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Ferroglaucophane and chloritoid-bearing metapelites from the phyllite series, southern Peloponnese, Greece

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SUMMARY. The unusual assemblage ferroglaucophane-chloritoid-paragonite-garnet-muscovite-chlorite-quartz has been found in metapelites of the phyllite series, north-east of Neapolis, southern Peloponnese, Greece. The chemical compositions of the coexisting phases are given, and the physical and chemical constraints which may control the appearance of this assemblage are briefly discussed.

THE mineral association chloritoid-glaucophane is very rare and, to the author's knowledge, it has been only reported by Lasaulx (1883), Velde (1967), and Makanjuola and Howie (1972) from Île de Groix, Roever and Nijhuis (1964) from Spain, Tshcopp (1923) from the Val de Bagnes, Ktenas (1907) from the Kyclades islands, Aegean Sea, Greece, and by Bearth (1963, 1967) from Switzerland.

The rock described here has been collected in the course of the study of the metamorphic rocks of the phyllite series in the southernmost part of Lakonia, Peloponnese, Greece. The occurrence of glaucophane in the phyllite series of Peloponnese has been also reported by Paraskevopoulos (1950), Richter and Thorbecke (in Jacobshagen *et al.*, 1976), and by Thiébault (1976). The present sample has been found north-east of Neapolis town at an altitude of 560 m and at 23° 05′ 20″ east longitude and 36° 32′ 05″ north latitude. Numerous other samples with various glaucophane assemblages have been collected from the roadcuts between Faraclo and Kastania villages.

The phyllite series in this part of its exposure consists mainly of strongly foliated mica schists and muscovite-bearing quartzites. Fossils in the metasediments from other parts of the series indicate Carboniferous and Permian age of deposition (Paraskevopoulos, 1964; Fytrolakis, 1971; Lys and Thiébault, 1971). The age of metamorphism of the phyllite series is disputed. Paraskevopoulos (1964) and Thiébault (1975) ascribe an Alpine age; however, sedimentary contacts found in some places and differences in deformation and metamorphic grade observed between various elements of the series (e.g. Ktenas, 1924, 1926; Richter, 1975; Panagos *et al.*, 1979) suggest that the phyllite series is not uniform but consists of parts metamorphosed during Hercynian and/or Alpine events.

Petrography

The major mineral constituents of the rock described here, besides chloritoid and glaucophane, are quartz, muscovite, and chlorite. Paragonite and garnet occur in lesser amounts and fine-grained graphite is dispersed in the rock, sometimes forming trains of inclusions, particularly in the white micas. White micas and chlorite are usually interleaved defining the foliation. Quartz occurs in small crystals forming microscopic layers parallel to the foliation. Glaucophane shows faint pleochroic colours and commonly occurs in the form of slender prisms. Chloritoid occurs in porphyroblasts showing twinning and, very frequently, bow-tie structure.

Specimens collected from outcrops adjoining the one of sample L224 may contain the following assemblages besides quartz, chlorite, and muscovite which are always present.

paragonite-glaucophane
paragonite-chloritoid
glaucophane-chloritoid
paragonite-chloritoid-albite
paragonite-chloritoid-glaucophane ± albite
paragonite-garnet
glaucophane-garnet

At least two episodes of crystallization and deformation seem likely for the studied samples. An early foliation S_1 is visible rarely and its trend is defined by the outlines of multi-crystal pseudomorphs of chlorite after biotite which are wrapped

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around by S_2. The S_2 foliation is apparently outlined by interleaved, coarse muscovite-paragonite-chlorite flakes but also by chloritoid and glaucophane prismatic crystals participating in the formation of asymmetrical microfolds. Most of the sheet silicate minerals seem to be syntectonic to F_2; however, some of these minerals may in fact be post-tectonic to F_2 but grown mimetically along the pre-existing S_2 foliation. This is supported by the fact that some crystals with idiomorphic outlines seem to have formed by partial replacement of pre-oriented glaucophane and chloritoid porphyroblasts which are now seen to be too highly corroded. Garnet, in the examined specimen, is present in rare small idiomorphic crystals which cut the S_2 foliation; it is therefore considered to be post-tectonic with respect to F_2. A third minor tectonic phase produces a strain slip cleavage S_3 but no crystal growth has been observed.

Mineral chemistry

Analyses of minerals were performed at the Department of Geology, University of Manchester, using a Link Systems energy-dispersive analyser attached to a Cambridge Geoscan microprobe. Several crystals of each mineral have been analysed and on each crystal analyses of at least three spots have been performed. Representative analyses of minerals coexisting in sample L224 are given in Table I.

Ferroglaucophane. Analyses of several spots reveal that the sodic amphiboles are very homogeneous. The analysis given in Table I has been recalculated on the basis of 23(O) assuming all the Fe as FeO. This is justified, however, because the M_2 position is nearly filled by Al, and there is no substitution of Si^{4+} by Al^{3+} since Z is filled by Si. Thus Fe^{3+} is present in minor amounts only. The substitution between Na^+ and Ca^+ in M_4 is also negligible and only the $Mg \rightleftharpoons Fe^{2+}$ substitution in the M_3 site is extensive leading to ferroglaucophane composition.

