe}^{II}$  (0.74) and of Mg (0.67) would suggest a positive correlation between  $\text{Fe}^{II}$  content and cell parameter values, the opposite appears on the diagrams. This could be interpreted through a polarization power control, as proposed by VON ENGELHARD (1942) for chlorite, and by GOWER (1955) for biotite: Fe would polarize the OH layer more intensely, and thus reduce the distance between apical O atoms.

The  $c_0$  parameter is related to  $\text{Fe}^{II}$ , not to  $\text{Fe}^{III}$  content.

As a product of these three parameters, the cell volume corresponds more closely to the  $\text{Fe}^{III}$  content.

The  $\beta$  angle varies only from  $103.36^\circ$  to  $103.82^\circ$ , and does not appear to be related to the composition (no diagram is presented).

ERNST (1963, 1968), and COLVILLE et al. (1966) emphasized the different cell parameters of both disordered and ordered forms, the former being the

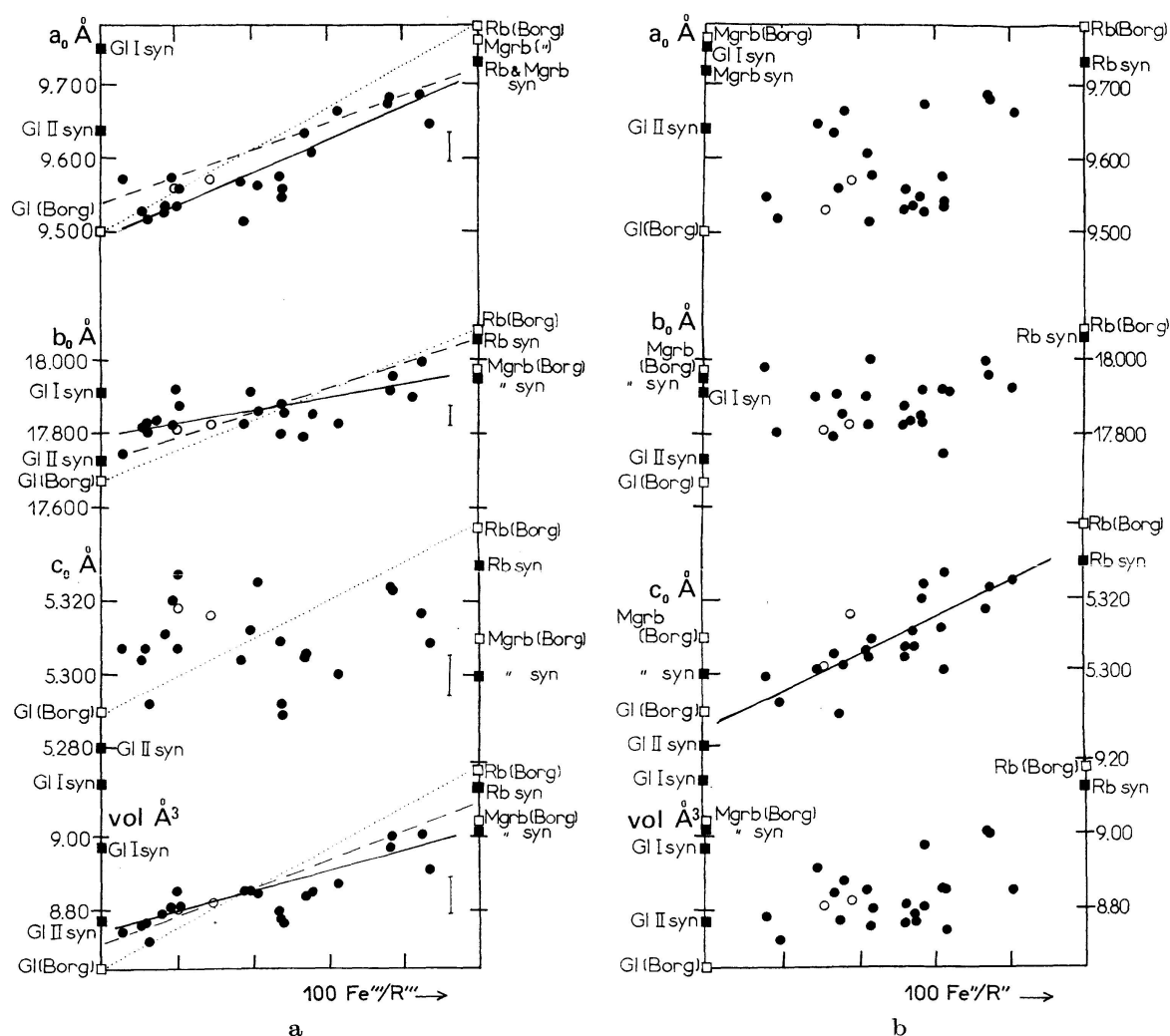


Fig. 9. Variation of cell parameters with (a)  $\text{Fe}'''$ , and (b)  $\text{Fe}''$  content (in atomic proportions). Full lines drawn from author's data. Dotted lines: BORG's (1967) regression lines. Dashed lines: COLEMAN and PAPIKE's (1968) regression lines. The error limit shown is the maximum computed standard deviation. Solid circles are author's data, open circles are literature data (CHATTERJEE 1971). Values of synthetic I and II polymorphs (solid squares), and BORG's end-members (open squares) are also plotted. Rb: riebeckite; Mgrb: magnesioriebeckite; Gl: glaucophane.

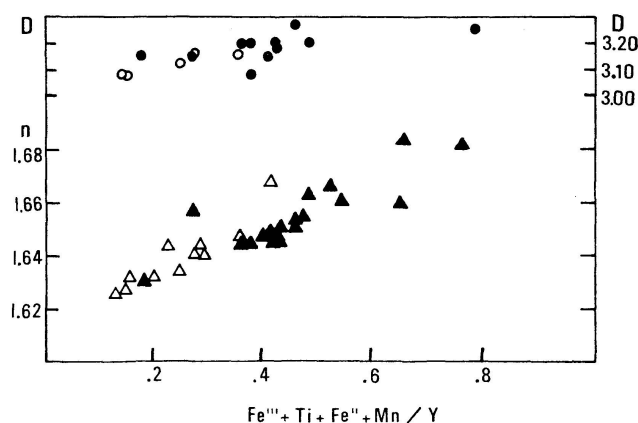
synthetic one. The structure of the ordered form is made of alternating (Mg, Fe) and (Al, Fe) octahedra (PAPIKE and CLARK 1968). Judging from their small cell parameters, all of the Western Alpine blue amphiboles belong to the ordered form.

