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# Sulphides and sulpharsenides in the emerald-hosting rocks from the Indus suture zone in Swat, NW Pakistan

Mohammad Arif<sup>1</sup>

## Abstract

In the Swat valley the ophiolitic member of the Indus suture melanges contains carbonate-rich assemblages, which in some places, e.g. in the Mingora and Gujar Kili areas, host emerald deposits. Abundant quartz veins crosscut these rocks and locally constitute stockworks. Evidently derived by talc-carbonate alteration of spatially associated ultramafic rocks, these assemblages essentially consist of magnesite and/or dolomite, and talc or quartz. Besides, chrome spinel (chromite, ferrite-chromite and/or Cr-magnetite) is a common accessory constituent. Some of the rocks, especially those invaded by quartz veins, contain tourmaline and/or fuchsite. Furthermore, some emerald-hosting, magnesite-rich rocks of the Gujar Kili area contain highly reflectant opaque phases. A detailed chemical investigation reveals that these are sulphide and sulpharsenide phases. The sulphides include pyrrhotite, pentlandite, pyrite, violarite and mackinawite. Gersdorffite and, rarely, cobaltite are the two sulpharsenides that occur in the emerald-hosting magnesite-rich rocks of the Gujar Kili area. Opaque mineral assemblages with such a modal abundance are unlikely to form under the high  $fO_2$  (and  $fS_2$ ) conditions that prevail during the talc-carbonate alteration of ultramafic rocks. Furthermore, besides being finely disseminated, the investigated phases locally occur as veins, which cut across the magnesite-rich matrix of the host rocks. Hence they are most probably epigenetic, i.e. formed as a result of late-stage hydrothermal alteration. Some of these phases, e.g. gersdorffite, are reported to occur as inclusions in the Swat emeralds. It thus appears that the same postorogenic hydrothermal activity related to granitic magmatism, which produced emerald in the region, is responsible for the formation of the sulphides and sulpharsenides as well.

**Keywords:** hydrothermal nickeliferous phases, emerald-hosting rocks, Indus suture zone, NW Pakistan.

## 1. Introduction

The occurrence of three drastically different types of melanges, namely the blueschist melange, the greenschist melange and the ophiolitic melange, marks the westward continuation of the Indus suture zone in northwestern Pakistan. The ophiolitic melange occurs as blocks that are distributed within and along the metamorphosed sedimentary rocks of the northern margin of the Indo-Pakistan plate. In addition to typical ophiolitic lithologies, e.g. mafic-ultramafic plutonic rocks, pillow lavas and pelagic sediments, the ophiolitic melange in the Swat valley contains carbonate rich lithologies that at places, such as the Mingora and Gujar Kili areas (Fig. 1), host emerald deposits. Petrographic, mineralogical and geochemical details about these rocks are available in the form of both unpublished and published reports (Arif, 1994; Arif and Moon, 1996a; Arif and Moon, 1999). Mineral chemical data on the major and some of the minor phases are also available (Arif and Moon, 1994, 1996b–d; Arif et al., 1996). The

current report describes some non-oxide opaque minerals that occur in trace to accessory amounts in some of the magnesite-rich rocks from the Gujar Kili emerald mines. In order to know about their genesis, the mode of occurrence, petrographic features and chemical characteristics of these phases are investigated in detail. Furthermore, the possibility of a genetic relationship of the investigated phases with emerald mineralization in the region is addressed.

## 2. Regional tectonics and general geology

In NW Pakistan, rocks of the intra-oceanic Kohistan island arc (KIA) separate the Indo-Pakistan and Asian plates, which are in contact along the Indus-Tsangbo Suture Zone (ITSZ) in India and Nepal (Gansser, 1964, 1980). The KIA was sutured to the southern edge of the Asian plate at ca. 90 Ma along the Shyok suture (Searle, 1991). The Himalayan collision in northwestern Pakistan at ca. 45 Ma was thus between the KIA and

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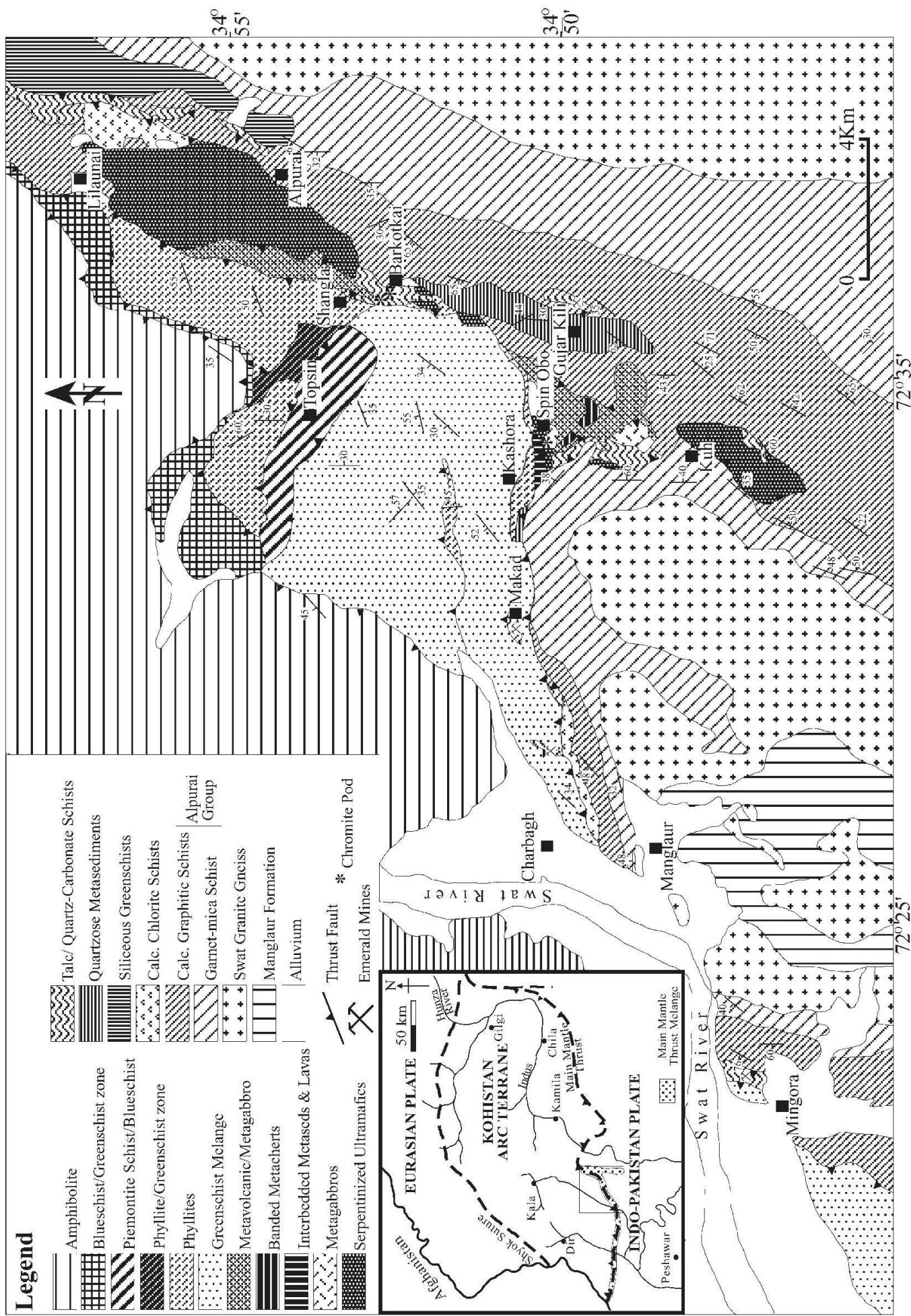


