Early-alpine ore parageneses in the serpentinites from the Balangero asbestos mine and Lanzo Massif (Internal Western Alps)

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ABSTRACT. — The ultramafites of the Balangero body and the adjacent Lanzo massif (Internal Piedmontese Zone) have been partly re-equilibrated by the early-alpine high pressure-low temperature metamorphism into serpentinites containing antigorite + diopside + olivine + Ti-clinohumite + magnetite ± Mg-chlorite. The petrological data, mainly derived from the parageneses of the associated metabasites, point to a temparature of 500-550°C and a minimum pressure of 15 kb for the early-alpine event.

The ore parageneses, mainly formed of the association of Ni and/or Fe sulphides + native metals (Ni-Fe and Fe-Co alloys) + magnetite, are clearly linked with the serpentinization process and mostly stable with the early-alpine silicate associations. Particularly, the association taenite ($\sim Ni_2Fe$) - awaruite (Ni_3Fe) - wairauite ($\sim Fe_3Co_2$) - troilite (FeS) - magnetite (for T = 550°C and P = 15 kb) is accompanied by fO_2 values 4-5 log units below the FMQ buffer, with fS_2 = 7-8 log units below the pyrite-pyrrhotite surface and with log fH_2S = 1.70 in the associated fluid. As far as the late-alpine retrogression is concerned, the presence of native iron in late chrysotile veins is evidence of distinct fall in fO_2 and fS_2 concomitant with the lowering of both temperature and pressure.

Key words: serpentinization, native metals, fluid phase, high pressure metamorphism, Western Alps.

Introduction

The characters and distribution of the opaque minerals in the ophiolitic ultramafites of the Central-Western Alps have been studied in depth (DE QUERVAIN, 1945; ZUCCHETTI, 1967, 1968, 1970: PERETTI and ZUCCHETTI, 1968). These Authors have demonstrated the presence of native metal (Ni-Fe alloy) + Fe-Ni sulphides parageneses and also established their genetic link with the serpentinization process. The many papers on the silicatic associations of the ophiolitic rocks published over the last fifteen years have led to outstanding results, especially with respect to assessment of the physical and chemical conditions that governed the formation of the metamorphic parageneses during alpine evolution (SANDRONE et al., 1986, with ref. therein). The importance of the part played by the fluid phase in petrogenesis is now unanimously recognized. This has served to foster an interest in the study of opaque minerals in equilibrium with silicates, as minor phase capable of supplying information on the composition of the fluid and its variations during the metamorphism.

This paper re-examines the ore parageneses within the serpentinized ultramafics of Balangero and Lanzo. Extensive use of microprobe as working tool has led to the discovery of hitherto unreported phases and exact description of the composition of each mineral. These data, combined with information concerning the parageneses of the silicates, are used to characterize the fluid phase within the metamorphic Alpine peridotites.

Geological framework

The Lanzo massif and Balangero body lie NW of Turin (Fig. 1) and belong to the innermost sector of the Western Alps. The
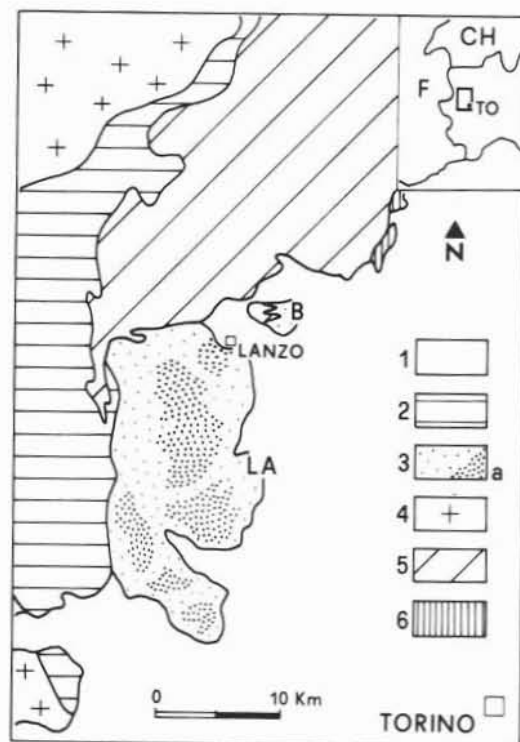
Fig. 1. — Geological sketch map of the inner sector of the Western Alps in the Lanzo area. 1: Quaternary deposits. 2: Piedmont ophiolite nappe. 3: Antigoritic serpentinites with (a) preserved peridotite cores of the Lanzo massif (LA) and Balangero body (B). 4: Paleozoic crystalline basement of the Gran Paradiso (upper left) and Dora Maira (lower left) massifs. 5: Sesia Zone. 6: South-alpine basement.

Lanzo massif covers an area of more than 200 km² and is in contact with the Sesia Zone and the Piedmont ophiolite nappe to the West.

