## Sodic Pyroxenes From Metabasites in the Eastern Mediterranean

## A.I. Okay

Department of Mineralogy and Petrology, Downing Place, Cambridge, Great Britain

Abstract. The compositions of sodic pyroxenes from blueschist metabasites in Northwest Turkey were investigated by electronprobe microanalysis. These are compared with sodic pyroxenes from high-grade blueschist terrains and eclogites with special reference to the island of Syros in Greece. Pyroxenes from lawsonite zone metabasites in Northwest Turkey are chloromelanites, aegerine augites and aegerine jadeites with the acmite contents ranging from 65% down to 30%. Epidote-garnet bearing high-grade blueschist metabasites of Syros on the other hand contain omphacite with the acmite content less than 30%. All the analyzed sodic pyroxenes from eclogites and high-grade blueschists in the literature are also omphacites with low acmite contents. It is argued that the acmite content of the sodic pyroxene decreases with rising temperature of metamorphism. This is almost entirely related to the appearance of epidote as an additional ferric ion bearing phase with an increase in temperature.

#### Introduction

Sodic pyroxenes are common minerals in the basic rocks of the blueschist facies and related eclogites. Their compositions fall within the ternary field of acmite-jadeite-augite.

A considerable amount of new data on sodic pyroxene compositions from blueschists and eclogites has become available in the last ten years. Each batch of new data has narrowed the "miscibility gaps", based on the apparent absence of sodic pyroxene compositions over certain regions in the sodic pyroxene ternary field (Dobretsov, 1962; Coleman and Clark, 1968), so that now almost the whole of the acmitejadeite-augite field is filled. The electron microprobe analyses presented here demonstrate the widely variable compositions of sodic pyroxenes. A new attempt is made to relate the composition of sodic pyroxene to the extensive, e.g., rock composition, and intensive variables, e.g., pressure and temperature, of metamorphism.

#### **Geological Environment**

In Northwest Turkey blueschists form a coherent, discontinuous belt of about 20 km in width and 300 km in length. They flank the margins of large ultramafic massifs in the Izmir-Ankara ophiolite zone (Brinkman, 1976). The rock types are dominantly metabasites and metacherts. The eastern part of the blueschist belt in the region of Mihallicik was studied by Cogulu (1967) who distinguished three metamorphic zones – lawsonite – albite, lawsonite – crossite, epidote – crossite – with an increase in grade northwards. The epidote zone truncates westwards. The studied areas, all entirely in the lawsonite zone, lie in the central portion of the blueschist belt in the districts of Tavsanli (area 1 in Fig. 1) and Gumele (area 2 in Fig. 1). In both areas metamorphism occurred during a single event and retrogressive readjustment has been minor. Plurifacial metamorphism, which complicates the interpretation of mineral assemblages in the Alps, is absent.

#### Method

Sodic pyroxene compositions were determined for twelve elements (Na, Ca, K, Fe, Mg, Mn, V, Ni, Cr, Ti, Al, Si) using an electronprobe microanalyzer with a Harwell Si(Li) detector and pulse processor (Statham, 1976). The correction procedures are given by Sweatman and Long (1969). Olivine and jadeite standards were used throughout.

The analyses were recalculated to a four cation formula unit. As there is no substitution of silicon by tetrahedral aluminium, the jadeite component equals to the aluminium in the formula unit. Acmite component was calculated assuming Ac = ferric ion = (Na-Al) in the formula unit. The remainder of the cations were included in the augite component. Transition elements such as Ti, Mn, Cr occur in amounts less than 0.01 of the formula unit, so that jadeite, acmite, diopside and hedenbergite components make up 98% or more of the sodic pyroxene.



# Mineral Assemblage and the Composition of the Sodic Pyroxene

#### Blueschist Metabasites From Northwest Turkey

This group comprises thoroughly recrystallized, often foliated, lawsonite bearing blueschist metabasites corresponding both in mineralogy and texture to "Type III" blueschists from California (Coleman and Lee, 1963).