Fig. 1 Geological map of the Lilaunai-Mingora area, Swat, NW Pakistan (after Kazmi et al., 1984). The inset map shows the general location of the study area.

the Indo-Pakistan plate along the Main Mantle Thrust (MMT), which is the westward extension of the ITSZ.

The occurrence of three fault bounded melanges, i.e. the blueschist melange, the greenschist melange, and the ophiolitic melange, marks the MMT in the Swat valley (Fig. 1) (Kazmi et al., 1984). The ophiolitic melange occurs as small to large lens-shaped masses distributed within and along the northernmost edge of the Indo-Pakistan plate (Fig. 1). The mostly blocky masses of the melange commonly contain variably altered ultramafic rocks whereas the other typical ophiolitic components, e.g. mafic cumulate rocks (largely gabbroic), pillow lavas and pelagic sediments, occur only locally.

The more or less pervasive hydration, leading to serpentinization, seems to be the main process responsible for the alteration of ultramafic rocks in the Swat area. Locally, however, carbonate alteration also has played a role in obscuring their original mineralogical composition. Textural relations (i.e. thin microscopic veins of magnesite cutting across matrix serpentine) suggest that carbonation took place after hydration. The varying nature and degree of alteration has in places (e.g. near Barkotkai village) (Fig. 1) resulted in a zonal pattern. The various zones include (1) a core of least altered (serpentinized) ultramafics that is surrounded by (2) a broad and extensively developed zone of mostly to totally serpentinized rocks followed by (3) a locally formed peripheral shell of carbonate-rich (talc-carbonate and quartz-carbonate) lithologies. At places (i.e. Gujar Kili village and Mingora town), the alteration seems to be more pervasive with the result that only the wholly transformed (serpentinites and/or talc-carbonate schists) equivalents of the ultramafic rocks can be seen. The Gujar Kili emerald mining area exemplifies an extreme case of carbonate alteration. Here, serpentinites are lacking and only the carbonate-rich rocks occur.

The carbonate-rich lithologies surface in a number of places in the Swat valley, e.g. the Al-purai-Lilaunai area, the Barkotkai and Gujar Kili villages, the Spin Obo-Kuh area, and north of the Mingora town (Fig. 1). In all these occurrences, except the Gujar Kili village, these rocks are spatially associated with variably serpentinized ultramafic rocks. Although also occurring as small patches within the serpentinized rocks in some places, these carbonate-rich rocks are mostly distributed along the contact between the serpentinites and metamorphosed pelitic rocks carrying carbonate  $\pm$  graphite. Quartz veins, which are locally very abundant and thus form stockworks, traverse these rocks (Bowersox and Anwar, 1989).

### 3. Samples and methods

About 20 rock samples were collected from the Gujar Kili emerald mine area. All of the samples were studied petrographically, and those containing grains of nickeliferous phases were selected for microprobe analyses and a detailed SEM investigation.

The microprobe analyses were performed with Jeol Superprobe model JXA-8600 using natural and synthetic standards. Analytical conditions were 15 kV accelerating voltage; 30 nA beam current; 20 seconds peak, 10 seconds negative background and 10 seconds positive background counting times. A focused electron beam ( $<1\text{ }\mu\text{m}$  in diameter) was employed to analyze Ni-rich phases.

### 4. Host rock characteristics

The emerald hosting carbonate-rich rocks of the Gujar Kili area are fine-grained and relatively soft with a white to greyish white colour locally having a reddish brown tint due to oxidation. They invariably consist of magnesite and accessory to trace amounts of spinel (mostly Cr-magnete, ferrite-chromite and, in some cases, chromite) accompanied by talc, quartz  $\pm$  dolomite. The different relative proportion of these minerals gives rise to three major types of assemblages (Kazmi et al., 1986): (1) talc-magnesite (or magnesite-talc, with one or the other more abundant); (2) talc-magnesite-dolomite; and (3) quartz-magnesite. The texture of these rocks depends on modal mineralogy, especially the absence or presence of talc. Whereas the talc-free or talc-poor quartz-magnesite assemblages are massive, the talc-magnesite rocks are strongly foliated. At places, especially where traversed by abundant quartz veins, these rocks contain fuchsite-tourmaline veins and clusters. Both fuchsite and tourmaline also occur finely disseminated in the host rocks and are, in some cases, associated with vein quartz. Besides, magnesite and talc enclose tiny grains of tourmaline.

In addition, magnesite rich rocks of the Gujar Kili area contain trace to accessory amounts ( $<0.5$  to 2 vol%) of a number of non-oxide opaque phases. These include pyrrhotite, pentlandite, pyrite, gersdorffite-cobaltite, mackinawite and violarite. Besides, optically and chemically inhomogeneous (mixed) grains also occur in some of the studied samples. These are reddish brown in transmitted light and show higher reflectance than the associated carbonate and silicate phases: they appear to be garnierite (Arif and Moon, 1996c).