The decidedly smaller Balangero body (about 7 km²) is also in tectonic contact with the Sesia Zone, and at present level of exposure is separated from the Lanzo massif by a band of quaternary terrains several kilometres wide.

The Lanzo massif is a large body of tectonitic peridotite, mainly lherzolite with subordinate harzburgite and dunite, that also contains various kinds of gabbros and basalt dykes (NICOLAS et al., 1972). It is only in the peripheral areas of the body and along some foliation bands that the peridotites are transformed into antigoritic serpentinites.

The Balangero body is mostly transformed into antigorite serpentinite, locally displaying a thick network of chrysotile veins. Peridotites similar to those of the Lanzo massif are locally preserved inside this body, suggesting a close genetic relationship between the Balangero and Lanzo massifs (SANDRONE and COMPAGNONI, 1986).

The structural position of the massif peridotites continues to be the centre of an extensive debate (see POGNANTE et al., 1985). What is certain, is that the original spinel peridotites, following their partial transformation to plagioclase peridotites during a prealpine evolution, were involved in the alpine tectonic and metamorphic evolution from the start, in the same way as the inner sectors of the Piedmontese and Sesia Zones (SANDRONE and COMPAGNONI, 1983). Studies of the parageneses of the silicates in the mafic and ultramafic rocks show that they have been mostly re-equilibrated during the early-alpine event in $T = 500$-$550°C$ and $P = 15$ kb conditions (SANDRONE and COMPAGNONI, 1983).

The chrysotile veins of the Balangero deposit, on the other hand, belong to a subsequent, late-alpine stage (COMPAGNONI et al., 1980).

Analytical methods

A significant sampling was made of the fresh peridotites and serpentinites. These samples were examined in the form of polished thin sections to enable determination of the metal and accompanying silicate parageneses to be carried out at the same time. All the phase were analysed in an ARL SEMQ wavelength-dispersive instrument. The analytical procedures and the mineral chemistry data are described and discussed in a separate note (ROSSETTI and ZUCCHETTI, 1987, in press) and only the essential analytical data will be mentioned here.

Nomenclature and chemistry of the metal phases

Apart from the spinel, which will not be dealt with here, the Lanzo and Balangero

fresh peridotites are almost devoid of ore minerals. These, on the other hand, appear in by no means negligible quantities in the serpentinized ultramafites.

The following metal phases were detected and analysed:

— native metals: native copper (Cu), native iron (Fe), awaruite (Ni$_3$Fe), taenite (~ Ni$_2$Fe), wairauite (~ Fe$_3$Co$_2$);

— sulphides: troilite (FeS), pentlandite [(Fe, Ni)$_9$S$_8$], heazlewoodite (Ni$_3$S$_2$);

— oxides: magnetite (Fe$_3$O$_4$).

Of the metal alloys, native Cu, native Fe, taenite and wairauite had not been previously reported in this sector of the Alps and the last three have only been occasionally observed in terrestrial ultramafic rocks (CHALLIS and LONG, 1964; CHAMBERLAIN et al., 1965; BOTTO and MORRISON, 1976; HARDING et al., 1982). Awaruite and sulphides, on the other hand, have already been described for the Balangero deposit and elsewhere in the Western Alps (ZUCCHETTI, 1967, 1970).

The location of the ore minerals (with the exception of magnetite and native Cu) in the S-Fe-Ni and Co-Fe-Ni diagrams is indicated in Fig. 2. The points refer to the average composition of these phases from the Balangero and Lanzo rocks.

The following points should be noted with regard to the subsequent discussion:

— native Fe and native Cu are regarded as pure phases (> 99 per cent Fe and Cu respectively);

— wairauite (Wa, a Fe and Co alloy) from the Balangero body has the general formula Fe$_3$Co$_2$, but its iron content range is between 57 and 63 wt%. It does not contain appreciable amounts of other components. Such a Fe-Co alloy composition differs from those reported from other localities (CHALLIS and LONG, 1964; CHAMBERLAIN et al., 1965; BOTTO and MORRISON, 1976), which are characterized by formula close to CoFe; on the other hand, the composition range mentioned above is similar to that reported by LEAVELL (1983);