#### OPTICAL CHARACTERS

Macroscopically, the bluish black to dark blue needles frequently occur as rosettes. Sometimes they are a few centimeters long in fibrous, crocidolite-like vein-fillings. The bigger crystals come from the eastern and northeastern part of the Western Alps.

The optical orientation, noted in Borg's classification as G (glaucophane), C (crossite), O (osannite), and R (riebeckite) is given in Table 2. Ferroglaucophane has a G-orientation, i. e. Z near the c axis. When its pleochroism is related to the a-b-c crystallographic axes instead of the X-Y-Z indicatrix' axes – as suggested by DE BÉTHUNE and JANS (1966) –, it appears to be similar to the pleochroism of glaucophane or of crossite. The change from G- to C-orientation seems to occur for about:  $40 < (\text{Fe}_{\text{total}} + \text{Ti} + \text{Mn}) : \text{total Y atoms} < 45$ .

Fig. 10. Refractive indices and density of blue amphiboles as a function of the iron-titanium-manganese content (in atomic proportions). Solid symbols refer to author's data, open symbols to literature data.



Refractive indices are of course those of the outer margin of the zoned grains, and this might explain the rather low values of some indices as compared with data from the literature. In Fig. 10 which shows a plot of the  $n_z$  and  $n_x$  values against the amount of total iron, titanium and manganese, with respect to total Y atoms, most points lie slightly below BORG'S curve (1967).

The 2 V values are not given, as the frequent zonation and fibrous habit too often prevented satisfactory measurements.

#### DENSITY

A few density values are given at the top of Fig. 10. They show the common increasing trend with the iron content.