The mineral assemblage in the metabasites is "sodic amphibole (often crossite or glaucophane) + lawsonite  $\pm$  sodic pyroxene  $\pm$  chlorite  $\pm$  quartz + phengite + sphene". Sodic pyroxene is a common part of the metabasic mineral assemblage in Northwest Turkey making up approximately 5 to 25 modal percent of the rock. Out of 86 thin sections of the metabasites examined 50 contained sodic pyroxene that usually occurred as small subhedral grains, occasionally showing a reaction relationship to sodic amphiboles.

Sodic pyroxene is, along with the lawsonite, one of the first metamorphic minerals to form in Northwest Turkish metabasites. As observed in the less well recrystallized parts of the blueschist terrain in Northwest Turkey, initially spilitic dolerites are transformed to an assemblage of lawsonite, chlorite, acmitic sodic pyroxene and quartz with incipient crossite. At this stage the original igneous texture is still intact with plagioclase pseudomorphed by an assemblage of lawsonite, quartz and chlorite while augite is largely replaced by an acmite rich sodic pyroxene. With further recrystallization crossite forms at the expense of sodic pyroxene, quartz and chlorite and the rock loses its ghost texture with the development of a distinct schistosity.

Sodic pyroxenes from ten blueschist metabasites were analyzed by electron-microprobe and plotted on the jadeite-acmite-augite ternary diagram in Fig. 2. Specimens with numbers starting with 93 come from major ophiolite occurrences (black) and blueschist outcrops in Northwest Turkey (ruled). The ophiolite outcrops in Western Turkey after Bingol (1976)

Fig. 1. Map of Aegean and surrounding areas showing

the area Gumele (area 2 in Fig. 1). Blueschists from Gumele were studied, especially with regard to their whole rock geochemistry, by Lunel (1967). The remainder of the specimens with prefixed K come from the district north of Tavsanli (area 1 in Fig. 1). All the analyzed rocks contain the assemblage "lawsonite+crossite+phengite+sphene". Additionally specimens K47, K75, K54, K29, 93163 contain primary chlorite, K47, K54 and 93180 contain quartz and K33, K29, K114 contain calcite. However these latter minerals occur in very small quantities, crossite, lawsonite, and sodic pyroxene making up 90% or more of the metabasites.

Compositions plotted in Fig. 2 demonstrate that sodic pyroxenes with similar parageneses show a wide range of compositions both within and between different metabasites. Zoning in sodic pyroxenes, like most other minerals with variable compositions from blueschist, is very common. The sodic pyroxenes from Northwest Turkey using the terminology adopted for sodic pyroxenes by Essene and Fyfe (1967), plot in the fields of chloromelanite, aegerine augite and aegerine jadeite with the acmite contents ranging from 65% down to 30%. Compositions of sodic pyroxenes are apparently rather rare in this range, such that a miscibility gap was proposed (Dobretsov, 1962; Coleman and Clark, 1968), which the new analyses fill at least in the ferric-rich portion.

## High-Grade Blueschist Metabasites From Other Terrains

This group includes thoroughly recrystallized epidotegarnet bearing blueschist metabasites and eclogites. The mineral assemblage is "glaucophane+epidote +sodic pyroxene+garnet+white mica $\pm$ quartz+rutile". They grade into eclogites with the dominance of sodic pyroxene and garnet in the mineral paragen-



Fig. 2. Compositions of sodic pyroxenes from lawsonite-bearing metabasites, Northwest Turkey



Fig. 3. Compositions of sodic pyroxenes from epidote-garnet bearing high-grade blueschists, Syros

esis. These differ from the blueschist metabasites of Northwest Turkey in the coarser grain size, the replacement of lawsonite and sphene by epidote and rutile respectively and the occurrence of almandine garnet. The eclogitic exotic blocks from the Franciscan terrain in California, Type IV of Coleman and Lee (1963), are a good example for these types of rocks.

The blueschists from the island of Syros in the Aegean provide another good example of high grade blueschists. They were studied in detail by Dixon (1967). The island consists of an alternating sequence of pelitic blueschists and marbles with rare intercalations of metabasic gneisses, metagabbros and serpentinite (Dixon, 1976). The sodic pyroxene analyses have been performed on the metagabbros and gneisses. These sodic pyroxenes are currently under study for their microstructure (Carpenter, 1978).