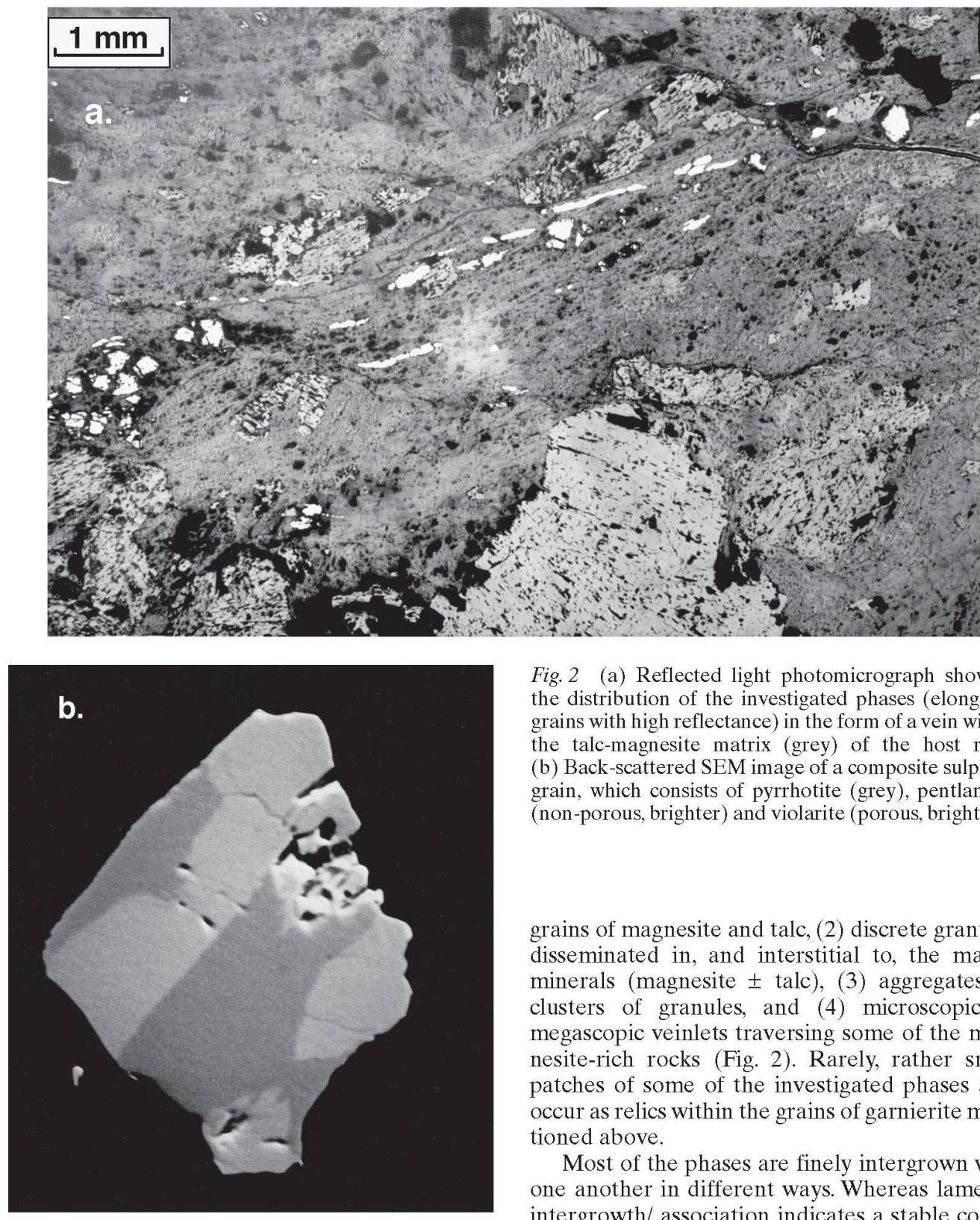


Fig. 2 (a) Reflected light photomicrograph showing the distribution of the investigated phases (elongated grains with high reflectance) in the form of a vein within the talc-magnesite matrix (grey) of the host rock. (b) Back-scattered SEM image of a composite sulphide grain, which consists of pyrrhotite (grey), pentlandite (non-porous, brighter) and violarite (porous, brightest).

grains of magnesite and talc, (2) discrete granules disseminated in, and interstitial to, the matrix minerals (magnesite  $\pm$  talc), (3) aggregates or clusters of granules, and (4) microscopic to megascopic veinlets traversing some of the magnesite-rich rocks (Fig. 2). Rarely, rather small patches of some of the investigated phases also occur as relicts within the grains of garnierite mentioned above.

Most of the phases are finely intergrown with one another in different ways. Whereas lamellar intergrowth/ association indicates a stable co-existence of some of the minerals (pentlandite and pyrrhotite), the cross-cutting relationship of some of the others, e.g. violarite, suggests their secondary origin (Fig. 2). The two major types of assemblages that occur in the samples studied are (1) pyrrhotite-pentlandite-violarite-pyrite  $\pm$  mackinawite and (2) pyrrhotite-pentlandite-violarite-gesdorffite-cobaltite  $\pm$  mackinawite. Both of these assemblages also contain magnetite as an additional ore mineral.

## 5. The non-oxide opaque phases

### 5.1. Mode of occurrence

The very high reflectance of the various non-oxide opaques facilitates their distinction from the associated silicate, carbonate and oxide phases. The non-oxide opaque phases occur in four different modes: (1) tiny granules enclosed within

## 5.2. Phase chemistry and comparison

### 5.2.1. Pyrrhotite

The amount of S in the studied pyrrhotite is relatively uniform (52.5–54.1 at%) (Table 1). The Fe content mostly falls between 45.0 and 46.7 at% with three of the analyses containing relatively low amounts (41.2–43.4 at% Fe). The latter analyses show significantly higher amounts of Ni (3.4–4.8 at%) (Fig. 3), hence Ni for Fe substitution. Ni concentrations in the remaining pyrrhotites are about 1 at%. Analytical data on pyrrhotite reported by most earlier workers (Papunen, 1970; Vaughan et al., 1971; Graterol and Naldrett, 1971; Harris and Nickel, 1972; Misra and Fleet, 1973) show  $\leq 1$  at% Ni contents, but Vaughan et al. (1971) and Batt (1972) found higher Ni concentrations in hexagonal than in monoclinic pyrrhotite. In contrast, monoclinic pyrrhotite that occurs as inclusions in olivine and pyroxene of the variably serpentinized peridotites from Beni Bousera (northern Morocco) and Ronda (southern Spain) contains appreciable Ni, occasionally reaching up to 8 wt% ( $\sim 6$  at%) (Lorand, 1985). Experimental studies suggest that the substitution of Ni in monoclinic pyrrhotite increases with temperature (Misra and Fleet, 1973). It is believed that monoclinic pyrrhotite can accommodate up to 5 wt% Ni at 260–300 °C (Naldrett, 1966, unpublished data quoted by Naldrett and Kullerud, 1967). Although the pyrrhotites under discussion were not investigated by X-ray diffraction, their chemical characteristics, especially S content, are more like the monoclinic ( $\text{Fe}_7\text{S}_8$ ; S = 53.33 at%) than the hexagonal variety ( $\text{Fe}_9\text{S}_{10}$ ; S = 52.63 at%) (cf. Misra and Fleet, 1973; Lorand, 1985). That is also perhaps why some of the analyses contain high Ni. The amount of Co is low (0.04–0.32 at%) while that of Cu is very low, i.e. near the detection limit.