— the Ni-Fe alloys show a large range in the Ni/Fe ratios. The ratio varies between 3.15 and 1.70 (at.%), but is not continuous. Rather, it shows a compositional gap between
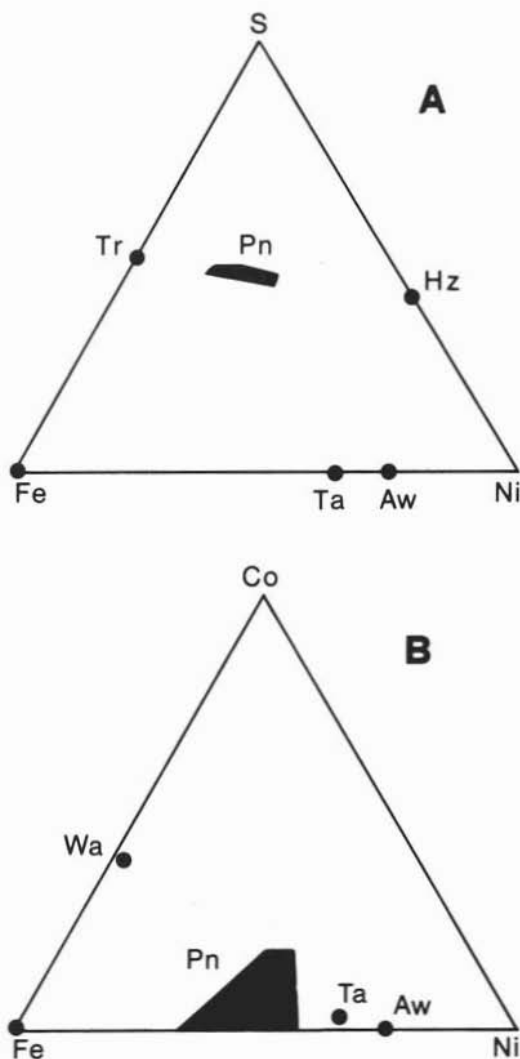

Fig. 2. — S-Fe-Ni and Co-Fe-Ni (at.%) plots of the opaque phases from the Lanzo massif and Balangero body. Magnetite and spinel compositions are not included. Points stand for the corresponding average compositions (see text for symbols). Among the sulphides, only pentlandite is reported in Fig. 2B, in order to show its compositional range in the Co-Fe-Ni system.

2.12 and 2.44. A similar gap was found, by BOTTO and MORRISON (1976), in pebbles from Josephine County. Moreover, in our rocks some Co (up to 6%) is often present, with its abundance being higher in the alloys with a lower Ni/Fe ratio.

As suggested by BOTTO and MORRISON

(1976), our data point to the presence of two different Ni-Fe alloys:

a) awaruite (Aw), nickel-rich ordered phase of the Fe-Ni system, with an average formula close to Ni_3Fe;

b) taenite (Ta), nickel-poor disordered phase, with an average formula close to Ni_2Fe.

This conclusion is substantiated by the fact that the disordered phase (i.e. taenite) contains more Co than does the ordered phase (i.e. awaruite)

— troilite (Tr, with Fe:S = 1:1) and heazlewoodite (Hz) are regarded as pure phases;

— pentlandite (Pn) is shown on the S-Fe-Ni diagram (Fig. 2A) as an area instead of a point on account to its very variable composition, ranging the Fe/Ni ratio from 0.8 to 2.10 (at.%). The Fe/Ni ratio is higher when pentlandite occurs in association with troilite and/or Ni-Fe alloys; conversely, it is lower in heazlewoodite-bearing assemblages, in agreement with the data reported by MISRA and FLEET (1973). The Co content is usually low (Co < 1 wt.%). Sometimes a more Co-rich pentlandite (Co up to 12 wt.%) occurs in the Lanzo massif (Fig. 2B).

In the Fe-Ni-Co-S system (experimentally studied by KANEDA et al., 1986, at $P_{H2O} \simeq$ 500 bars) our compositional data would fall within the pentlandite solid-solution field, close to the Fe-Ni binary, at $T = 500°C$. Despite of the higher pressures estimated in the Lanzo and Balangero ultramafics, the wide range of the Fe/Ni ratio strongly suggests changes of T and/or fS_2 conditions (KANEDA et al., 1986; see discussion below);

— magnetite (Mt) is practically pure.

Ore parageneses

The definition of the equilibrium in ore associations requires some more discussion. In fact, opaque minerals occur as minor phases, irregularly disseminated in the rock and are rarely in contact. On the other hand, the serpentinization process itself is generally considered a non-equilibrium process. Thus, when the ore minerals are not in contact, the following criteria for the definition of

equilibrium association were adopted (see ECKSTRAND, 1975):

— minerals are in the same section, or better in small domains — generally at a centimetric scale — where the silicates are in equilibrium;

— there are not textural indications of disequilibrium.

The most frequent and typical associations of early-alpine age (i.e., not including late-alpine veins) are the following:

(1) Ta - Aw - Wa - Tr - Mt
(2) Ta - Aw - Tr - Mt
(3) Ta - Wa - Tr - Mt
(4) Ta - Tr - Mt
(5) Aw - Tr - Mt
(6) Aw - Tr - Pn - Mt
(7) Aw - Pn - Mt
(8) Tr - Pn - Mt
(9) Aw - Pn - Hz - Mt
(10) Aw - Hz - Mt

It may be argued that at least the heazlewoodite-bearing assemblages, although not inside the late-alpine veins, could reflect the effect of a retrogressive stage (i.e., greenschist stage). The following facts should, however, be considered:

— in this sector of the Western Alps the early-alpine assemblages are normally extremely well preserved, the effect of retrogression being mostly confined to sheared zones;

— the petrography of silicates in these ultramafics does not suggest the occurrence of post-eclogitic recrystallization;

— particularly, in mafic dykes cutting the Lanzo peridotite the early-alpine assemblages are extremely well preserved (POGNANTE and KIENAST, 1987), suggesting that most of the massif did not suffer the effect of retrogression.