Sodic pyroxenes from four metabasic rocks from Syros are shown in the acmite-jadeite-augite ternary diagram in Fig. 3. All four rocks have the mineral assemblage "glaucophane+epidote+sodic pyroxene-+garnet+white mica+quartz" and all except 97506 contain rutile. Specimen 97542 also contains some actinolite. The jadeite rich pyroxenes from specimens with numbers 97503 and 97667 have recrystallized in plagioclase rich portions of the original coarse grained protolith (Dixon, 1968). They represent an unusually aluminous environment for a metabasic rock.

Sodic pyroxenes from analyzed Syros metabasites fall largely in the omphacite field with the acmite contents ranging from 30% down to 2%. Omphacitic pyroxenes of these compositions are characteristic of eclogites and high-grade blueschists.

## Discussion

Sodic pyroxenes from both terrains show a wide range of compositions within a relatively uniform bulk rock chemistry. In the metabasites the absence of albite is reflected in the highly variable jadeite contents of pyroxenes, even within a single rock, preventing any geobarometric deductions. Although the jadeite contents of pyroxenes from metabasites in Syros and Northwest Turkey are similar the pressure has been considerably higher in Syros as indicated by the presence of jadeite+quartz assemblages in rocks of appropriate chemistry (Dixon, 1976).

However there is a distinct difference in the acmite contents of the sodic pyroxenes between lawsonitebearing metabasites from Northwest Turkey and other high-grade epidote-garnet bearing blueschists and eclogites, including those from Syros. Such a difference between lawsonite-zone metabasites on the one hand and epidote-zone metabasites on the other hand seems to be a general case (see Fig. 4). This difference must lie in the intensive variables of metamorphism, e.g., pressure and temperature, as the bulk rock chemistry is approximately the same in both cases. Both oxygen isotope studies (Black, 1974; Tay10

lor and Coleman, 1968) and experimental work on the stability of lawsonite (Nitsch, 1974) show that epidote-garnet-rutile bearing blueschists have recrystallized at considerably higher temperatures ( $380^\circ$ - $550^\circ$ C) than lawsonite-sphene bearing blueschists ( $270^\circ$ -400°C). The lawsonite/epidote transformation, being a dehydration reaction, has a steep slope on the *P*-*T* diagram, making it a good geothermometer.

The effect of pressure on sodic pyroxene compositions in metabasalts is more difficult to assess. The absence of primary albite and the presence of jadeite-+ quartz assemblages in Syros (Dixon, 1968) indicate considerably higher pressures (12 to 15 kbar) for blueschists from Syros than those from epidote zone blueschists in New Caledonia, which show a very similar mineral paragenesis with the exception of the stability of albite (Brothers, 1974), indicating lower pressures of recrystallization. However the range of observed acmite content in the epidote-zone sodic pyroxenes from the blueschist metabasites in New Caledonia is nearly the same as those from Syros, 30% down to 5% (Black, 1974), suggesting that temperature has the dominant effect on the acmite content of the sodic pyroxene.

This trend of decreasing acmite content in the sodic pyroxene with rising temperature may be related either to the formation of an additional ferric bearing phase or to reduction during the progressive metamorphism. Omphacitic pyroxene is not thought to be inherently unstable in the lawsonite-zone conditions as indicated by its presence in some partially recrystallized basic rocks (Carpenter and Okay, in prep.).

Blueschist metabasites generally do not contain any iron oxides, as ferric ion has alternative sites in the sodic amphiboles and sodic pyroxenes. Therefore the major ferric iron bearing minerals in lawsonite-zone blueschists are sodic pyroxenes and sodic amphiboles. In the epidote-zone blueschists, epidote itself is an additional  $Fe^{3+}$  bearing phase. Thus the formation of epidote in the temperature interval of 355–400 C would be expected to affect the ferric iron contents of the associated sodic pyroxene and sodic amphibole.