### 5.2.2. Pentlandite

The variation in sulphur content of the studied pentlandite is restricted, with most of the analyses containing between 46.5 and 47 at% S (Table 1). Only two of the analyses with 46.1 and 47.3 at% S fall outside this range. Thus the amounts of sulphur are mostly below the ideal value of 47.06 at% S for stoichiometric pentlandite ( $\text{M}_9\text{S}_8$ ) (Fig. 3). This is in accordance with the conclusion that most of the natural pentlandites seem to be S-deficient (cf. Misra and Fleet, 1973). The amount of iron ranges from 17.4 to 25.2 at%, while Ni varies between 27.5 and 33.8 at%. The specimens thus belong to the Ni-poor part of the pentlandite compositional range (18–34 at% Ni) noted by

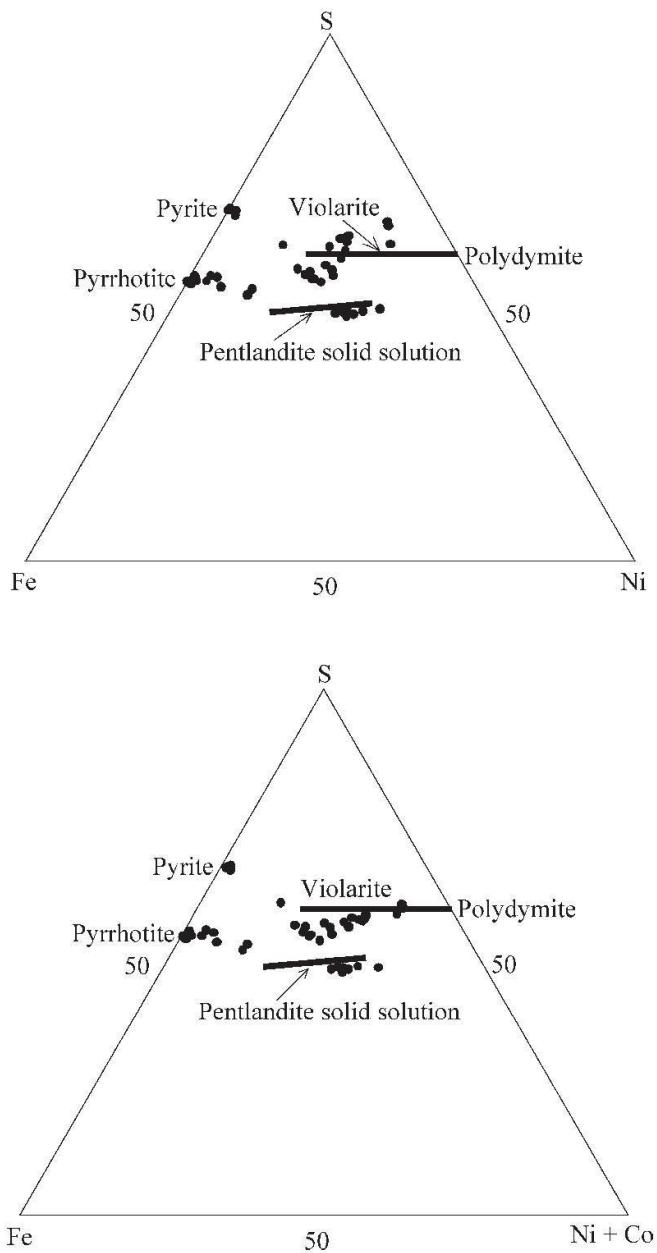


Fig. 3 Compositional characteristics of the studied sulphide phases. The compositional bars are after Misra and Fleet (1974).

Misra and Fleet (1973). These authors postulated that the Ni content of natural pentlandites depends on the assemblage: Ni-rich pentlandites occur in Ni-rich environments, i.e. heazlewoodite and millerite-bearing assemblages, and Ni-poor (Fe-rich) pentlandite occurs in Fe-rich, i.e. troilite-bearing assemblages. The present data support this conclusion.

The results of experimental work by Misra and Fleet (1973) suggest that the Ni and Fe contents of pentlandite also vary with temperature of re-equilibration. The amount of Ni decreases from a maximum of 41 at% at 600 °C to a minimum of 34 at% at 300 °C, while that of Fe increases from 33 at% at 600 °C to 40 at% at 285 °C. Based on these experimental data, pentlandite in this study may

Table 1 Representative analyses of pentlandite and pyrrhotite.

S. No. Phase	1 Po	2 Po	3 Po	4 Po	5 Po	6 Po	7 Po	8 Po	9 Po	10 Po	11 Pn	12 Pn	13 Pn	14 Pn	15 Pn	16 Pn
Atomic percent																
S	53.40	53.08	53.18	53.07	53.34	53.27	54.11	53.62	53.04	52.92	46.99	46.78	47.06	46.15	47.28	46.79
Fe	45.60	45.88	45.80	45.12	45.58	45.11	42.16	41.21	43.37	46.72	17.39	22.51	23.53	23.73	20.67	25.23
Co	0.07	0.08	0.08	0.08	0.08	0.04	0.08	0.32	0.16	0.11	1.67	0.06	0.44	0.63	0.21	0.44
Ni	0.92	0.95	0.93	1.72	0.99	1.57	3.63	4.81	3.40	0.25	33.82	30.62	28.94	29.48	31.81	27.51
Cu	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.01	0.01	0.13	0.02	0.03	0.01	0.02	0.04	0.04
Number of cations on the basis of eight sulphur ions																
Fe	6.830	6.914	6.889	6.802	6.836	6.775	6.234	6.149	6.541	7.062	2.961	3.849	3.999	4.114	3.497	4.313
Co	0.010	0.012	0.012	0.011	0.011	0.006	0.011	0.048	0.025	0.016	0.284	0.011	0.075	0.110	0.036	0.075
Ni	0.138	0.143	0.139	0.259	0.148	0.236	0.537	0.718	0.513	0.038	5.759	5.237	4.919	5.110	5.383	4.703
Cu	0.002	0.002	0.001	0.001	0.002	0.001	0.003	0.005	0.002	0.001	0.023	0.004	0.005	0.001	0.004	0.006

Po = Pyrrhotite, Pn = Pentlandite

Table 2 Representative analyses of mackinawite and violarite.

S. No. Phase	1 Mw	2 Mw	3 Mw	4 Mw	5 Viol	6 Viol	7 Viol	8 Viol	9 Viol
Atomic percent									
S	51.89	51.89	52.93	51.90	56.91	56.45	56.42	57.15	59.43
Fe	41.58	24.32	25.99	6.88	14.54	17.05	14.89	9.30	27.28
Co	0.16	1.27	0.88	7.26	7.76	4.16	8.36	4.94	0.80
Ni	6.35	21.89	18.54	22.86	20.76	22.29	20.32	28.58	12.47
Cu	0.01	0.63	1.66	11.11	0.02	0.05	0.01	0.04	0.02
Number of cations on the basis of eight sulphur ions									
Fe	6.411	3.750	3.928	1.060	2.044	2.416	2.112	1.301	3.672
Co	0.024	0.196	0.133	1.119	1.092	0.590	1.186	0.692	0.107
Ni	0.979	3.374	2.802	3.524	2.918	3.159	2.881	4.000	1.678
Cu	0.002	0.097	0.251	1.712	0.003	0.007	0.001	0.005	0.003

Mw = Mackinawite, Viol = Violarite

have formed or equilibrated at or below 300 °C.

Kaneda et al. (1986) suggest that the S content and hence M : S ratio of pentlandite strongly depend on the relative concentration of Fe and Ni. Whereas Fe-rich compositions tend to be S-deficient, i.e. metal-rich, high Ni contents show the opposite effect. However, the data presented here do not indicate such a relationship.