#### CONCLUDING REMARKS

The chemistry of the Western Alpine sodic amphiboles is summarized as consisting of:

- glaucophane, with some crossite, in the Piemont meta-ophiolites (Mesozoic rocks);
- glaucophane, ferroglaucophane, and crossite in the quartz-, mica- and glaucophane-schists of the Piemont zone (Mesozoic rocks);

- ferroglaucophane and crossite in the mica- and glaucophane-schists of the Briançon basement (polymetamorphic rocks exhibiting relicts of a pre-Alpine, pre-Westphalian metamorphism, which escaped Alpine metamorphisms and deformations);
- crossite, magnesioriebeckite and riebeckite in Briançon carbonate rocks and in Piemont iron formations (Mesozoic rocks).

The rather common occurrence of ferroglaucophane is emphasized. In the Western Alps ferroglaucophane is associated with paraschists of pelitic composition, and with orthogneisses and schists, which are chemically gabbros and diorites (BOCQUET, in prep.). However, it is also reported to occur in other rock-types: in alkali basalt (HOFFMANN 1970), and in acid metavolcanics (BLACK 1970). Favourable host-rock composition seems to be Mg- and Fe<sup>3+</sup>-poor.

The chemical variations among blue amphiboles have been shown to be related to both iron content and oxidation state of the host-rock. However, as blue amphibole is the only iron-bearing mineral present in many host-rocks, one may ask whether the commonly assumed zoneographic control of blue amphibole Fe-Mg-Al content is concealed by this relationship. Being given no choice of Fe-Mg-Al ratios from the host-rock, the amphibole would only crystallize in those rocks whose bulk chemistry allows that definite amphibole composition which is stable under the other existing environmental conditions. Unfortunately, rock-types of constant bulk composition, which might allow detection of zoneographically controlled chemistry of sodic amphibole, are not common throughout the Western Alpine blueschists area. Moreover, the number of analyses from both blue amphiboles and host-rocks is still too limited.

General evidence toward such a zoneographic control is:

1. It has been advanced in other parts of the world: e. g. for Californian blueschists compared to Japanese blueschists, where it is supported by associated parageneses: jadeite-rich pyroxene in California, or diopsidic-acmitic pyroxene in Japan, etc. (ERNST and SEKI 1967, ERNST et al. 1970); in New Caledonia, where the blue amphibole chemistry varies from a lawsonite-free zone, through a lawsonite-bearing area, to an epidote zone (BLACK 1973).

2. ERNST's experimental work (1960, 1961, 1962, 1963, see also 1968) would support the assumption of glaucophane requiring higher temperature than do the iron-rich end-members, but his data strictly apply only to the synthetic, disordered forms, some of them also displaying optical characters apart from those of the natural minerals (synthetic riebeckite has a "crossite" optic orientation). In later works, ferroglaucophane stability relations have been studied (HOFFMANN 1972), and investigations on the lower breakdown relationships of a crossitic material initiated (BOCQUET and MOH 1972). The upper tempera-

ture limit was shown to be much lower for ferroglaucophane than for pure Mg-glaucophane (about 390° C for  $\text{Fe}_{70}\text{Gl}_{30}$  against 864° C for  $\text{Gl}_{100}$ ), the reactions being almost pressure-independent. However, the ferroglaucophane synthesized was a disordered form again, as the cell parameters are much larger than the natural ferroglaucophanes.

In the western Alpine blueschists area, a zoneographic gradient does exist between (a) the eclogites- and kyanite- (DAL PIAZ 1971 a) bearing Sesia zone, Zermatt-Saas zone and inner Penninic massifs, and (b) the westernmost parts, devoid of both eclogites and kyanite (but still jadeite-bearing).

1. In the Aosta valley two metamorphic areas have been distinguished in the Piemonte zone, which also coincide with paleogeographical and structural features (DAL PIAZ 1971 b, 1974 a and b, ELTER 1971, 1972, see also BORTOLAMI and DAL PIAZ 1970). The Zermatt-Saas zone (a denomination initially applied only to the Zermatt region, BEARTH 1967) is separated from the more westerly Combin zone: the former contains abundant ophiolites (serpentinites, metabasalts, and meta-pillows, regarded as original oceanic crust and lavas), associated with scarce micaschists; in the latter zone the "prasinities"<sup>1)</sup>-bearing calcschists are thought to have deposited on a sialic crust. Blue amphiboles and sodic pyroxenes are common in the Zermatt-Saas zone, scarce or absent in the Combin zone. The differences in the metamorphism have been related by DAL PIAZ et al. (1972) to unequal subduction depths attained by differentially moving units of a composite plate. According to them, the Combin zone remained on a superficial level, and was sheltered from the Eoalpine high pressure conditions.