Thus, the occurrence of heazlewoodite-bearing metamorphic assemblages in the Lanzo massif confirms their genetic link with the early-alpine stage. The analogous assemblages within the more transformed Balangero body are likely to belong to the early-alpine stage as well. However, we cannot exclude that part of them could represent the product of a retrogression stage (although any

evidence of it is lacking), as they surely are stable also at lower temperature and pressure.

The relations among the opaque phases can be best shown on a Fe-Ni-S chemographic projection from oxygen (Fig. 3)[1]. On such a projection the stability of assemblages with magnetite (the only oxide in the assemblages) will expand with increasing fO_2. Thus an infinite number of such projections are possible, with each one showing tie-lines stable at different oxygen fugacity. For topologic

All these topologies are present in the Balangero and Lanzo ultramafics (heavy tie-lines in Fig. 3). It is worth to note that in all the parageneses magnetite is stable, and that the Ni-Fe alloys cover a small part of the compositional range shown in the different topologies. Particularly, taenite is always Ni-rich, while awaruite tends to be Fe-rich.

The assemblages (1) to (5) belong to the topology 3a. In such assemblages, awaruite shows generally a lower Ni/Fe ratio than
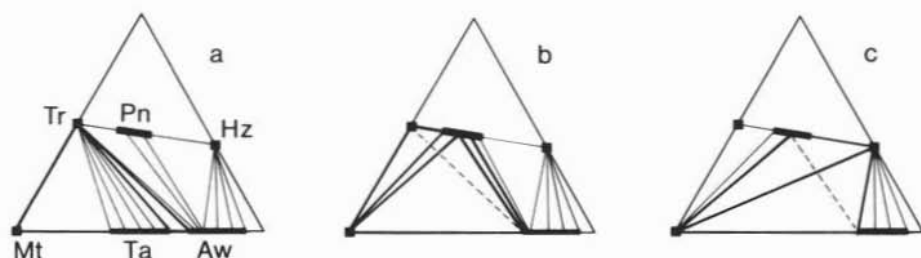

Fig. 3. — Relations among the opaque phases on a Fe-Ni-S chemographic projection from oxygen, with increasing fO_2 from (a) to (c). Symbols in Figg. (b) and (c) are the same indicated in Fig. (a). Heavier tie-lines correspond to the early-alpine assemblages from the Lanzo and Balangero rocks. Ta is stable only in topology (a); the Ni content in Aw increases from (a) to (c) (see text for discussion). The dashed lines in the Figg. (b) and (c) show the chemographic relations in the low-variance assemblage (6) and (9), respectively, where the activities of oxygen and sulphur are fixed.

purposes, however, only three projections are necessary, one at relatively low fO_2 (Fig. 3a), another at intermediate values (Fig. 3b), and one at relatively high fO_2 (Fig. 3c). At relatively low fO_2 there is an extensive stability range of iron-nickel alloys, with both taenite and awaruite stable with troilite. With increasing oxygen fugacity, the alloy coexisting with magnetite moves to more Ni-rich compositions. The topology shown in Fig. 3b is established when the oxygen fugacity is high enough to stabilize the assemblage magnetite-pentlandite by the reaction:
awaruite + troilite + O_2 = magnetite + pentlandite.

Further increases in oxygen fugacity restrict the alloy to even more Ni compositions and once the heazlewoodite-magnetite assemblage is stabilized, the topology shown in Fig. 3c is established.

observed in topologies 3b and 3c.

The assemblages (6) to (8) are instead referred to the topology 3b, while those indicated as (9) and (10) belong to the topology 3c. The nickel content increases in the Ni-Fe alloys from the first topology to the third.

As for is the distribution of these assemblages, the parageneses belonging to topology 3a are the most common and mainly occur in partially serpentinized peridotites, containing relics of primary olivine. Taenite and Fe-Co alloy are exclusively associated to these parageneses.

Parageneses belonging to the topologies 3b and 3c mostly occur in more serpentinized peridotites, or in any case in antigoritic domains. Alternatively, heazlewoodite - magnetite parageneses (with or without awaruite and pentlandite), which belong to topology 3c, occur sometimes in poorly serpentinized peridotites. Only in this case native Cu is present. These parageneses are mostly inside primary, non metamorphic

minerals and are at times in association with relics of primary spinel.