Chloritoid. Apart from its characteristic high Al_2O_3 and FeO contents, chloritoid was found to contain low amounts of MgO and MnO. The analysis has been recalculated on the basis of 12(O) to the structural formula $X_2YAl_3O_2(SiO_4)_2(OH)_4$.

TABLE I. *Representative electron-microprobe analyses of coexisting phases in sample L224*

	Ferro-glaucophane	Chloritoid	Chlorite	Muscovite	Paragonite	Garnet Core	Garnet Rim
SiO_2	57.39	24.12	25.46	50.10	47.15	38.03	38.06
TiO_2	—	—	—	—	—	—	—
Al_2O_3	11.44	40.73	20.34	27.95	37.72	21.19	21.43
FeO^+	15.24	25.16	29.87	3.34	0.40	23.84	26.45
MnO	—	0.24	0.25	—	—	9.06	5.22
MgO	6.25	1.91	11.92	2.54	0.21	0.38	0.55
CaO	0.35	—	—	0.18	—	8.06	8.91
Na_2O	7.14	—	—	0.51	7.19	—	—
K_2O	—	—	—	9.98	0.76	—	—
Total	97.81	92.16	87.84	94.86	94.43	100.62	100.63
	23(O)	12(O)	28(O)	22(O)	22(O)	12(O)	
Si	8.03	2.01	5.49	6.74	6.13	3.03	3.02
Al	—	3.0	2.51	1.26	1.87	—	—
Al	1.89	0.99	2.66	3.17	3.91	1.99	2.01
Ti	—	—	—	0.03	—	—	—
Fe^{+2}	1.78	1.75	5.39	0.37	0.04	1.59	1.76
Mn	—	0.01	0.05	—	—	0.61	0.35
Mg	1.30	0.24	3.83	0.51	0.04	0.05	0.06
Na	1.94	—	—	0.13	1.81	—	—
K	—	—	—	1.71	0.13	—	—
Ca	0.05	—	—	0.02	—	0.69	0.76
					Pyrope	1.70	2.05
					Almandine	54.08	60.07
					Spessartine	20.75	11.95
					Grossular	23.47	25.93

The tetrahedral site is occupied by Si; three Al atoms are in the corundum type octahedral sites, whereas the excess Al and Fe, Mg and Mn, with a sum very close to the ideal 3, occupy the brucite-type octahedral site.

Chlorite. The most important cations in this mineral are the pair Fe^{2+} and Mg. With Fe prevailing over Mg, these cations occupy more than nine out of twelve octahedral sites. The tetrahedral substitution by Al is lower than that of octahedral, it is therefore suggested that Fe in the ferric state may not be present in this mineral. According to its $Fe^{2+}/(Fe^{2+}+Mg)$ ratio and tetrahedral Si-Al^{IV} content, the present chlorite is a ripidolite.

Muscovite. The muscovite is highly celadonitic. Its Si content (6.74) is well above the ideal six per structural formula. The replacement of Al^{3+} by Si^{4+} in the tetrahedral site is compensated by concomitant replacement of Al^{3+} by Fe^{2+} and Mg^{2+} in octahedral sites to balance the charges. The total octahedral occupancy, however, (4.08) shows no tendency for a miscibility towards trioctahedral micas. The paragonite and margarite solid solution in muscovite is 7 mol% and 1 mol% respectively.

Paragonite. Paragonite is nearly pure and the only solid solution observed is towards muscovite. Margarite solid solution has not been detected and the celadonite component is almost negligible.

Garnet. Garnets are compositionally zoned and consist predominantly of almandine, spessartine, and grossular components. Core and rim compositions are given in Table I. The cores of all garnets are enriched in Mn relative to Fe and the rims are enriched in Fe and depleted in Mn. The grossular and pyrope components seem also to increase slightly towards the rims. The andradite component, judging from the amount of Fe required to fill the *Y*-position ($Al^{VI}+Fe^{3+}=2$), is negligible in the core and absent from the rim.

Bulk rock composition—discussion

XRF major-element analysis of the examined sample, computed on volatile-free basis, is given in Table II, together with the average composition of shales from geosynclines given by Wedepohl (1969), recalculated also to a volatile-free basis. The bulk-chemical composition of the sample shows some important deviations from the average shales of geosynclines; CaO and MgO are distinctly lower, whereas Na_2O is considerably higher compared with the average shale composition. The Fe^{2+}/Fe^{3+} has not been determined; however, it is considered to be much higher than that of the average shale since the analyses of the minerals presented in Table I show that Fe^{2+} is the dominant Fe cation in their structures. Furthermore, the opaque minerals are represented by small pyrite blebs and only occasional secondary hematite, occurring as alteration product, has been observed.

