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The Behaviour of the Upper Mantle Sulfide Component During the Incipient Alteration of "Alpine"-Type Peridotites as Illustrated by the Beni Bousera (Northern Morocco) and Ronda (Southern Spain) Ultramafic Bodies

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With 9 Figures

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Summary

A volumetrically minor Cu-Fe-Ni-S component derived from the uppermost mantle is found within the Beni Bousera (northern Morocco) and Ronda (southern Spain) "Alpine"-type peridotites; it occurs today as inclusions within primary silicates or as assemblages disseminated in the intergranular sites of the host rocks. Detailed microtextural and microprobe data indicate that inclusions and intergranular assemblages behaved as two contrasting systems during the low temperature, incipient serpentinization of the host rocks. The former were equilibrated in closed systems whereas the latter behaved as open systems with respect to hydrothermal fluids; as a result, intergranular assemblages were controlled by redox conditions generated by serpentinization. An early stage of alteration is characterized by a slight decrease of the sulfur content and would be due to the first influx of water inside peridotites; a further transformation was produced by anomalous highly reducing conditions responsible for the crystallization of native iron-bearing alloy assemblages as well as for a preferential partioning of Fe from silicate into pentlandite. The production of anomalous, reducing conditions during incipient serpentinization is ascribed to a low permeability of the host rocks with respect to the diffusion of hydrogen out of the sites of serpentinization. Because of its low temperature behaviour, the intergranular sulfide component would not be of use reconstructing the initial composition of the upper mantle sulfide component; thus, it is concluded that only the sulfide inclusions would provide such informations.

Résumé

Le comportement du composant sulfuré du manteau supérieur pendant les premiers stades de serpentinisation des péridotites de type "alpin"; une discussion a partir de l'exemple des massifs ultramafiques de Beni Bousera (Maroc) et de Ronda (Espagne)

Des traces d'un composant sulfuré du système Cu-Fe-Ni-S d'origine mantellique sont présentes dans les péridotites "alpines" de Beni Bousera (Maroc) et Ronda (Espagne); il forme actuellement des inclusions dans les silicates primaires ou des plages intergranulaires disséminées dans les interstices des roches. Une analyse minéralogique et chimique détaillée démontre qu'inclusions et plages intergranulaires sulfurées ont eu un comportement opposé dès les premiers stades de serpentinisation des roches encaissantes. Les premières ont été reéquilibrées en système chimique ouvert vis-à-vis des fluides de serpentinisation; en conséquence les paragenèses intergranulaires résultent d'une suite de transformations du composant sulfuré mantellique, controlée par le degré d'oxydo réduction du fluide de serpentinisation. Dans un premier stade, l'entrée de l'eau dans les péridotites a provoqué une légère baisse de la fugacité du soufre et la cristallisation d'assemblages sulfurés riches en mackinawite. L'augmentation du degré de serpentinisation a ensuite engendré des conditions inhabituellement réductrices responsables d'un important fractionnement du fer libéré par la serpentinisation de l'olivine dans la pentlandite ainsi que de la cristallisation d'une paragenèse complexe de phases métalliques incluant localement le fer natif; ces conditions anormalement reductrices sont imputées à une faible perméabilité des roches encaissantes vi-à-vis de la diffusion de l'hydrogène en dehors dessites de serpentinisation. En raison de leur comportement à basse température, les plages sulfurées intergranulaires sont inutilisables pour reconstituer le composant sulfuré du manteau supérieur; sur ce plan, on conclut que seules les inclusions blindées dans les silicates peuvent apporter des informations.

Pentlandite and other (Cu)-Fe-Ni-S minerals have been found to occur as intergranular assemblages among the primary silicates and spinel within "alpine"-type peridotites (*Besson*, 1975; *Lorand*, 1983a and b; *Garuti* et al., 1984). Some authors assume that this kind of sulfide occurrence represents the product of an almost isochemical subsolidus reequilibration of the upper mantle sulfide component (*Garuti* et al., 1984). However, a preliminary investigation on more than 300 samples of alpine-type peridotites from various localities has shown that intergranular sulfide assemblages may have suffered low temperature exchange reactions as soon as the degree of serpentinization is greater than 5–10% by volume of the host rocks (*Lorand*, 1983a and b). The present paper documents these reactions on the basis of a detailed study of the sulfide component in the Beni Bousera (northern Morocco) and Ronda (southern Spain) alpine-type peridotites. Owing to their moderate but highly variable degree of serpentinization, such occurrences of peridotites provide the opportunity to examine the behavior of the sulfide component during the incipient alteration of primary silicates into serpentine minerals.

For each sample, the microscopic and microprobe investigations were performed not only on the intergranular Cu-Fe-Ni-S assemblages but on the sulfides fully enclosed within primary silicates as well; furthermore, the compositional variation of pentlandite has received special attention. A general appraisal of sulfide alterations connected with incipient serpentinization has been attempted with references to the models of *Chamberlain* et al. (1965) and *Eckstrand* (1975). Relationships between the present sulfide assemblages from "alpine" type peridotites and the upper mantle sulfide component are also discussed.

I. Geological Setting and Main Petrographic Characteristics

The Beni Bousera (northern Morocco) and Ronda (southern Spain) ultramafic bodies, respectively 70 and 300 km^2 across, occur as two tectonic lenses within the Betico Rifean cordillera situated on either side of the straits of Gibraltar (Fig. 1). The works of *Kornprobst* (1969) and *Obata* (1980) and the recent structural and petrographic review by *Kornprobst* and *Vielzeuf* (1984) indicate that these lenses are portions of the subcontinental upper mantle which have undergone a complex history of partial melting and solid state recrystallizations before their tectonic emplacement within the continental crust. Both consist of layered tectonic peridotites with few percent of conformable pyroxenite and (or) gabbroic layers. The peridotites are spinel lherzolites grading locally into spinel harzburgites at Beni Bousera whereas garnet and plagioclase peridotites occur together with spinel lherzolites at Ronda. Whatever their mineralogy, the peridotites show the porphyroclastic and granuloblastic textures typically formed within upper mantle peridotites during their solid state deformation and recrystallization at high temperature (*Mercier* and *Nicolas*, 1975).

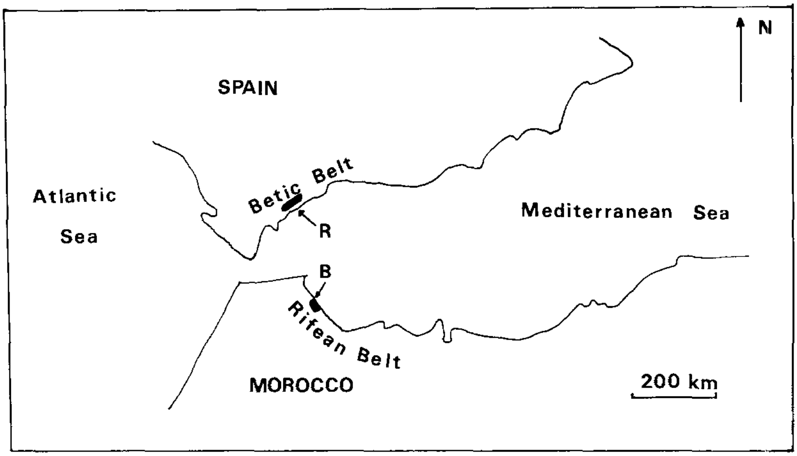

Fig. 1. Location of the Beni Bousera (*BB*) and Ronda (*R*) ultramafic bodies

Fifty five spinel lherzolites samples from Beni Bousera and forty five plagioclase and spinel lherzolites samples from Ronda have been studied. Some of them show only traces of serpentine minerals invading the primary olivine along fractures and grain boundaries; others are more altered and contain relict cores of olivine within a mesh-textured serpentine matrix and orthopyroxene partly replaced by a "bastite" product (Al lizardite according to *Wicks* and *Plant*, 1979) as well as rims of "ferritchromite" on Al-Cr spinel. Magnetite forms as tiny grains within serpentine veinlets in the serpentinized samples while clinopyroxene and plagioclase remain unaltered. Although it shows considerable variation at the hand-sample scale, the magnitude of serpentinization will be treated hereafter in terms of the percentage of serpentine-group minerals occurring within each sample. Different estimates (visual estimates under the microscope and values of the ignition loss of whole rock analyses; *Kornprobst*, unpublished data) show it to range from less than 10% by volume in the least serpentinized samples to 70% by volume in the more altered peridotites, the Ronda samples appearing more altered than those from Beni Bousera.

The physical conditions (temperature, total and fluid pressures) which have controlled serpentinization in the two bodies investigated are not yet documented. However, it has to be noted that whatever its magnitude, this alteration has faithfully preserved the grain boundaries of primary silicates and spinel so that it may be termed "pseudomorphic" according to the *Wicks* and *Whittaker* (1977) classification. Such a serpentinization is thought to have occurred at a temperature below 200–300 °C (*Moody*, 1976; *Wicks* and *Whittaker*, 1977).

II. Petrography of the Cu-Fe-Ni-S Assemblages

A) *Mode of Occurrence*

Previous papers by *Conquéré* (1969), *Barrakad* (1971), *Conquéré* and *Kornprobst* (1972) and *Mikkailov* (1975) reported a (Cu)-Fe-Ni-S component within the mafic layers at Beni Bousera. The present study, based on more than 160 polished thin sections, found it in most of the peridotite samples, occurring preferentially in lherzolites and averaging generally less than 0.2% by volume of the host rock. In this respect, no significant differences are seen between the Beni Bousera and Ronda peridotites.