Origin of the ore parageneses

In the fresh peridotites the opaque minerals are only present in small amounts, thus only a some proportion of the opaque assemblages could possibily derive from «in situ» transformation of pre-alpine ores. Conversely, since the first stages of serpentinization several small grains of opaque minerals (principally Ni-Fe alloys) tend to contour the relics of primary olivine. These facts prove the existence of a close connection between the genesis of the metal phases and the serpentinization process, as now generally accepted (NICKEL, 1959; KRISHNARAO, 1964; CHAMBERLAIN et al., 1965; RAMDOHR, 1967; ZUCCHETTI, 1970; ECKSTRAND, 1975; FROST, 1985). In particular, most of nickel in the opaque minerals is considered to be released by primary olivine during serpentinization.

The petrography of the ultramafites indicates that serpentinization has primary occurred during the regional alpine metamorphism and has produced parageneses with antigorite + diopside + olivine + Ti-clinohumite + magnetite ± Mg-chlorite. The data for the silicatic parageneses in the ultramafic and mafic rocks (SANDRONE and COMPAGNONI, 1983) point to a temperature and pressure combination (T = 500-550°C, P = 15 kb) [2] attributable to the early-alpine stage of the orogeny. The effect of the subsequent late-alpine retrocession is negligible here and confined to the late chrysotile veins.

Most of the ore associations are in equilibrium with the early-alpine silicatic parageneses and the same T and P conditions can be postulated for them.

If, as is certain, the ore minerals are linked

with the serpentinization process, then a mobilization of both oxygen and sulphur in the rock must be taken into account for their origin. Thus, assessment of significance of the ore parageneses requires the consideration, at fixed T and P, of oxygen and sulfur fugacity (fO_2 and fS_2) (ECKSTRAND, 1975). In other words, under certain temperature and pressure conditions the stability of the metal parageneses depends on the composition of the associated fluid.

The composition of the fluid phase during the early-alpine metamorphism was determined on the association Ta - Aw - Wa - Tr - Mt. The criteria underlying the choice of this paragenesis were:
— the certainty that this association is stable with the early-alpine silicate parageneses. This certainty rests on the petrographical and minerographical data and is confirmed by the presence of taenite, the «high temperature» disordered Ni-Fe alloy (see FROST, 1985);
— the existence of the albeit scanty thermodynamic data for the minerals mentioned above;
— the fact that this paragenesis belongs to the topology 3a, the most common in our rocks;
— the fact that it is a low variance assemblage.

Analysis of fO_2 and fS_2

In the calculation of fO_2 and fS_2 values for the association mentioned above the method described by FROST (1985) was adopted, using the equilibria listed in Table 1. The equilibrium constant for each reaction was determined from the relation (FROST, 1979):

$$\log K = A/T + B + C(P-1)/T$$

where $A = -\Delta H°/2.303\ R$
$\quad\quad B = \quad \Delta S°/2.303\ R$
$\quad\quad C = -\Delta V°/2.303\ R$
$\quad\quad$ T = temperature in degrees Kelvin
$\quad\quad$ P = total fluid phase pressure in bars.

The water fugacity coefficient ($\gamma H_2O \simeq 3.0$) in reaction 5 was determined using the MODRK, namely a computer program kindly

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[2] Recently, lower T-P values (T = 450-500°C and P_{min} = 12-13 kb) have been suggested, by POGNANTE and KIENAST (1987), for the dykes of Fe-Ti metagrabbro which crosscut tectonite lherzolites in the Lanzo massif. However, these differences in the T-P estimations will have only negligible effects in the following discussion.

TABLE 1

List of the equilibria used in the calculation of the composition of the fluid phase

	A	B	C
$2\ Fe_3O_4 + 3\ SiO_2 = 3\ Fe_2SiO_4 + O_2$	-27271.3	11.625	.092
$FeS + .5\ S_2 = FeS_2$	7322.6	-7.053	-.03
$Fe + .5\ S_2 = FeS$	8267.2	-3.316	-.058
$.5\ Fe_3O_4 = 1.5\ Fe + O_2$	-29427.8	10.028	.061
$2\ H_2S + O_2 = 2\ H_2O + S_2$	8207.6	-.302	—

supplied by R.B. Frost and described in FROST (1979).

Let us consider the association:
Ta (~ Ni$_2$Fe) - Aw (Ni$_3$Fe) - Wa (~ Fe$_3$Co$_2$) - Tr (FeS) - Mt (Fe$_3$O$_4$). In this association at equilibrium, the Fe activity values (a_{Fe}) must be the same for all three alloys. This means that the activity-composition relationship in the alloys surely is not ideal; in fact, assuming $a_{Fe}^{alloy} = X_{Fe}^{alloy}$, the resulting a_{Fe} in the alloys would be very different ($X_{Fe}^{Aw} = .24$—$.32$; $X_{Fe}^{Ta} = .47$—$.44$; $X_{Fe}^{Wa} = .58$). Most authors indicate a large negative ΔHmix at high temperature for the Ni-Fe alloys (DALVI and SRIDHAR, 1976; RAMMENSEE and FRASER, 1981); therefore, a_{Fe} in the Ni-Fe alloys should be lower than .47.