Kaneda et al. (1986) further postulate that the extent of pentlandite solid solution is temperature-dependent. Pentlandite forms a complete solid solution between  $(\text{Fe}, \text{Ni})_{9\pm 3}\text{S}_8$  and  $\text{Co}_{9\pm 3}\text{S}_8$  in the 600–300 °C temperature range, but this is presumed to decompose into two fields toward the  $(\text{Fe}, \text{Ni})_9\text{S}_8$  and  $\text{Co}_9\text{S}_8$  members at 200 °C. The field of solid solution at 500 °C is the most extensive and includes all of the other solid solution fields (Kaneda et al., 1986).

The concentration of Co in pentlandite is low (0.06–0.65 at%) in all but one (1.67 at%) of the analyses presented here. The analysis with highest Co is also the one characterized by maximum Ni

(33.8 at%) and correspondingly minimum Fe (17.4 at%) contents. The Cu content of most of the analyses is around the minimum detection limit. Similarly, the amount of As is consistently low, i.e. below or around the minimum detection level.

### 5.2.3. Pyrite

In addition to sulphur (65.5–66.4 at%) and iron (32.0–32.9 at%), pyrite from the studied rocks contains small but significant amounts of Ni (0.24–1.92 at%) and Co (0.05–0.84 at%). Cu contents are around the detection limit.

The solubility of Ni in pyrite has not been determined experimentally as a function of temperature, but the experiments of Clark and Kullerud (1963) indicate 1 wt% Ni in pyrites at 143–148 °C. The Ni contents of most natural pyrites are generally <1.0 at%, consistent with low temperature equilibration (Mirsa and Fleet, 1973). Pyrite with up to 3.7 and 7 wt% Ni has been reported from

Table 3 Representative analyses of sulpharsenides<sup>a</sup>.

S. No.	1	2	3	4	5	6
Atomic percent						
S	38.51	38.55	32.64	33.68	33.14	33.51
As	27.19	27.29	33.22	32.47	32.15	31.96
Fe	2.12	2.06	4.19	2.64	2.81	3.59
Co	3.87	3.81	3.54	3.43	3.42	17.03
Ni	28.26	28.27	26.38	27.76	28.46	13.89
Cu	0.04	0.03	0.03	0.02	0.02	0.02
Number of ions on the basis of two anions (S + As)						
S	1.172	1.171	0.991	1.018	1.015	1.024
As	0.828	0.829	1.009	0.982	0.985	0.976
Fe	0.062	0.060	0.123	0.078	0.081	0.104
Co	0.113	0.111	0.104	0.101	0.099	0.493
Ni	0.824	0.828	0.773	0.820	0.820	0.402
Cu	0.001	0.001	0.001	0.001	0.001	0.001

<sup>a</sup> Gersdorffite (1-5) and cobaltite-gersdorffite (6)

northwest Nelson, New Zealand (Grapes and Challis, 1999) and English Lake, Manitoba (Karup-Møller, 1969), respectively. The data presented by Nickel et al. (1974) show that secondary pyrite contains distinctly higher amounts of Ni that may range up to 12 wt%.

#### 5.2.4. Mackinawite

The concentration of S ranges from 50.4 to 53.0 at% (Table 2). The amounts of both Fe (24.3–41.6 at%) and Ni (6.4–21.9 at%) are highly variable. In terms of these two components, some of the analyses approach pentlandite, however, their higher S contents distinguish them from the latter. The analyses also contain notable amounts of Co that range up to 1.27 at%. Although slightly low, S contents of most of the mackinawite analyses closely approximate those of pyrrhotite. However, their distinctly higher Ni, Co and occasionally Cu, and correspondingly low Fe contents serve to distinguish them from pyrrhotite (cf. Lorand, 1985). Textural relationships, spatial association and a strong negative correlation of both Ni and Co with Fe suggest that mackinawite formed from pyrrhotite as a result of Ni and Co substitution for Fe.

The Cu content of most of the analyses is low and does not exceed 1.66 at%. Two of them, however, contain markedly high amounts (10.6 and 11.1 at% Cu, respectively). Although mackinawite can contain Cu, such cuprian varieties of the mineral seem to occur rarely in nature.

Whereas mackinawite is generally believed to have an M : S > 1, the M : S ratio of virtually all of

the analyses presented here is consistently less than one. Some of the workers (e.g. Taylor and Finger, 1971) have shown that there is a deficiency of S in the structure of mackinawite rather than an excess of metal, so the formula is properly written  $Fe_{1-x}S$ . Although originally considered to be an iron sulphide with tetragonal symmetry (Evans et al., 1964), mackinawite can accommodate a number of other metals, e.g. Ni, Co, Cu and even Cr (cf. Clark, 1970; Lorand, 1985; Mukherjee and Sen, 1991). The mode of occurrence and intimate association of the phase under discussion with pyrrhotite and pentlandite indicate that it is likely to be mackinawite.

#### 5.2.5. Volarite

The composition of the studied violarite is highly variable in terms of almost all the major components. This is particularly true for Ni, Fe and Co (Table 2, Fig. 3). The variation in Ni contents (17.1–28.6 at%) except for one analysis (with 12.5 at% Ni) falls within the range observed by Misra and Fleet (1974). The amount of Fe mostly varies between 14.5 and 21.8 at%, only five of the analyses fall outside this range. One of them has lower (9.3 at%) and the remaining four have higher Fe contents (25.6–27.3 at%). The amounts of Co (0.12–8.36 at%) in the present violarite analyses also show considerable variation, but they fall within the range reported by Misra and Fleet (1974). Like the other metals, Cu in the investigated violarite shows considerable variation (from below detection limit to 1.9 at%).

The concentration of S shows minor but significant variation (53.2–57.1) as well. The sulphur content of one of the analyses is rather high (59.4 at%). This particular analysis has markedly low Ni (12.5 at%) and abnormally high Fe contents (27.3 at%). Relative to the ideal value (57.14 at% S) required by the stoichiometry  $[(Fe, Ni)_3S_4]$  of violarite, all but two of the analyses are apparently S-deficient (Fig. 3). Most of these values, however, fall within the range of S contents of violarite (55.1–57.5 at%) reported by Misra and Fleet (1974). The anomalously low S contents (down to 53 at%) of a few of the violarite analyses with low totals from the present study most probably reflect inaccuracy due to analytical problems arising from the porous nature of the analyzed grains.

Violarite mostly appears to replace pyrrhotite (and pentlandite) (Fig. 2). This and a reasonably good negative correlation of both Ni and Co with Fe indicate that violarite might have formed from pyrrhotite due to substitution of variable amounts of Ni and Co for Fe.