2. The distinction between an inner and an outer Piemonte zone can be easily recognized as far southward as the Arc and Dora Riparia valleys.

3. Further to the south, the currently proposed subdivisions of the Piemonte zone (LEMOINE and MICHARD 1963, LEMOINE 1971, CARON 1971, MICHARD and SCHUMACHER 1973, CARON et al. 1973) are of a paleogeographical character only. Here the metamorphic conditions are no longer the same as in the north: lawsonite is wide-spread in the meta-ophiolites and associated paraschists. Moreover, the later greenschist facies left a much weaker mark than in the N and NE parts of the blueschist area. The scarcity of prasinities and ovardites in this region must also be mentioned. Here eclogites are only known in the easternmost part (Mte Viso). More evidence seems still needed to make long-distance paleogeographical and metamorphic correlations.

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<sup>1)</sup> Alpine word applying to amphibole-poecilite albite-epidote schists, mainly metatuffs and metadiabases; when chlorite appears instead of amphibole, it is called ovardite (NOVARESE 1895).

In fact, the available analyses of the Zermatt-Saas zone are of glaucophanes. For the Sesia zone, there is only one, somewhat questionable (from a morainic boulder), analysis (ZAMBONINI 1902): the analysis has not been quoted above, owing to Fe<sup>II</sup> and Fe<sup>III</sup> not being distinguished, but the Al and Mg contents are high enough for glaucophane. The term gastaldite, used in Italy, which refers to a very pale blue amphibole, points to a likely similar glaucophanitic composition for Italian specimens, i. e. those from the Sesia zone, the Aosta and Susa valleys, etc. (see MICHEL 1953; VITERBO-BASSANI and BLACKBURN 1968, and earlier descriptions of Italian occurrences).

In the lawsonite-bearing part of the Western Alps (BOCQUET 1971; SALIOT 1973), the chemistry of blue amphiboles varies from glaucophane to crossite. The difference has already been noticed by BEARTH (1967, p. 91). In this lawsonite area the temperature must not have reached values as high as in the zoisite-, kyanite-, and eclogite-bearing areas of the E and NE parts of the Western Alps. The transition from lawsonite ( $\pm$  quartz) to zoisite ( $\pm$  Al-silicate + pyrophyllite + H<sub>2</sub>O) has been experimentally determined at 360° C for 4 kb, to 410° C for 7 kb (NITSCH 1972). Estimates of the P-T conditions in the Zermatt region still seem to deserve improvement and better-established experimental foundation.

If there was actually a temperature gradient decreasing from the northeast toward the south, DE ROEVER'S (1972) contradictory re-interpretation of Ernst's data might be somehow modified: crossite, ferroglaucophane, and glaucophane all require high pressure in order to crystallize in the ordered forms, the only ones currently known in nature, but crossite (and ferroglaucophane) might be the relatively low temperature phases, whereas the iron-poorer glaucophane s. str. would appear in higher grade environment (but still under low geothermal gradient).

The most common zonation pattern of sodic amphiboles in the Western Alps consists of decreasing iron towards the crystal rims. This type of zonation has also been mentioned in other blueschists belts of the world, e. g. in Calabria by HOFFMANN (1970).

If, on the one hand, the step-like variations suggest late leaching or diffusion processes along cleavage planes, on the other hand the general bell- or bowl-shaped profiles could suggest control by evolving environmental conditions. The assumption of some leaching phenomenon would also be supported by the fact that alteration of blue amphibole crystals into chlorite + albite may occur selectively on some zones, leaving some of them unaltered.

#### *Acknowledgments*

I have benefited from stimulating discussions with some Alpine colleagues, particularly Prof. G. V. Dal Piaz of Turin, and Dr. J. C. Hunziker of Bern.

Best thanks are due to Mr. Morlevat and Mr. Roussignol, of the C.E.N. Grenoble, who

performed the microprobe profiles. I am also grateful to Miss Chion, of the Physics Institute of Grenoble University, and to Mr. Nuber, previously at the Mineralogisch-Petrographisches Institut in Heidelberg, for their kind assistance in the computing of the cell parameters. Mr. Girault, of the Grenoble Geological Institute, and Mr. Pirouz have kindly checked the form of this paper.

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Manuscript received November 6, 1973.