The sulfide component of the peridotites has basically two modes of occurrence. It is found as small droplets fully enclosed within primary silicates and as coarser anhedral aggregates up to 500 μm across, interstitial with respect to primary silicates and largely predominating over the sulfides enclosed within primary silicates. These two sulfide occurrences may be observed together in a single polished thin section and correspond to droplets of an early immiscible sulfide melt trapped either within or at the grain boundaries of primary silicates during their high temperature recrystallization in the uppermost mantle (for further details, see *Lorand*, 1983b). Sulfides enclosed within primary silicates and interstitial assemblages will be referred to respectively as *sulfide inclusions* and the *intergranular sulfide component*.

B) *The Sulfide Inclusions*

Sulfide inclusions are scarce, two or three inclusions per sample being a common average. They are hosted by olivine and pyroxene rather than by spinel and plagioclase. Some of them occur as rounded or euhedrally terminated droplets up to 40 μm across, within unbroken primary silicates (Fig. 2A). The others are smaller in diameter and occur as "trains" of globules along the sealed fracture planes of silicates. These two sorts of inclusions have respectively been referred to an early and late generation of sulfide melt trapped at high temperature within silicates (*Lorand*, 1983b).

Regardless of their origin, the inclusions contain the same sulfide assemblage (Fig. 3) typically described within unserpentinized ultramafic rocks (*Kullerud* et al., 1969). Pentlandite is predominant and coexists with minor pyrrhotite, chalcopyrite and bornite; a single inclusion in a Ronda sample also shows vermiform pyrite within pentlandite. Sulfide minerals are in sharp contact with each other, suggesting that they achieved equilibrium (Fig. 2A). On the other hand, their proportions show considerable variations among inclusions, sulfide inclusions

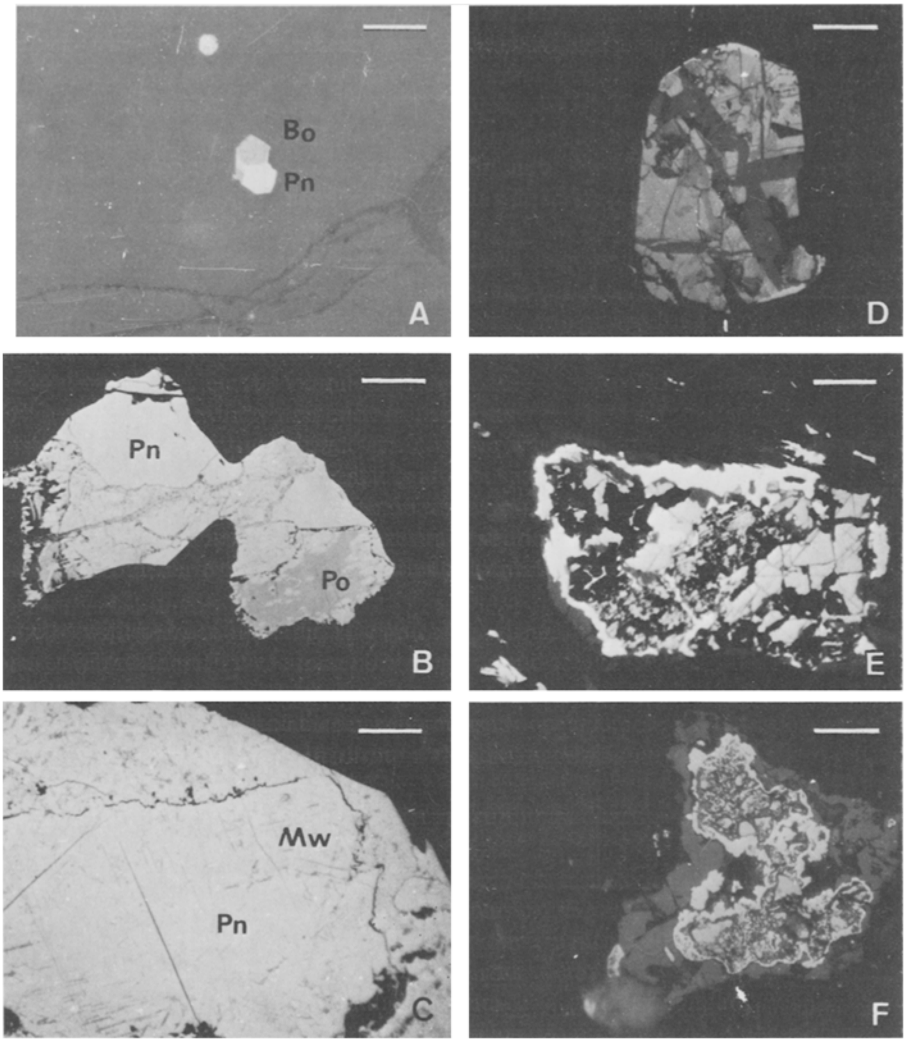

Fig. 2. Photomicrographs of Cu-Fe-Ni-S mineral assemblages (plane polarized reflected light; oil immersion). A) Two phase (*Pn* pentlandite; *Bo* bornite) inclusion in pyroxene; B) and C) intergranular assemblages from weakly-serpentinized peridotites (*Mw* vermicular mackinawite; *Po* pyrrhotite); D) to F) intergranular assemblages from partly-serpentinized samples; Fig. 2D shows coarse-grained mackinawite (medium grey) within pentlandite (light grey), veined by magnetite (dark grey); Fig. 2E corresponds to pentlandite (light grey) veined along the (100) cleavages by chalcopyrite and externally rimmed by native copper (white); Fig. 2E: pentlandite (medium grey) internally rimmed by awaruite (light grey) and externally surrounded by magnetite (dark grey). Scale bar on each photomicrograph is 50 μm except for C where it is 20 μm

being either one-, two- or three-phase (Fig. 2A). Such variations are clearly independent of the magnitude of serpentinization but may be ascribed to random variations in bulk chemistry of high temperature sulfide droplets as they were trapped (*Lorand*, 1983a and b).

C) *The Intergranular Component*

The intergranular component is randomly disseminated on the hand sample scale; within the same polished thin section, it is observed to occur either at the grain boundaries of unserpentinized primary silicates and Al-Cr spinel, or in close contact with the serpentine mesh lines, without any relationship to the magnitude of serpentinization. In contrast, the mineralogy of intergranular assemblages shows sympathetic variations with the alteration of the host rocks. On the basis of these assemblages, two groups of samples will be distinguished hereafter. The first include samples showing a magnitude of serpentinization broadly lower than 20% by volume and will be referred to as "weakly" serpentinized peridotites. The second group corresponds to the more serpentinized ones and will be termed "partly" serpentinized peridotites. Many of the Beni Bousera samples belong to the former group while the latter consists mainly of the Ronda samples.

1. Weakly-Serpentinized Peridotites

Intergranular assemblages are devoid of pyrite and bornite but contain abundant mackinawite coexisting with the predominant pentlandite and minor pyrrhotite and chalcopyrite. Thus, the resulting assemblage is slightly deficient in sulfur in comparison with the coexisting inclusions (Fig. 3). At this stage, many intergranular assemblages are single phase and consist of pentlandite; others are two, three or four phase and commonly show a core of pentlandite with a scalloped border, surrounded by pyrrhotite and (or) chalcopyrite (Fig. 2B). By analogy with the sulfide inclusions, it seems likely that most of the variations in average proportions of pentlandite, pyrrhotite and chalcopyrite are a primary feature of the intergranular assemblages. On the other hand, mackinawite which occurs as tiny wisps, 5–10 μm across, lying parallel to the (111) and (100) cleavage planes of pentlandite (Fig. 2C) is obviously related to a secondary process because of the following reasons i) grain margins of pentlandite are always richer in mackinawite than grain cores (Fig. 2C) ii) some sulfide grains are complete pseudomorphs of mackinawite after pentlandite. These features suggest a replacement of pentlandite by mackinawite (*Blain*, 1978) rather than exsolution of the latter sulfide from the former as previously postulated by *Conquéré* (1969). Such an interpretation is supported by the lack of an experimentally demonstrated solvus between these sulfides (*Power* and *Fine*, 1976).

2. Partly-Serpentinized Peridotites

They show intergranular assemblages drastically different from those enclosed within silicates or occurring within the weakly serpentinized samples. Although pentlandite is always predominant, pyrrhotite is no longer present while the overall abundance of chalcopyrite and mackinawite largely decreases. The disappearance of these sulfides is balanced by the crystallization of abundant