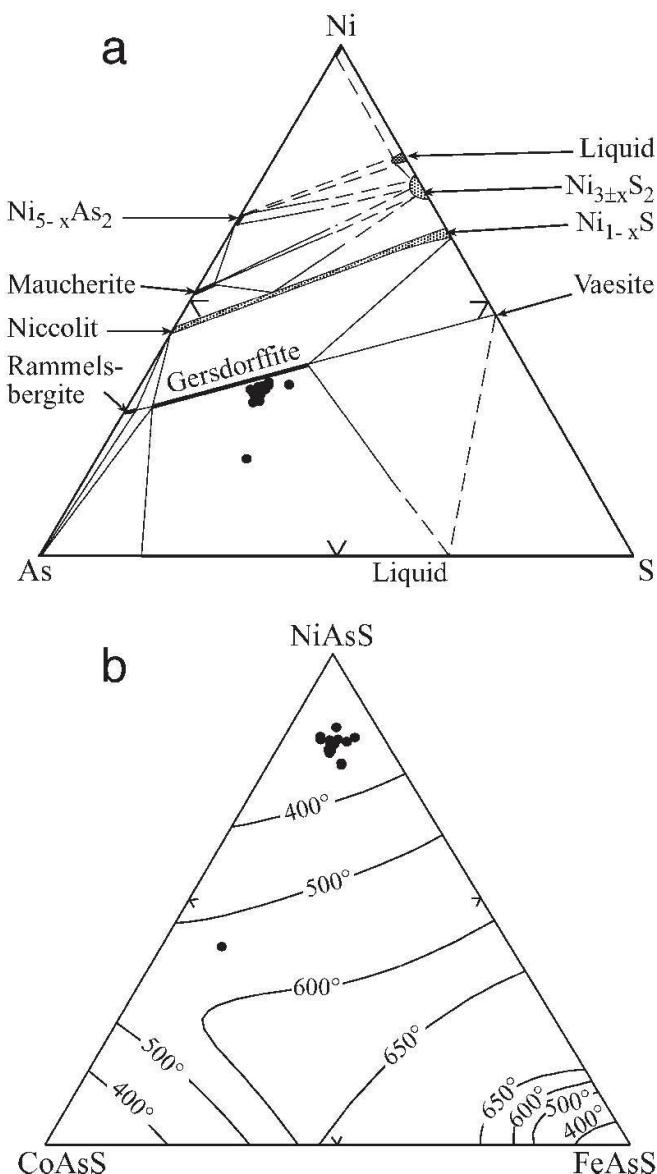


Fig. 4 Chemical characteristics of the studied sulpharsenides. (a) Condensed phase relations in the Ni-As-S (wt%) system at 700 °C (after Yund, 1962). The apparent departure of the plotted analyses from the stoichiometric gersdorffite (compositional bar) is due to their Fe and Co contents. (b) Solvus in the condensed NiAsS-FeAsS-CoAsS system at 400, 500, 600 and 650 °C (after Klemm, 1965). All of the gersdorffite analyses from the present study fall below the 400 °C immiscibility region. Only the single cobalt-rich composition falls above the 500 °C region.

#### 5.2.6. Gersdorffite-cobaltite solid solution

The sulphur and arsenic contents of gersdorffite mostly range from 30.9 to 34.1 at% and 30.2 to 33.6 at%, respectively (Table 3). Three of the analyses, however, contain markedly high S (~38 at%) and correspondingly low As (~27 at%). In addition to Ni (26.4–29.5 at%), the investigated gersdorffite contains relatively low but notable amounts of Fe (2.1–4.2 at%) and Co (1.8–4.0 at%) (Fig. 4). Natural examples of gersdorffite

with significant amounts of Fe (up to 9.86 wt%) and/or Co (up to 8.82 wt%) are known and quoted in the published literature (cf. Yund, 1962). More recently, gersdorffite with up to 12 wt% Co has been reported to occur in a sample of fuchsite quartzite from NW Nelson, New Zealand (Grapes and Challis, 1999). The concentration of Cu in the analyses of gersdorffite from the present study is invariably below the detection limit. These compositions closely approximate those reported from similar host rocks from NW Nelson, South Island of New Zealand (Grapes and Challis, 1999). Gersdorffite also occurs in mineralized talc-carbonate rocks of the Phenga complex, Russia (Abzalov et al., 1997).

Beside typical gersdorffite, described above, one of the sulpharsenide analyses is intermediate between gersdorffite and cobaltite (Table 3). Its composition, recalculated on the basis of two anions, is  $[Co_{0.519}Ni_{0.424}Fe_{0.110}](S_{1.023}As_{0.977})$ . Notable features of the composition, compared to typical cobaltite, are its relatively low Co : Ni and As : S ratios. A cobaltite-gersdorffite solid solution with a compositional range of  $(Co_{0.05-0.59}Ni_{0.27-0.66}Fe_{0.14-0.32})As_{0.97-1.07}S_{0.89-0.97}$  has been reported to occur enclosed within phenocrysts and in the matrix of spessartite sills in the Lacauna area of Montagne Noire, France (Beziat et al., 1996). Some of the cobaltite-gersdorffite analyses reported from O'Toole, Brazil (Marchetto, 1990) approach the composition presented here.

#### 6. Discussion and conclusions

Field association, mineralogical composition, mineral and whole-rock chemical characteristics all suggest that the rocks which host the investigated opaque mineral assemblages formed by talc-carbonate alteration of originally ultramafic rocks (cf. Arif, 1994; Arif and Moon, 1999; Schandl and Naldrett, 1992). The oxygen and sulphur fugacities under which such an alteration of ultramafic rocks takes place have been investigated in detail (Eckstrand, 1975; Frost, 1985). It is concluded that, unlike serpentinization, talc-carbonate alteration of ultramafic rocks occurs under strongly oxidizing conditions (high  $fO_2$ ) (Fig. 5). Furthermore, these studies demonstrated that the  $fS_2$  profile is essentially a function of the  $fO_2$  profile. In view of the strong metasomatism, the amounts of infiltrated fluid are likely to have been relatively large. Because the modal abundance of the opaque minerals is low, interaction of infiltrating hydrothermal fluid with the ultramafic host rock is expected to yield opaque assemblages that expresses the high  $fO_2$  (and  $fS_2$ ) during this process.