On the other hand, also for the Co-Fe alloys the few experimental data indicate an activity coefficient lower than unity (RAMMENSEE and FRASER, 1981).

Unfortunately, all the experimental data are referred to T and P conditions very different from those supposed for our association. The following assumptions seem, however, to be reasonable:

— $a_{Fe}^{alloys} < .6$. An a_{Fe} value higher than .6 would mean positive ΔHmix for both Fe-Co and Ni-Fe alloys, contrarly to all experimental data;

— $a_{Fe}^{alloys} > .25$. An a_{Fe} value of .25 corresponds to X_{Fe} in awaruite, the low temperature phase in the Ni-Fe system; a lower value would mean an extreme deviation from ideality for both taenite and wairauite.

In consequence, we decided to calculate the fO_2 and fS_2 values in the whole range between $a_{Fe} = .25$ and $a_{Fe} = .6$. Troilite and magnetite are practically pure phases. a_{FeS}^{Tr} and a_{Fe3O4}^{Mt} are therefore taken as equal to 1.

Once defined the range of a_{Fe}^{alloys}, the fO_2 value can be calculated considering that awaruite, taenite and wairauite are in equilibrium with magnetite. Thus, the following equilibrium reaction can be written:
$.5\ Fe_3O_4 = 1.5\ Fe_{alloy} + O_2$
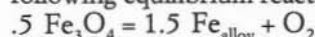
The log fO_2 values obtained vary (at T = 550°C and P = 15 kb) between —23.72 (if $a_{Fe} = .25$) and —24.29 (if $a_{Fe} = .6$). These values are greatly influenced by T and only to a subordinate degree by P (see Table 2), and lie between 3.88 and 4.45 log units below the surface represented by the FMQ buffer (Fig. 4 and following discussion).

The fS_2 value can be calculated in the same way, being the Ni-Fe and Fe-Co alloys in equilibrium with troilite, through the following equilibrium reaction:
$Fe_{alloy} + .5\ S_2 = FeS$
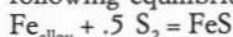
The corresponding log fS_2 values at the same T and P conditions are —11.14 and

TABLE 2

List of fO_2 and fS_2 values at different P-T conditions

T°C	Pkb	log fO_2	Δlog fO_2	log fS_2	Δlog fS_2
550	15	-23.72	-3.88	-10.14	-7.54
		-24.29	-4.45	-10.90	-8.30
550	10	-24.08	-3.69	-10.84	-7.88
		-24.65	-4.26	-11.60	-8.64
500	15	-25.96	-4.08	-11.30	-7.62
		-26.53	-4.65	-12.06	-8.38
500	10	-26.35	-3.88	-12.05	-7.99
		-26.92	-4.45	-12.81	-8.75
500	5	-26.74	-3.68	-12.80	-8.35
		-27.31	-4.25	-13.56	-9.11
400	8	-32.07	-4.27	-15.35	-8.41
		-32.64	-4.83	-16.11	-9.17
400	5	-32.34	-4.13	-15.87	-8.66
		-32.91	-4.70	-16.63	-9.42
300	5	-39.89	-4.72	-20.01	-9.08
		-40.46	-5.29	-20.77	-9.84
300	2	-40.21	-4.57	-20.61	-9.37
		-40.78	-5.13	-21.37	-10.13

For each T-P combination, the first value refers to $a_{Fe}^{alloys} = .25$, the second to $a_{Fe}^{alloys} = .6$. The conditions suggested for the early-alpine assemblages are T = 500-550°C and P = 15 kb: calculations for other T-P values are only given in order to show the dependence of fO_2 and fS_2 on T and P (see text).

—11.90 respectively. These, too, are strongly influenced by T and only subordinately by P (see Table 2). If the pyrite-pyrrothite surface is used as reference, log fS_2 values are 7.54—8.30 log units below it (see discussion).

In carbonate-free metaperidotites the dominant species in the fluid will be H_2O and H_2S (FROST, 1985); the fH_2S in the fluid depends on the fO_2 and fS_2 values and, if these are known, it can be calculated. The log fH_2S value in the fluid phase can be obtained considering the following equilibrium between fluid species:

$$2\ H_2S + O_2 = 2\ H_2O + S_2$$
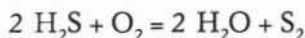
Such a value is comprised between 1.77 ($a_{Fe} = .25$) and 1.67 ($a_{Fe} = .6$) (for $T = 550°C$ and $P = 15$ kb).