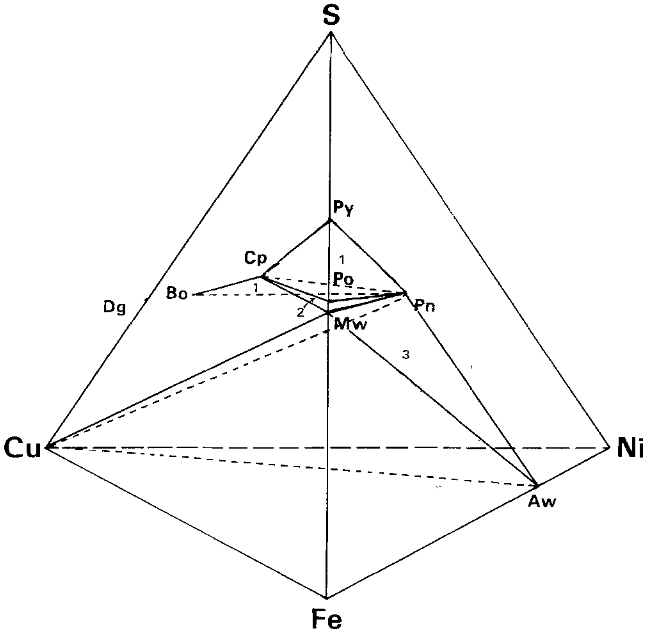

Fig. 3. Schematic phase relations of the Cu-Fe-Ni-S assemblages (theoretical phase composition after *Kullerud* et al., 1969). *1* Sulfide inclusions; *2* intergranular assemblages from weakly-serpentinized peridotites; *3* intergranular assemblages from partly-serpentinized peridotite. Abbreviations as in Fig. 2; *Cp* chalcopyrite; *Py* pyrite; *Dg* digenite; *Cu* native copper; *Aw* awaruite

metallic phases (native copper and awaruite) and by secondary sulfides (digenite, valleriite). Consequently, the intergranular assemblages become strongly sulfur-deficient with respect to sulfide inclusions (Fig. 3) and resemble those extensively documented by *Chamberlain* et al. (1965), *Ramdohr* (1967), *Eckstrand* (1975), *Groves* and *Keays* (1979) and *Ahmed* and *Hall* (1982) in serpentinites. As well as these minerals, unusual assemblages or unknown products were found both at Beni Bousera and Ronda. The unusual assemblage native iron + wairauite (FeCo) occurs instead of awaruite in a single sample from Ronda (*Lorand* and *Pinet*, 1983). Nickel arsenide orcelite ($Ni_{5+x}As_2$) and maucherite have been observed in four samples from Beni Bousera and Ronda, sometimes coexisting with heazlewoodite (*Lorand* and *Pinet*, 1984); however, even when they occur, these minerals are negligible in volume with respect to the (Cu)-Fe-Ni-S component, so that they will not be further referred to. In addition, many samples show an unknown fibrous product after pentlandite, exhibiting optical properties identical to those of valleriite except for higher reflectivity. Microprobe analyses show it to contain Ni, Fe, Mg, Al and Si as dominant elements but sulfur is only present as traces (*Lorand*, research in progress).

On the hand-sample scale, pentlandite and the coexisting Cu-Fe-Ni-S minerals form various assemblages which are one-, two-, three-, four- or five-phase. Despite these variations, many intergranular assemblages display a complete sequence of sulfide replacement which is roughly constant in all the samples studied here.

The core of intergranular assemblages is composed of relict pentlandite enclosing a rare, coarser-grained mackinawite up to 50 μm across (Fig. 2D); many pentlandite grains are veined along the (100) and (111) cleavages by chalcopyrite (Fig. 2E). This occurrence of chalcopyrite can only be observed under the highest magnifications but is readily demonstrated during microprobe analyses by drastic increases of the Cu content of pentlandite.

The pentlandite + mackinawite + chalcopyrite admixtures are generally rimmed by awaruite and (or) native copper (Fig. 2D, 2E, 2F), apart from the strongest serpentinized sample from Ronda wherein pentlandite is surrounded by an internal rim of wairauite and an external rim of native iron (*Lorand* and *Pinet*, 1983). Awaruite is always found in close contact with pentlandite, suggesting that it has formed by replacement of this sulfide rather than by Ni release of silicates during serpentinization. Native copper was crystallized after chalcopyrite but, as well as occurring within the composite sulfide aggregates, it is also observed intergrown with the serpentine veinlets, ranging from 10 to 50 μm across. This heterogeneous distribution on the hand-sample scale may reflect the random distribution of chalcopyrite or indicates that native copper was mobile during serpentinization.

Magnetite is found as intergrowths with pentlandite (Fig. 2D) but generally forms overgrowths on metallic phases (Fig. 2E and 2F) as soon as intergranular assemblages are in close contact with serpentine veinlets. Such a distribution shows that magnetite associated with intergranular assemblages was released during the serpentinization of olivine rather than originated through the oxidation of Cu-Fe-Ni-S minerals.

Digenite and valleriite occur in trace amounts in most of the partly serpentinized samples, ranging in size from 10 to 40 μm. Digenite is a replacement product of native copper, whereas valleriite is intergrown with serpentine veinlets as well as with magnetite rims on the intergranular assemblages. Apart from intergranular pentlandite, two of the most serpentinized peridotites from Beni Bousera contain minute, euhedral pentlandite crystals up to 30 μm across. Significantly, this kind of pentlandite is not found at the boundaries of unserpentinized primary silicates but always occurs within the serpentine veinlets, suggesting that it was crystallized "in situ" during serpentinization, an hypothesis previously advanced by *Eckstrand* (1975) in the Dumont serpentinite, Canada. Formation of digenite, valleriite and secondary pentlandite requires the presence of free sulfur, which is ascribe to the breakdown of pentlandite, pyrrhotite and chalcopyrite into metallic phases.

III. Phase Chemistry

In order to test the equilibrium state achieved by both the inclusions and the intergranular component, microprobe analyses were performed on primary and secondary Cu-Fe-Ni-S minerals at the National Museum in Paris, France, using a CAMEBAX automated instrument under experimental conditions as indicated in Table 1. Pentlandite was probed on 200 sulfide aggregates consisting of in-

Table 1. *Representative Microprobe Analyses of Pentlandite from Beni Bousera*

No.	1	2	3	4	5	6	7	8	9	10
wt.%										
Fe	27.14	24.56	29.86	35.60	30.92	42.36	42.11	42.61	40.79	30.88
Ni	39.49	41.13	36.26	30.25	35.56	24.88	23.97	23.52	25.62	23.63
Co	0.32	0.32	0.18	0.32	0.06	0.31	0.44	0.26	0.77	12.07
Cu	–	0.08	–	0.01	0.54	0.15	0.09	0.03	–	–
S	33.63	33.88	33.46	33.78	34.18	33.10	33.90	33.11	33.48	33.71
	99.60	99.87	99.78	99.91	99.27	99.80	100.54	98.96	100.24	100.29
at.%										
Fe	22.12	19.95	24.31	25.92	25.16	33.60	33.64	34.34	32.85	25.00
Ni	29.86	31.79	28.09	25.47	25.97	19.22	18.21	18.29	19.62	18.20
Co	0.23	0.24	0.14	0.24	0.04	0.24	0.33	0.20	0.61	9.26
Cu	–	0.05	–	–	0.39	0.11	0.06	0.02	–	–
S	47.77	47.95	47.46	46.29	48.44	46.83	47.90	47.14	46.93	47.54
$\frac{Fe}{Ni}$	0.740	0.627	0.865	1.018	0.968	1.748	1.880	1.877	1.674	1.373
	Pn+Po +Cp	Pn+Bo +Cp	Pn	Pn+Mw +Po+Cp	Pn+Cu	Pn	Pn+Po +Mt+Mw	Pn+Cu	Pn+Aw	Pn

1–3 pentlandite enclosed primary silicates. 3–5 intergranular pentlandites in close contact with unserpentinized primary silicates. 6–9 intergranular pentlandites adjacent to serpentine veinlets. 10 euhedral pentlandite crystal within serpentine. The opaque assemblage in which pentlandite occurs is indicated at the bottom of the table. Abbreviations as in Figs. 2 and 3. Analytical conditions: Accelerating potential 15 kV; counting time 6 s:element. Standards; natural pyrite and pure metals (Ni, Co, Cu).

clusions and intergranular assemblages either adjacent to primary silicates or in close contact with serpentine minerals. On the contrary, the restricted size of the coexisting Cu-Fe-Ni-S minerals permitted only a few microprobe analyses, but carefully repeated several times on each mineral to reduce the possibility of spurrious counts from the associated species. Compositional variations of the Cu-Fe-Ni-S minerals are quite similar at Beni Bousera and Ronda, especially those of pentlandite which covers the entire field of solid solution known from the Co-poor pentlandites.

A) *Sulfide Inclusions*

Copper sulfides are close to stoichiometry (Table 3 and 4) while pentlandite is characterized by the lowest Fe/Ni atomic ratio and the lowest Co content of all the probed pentlandites (Figs. 4 and 5). Its Fe/Ni ratio is close to 0.75 at Beni Bousera whereas the Ronda samples exhibit more scattered values, irrespective of the composition of the sulfide assemblage containing pentlandite (Tables 1 and 2).

Table 2. *Representative Microprobe Analyses of Pentlandite from Ronda*

No.	1	2	3	4	5	6	7	8	9	10
wt.%										
Fe	30.32	23.19	31.52	36.53	41.93	39.04	43.47	42.88	43.82	46.28
Ni	35.41	42.24	33.48	30.13	24.25	26.48	21.98	22.53	22.43	18.78
Co	0.23	0.23	0.39	0.55	0.37	1.14	0.44	0.30	0.12	2.89
Cu	0.09	0.29	0.01	0.55	–	–	0.07	0.53	0.01	0.42
S	33.79	33.45	33.58	33.29	33.49	33.36	33.81	33.62	32.71	33.17
	99.77	99.40	98.98	100.58	100.03	100.02	99.87	99.87	99.10	99.05
at.%										
Fe	26.44	18.99	27.60	29.51	33.90	32.86	35.09	34.68	35.65	37.76
Ni	27.38	32.91	25.00	22.16	18.65	20.41	16.91	17.34	17.45	14.57
Co	0.17	0.19	0.73	0.42	0.28	0.88	0.33	0.23	0.09	0.31
Cu	0.02	0.19	0.42	0.06	–	–	0.04	0.38	–	0.30
S	47.78	47.70	48.08	46.85	47.17	45.85	47.62	47.37	46.60	47.67
$\frac{Fe}{Ni}$	0.90	0.827	1.04	1.274	1.82	1.55	2.074	2.00	2.054	2.59
	Pn+Py +Po+Cp	Pn+Bo +Cp	Pn	Pn+Cu	Pn	Pn+Dg +Mt	Pn+Po +Mw+V	Pn+Cu	Pn+Fe Wa+Mt	Pn+A +Mt

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1–2 pentlandite enclosed in primary silicates. 3 and 4 intergranular pentlandites adjacent to unserpentinized primary silicates. 5–10 intergranular pentlandites in close contact with serpentine veinlets. Abbreviations as in Figs. 2 and 3. Fe: native iron; Wa: wairauite; V: valleriite.