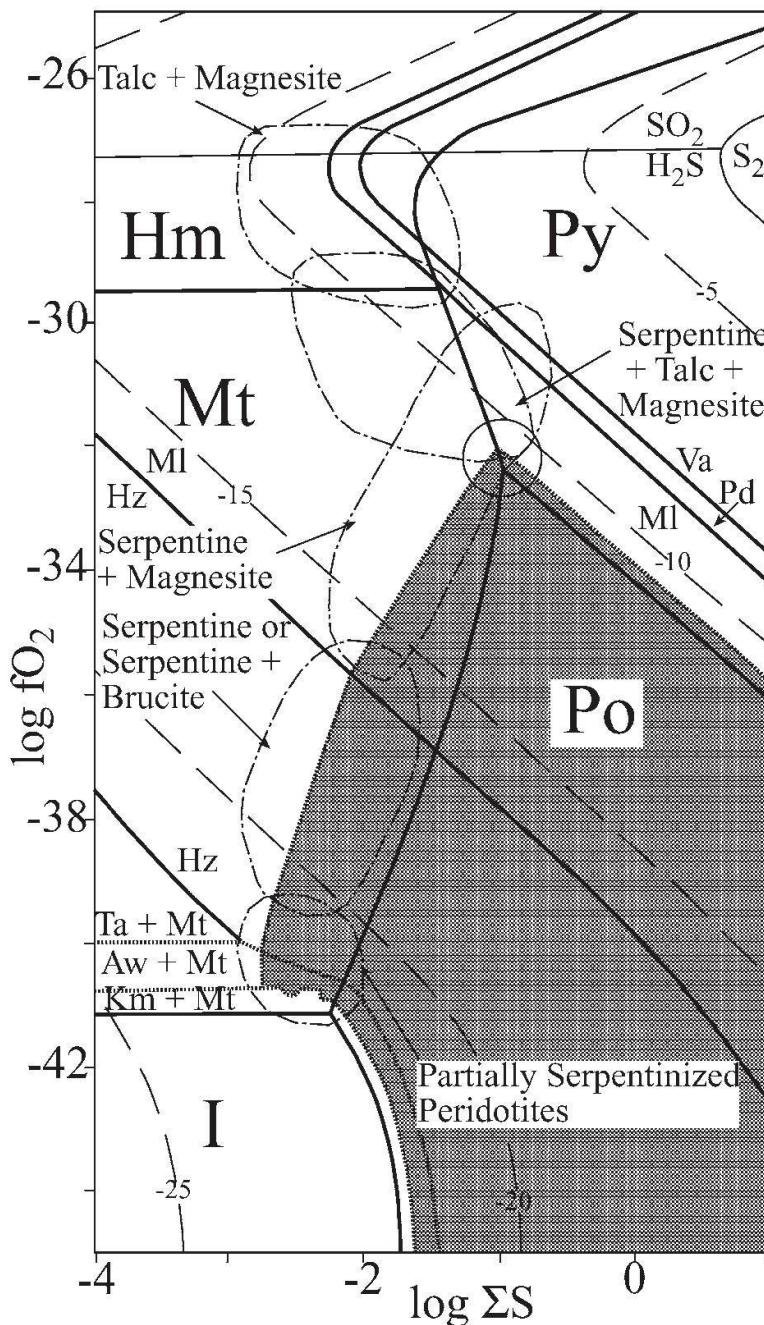


Fig. 5 Log  $f\text{O}_2$  – log  $\Sigma\text{S}$  diagram showing sulphide and oxide stabilities at 300 °C and 2 kbar. The circle shows the sulphide-oxide assemblage from this study, all other information from Frost (1985). Solid lines represent reactions between solid phases calculated from thermodynamic data, finely dotted lines are boundaries inferred from petrologic data, light solid lines delineate fields where various sulphur species dominate, and dashed lines are contours for log  $f\text{S}_2$  in the fluid. Stippled area is the stability field for pentlandite based on petrologic data. Fields occupied by sulphide-oxide-metal assemblages from low temperature metaperidotite are demarcated by dash-dot lines. Abbreviations: Aw – awaruite, Hm – hematite, Hz – heazlewoodite, I – iron, Km – kamacite, MI – millerite, Mt – magnetite, Pd – polydymite, Po – pyrrhotite, Py – pyrite, Ta – taenite, and Va – vaesite.

If so, the opaque mineral assemblages are indicators of the  $f\text{O}_2$  that prevailed during the process of talc-carbonate alteration of their host rock.

Talc-carbonate alteration at high  $f\text{O}_2$  (and  $f\text{S}_2$ ) should lead to the formation of Fe-sulphide-free, pentlandite-millerite assemblage in weakly mineralized rocks and pyrite-pentlandite assemblage in moderately mineralized ultramafic rocks (dunites). Fe-sulphides (pyrrhotite or pyrite) in assemblages of weakly mineralized ultramafic rocks reflect alteration under intermediate  $f\text{O}_2$  (Fig. 5). As pointed out above, the samples studied are talc-carbonate-altered ultramafics, totally free of serpentine, essentially consisting of talc and magnesite. Rocks with such a mineralogical composition can originate only under high  $f\text{O}_2$  and  $f\text{S}_2$  conditions and, therefore, their opaque

mineral assemblages should include neither pentlandite nor pyrrhotite (Fig. 5). Yet the opaque mineral assemblages found in the serpentine-free, talc-magnesite rocks from the study area essentially consist of pentlandite and pyrrhotite with or without pyrite, violarite, gersdorffite and rather rarely cobaltite-gersdorffite.

It seems that the apparently anomalous occurrence of sulphide phases in the talc-magnesite rocks from the study area reflects either of the following two possibilities:

- (1) The original ultramafic rocks were neither barren nor weakly mineralized, rather they were at least moderately well mineralized.
- (2) The prevailing  $f\text{S}_2$  is not determined by  $f\text{O}_2$  and, therefore, by the talc-carbonate alteration reactions. At least part of the sulphur may

have been introduced from some external source as dissolved species.

The relative sparseness of ore minerals in the rocks studied negates the first possibility. Hence the investigated phases appear to have formed by the process separate from the talc-carbonate alteration. The sulphide and sulpharsenide assemblages are epigenetic and formed by late-stage hydrothermal activity. S (and As)-rich hydrothermal fluids infiltrated the original ultramafic rocks and by wall rock alteration extracted from them the various ore elements. Contribution of metals from the host rock is indicated by the composition of the phases. For example, the presence of relatively high amounts of Ni in some of the pyrrhotite analyses point to such a possibility. Nevertheless the presence of Cu in some of the other minerals, e.g. mackinawite, suggests that the fluids rich in S and As probably also contained some amounts of the ore-forming metals as dissolved species from their source.

The overall composition of the non-oxide opaque assemblage suggests that it might have originated largely as a monosulphide or metal sulphide solid solution (MSS). The intimate spatial association of the various sulphide phases shows that they formed from the original MSS through low-T subsolidus re-equilibration of the latter. Some of the investigated phases, e.g. pyrrhotite and gersdorffite, also occur as inclusions in grains of emerald from the Swat region (Gübelin, 1989). Hence it seems that the emerald-forming hydrothermal activity in the Swat region also produced the investigated non-oxide opaque mineral assemblage. The mineralogical association and stable isotope data suggest that the hydrothermal fluids that formed the Swat emerald were most probably magmatic in origin, i.e. related to young granitic magmatism in the Swat-Malakand region (Arif et al., 1996; Arif and Moon, 1999). This interpretation regarding the origin of Swat emerald is in accordance with the conclusion by Snee and Kazmi (1989) that beryllium for the formation of Swat emerald was supplied in hot, saline solutions derived from the solidification of melt parental to post-collisional granites in the region.