Lawsonite and ferric iron rich epidote are expected to coexist over a certain range of temperature and pressure. Sodic pyroxenes coexisting stably with lawsonite and ferric iron rich epidote should have an acmite content of around 30% and plot in the acmitejadeite-augite ternary diagram in the intermediate region between lawsonite and epidote zone metabasic pyroxenes (Fig. 4). Unfortunately the scarcity of pyroxene analyses over such transitional terrains prohibits the testing of this hypothesis. A.I. Okay: Sodic Pyroxenes From Metabasites in Turkey



Fig. 4. Compositions of metamorphic sodic pyroxenes; filled triangles: Pyroxenes from iron-rich metasediments and metacherts; filled circles: pyroxenes from lawsonite bearing metabasites; open circles: pyroxenes from epidote-garnet bearing blueschist metabasites and eclogites, open triangles: pyroxenes from aluminuous blueschists; filled squares: pyroxenes from metagreywackes (this paper, Muir Wood (1977); Ernst (1976), Black (1974); Abraham et al. (1974); Kerrick and Cotton (1971); Ernst et al. (1978); Onuki and Ernst (1969)

It is known that the epidote compositional field extends towards lower ferric contents with rising temperature during progressive metamorphism (Miyashiro and Seki, 1958), such that epidotes from eclogites usually have low pistacite components. This implies a certain amount of reduction during metamorphism, leading to the highly reduced two phase-almandineomphacite-eclogite. Such a progressive reduction with increasing grade has been observed in some high pressure metamorphic terrains, e.g., in Hohe Tauern window (Abraham et al., 1974).

Although reduction may be of importance in highgrade blueschists and eclogites, the regular and sharp break in sodic pyroxene compositions between two types of metabasalts, indicate that the temperature related lawsonite/epidote transformation is mainly responsible for the observed difference between lawsonite and epidote-garnet bearing metabasites.

## Compositional Range of Sodic Pyroxenes From Blueschists

Sodic pyroxene analyses from blueschists and related eclogites are shown in acmite-jadeite-augite ternary diagram in Fig. 4. The range of sodic pyroxene compositions for different major rock types, iron-rich rocks, metabasalts and metagreywackes, are also indicated.

#### A.I. Okay: Sodic Pyroxenes From Metabasites in Turkey

Acmite and aegerine have a very wide pressuretemperature stability field. They are found in iron-rich rocks and metacherts from both lawsonite and epidote zone blueschists in Northwest Turkey, California and other blueschist terrains. The occurrence of aegerine in igneous rocks is a further testimony of its large P-T stability field. Most of the analyses of sodic pyroxenes from iron-rich rocks come from Muir-Wood (1977) who also reports Mn as a major component in some of the aergerines.

Metabasites on account of their calcium and ferromagnesium rich character do not contain any jadeite or jadeite-rich pyroxenes either in lawsonite or epidote zones. However lawsonite is stably associated with jadeite rich pyroxenes in some metagreywackes from the Franciscan terrain in California (Ernst et al., 1970). The occurrence of jadeite in appropriate bulk rock compositions depends on the prevailing pressure of metamorphism.

There is an apparent lack of sodic pyroxene compositions in a small region between jadeite and omphacite. A much larger area extending towards more ferric-rich compositions and including this region was interpreted by several workers as a miscibility gap in the sodic pyroxene system (Dobretsov, 1962; Coleman and Clark, 1968). However from the extensive range of compositions plotted in Fig. 4, it is likely that the apparent lack of sodic pyroxene compositions in this region is due to the absence of suitable rock compositions. Immiscibility, as demonstrated in exsolution, in such low temperature minerals as sodic pyroxenes, is likely to be on a submicroscopic scale. As a result, microprobe analyses should not be expected to reveal the limits of immiscibility in the sodic pyroxene ternary system.

Acknowledgements. This work was carried out while in receipt of a grant from the Mineral Research and Exploration Institute of Turkey (MTA) which is gratefully acknowledged. The analyses of sodic pyroxenes from the high-grade blueschists of Syros and from iron rich metasediments were kindly provided by M.A. Carpenter and R. Muir Wood respectively. I thank R. Muir Wood, M.A. Carpenter, and S.O. Agrell for critical comments on this paper.