Table 3. *Representative Microprobe Analyses of Cu-Ni-Fe-S Opaque Minerals Coexisting with Pentlandite from Beni Bousera*

	Po (*)	Cp (*)	Bo (*)	Po	Mw1	Mw2	Dg	Aw	Cu
wt.%									
Fe	55.15	30.41	11.09	63.30	43.78	56.56	2.44	22.70	4.68
Ni	5.85	–	0.02	–	20.13	4.52	1.18	72.81	2.29
Co	–	0.13	0.83	0.10	0.28	0.41	0.08	–	–
Cu	–	33.72	60.87	–	0.15	0.24	73.66	0.15	92.06
S	39.82	35.48	26.79	36.33	35.25	36.11	22.75	0.15	0.34
	99.50	99.73	99.59	99.79	99.60	99.85	100.13	100.81	99.37
at.%									
Fe	42.44	24.92	9.91	49.97	35.10	46.39	2.27	28.46	5.30
Ni	4.16	–	0.02	–	15.36	3.38	1.02	71.15	2.46
Co	–	0.1	0.66	0.05	0.20	0.30	0.07	–	–
Cu	–	24.31	47.77	–	0.10	0.15	59.84	0.11	91.55
S	53.40	50.65	41.65	49.98	49.24	49.73	36.68	0.28	0.69
	0.873	0.972	1.40	1.000	1.03	1.008	1.726	–	–

The stars refer to sulfide inclusions. The values at the bottom of the table indicate the metal:sulfur atomic ratio. Abbrevations as in Figs. 2 and 3.

Pyrrhotite averages a monoclinic pyrrhotite in composition (Figs. 6 and 7), as espected for this sulfide when it coexists with pyrite (*Misra* and *Fleet*, 1973). It contains appreciable Ni, occasionally reaching 8% by weight (Tables 3 and 4). According to the few-experimental data, Ni substitution in monoclinic pyrrhotite shows a positive temperature dependance (*Misra* and *Fleet*, 1973). *Naldrett* (1966, unpublished data quoted by *Naldrett* and *Kullerud*, 1967) has established that monoclinic pyrrhotite can accommodate up to 5% by weight of Ni at 260–300 °C; this temperature may accordingly represent the upper temperature limit of the final equilibration of sulfide inclusions. However, variations in the Ni content of pyrrhotite together with the lack of correlation of this element with the chemistry of coexisting pentlandite (Fig. 6) suggest that the final equilibration of inclusions has occurred at temperatures displaying large variations between inclusions.

Table 4. *Representative Microprobe Analyses of Cu-Fe-Ni-S Opaque Minerals Coexisting with Pentlandite from Ronda*

	Po (*)	Cp (*)	Bo (*)	Po	Mw2	Dg	Aw	Aw	Cu
at.%									
Fe	58.37	30.00	5.01	63.40	61.14	3.24	41.86	25.78	1.57
Ni	2.11	0.10	1.91	0.02	3.34	1.84	56.33	73.56	0.26
Co	0.27	0.01	–	0.03	0.32	0.06	0.70	0.01	–
Cu	0.28	33.63	67.77	0.05	0.31	71.86	0.07	0.89	97.52
S	39.85	35.15	23.96	36.97	35.79	23.65	0.02	0.34	–
	100.88	98.87	98.65	100.47	100.89	100.66	99.00	100.59	99.30
at.%									
Fe	44.97	24.82	4.63	49.59	48.05	2.97	43.53	27.46	1.78
Ni	1.12	0.08	1.65	0.01	2.49	1.58	55.52	71.11	0.19
Co	0.02	–	–	0.02	0.24	0.04	0.70	0.01	–
Cu	0.02	24.44	55.09	0.04	0.20	57.77	0.06	0.79	97.97
S	53.44	50.66	38.60	50.34	48.99	37.64	0.04	0.62	–
	0.87	0.974	1.59	1.013	1.04	1.65	–	–	–

Symbols as in Table 4.

B) *Intergranular Assemblages*

Pyrrhotite and pentlandite show compositional variations that are markedly different from those probed within inclusions. Pyrrhotite is almost Ni-free (Tables 3 and 4), suggesting that the intergranular component was reequilibrated down to lower temperature than inclusions. On the other hand, its iron:sulfur ratio increases from 7:8 in the least serpentinized samples to 1 in the other weakly-serpentinized samples where pyrrhotite approachs troilite in composition (Figs. 6 and 7). Unfortunately, the small size of this mineral do not permit to confirm the

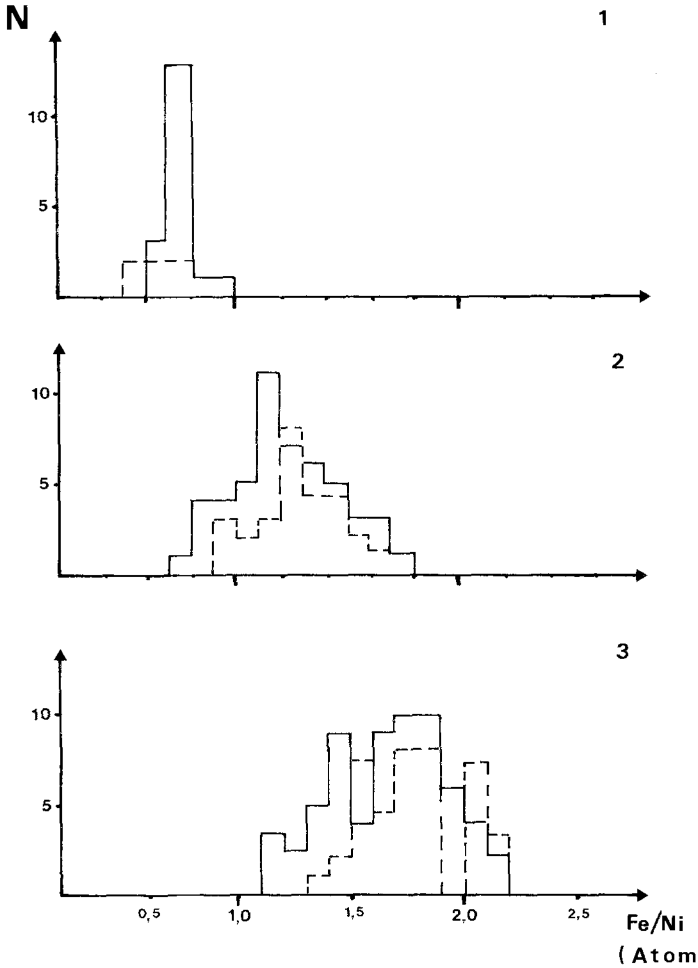

Fig. 4. Frequency distribution of pentlandite compositions (*N* is the number of probed grains for which composition has been averaged on five microprobe analyses). Full lines correspond to the Beni Bousera samples and dashed lines to the Ronda samples. *1* Pentlandite inclusions; *2* intergranular pentlandites adjacent to unserpentinized primary silicates; *3* intergranular pentlandites in close contact with serpentine veinlets

occurrence of troilite by using X-rays diffraction pattern; the drop of the sulfur content of intergranular pyrrhotite with respect to the inclusions is, however, a further evidence of the slight decrease of the overall sulfur content within the intergranular component in weakly-serpentinized peridotites.

Taken as a whole, the intergranular pentlandites are higher in Fe and Co than the pentlandite inclusions (Figs. 4 and 5) and their compositional ranges are clearly dependent on textural sites which they occupy in the host rock. Despite some scatter in the values, the histograms in Fig. 4 show that the Fe/Ni atomic ratio of intergranular pentlandites adjacent to the unaltered primary silicates