Discussion

The widespread occurrence of native metals-sulphides-magnetite assemblages in the serpentinized peridotites corresponds to low fO_2 and fS_2 values. Such highly reducing conditions are related to the transformation of olivine into serpentine + magnetite, since
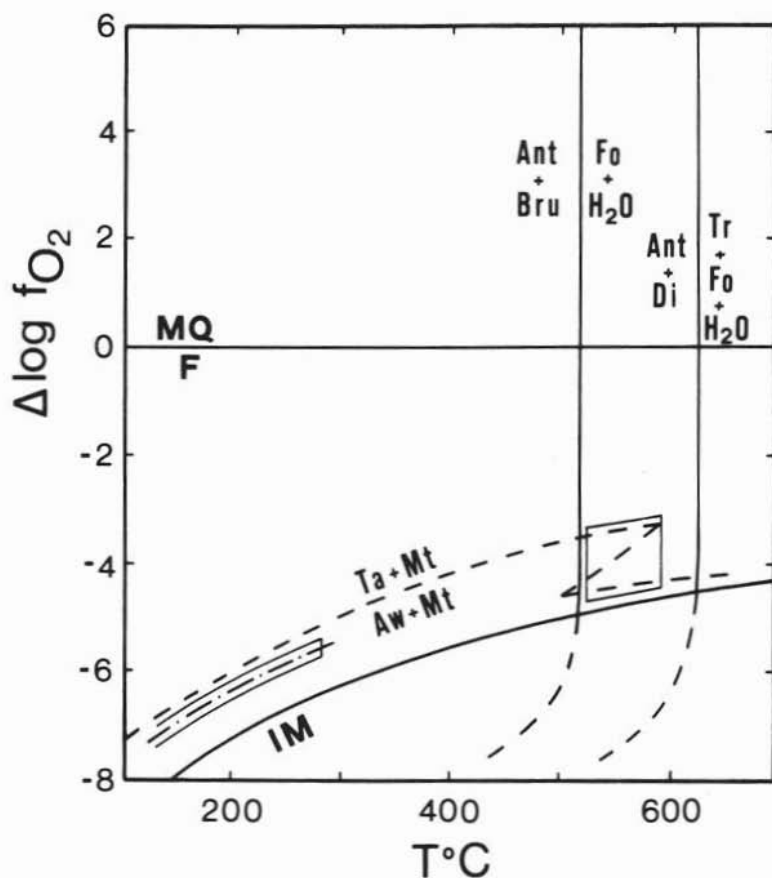

Fig. 4. — $\Delta \log fO_2$-T projection showing equilibrium relations in serpentinites at $P_{H2O} + P_{H2} = 15$ kb. Ant = antigorite; Bru = brucite; Di = diopside; Fo = forsterite; Tr = tremolite. FMQ and IM are the fayalite - magnetite - quartz and the iron-magnetite buffer, respectively. The dashed curves show the stability range of the Ni-Fe alloys and the portions of the dehydration equilibria where they may be displaced due to the presence of H_2 in the fluid. The box between the two dehydration reactions shows the fO_2 conditions of the early-alpine assemblage Ta - Aw - Wa - Tr - Mt in the Lanzo and Balangero rocks. The dotted-dashed curve is the iron-magnetite buffer at $P_{H2O} + P_{H2} = 2$ kb. The open box estimates the fO_2 conditions for the late alpine veins as inferred by the occurrence of native iron.

the production of magnetite induces reduction of the associated fluid phase (see FROST, 1985, with ref. therein).

Our observations on the ore parageneses in the Lanzo and Balangero rocks seem to suggest that at T = 550°C and P = 15 kb the system is of much the same type as that observed at lower temperatures (ECKSTRAND, 1975; FROST, 1985).

The composition of the fluid phase associated to the early-alpine taenite - awaruite - wairauite - troilite - magnetite assemblage, however, is marked by log fO_2 and log fS_2 values appreciably higher than those calculated by FROST (1985) for similar associations in serpentinized peridotites formed at lower temperatures and pressures.

The apparent discrepancy is due to the strong dependence of the log fO_2 and log fS_2 values on temperature, since they increase by about 6 and 3 log units respectively per 100°C. Their changes due to pressure are less marked (about 0.5 and 0.8 log units per 5 kb, see Table 2), although not negligible because of the very high pressure values estimated for these ultramafics.

In order to lower the influence of temperature, fO_2 and fS_2 have been referred to the FMQ buffer and to the Py-Po surface respectively (Fig. 4). Our values are comparable with those provided by FROST (1985, Fig. 4) on native metals + sulphides associations at lower T and P, though the corresponding absolute values are very different.

The study of the Ta - Aw - Wa - Tr - Mt paragenesis gives values of fO_2 and fS_2 that can be extrapolated, excepted for small differences, to all the associations occurring in the topology shown in Fig. 3a.