#### References

- Abraham, K., Hormann, P.K., Raith, M.: Progressive metamorphism of basic rocks from the southern Hohe Tauern area, Tyrol (Austria). N. Jb. Abh. **122**, 1–35 (1974)
- Bingol, E.: Evolution geotectonique de l'Anatolie de l'Ouest. Bull. Soc. Geol. France. Ser. 7, 18, 431-450 (1976)

- Black, P.M.: Mineralogy of New Caledonian metamorphic rocks III. Pyroxenes. Contrib. Mineral. Petrol. 45, 281–288 (1974)
- Black, P.M.: Oxygen isotope study of metamorphic rocks from the Ouegoa district, New Caledonia. Contrib. Mineral. Petrol. 47, 197-206 (1974b)
- Brinkman, R.: Geology of Turkey. Amsterdam: Elsevier Pub. Company. 158 (1976)
- Brothers, R.N.: High-pressure schists in northern New Caledonia. Contrib. Mineral. Petrol. 46, 109-127 (1974)
- Carpenter, M.: Kinetic control of ordering and exsolution in omphacite. Contrib. Mineral. Petrol (1978, in press)
- Cogulu, E.: Etude petrographique de la region de Mihalliccik (Turquie). Schweiz. Mineral. Petrogr. Mitt. 47, 683-824 (1967)
- Coleman, R.G., Clark, J.R.: Pyroxenes in the blueschist facies of California. Am. J. Sci. 266, 43-59 (1968)
- Coleman, R.G., Lee, D.E.: Glaucophane-bearing metamorphic rock types of the Cazadero area, California. J. Petrol. 4, 260–301 (1963)
- Dixon, J.E.: Glaucophane schists of Syros, Greece (abstract). Bull. Soc. Geol. France. Ser. 18, 280 (1976)
- Dixon, J.E.: The metamorphic rocks of Syros, Greece. Ph.D. Thesis (unpublished), University of Cambridge (1968)
- Dobretsov, N.L.: Miscibility limits and mean compositions of jadeite pyroxenes. Dokl. Akad. Nauk. SSSR 146, 118-120 (1962)
- Ernst, W.G.: Mineral chemistry of eclogites and related rocks from the Voltri group, Western Liguria, Italy. Schweiz. Mineral. Petrogr. Mitt. **56**, 293–343 (1976)
- Ernst, W.G., Seki, Y., Onuki, H., Gilbert, M.C.: Comparative study of low-grade metamorphism in the California Coast Ranges and the outer metamorphic belt of Japan. Geol. Soc. Am. Mem. 70, 259 (1970)
- Essene, E.J., Fyfe, W.S.: Omphacite in Californian metamorphic rocks. Contrib. Mineral. Petrol. 15, 1-23 (1967)
- Kerrick, D.M., Cotton, W.R.: Stability relations of jadeite pyroxene in Franciscan metagreywackes near San Jose, California. Am. J. Sci. 271, 350–369 (1971)
- Lunel, T.: Geology of Subren-Karaalan area, Eskisehir (Turkey). Ph.D. Thesis (unpublished), University of Bristol (1967)
- Miyashiro, A., Seki, Y.: Enlargement of the composition field of epidote and piemontite with rising temperature. Am. J. Sci. 256, 423-430 (1958)
- Muir Wood, R.: Iron rich sediments in blueschist facies metamorphism. Ph.D. Thesis, University of Cambridge (unpublished) (1977)
- Nitsch, K.H.: Das P-T- $X_{CO_2}$  Stabilitätsfeld von Lawsonit. Contrib. Mineral. Petrol. **34**, 116–134 (1972)
- Onuki, H., Ernst, W.G.: Coexisting sodic amphiboles and sodic pyroxenes from blueschist facies metamorphic rocks. Mineral. Soc. Am. Spec. Paper 2, 241–250 (1969)
- Statham, P.J.: A comparative study of techniques for quantitative analysis of the X-ray spectra obtained with a Si(Li) detector. X-ray Spectrom. 5, 16–28 (1976)
- Sweatman, R.R., Long, J.V.P.: Quantitative electron probe microanalysis of rock forming minerals. J. Petrol. 10, 332–379 (1969)
- Taylor, H.P., Coleman, R.G.: O<sup>18</sup>/O<sup>16</sup> ratios of coexisting minerals in glaucophane-bearing metamorphic rocks. Geol. Soc. Am. Bull. 79, 1727–1756 (1968)

Accepted October 12, 1978