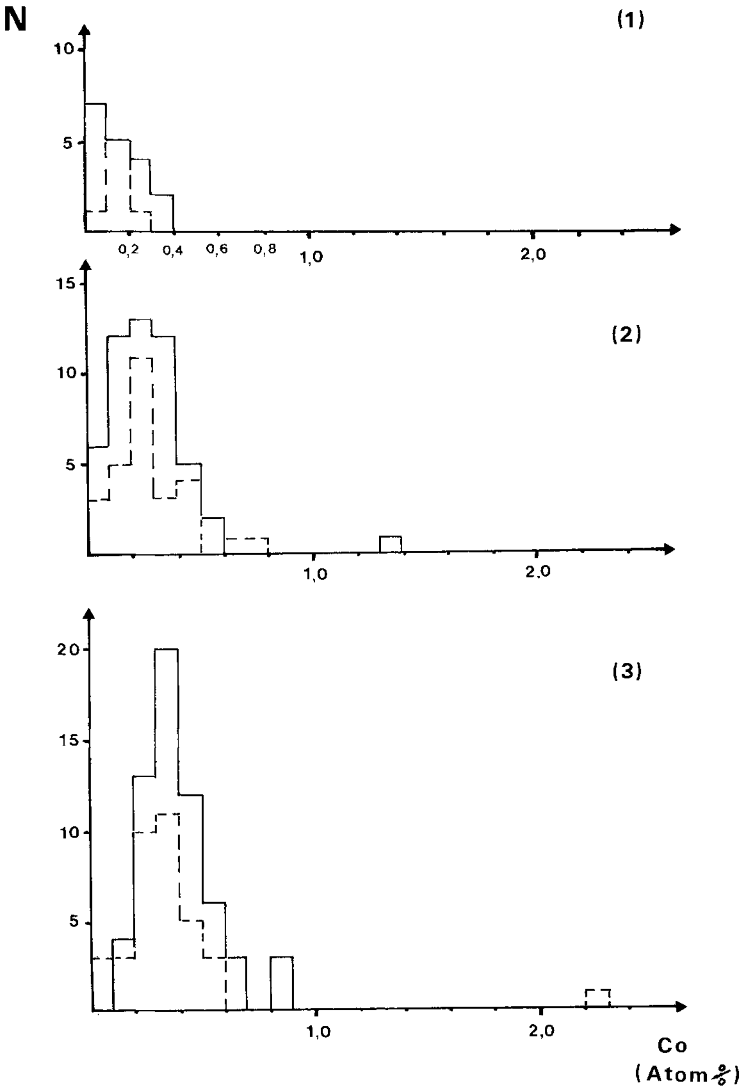

Fig. 5. Frequency distribution of pentlandite compositions. Caption as in Fig. 4

averages 1.15. On the other hand, the intergranular pentlandites in close contact with serpentine are strongly enriched in Fe (Fig. 4), the highest Fe content (up to 46% by weight) being observed in a pentlandite grain from Ronda (Table 2). Within each compositional range in Fig. 4, isolated pentlandite exhibits compositional variations roughly similar to those of pentlandite occurring within polyphase aggregates (Tables 1 and 2); consequently, this sulfide does not seem to obey the general principle of *Misra* and *Fleet* (1973) in which the Fe/Ni ratio of pentlandite from ultramafic rocks should be characteristic of the particular sulfide assemblage containing this mineral. The Co content of intergranular

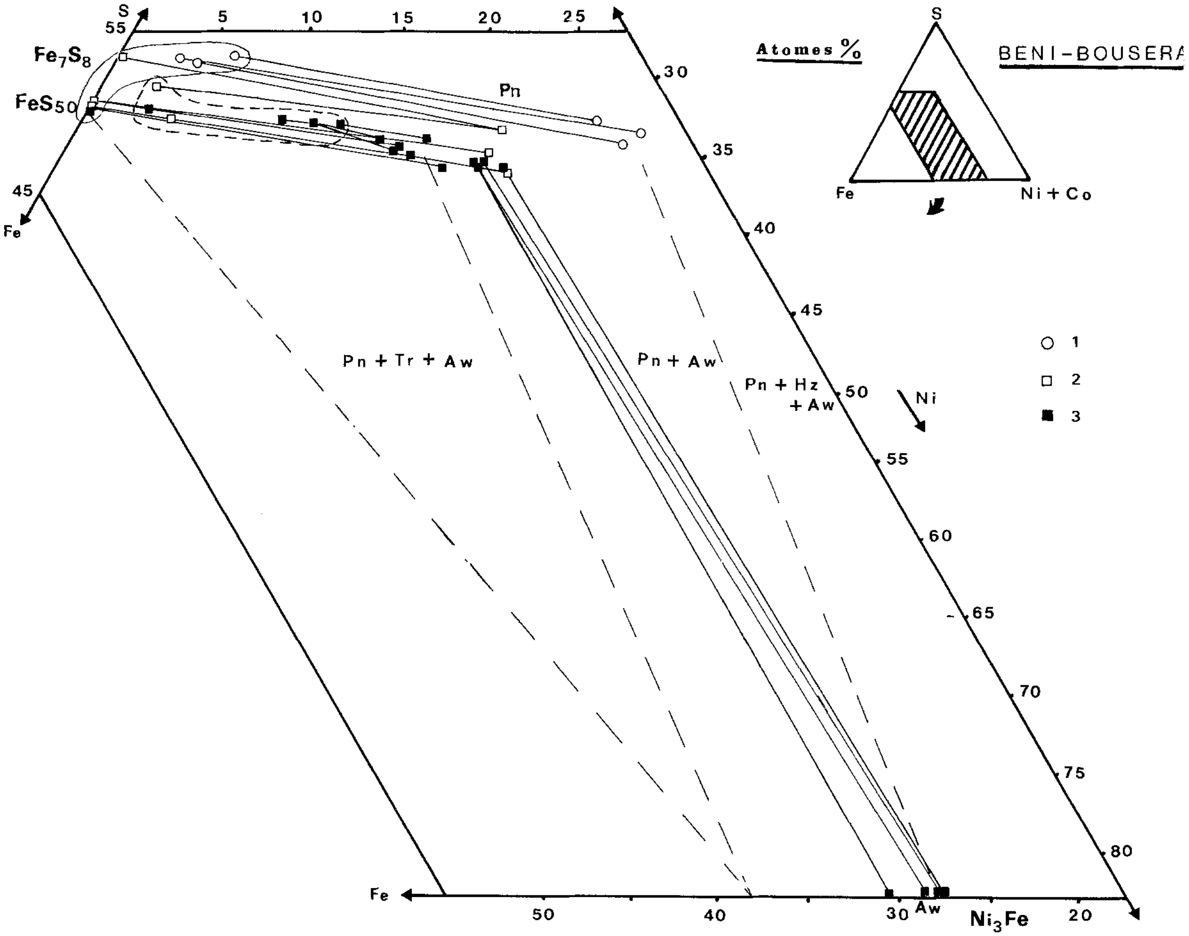

Fig. 6. Plot of representative analyses of pentlandite, pyrrhotite, mackinawite and awaruite in the Fe-Ni-S system. Full and dashed lines area respectively surround the compositional variations of pyrrhotite and mackinawite. The interpretative low temperature phase fields of the sulfur-deficient portion of the Fe-Ni-S system given by *Misra* and *Fleet* (1973). *1, 2, 3* as in Fig. 4 and other abbreviations as in Fig. 2 and Table 1

pentlandite displays a slight increase with respect to the inclusions although its variations are less evident (Fig. 5); the highest Co content of all tne probed pentlandites is found within euhedral pentlandite crystals (Table 1).

The occurrence of these compositional ranges in both the weakly and partly serpentinized samples, sometimes observed in a single sample, is noteworthy and may be ascribed to processes which have been active at different cooling stages of the sulfide component. A final equilibration of intergranular assemblages at a lower temperature than the inclusions may be responsible for the first step of the Fe-enrichment observed at the grain boundaries of primary silicates. On the other hand, the chemistry of intergranular pentlandites in close contact with serpentine has obviously been controlled by the serpentine-

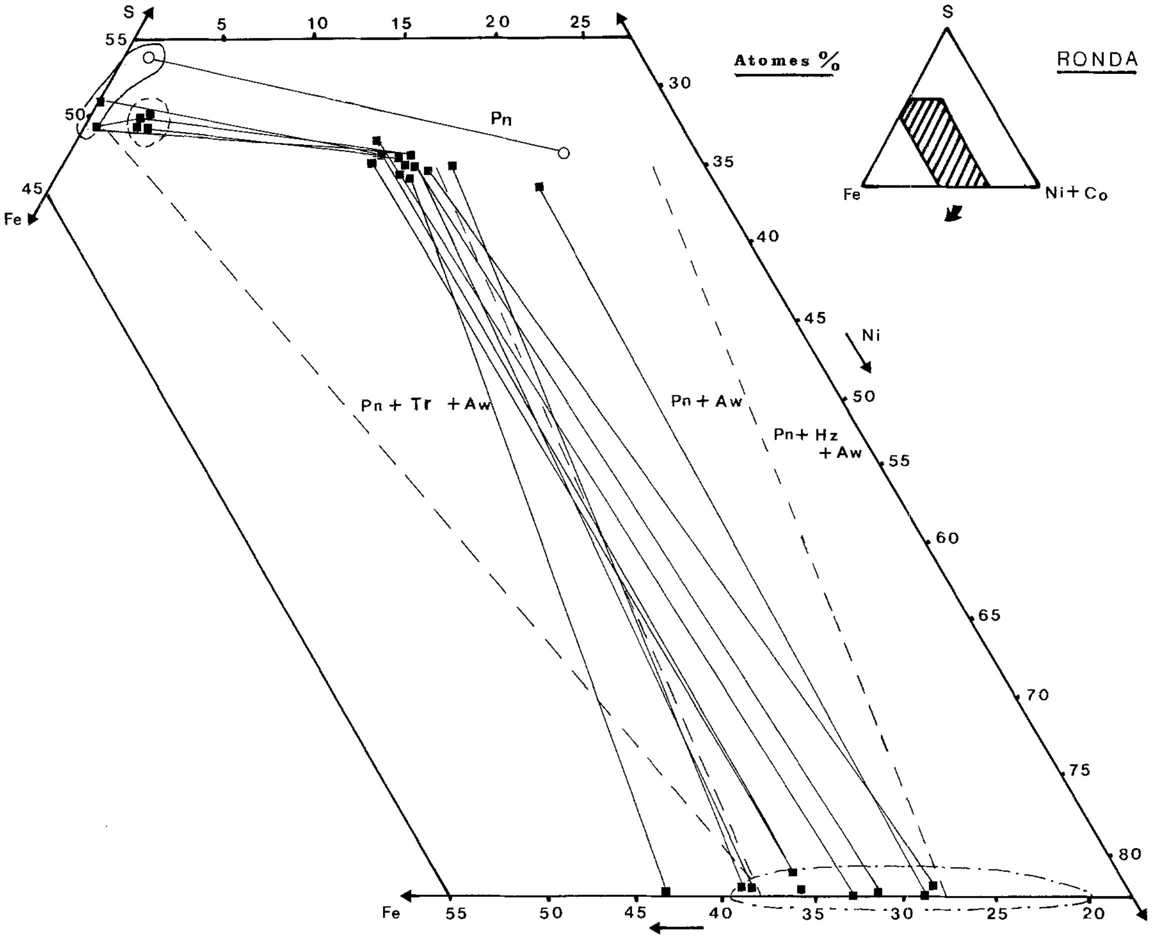

Fig. 7. Legend as in Fig. 6. Compositional variations of awaruite are surrounded by a dashed-dotted line

producing reactions. Then, their strong enrichments in Fe and Co may have been produced either by a selective leaching of Ni from pentlandite by aqueous fluids involved during serpentinization or by the partitioning of Fe and Co from silicates into pentlandite. In the former process, the leaching of Ni together with a parallel shrinkage of the volume of initial pentlandite would indeed generate high residual concentrations of Fe and Co. However, it also implies that the Fe and Co would vary sympathetically in the residual pentlandite, and this is not the case (Tables 1 and 2); moreover, there is no textural evidence suggesting that the Fe- and Co-rich pentlandites are smaller in volume that those adjacent to primary silicates. Consequently, the second hypothesis seems more likely; in that hypothesis, the spread values shown in histograms (Figs. 4 and 5) would suggest that pentlandite only achieved a grain by grain equilibrium with its neighboring silicates.