Calculations of the corresponding values of fO_2 and fS_2 for the two last topologies are difficult, because of the paucity of thermodynamic data on all the compositional range of pentlandite and because of the uncertainly due to the choice of the a_{Fe} values in the alloys. However, in topology 3c the association of awaruite with both heazlewoodite and magnetite suggests fO_2 and fS_2 values 0.5 and 0.3 log units higher, respectively, than those referred to the topology 3a. Higher fS_2 values for topology 3c are also suggested, on the other hand, by the low Fe/Ni ratio in pentlandite associated with heazlewoodite (see KANEDA et al., 1986).

Such differences, at the same T and P conditions, can be explained in several ways:

— the equilibrium controlling oxygen fugacity:

$$12 \ Fe_2SiO_4 \ (in \ olivine) + 12 \ H_2O + O_2 = 6 \ Fe_3Si_2O_5(OH)_4 \ (in \ serpentine) + 2 \ Fe_3O_4$$

is dependent on changes in minor elements concentration. Changes in Mg/Fe in the silicates, Al, Cr, F content of serpentine, and Cr content of magnetite could all cause variations in oxygen fugacity from rock to rock (FROST, 1986, pers. comm.);

— during the same metamorphic event, the degree of serpentinization was not uniform. As shown by FROST (1985) and confirmed in our study, at the same T and P conditions we must expect lower fO_2 values in non completely serpentinized peridotites, which still contain relics of olivine;

— on the contrary, mineral assemblages referred to the topology 3c occur sometimes in poorly serpentinized peridotites, where, however, magnetite contains some Cr, and heazlewoodite some Fe and/or Cu. These particular compositions, as mentioned above, could explain such an occurrence. Moreover, textural relationships suggest that at least part of these assemblages grew on older sites (pre-alpine, perhaps primary blebs?), as it could be confirmed by the local abundance of Cu, which is always diffused in the rock during the following stage. Elsewhere, heazlewoodite - magnetite parageneses grew on a primary spinel. Thus, the higher fO_2 assemblages in the poorly serpentinized peridotites could be related to the presence of minor elements in the ore phases, and/or to the derivation from older associations perhaps partially re-equilibrated during the alpine metamorphism.

The log fH_2S value for the fluid associated with the paragenesis studied in detail may appear excessively high. The explanation lies in the fact that it is accompanied by a low fO_2. In a hydrated environment with low fO_2, such as that considered, a hypothetical reaction as:

$Fe_{alloy} + H_2S + .5\ O_2 = FeS + H_2O$
would proceed to the left, promoting the stability of the native metals and releasing H_2S as product. The presence of local concentrations of late sulphides in some areas of the Balangero body (PERETTI and ZUCCHETTI, 1968) may indeed be ascribable to migration of such a H_2S-rich fluid to areas favorable to deposition.

Although the study of transformations linked to late alpine retrogression has not been examined in this paper, the discovery of native iron in late chrysotile veins is infomative in this respect. These veins are attributed to a late alpine stage, at low temperature and pressure. Native iron has been already reported, although rarely, from partially serpentinized peridotites (CHAMBERLAIN et al., 1965; HARDING et al., 1982). The occurrence of native iron suggests that a marked fall in fO_2 by at least 1 log unit with respect to the FMQ buffer during the retrogression occurred (Fig. 4). However, these extremely reducing conditions are not likely to reflect equilibrium, but rather are due to partial retrogression of olivine-bearing assemblages.

Conclusions

This study of the partially serpentinized peridotites in the Lanzo massif and the Balangero body has elicited a compositional spectrum for the metal parageneses, especially for the native metals, that is among the widest so far observed in rocks of this kind.

Opaque mineral associations, attributable to the early-alpine event (T = 500-550°C and P = 15 kb) in the light of the silicate parageneses, suggest that the topologies in the Fe-Ni-S-O system are not very different from those reported at lower temperatures and pressures (ECKSTRAND, 1975; FROST, 1985).

These same associations, however, are stable for much higher fO_2 and fS_2 values. On the other hand, the relative shifts of fO_2 and fS_2 with respect to the FMQ buffer and pyrite-pyrrothite reference surface are comparable with the low temperature data.

The composition of the fluid phase in the serpentinized peridotites of Balangero during the early-alpine stage, as shown by the low variance association taenite - awaruite - wairauite - troilite - magnetite, was marked by fO_2 values about 4-5 log units below the FMQ buffer and by fS_2 values corresponding to 7.5-8.3 log units below the pyrite-pyrrothite surface, with log $fH_2S = 1.70$.

In these ranges, higher fO_2 mineral associations could reflect different degrees of serpentinization, the distribution of minor elements and, possibly, the partial re-equilibration of pre-alpine ore assemblages.

In the last retrogression stage following the early-alpine, at least locally, extremely reducing conditions — with production of native iron — were reached. They are likely to reflect a disequilibrium process, linked with the partial transformation of olivine-bearing assemblages.

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