As can be seen from the rock analysis its bulk composition is not particularly unusual. Even if all the Fe is expressed as FeO, its chemistry possesses the compositional restrictions for the appearance of chloritoid set up by Hoschek (1969) and plot into the appropriate fields of all the three triangular diagrams used by the above author for chloritoid-bearing metapelites. The appearance of ferroglaucophane may be related to the higher than the average Na_2O content of the rock but also to a high FeO/Fe_2O_3 ratio. (cf. Hoffman, 1972).

To illustrate reaction relationships in the rock described here, as well as many of the observed assemblages, a composition-paragenesis diagram analogous to the Thompson AFM diagram may be constructed. If the rock is regarded as composed of six components (SiO_2, Al_2O_3, MgO, FeO, Na_2O, and H_2O), a projection from paragonite enables representation of assemblages that also contain paragonite + quartz + H_2O. A representation of the compositions of minerals present in the studied rock on the plane Al_2O_3-FeO-MgO of the tetrahedron Al_2O_3-MgO-FeO-Na_2O is given in fig. 1. It is evident from this figure that the chlorite-garnet tie line is incompatible with the chloritoid-ferroglaucophane tie line, suggesting that the sample L224 was possibly formed close to the reaction:

$$\text{quartz}+\text{paragonite}+\text{garnet}+\text{chlorite} = \text{chloritoid}+\text{ferroglaucophane}+H_2O$$

TABLE II. *Bulk rock composition*

	L224	Average shale*
SiO_2	65.20	63.24
Al_2O_3	18.33	17.93
Fe_2O_3	7.03*	3.01
FeO		3.97
MgO	2.01	2.79
CaO	0.44	2.36
Na_2O	2.21	1.72
K_2O	3.82	3.87
TiO_2	0.86	0.84
MnO	0.08	0.10
P_2O_5	0.18	0.17
Total	100.16	100.00

* Wedepohl, 1969.

Textural relationships between the phases suggest that the left side of the reaction is growing at the expense of the right. In the area of Zermatt, Bearth (1967) has shown that a similar reaction

chlorite + paragonite + quartz = chloritoid + glaucophane + H_2O

has also proceeded to the left (cf. Hoschek, 1969).

According to Hoschek (1969) the stability region of chloritoid + glaucophane corresponds to the glaucophanitic-greenschist facies. Some evidence on the conditions prevailed during the metamorphism of the rock described here is presented below.

The muscovite-paragonite solvus geothermometer (Eugster *et al.*, 1972) when applied to the coexisting muscovite-paragonite pair of the present sample, indicates minimum temperatures of about 350 and 510 °C from the muscovite and paragonite limb respectively. The occurrence of ferroglaucophane and of the paragenesis paragonite + quartz provide further evidence on the possible conditions of metamorphism. The upper temperature limit of ferroglaucophane in the pressure range 3–5 kb and at relatively low oxygen fugacities is about 360 ± 10 °C (Hoffman, 1972). The lower stability of the assemblage paragonite + quartz (determined by Chatterjee, 1973) is 335–315 °C at 2 to 7 kb. Thus a rather narrow range of possible temperature conditions is indicated. Pressure conditions, however, are uncertain. Hoffman's experiments demonstrate with a reversible reaction that the natural ferroglaucophane is stable at about 3 kb/350 °C; the determined stability curve, however, is extremely steep in the pressure-temperature field.

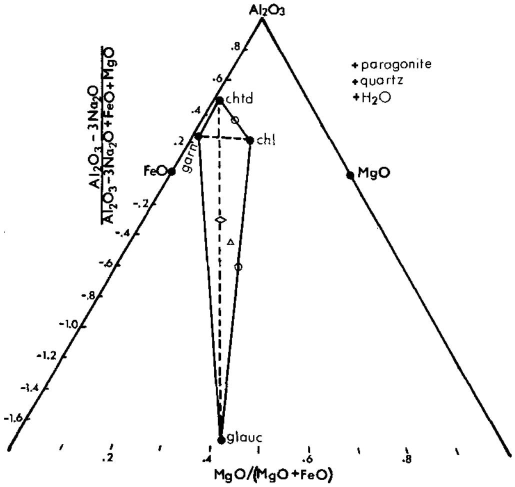

FIG. 1. Representation of the compositions of coexisting minerals in sample L224 on the plane Al_2O_3–FeO–MgO of the tetrahedron Al_2O_3–MgO–FeO–Na_2O, using paragonite as projection point. Open symbols indicate observed assemblages; rhomb denotes the assemblage garnet chlorite-ferroglaucophane; and triangle the assemblage chloritoid-chlorite-ferroglaucophane.

It is evident from the above discussion that more data are needed before we are able to define the physical and chemical constraints controlling the appearance of this unusual assemblage and its connection to the other mineral associations observed in this area. It is hoped that work now in progress will elucidate some of these problems.

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