Among the Cu-Fe-Ni-S opaque minerals formed during serpentinization, native copper, mackinawite and awaruite display significant compositional variations. Native copper is compositionally similar to those described by *Botto* and *Morisson* (1976) in the Josephine Peridotite, Oregon (U.S.A.) and shows up to 4.8% by weight of Fe (Tables 3 and 4). As experimentally demonstrated by *Morimoto* and *Koto* (1970), a significant amount of Fe is also required to stabilize digenite at low temperature (Tables 3 and 4).

The Fe/Ni ratio of mackinawite and awaruite increases with the degree of serpentinization (Tables 3 and 4). The vermicular mackinawite (Mw_1) occurring within weakly-serpentinized peridotites is Ni-rich and similar to that previously described by *Conquéré* (1969) in a mafic layer from Beni Bousera. The coarser grained mackinawite (Mw_2) is poorer in Ni, resembling mackinawite often described in serpentinites (*Ashley*, 1975).

Awaruite is close to Ni_3Fe at Beni Bousera and its composition plots exactly within the room temperature phase field assumed by *Misra* and *Fleet* (1973) for this mineral when it only coexists with pentlandite (Fig. 6). In comparison, awaruite from Ronda displays intermediate compositions between Ni_3Fe and native iron as well as a slight departure from the solid solution limits of natural awaruite compiled by *Ahmed* and *Hall* (1982) (Fig. 7). Another interesting feature at Ronda is the intersection of tie lines existing between awaruite and the coexisting pentlandite (Fig. 7), which supports the grain by grain equilibrium hypothesis suggested above. In this regard, it is evident from a comparison of Fig. 6 with Fig. 7 that the higher average degree of serpentinization displayed by the Ronda samples is partly responsible for this particular equilibrium state achieved by the intergranular component.

IV. Discussion

Textural relations and phase chemistry of the Cu-Fe-N-S minerals show that inclusions and the intergranular component were composed of the same sulfide assemblage prior to serpentinization but they behaved as different physical and chemical systems with respect to hydrothermal fluids involved in serpentinization.

The sulfide inclusions escaped contamination by low temperature fluids, as demonstrated by the occurrence of a sulfide assemblage commonly found in ultramafic rocks not subject to serpentinization; on the other hand, the presence of monoclinic pyrrhotite, sometimes associated with pyrite indicates that they were equilibrated at high of values fS_2 (*Eckstrand*, 1975). It is therefore concluded that the sulfide inclusions behaved as closed systems with respect to hydrothermal fluids so that fS_2 within inclusions was internally controlled by the sulfide assemblage. In that case, the variations of equilibrium temperatures suggested above may have been produced either by low temperature thermal gradients within the host silicates or by the presence of minor elements in variable amounts within the sulfide component not detected by the electron microprobe analyses; as discussed by *Yund* and *Hall* (1970), minor elements can reduce the rates of the subsolidus reactions occurring within sulfide minerals on cooling.

The question of whether the mackinawite-bearing intergranular assemblage from weakly serpentinized peridotites behaved as a closed or as an open system with respect to low temperature fluids is of particular interest because this assemblage forms the main part of the intergranular sulfide component found within alpine type bodies (*Besson*, 1975; *Lorand*, 1983a and b; *Garuti* et al., 1984). *Garuti* et al. postulated that it would be the product of an almost isochemical subsolidus reequilibration of the upper mantle sulfide component. Nevertheless, this opinion can hardly be reconciled with the present data. Firstly, two lines of evidence suggest that mackinawite-bearing assemblages behaved as open systems with respect to both fluids, and the silicate matrix during serpentinization 1) their final equilibration occurred at values of lower fS_2 than inclusions, 2) they contain Fe- and Co-rich pentlandites indicative of exchange reactions with the surrounding serpentines. In addition, microtextural relationships show that mackinawite originated through a replacement reaction involving pentlandite. The slightly different sulfur contents between these two sulfides imply that the conversion of pentlandite has required sulfur addition which is logical to be ascribed to the parallel breakdown of pyrite and monoclinic pyrrhotite into troilite. Although its stability field is not accurately known, mackinawite is generally believed to be stable at or below 200 °C (*Power* and *Fine*, 1976); it seems therefore likely that the internal redistribution of sulfur as well as the crystallization of mackinawite have been produced by fluids involved in serpentinization. This opinion is supported by the common occurrence of mackinawite in serpentinized ultramafic rocks (*Ashely*, 1975; *Blain*, 1978) as well as by experimental works of *Zoka* et al. (1973) and *Sweeney* and *Kaplan* (1973) emphasizing that the crystallization of this sulfide is possible only under hydrous conditions. On the basis of these results, it is postulated that mackinawite-bearing assemblages would represent the earliest alteration product of the intergranular upper mantle sulfide component by low temperature hydrothermal fluids. That the final equilibration of these assemblages has occurred in the presence of fluids is also demonstrated by their equilibrium temperatures systematically lower than those of the inclusions; owing to its probable "catalytic" effect on the solid state reactions, the fluid phase would account for such a discrepancies.

Concerning the partly-serpentinized samples, there are three sets of arguments demonstrating that intergranular assemblages were generated through a strong alteration of the upper mantle sulfide component by serpentinization. Exchange reactions within pentlandite as well as the distribution of secondary sulfides show that all the ore-forming elements (Fe, Ni, Co, Cu and S) underwent a redistribution, at least on the hand sample scale. The second line of evidence is provided by the temperatures which have controlled the crystallization sequence of intergranular assemblages, as deduced from textural relationships between sulfides and native metals. Because they clearly postdate the replacement of pentlandite by mackinawite, native metals are assumed to have formed at or below 200 °C; on the other hand, the replacement of native copper by digenite was only possible below 80 °C, as indicated by the stability field of this sulfide (*Roseboom*, 1966; *Morimoto* and *Koto*, 1970). It has to be noted that this temperature range, even if it cannot be known with more accuracy, is in good agreement with those assumed for the formation of lizardite-bearing serpentine assemblages (*Moody*, 1976). Lastly, the mineralogical changes observed through the crystallization sequence of intergranular assemblages is entirely consistent with a control of the minor sulfide component by Fe-related redox mechanisms occurring within the dominant silicate + fluid portion during serpentinization, as previously suggested by the models of *Chamberlain* et al. (1965), *Eckstrand* (1975), and *Groves* and *Keays* (1979). This process may be depicted by the fS_2 vs. fO_2 diagrams of *Eckstrand* (1975) (Fig. 8) which is valid at a temperature comparable to those derived above; starting from the sulfide assemblage in inclusions, it shows that the intergranular assemblages were externally buffered by three different redox conditions through increasing degree of serpentinization.

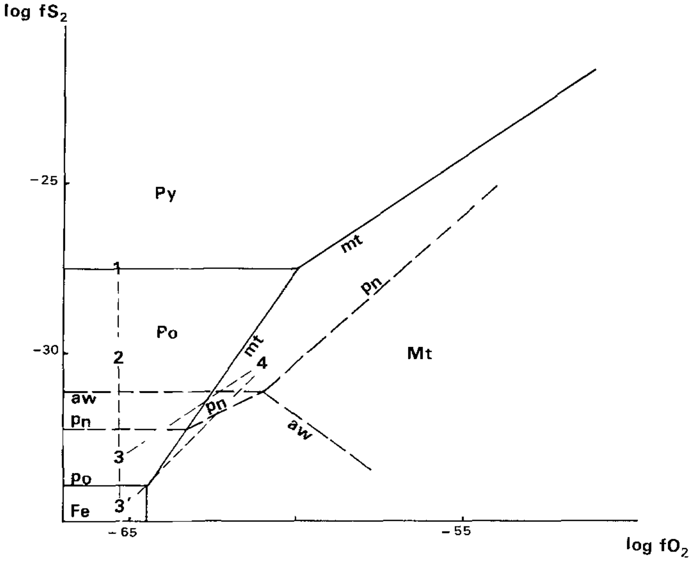

Fig. 8. Crystallization sequence of intergranular assemblages from the partly-serpentinized peridotites plotted in the fO_2 versus fS_2 diagram of *Eckstrand* (1975). *1* Sulfide inclusions; *2* mackinawite – bearing assemblages (early stage of serpentinization); *3* to *3'* native metals (middle stage of serpentinization); *4* magnetite and secondary sulfides (late stage of serpentinization)

The slight decrease of fS_2 suggests that the early stage of serpentinization involved moderately reducing fluids or near neutral water. On the contrary, the drop of fS_2 and the low fO_2 during the crystallization of metallic phases allow a middle stage of serpentinization characterized by reducing fluids to be defined, becoming more reducing with the magnitude of serpentinization until native iron was formed (*Lorand* and *Pinet*, 1983). The crystallization of secondary sulfides and magnetite after metallic phases indicates a late increase of both fS_2 and fO_2, suggesting that the latest stage of serpentinization produced more oxidizing fluids. As discussed below, no unique explanation may be offered for the late increase of fO_2 but, at least, the development of reducing fluids is in agreement with the reaction of anhydrous olivine containing Fe^{2+} with water to produce magnetite and residual concentrations of H_2 as follows:

(A) $2\,Fe^{2+}$ (in olivine) + $H_2O \rightleftharpoons 2\,Fe^{3+}$ (in magnetite) + O^{2-} + H_2
(*Wicks* and *Whittaker*, 1977).

Petrogenesis of Opaque Assemblages

The above data allow a model involving a three-stage alteration of intergranular assemblages through the increasing degree of serpentinization to be proposed. Assuming that they occurred only in the presence of an aqueous fluid or its breakdown products, alteration reactions of opaque assemblages corresponding to each stage have been written on the basis of textural relationships and composition of each Cu-Fe-Ni-S opaque mineral, as given by microprobe analyses (Table 5). Because of the possible grain by grain compositional variations of the sulfide component prior to serpentinization and the mobility of ore-forming elements during this alteration, the reactions in Table 5 are only empirical; in addition, the grain-by-grain equilibrium stage achieved by the intergranular component suggests that each intergranular assemblage was in itself a physical system isolated from the others by the surrounding non-sulfide minerals so that the writing of more accurate reactions is precluded. Reactions such as those proposed here and a part of that is discussed below have previously been proposed in various forms for other occurrences of serpentinites (see *Ashley*, 1975 for an example); nevertheless, the present model has to account for the following unique features.

1) The whole sequence of events from unaltered primary sulfides to complete alteration of intergranular assemblages is displayed in a single polished thin section as well as between samples; the present appraisal should therefore be valid on the hand sample scale as well as on a larger scale.

2) The presence of mackinawite-bearing assemblages in samples displaying only 10% by volume of serpentine minerals suggests that alteration of intergranular opaque assemblages began at an earlier serpentinization stage than commonly assumed.

3) The average degree of serpentinization is lower but conditions were more reducing than in most of the serpentinites occurrences previously studied, as demonstrated by the occurrence of metallic phases for a degree of serpentinization not higher than 20% by volume as well as by native iron.

4) Intergranular assemblages achieved a grain by grain equilibrium state as the magnitude of serpentinization has increased.

5) Low temperature exchange reactions between sulfides and silicates have involved mainly Fe, and, to a lesser degree, Co whereas serpentinization is generally believed to partition Ni from altered silicates into Cu-Fe-Ni opaque assemblages (*Eckstrand*, 1975).

a) Early Stage of Serpentinization

The absence of magnetite in weakly serpentinized peridotites suggests that reaction (A) was not active in the early stage of serpentinization; this supports the above assumption that moderately reducing fluids were generated at this stage. Of special interest for understanding the early alteration of the intergranular sulfide assemblages is the low overall volume of the sulfide component in the Beni Bousera and Ronda samples. *Eckstrand* (1975) stressed that the effect of serpentinization on sulfide assemblages would increase as the ratio between the fluid + silicates portion and the sulfide component increases. It can accordingly be postulated that the volumetrically minor, upper mantle

Table 5. *Possible Reactions Occurring During Serpentinization*

Non-sulfide minerals	Intergranular sulfide component
	a) Early stage
olivine → serpentine	1) $\underset{\text{monoclinic Po}}{Fe_{0.787}Ni_{0.088}S} \rightleftharpoons \underset{\text{troilite}}{0.787\ FeS} + \underset{\text{fluid}}{0.213\ S + 0.088\ Ni}$
	2) $\underset{\text{pentlandite}}{Fe_{3.36}Ni_{5.14}S_8} + \underset{\text{fluid}}{2.82\ Fe + 1/2\ S_2} \rightleftharpoons \underset{\text{vermicular Mw}}{Fe_{6.68}Ni_{2.32}S_9} + \underset{\text{fluid}}{2.82\ Ni}$
	b) Middle stage
olivine → serpentine + magnetite	3) $\underset{\text{pentlandite}}{2\,(Fe_{6.8}Ni_{4.2})S_8} + \underset{\text{fluid}}{18\ H_2} \rightleftharpoons \underset{\text{awaruite}}{3\ Ni_{2.8}Fe} + \underset{\text{fluid}}{18\ H_2S + 6.6\ Fe}$
orthopyroxene → bastite	4) $\underset{\text{chalcopyrite}}{CuFeS_2} + \underset{\text{fluid}}{2\ H_2 + 0.1\ Ni} \rightleftharpoons \underset{\text{native copper}}{Cu_{0.96}Fe_{0.3}Ni_{0.1}} + 2\ H_2S + 0.93\ Fe + 0.04\ Cu$
CrAl-spinel → ferritchromite	5) $\underset{\text{troilite}}{FeS} + \underset{\text{fluid}}{H_2} \rightleftharpoons \underset{\text{fluid}}{Fe + H_2S}$
	c) Late stage
	6) $\underset{\text{native copper}}{Fe_{0.03}Ni_{0.01}Cu_{0.96}} + \underset{\text{fluid}}{0.615\ H_2S} \rightleftharpoons \underset{\text{digenite}}{1.62\,(Fe_{0.02}Ni_{0.01}Cu_{0.59}S_{0.38})}$ $\underset{\text{fluid}}{+\ 0.615\ H_2 + 0.024\ Fe + 0.0062\ Ni}$
	7) $\underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{fluid}}{3.637\ H_2S + 1.114\ H_2O + 0.171\ Ni + 1.119\ Cu + 2.416\ Mg} \rightleftharpoons$ $\underset{\text{valleriite}}{15.544\,(Fe_{0.192}Ni_{0.011}Cu_{0.072}S_{0.13}4Mg_{0.16}(OH_{0.229}))}$
	8) $\underset{\text{serpentine}}{4.59\ Fe + 3.53\ Ni + 0.88\ Co} + \underset{\text{fluid}}{8\ H_2S} \rightleftharpoons \underset{\text{euhedral pentlandite}}{(Fe_{4.59}Ni_{3.53}Co_{0.88})S_8} + 8\ H_2$

sulfide component no longer retains its "self buffering capacity" with respect to fS_2 as the water volume increases inside the peridotites; then, the increase of fH_2O would quickly lower the fS_2 and, accordingly, promote reactions (1) and (2) (Table 5). Fluids would also remove the coarse-grained, early chalcopyrite to form the chalcopyrite-pentlandite intergrowths as described in partly-serpentinized samples.

Iron largely predominates over nickel in upper mantle olivine (*Kornprobst*, 1969; *Obata*, 1980). On the other hand, *Moody* (1976) and *Wicks* and *Whittaker* (1977) have pointed out that serpentine pseudomorphs show Ni contents slightly lower than those of primary olivine but do not accommodate a large amount of Fe released by this silicate. Due to the lack of magnetite in weakly-serpentinized samples, it is postulated that Fe was in excess with respect to Ni in the sites of serpentinization during the early stage of alteration. This, and the low overall abundance of the sulfide component account for the occurrence of Fe-rich pentlandites in the least serpentinized samples.

b) Middle Stage of Serpentinization

In his model, *Eckstrand* (1975) noted that it remains unclear why serpentinization is locally sufficiently reducing to produce native iron, whereas in general it is only reducing enough to generate awaruite. On the other hand, *Abrajano* and *Pasteris* (1984) postulated that the crystallization of native iron and iron alloys during hydration of ultramafic rocks requires four conditions (1) the participation of olivine, stable or metastable in the low temperature redox reaction (2) a low water/protolith ratio ($\leqslant 0.18$); (3) a low silica activity, and (4) a high Fe^{2+}/Mg ratio in the initial olivine. As far as the Beni Bousera and Ronda samples are concerned, conditions (3) and (4) seem to be unnecessary to stabilize native iron and iron alloys, because the serpentinization of lherzolites generates a high silica activity (*Wicks* and *Plant*, 1979) and the Fe/Mg ratio of mantle olivine is very low (*Kornprobst*, 1969; *Obata*, 1980). On the contrary, the serpentinization of all the samples studied here is far from completion, so that the alteration process is believed to have involved a low water/protolith ratio. It is postulated that, in the case of a low water/protolith ratio, the volumetrically dominant primary silicates would act as a "screen" with respect to the diffusion of fluids; therefore, hydrogen produced by reaction (A) would slowly migrate out of the sites of serpentinization, thus increasing reducing conditions inside that site. This process accounts for the crystallization of reduced assemblages even for some low degree of serpentinization. Moreover, it is readily apparent from Fig. 9 that the crystallization of iron-rich awaruite and native iron instead of awaruite in the most serpentinized samples from Ronda may be explained by an increase of fH_2 roughly proportional to the magnitude of serpentinization; such an increase would require that conditions of slow diffusion of hydrogen are maintained through the entire range of serpentinization. To summarize, unusually reducing conditions produced during incipient serpentinization may at first be explained by the low permeability of the host rocks with respect to the diffusion of fluids.

At this stage, the bastitization of orthopyroxene (Table 5) has precluded the crystallization of brucite (*Wicks* and *Plant*, 1979) which could accommodate a

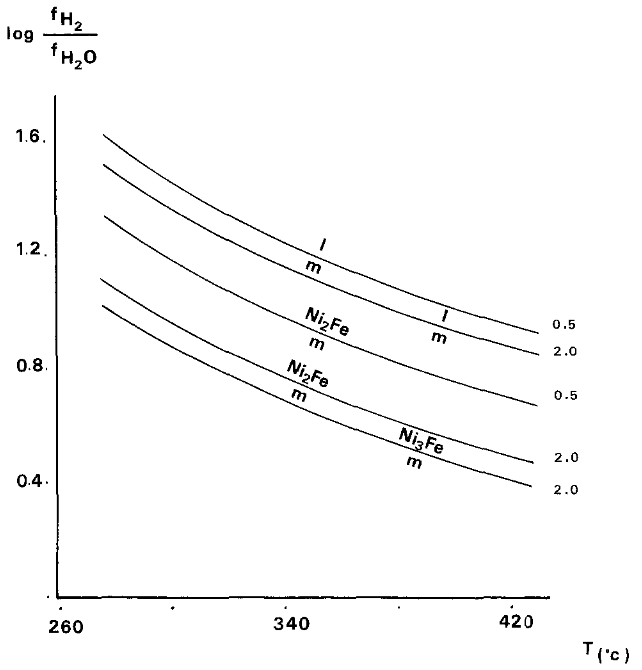

Fig. 9. Stability of iron-magnetite (IM) and magnetite-awaruite (Ni_2Fe-Fe_3O_4 and Ni_3Fe-Fe_3O_4) assemblages as a function of log fH_2/fH_2O and temperature for P_{total} = 0.5 and 2.0 kb (after *Moody*, 1976)

significant amount of Fe (*Moody*, 1976). Accordingly, the partitioning of Fe and Ni released by olivine would have been controlled by magnetite and pentlandite. As shown by reaction (A), a high fH_2/fH_2O would stabilize iron released by olivine as Fe^{2+}, making easier the entry of this element into pentlandite rather than into magnetite. Other evidence supporting this conclusion has been provided experimentally by *Philippidis* (1982) who obtained Fe-rich pentlandite coexisting with a Ni-bearing magnetite through the serpentinization of an Fe-Ni-Mg olivine with a reducing, sulfur-bearing fluid. Thus, the unusually reducing conditions produced during the middle stage of serpentinization are responsible for the strong partitioning of Fe into pentlandite, the primary composition of peridotites being another possible controlling factor.

Strongly reducing conditions may have also enhanced the partitioning of Fe from silicates into the fluid phase when the sites of serpentinization were devoid of pentlandite. A high activity of Fe in the fluid is needed by reaction 2 (Table 5) but also accounts for the absence of bornite from weakly serpentinized peridotites and for the high Fe content of most of Cu-Fe-Ni-S minerals formed during serpentinization. In addition, exchange reactions between intergranular pentlandites and the fluid cannot be ruled out and would be responsible for the slight Fe-enrichment of intergranular pentlandites adjacent to unserpentinized primary silicates. In that hypothesis, the two compositional ranges of pentlandite (Fig. 4) suggest that hydrothermal fluids were characterized by strong gradients of a_{Fe}

from the sites of serpentinization toward the boundaries of unserpentinized silicates. Assuming that the solubility of Fe was controlled by redox conditions, then, such gradients would reflect strong gradients of fH_2 on the hand-sample scale; this is in agreement with the above hypothesis that the low permeability of the host rocks would have constrained hydrogen to stay within the sites of serpentinization during the middle stage of serpentinization.

Several factors may be responsible for the grain-by-grain equilibrium state achieved by intergranular assemblages. An interesting feature in Fig. 9 is that the grain-by-grain compositional variations of awaruite from Ronda (Fig. 7) would obviously reflect microscale variations of the fH_2/fH_2O ratio in the fluid phase; it would especially be true if the pressure range controlling serpentinization was below 1 kb, because the difference between the $\log fH_2/fH_2O$ in the fluid necessary to stabilize Ni_2Fe instead of Ni_3Fe becomes very small (*Moody*, 1976). One of the possible factors controlling microscale variations of fH_2/fH_2O may be the alteration of Al-Cr spinel into ferritchromite which is capable of producing additional concentration of H_2 (*Ahmed* and *Hall*, 1982); on the other hand, an heterogeneous diffusion of H_2 and (or) H_2O enhanced by the highest degree of serpentinization is not unrealistic. Microscale variations of the fH_2/fH_2O ratio within fluids would produce microscale variations of a_{Fe} and, thus, the grain-by-grain compositional variations of pentlandite; however, the relative scatter in histograms in Fig. 4 could also be ascribed to local occurrences of bastite after *Opx* in close contact with intergranular pentlandites, this alteration reaction being not an Fe-producing one (*Wicks* and *Plant*, 1979). As a result, the equilibrium state of the intergranular component would be a complex function of both the diffusion of fluids and the solid state reactions of the surrounding non-sulfide minerals.

c) Late Stage of Serpentinization

A general decrease of the fH_2/fH_2O ratio in the fluid accounts for the late overgrowths of magnetite on metallic phases (Fig. 9) and, thus, for the oxidizing conditions which prevailed at this stage. Indeed, oxidizing conditions would bring a slowdown in the partitioning of Fe into pentlandite, by stabilizing Fe as Fe^{3+}; this is in good agreement with the decrease of the Fe/Ni ratio of secondary pentlandite (Table 1). Oxidizing conditions also constrain sulfur released as H_2S (*Philippidis*, 1982) by reactions (3) to (5) (Table 5) to recombine itself with ore-forming elements to form secondary sulfides, as previously postulated by *Ramdohr* (1967), *Ashley* (1975) and *Groves* and *Keays* (1979). Under these conditions, the distribution of secondary sulfides on the hand sample scale would reflect the mobility of ore-forming elements. The extent of redistribution remains unclear for Cu and S, especially as regards the distance should have migrated. Chalcopyrite, native copper, digenite and valleriite often occur together in the same polished thin section so that it seems unlikely that Cu could have migrated on more than the hand sample scale. Concerning sulfur, there is no textural evidence supporting the addition of this element from an external source, as pointed out for other occurrences of serpentinites (*Ashley*, 1975). On the other hand, the abundance of secondary sulfides shows a slight decrease at Ronda with respect to Beni Bousera, suggesting that the amount of sulfur escaping from intergranular assemblages was proportional to the degree of serpentinization. Reaction (6) in Table 5 is a possible one only below 80 °C owing to the stability field of digenite (see above); thus, it is assumed that sulfur was still mobile at this temperature.

A late decrease of the fH_2/fH_2O ratio in fluids causing late stage serpentinization has already been pointed out by *Kanehira* et al. (1964) and *Chamberlain* et al. (1965) for other occurrences. According to *Kanehira* et al. (1964), this would be the result of the diffusion of H_2 outside the sites of serpentinization; on the other hand, *Chamberlain* et al. (1965) postulated that the decrease of temperature controlling the latest stage of serpentinization would bring a slowdown in reaction (A) and, consequently, a decrease in the amount of H_2. The former hypothesis implies that the diffusion of fluids was easier at the end of serpentinization. That conclusion is supported by the behaviour of sulfur as discussed above as well as by the crystallization of valleriite which requires a late influx of water (Table 5; reaction 7); in the latter case, the decrease in the fH_2/fH_2O ratio would have been produced locally by the increase of fH_2O. Concerning the second hypothesis, textural evidence shows that magnetite was formed at a very low temperature, perhaps below 100 °C so that temperature may also be responsible for the drop of fH_2. However, a third possibility is that the fluid/opaque minerals volume ratio progressively decreased as the fluid was consumed by alteration reactions; consequently, intergranular opaque assemblages would have regained their "self-buffering capacity" with respect to redox conditions in the latest stage of serpentinization, thus allowing the fH_2 to be buffered by reactions (3) to (5) (Table 5).

V. Conclusions

A comparison between sulfide inclusions in primary silicates and coexisting intergranular sulfide assemblages appears to be a useful method to discuss the low temperature behaviour of the primary sulfide component of ultramafic rocks. In the present case, it shows that any sulfide component disseminated in the intergranular sites of a volumetrically dominant silicate matrix behaves as an open system with respect to hydrothermal fluids as soon as the degree of serpentinization is higher than 5–10% by volume. These results are believed to have implications for both the interpretation of alterations of opaque minerals connected with serpentinization and the relationships between the sulfide assemblages from upper mantle peridotites and the upper mantle sulfide component.

Concerning the first point, highly reducing conditions appear to be characteristic of the incipient stages of serpentinization; they are ascribed to a low permeability of the host rocks with respect to the diffusion of hydrogen produced by the breakdown of olivine. Apart from the early crystallization of metallic phases, the most important implication of these conditions is thought to be the preferential partitioning of Fe from silicates into pentlandite. Fe-rich pentlandites seem to be common in serpentinites (*Misra* and *Fleet*, 1973; *Ashely*, 1975; *Sinton*, 1976) so that the processes discussed here may have been active elsewhere.

Any study of the upper mantle sulfide component in "Alpine"-type bodies would be constrained by the following factors. Even in the absence of metallic phases, contamination of the intergranular sulfide component resulting from serpentinization must be expected when it contains the assemblage Fe-rich pentlandite + troilite + mackinawite; this conclusion is supported by separate observations from other "Alpine"-type bodies such as those from the Northern Pyrenean Zone, France (*Lorand*, 1983a and b). Because of its low temperature behaviour, the intergranular sulfide component from weakly serpentinized "Alpine"-type peridotites would give erroneous estimations as to the sulfur fugacity levels within the upper mantle. On the other hand, many features of the high temperature equilibration between the upper mantle sulfide component and the surrounding silicates may have been overprinted by low temperature exchange reactions of Fe and Ni. It is therefore suggested that in almost all "Alpine"-type peridotites, only sulfide inclusions in the primary silicates would preserve the initial composition of the upper mantle sulfide component.

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