The investigated non-oxide opaque mineral assemblage and its host rock characteristics are almost identical to those described by Grapes and Challis (1999) from NW Nelson, South Island of New Zealand. Grapes and Challis (1999) concluded that the opaque mineral assemblage from Nelson is genetically related to the talc-carbonate alteration process of the host rock. However, on the basis of the reasoning presented above, the Nelson assemblage also seems to be epigenetic and thus genetically similar to that of the present in-

vestigation. A regional metasomatic process that Challis et al. (1995) believe to have affected the Nelson area, has most probably also resulted in the formation of the ore assemblage described by Grapes and Challis (1999).

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### References

Abzalov, A.Z., Berwer, T.S. and Polezheva, L.I. (1997): Chemistry and distribution of accessory Ni, Co, Fe, As minerals in the Phenga Ni-Cu deposits, Kola Peninsula, Russia. *Mineral. and Petrol.* **61**, 145–61.

Arif, M. (1994): Mineralogy, geochemistry and stable isotope studies of ultramafic rocks from the Swat valley ophiolites, northwestern Pakistan: implications for the genesis of emerald and nickeliferous opaque phases. PhD thesis, Univ. Leicester, Unpubl., 300 pp.

Arif, M., Fallick, A.E. and Moon, C.J. (1996): The genesis of emeralds and their host rocks from Swat, northwestern Pakistan: a stable-isotope investigation. *Mineral. Dep.* **31**, 255–268.

Arif, M. and Moon, C.J. (1994): Occurrence, chemistry and genesis of the nickel-rich phases in the ultramafic rocks from Swat, northwestern Pakistan. *Geol. Bull. Univ. Peshawar* **27**, 29–41.

Arif, M. and Moon, C.J. (1996a): The platinum-group element geochemistry of chromitites and silicate rocks from Swat, NW Pakistan. *Geol. Bull. Univ. Peshawar* **29**, 1–8.

Arif, M. and Moon, C.J. (1996b): Chemical characteristics of chrome spinel in the magnesite-rich rocks from Swat, northwestern Pakistan. *Geol. Bull. Univ. Peshawar* **29**, 9–15.

Arif, M. and Moon, C.J. (1996c): Garnierites from the ultramafic rocks in Swat, northwestern Pakistan. *Geol. Bull. Univ. Peshawar* **29**, 69–79.

Arif, M. and Moon, C.J. (1996d): Chemistry of tourmaline from the emerald-hosting rocks in Swat, NW Pakistan. *Geol. Bull. Univ. Peshawar* **29**, 81–89.

Arif, M. and Moon, C.J. (1999): Geochemistry of magnesite-rich rocks from the Indus suture in Swat, NW Pakistan. *Geol. Bull. Univ. Punjab* **33/34**, 111–118.

Batt, A.P. (1972): Nickel distribution in hexagonal and monoclinic pyrrhotite. *Can. Mineral.* **11**, 892–897.

Beziat, D., Monchoux, P. and Tolland, F. (1996): Cobalt-gersdorffite solid solution as a primary magmatic phase in spessartite, Lacauna area, Montagne Noire, France. *Can. Mineral.* **34**, 503–12.

Bowersox, G.W. and Anwar, J. (1989): The Gujar Kili emerald deposit, Northwest Frontier Province, Pakistan. *Gems and Gemology* **25**, 16–24.

Challis, A., Grapes, R. and Palmer, K. (1995): Chromian muscovite, uvarovite, and zincian chromite: products of regional metasomatism in NW Nelson, New Zealand. *Can. Mineral.* **33**, 1263–84.

Clark, A.H. (1970): Nickelian mackinawite from Vlakfontein, Transvaal. *Am. Mineral.* **55**, 180–186.

Clark, L.A. and Kullerud, G. (1963): The sulphide-rich portion of the Fe-Ni-S system. *Econ. Geol.* **58**, 853–885.

Eckstrand, O.R. (1975): The Dumont serpentinite: a model for control of nickeliferous opaque mineral assemblages by alteration reactions in ultramafic rocks. *Econ. Geol.* **70**, 183–201.

Evans, H.T., Jr., Milton, C., Chao, E.C.T., Alder, I., Mead, C., Ingram, B. and Berner, R.A. (1964): Valleriite and the new iron sulphide mackinawite. *U.S. Geol. Surv. Prof. Pap.* **475D**, D64–69.

Frost, B.R. (1985): On the stability of sulphides, oxides, and native metals in serpentinite. *J. Petrol.* **26**, 31–63.

Gansser, A. (1964): Geology of the Himalaya. Wiley Intersci., New York, 289 pp.

Gansser, A. (1980): The significance of the Himalayan suture zone. *Tectonophysics* **62**, 37–52.

Grapes, R.H. and Challis, G.A. (1999): Gersdorffite with pentlandite, violarite, pyrrhotite and pyrite from northwest Nelson, New Zealand. *New Zealand J. Geol. Geophys.* **42**, 189–204.

Graterol, M. and Naldrett, A.J. (1971): The mineralogy of the Marbridge No. 3 and No. 4 nickel-iron sulphide deposits with some comments on low temperature equilibration in the Fe-Ni-S system. *Econ. Geol.* **66**, 886–900.

Gübelin, E.J. (1989): Gemological characteristics of Pakistani emeralds. In: Kazmi, A.H. and Snee, L.W. (eds): *Emeralds of Pakistan*, Van Nostrand Reinhold, New York, 75–92.

Harris, D.C. and Nickel, E.H. (1972): Pentlandite compositions and associations in some mineral deposits. *Can. Mineral.* **11**, 861–878.

Kaneda, H., Takenouchi, S. and Shoji, T. (1986): Stability of pentlandite in the Fe-Ni-Co-S system. *Mineral. Dep.* **21**, 69–80.

Karup-Møller, S. (1969): Secondary violarite and bravoite, English Lake, Manitoba. *Can. Mineral.* **9**, 624–643.

Kazmi, A.H., Lawrence, R.D., Dawood, H., Snee, L.W. and Hussain, S.S. (1984): Geology of the Indus suture zone in the Mingora-Shangla area of Swat. *Geol. Bull. Univ. Peshawar* **17**, 127–144.

Kazmi, A.H., Lawrence, R.D., Anwar, J. and Hussain, S. (1986): Mingora emerald deposits (Pakistan): suture-associated gem mineralization. *Econ. Geol.* **81**, 2022–2028.

Klemm, D.D. (1965): Synthesen und Analysen in den Dreieckdiagrammen  $FeAsS$ - $CoAsS$ - $NiAsS$  und  $FeS_2$ - $CoS_2$ - $NiS_2$ . *N. Jb. Miner. Mh.* **103**, 236–255.

Lorand, J.P. (1985): The behaviour of the upper mantle sulfide component during the incipient alteration of alpine-type peridotites as illustrated by the Beni-Bouchera (Northern Morocco) and Ronda (Southern Spain) ultramafic bodies. *Tscher. Mineral. Petrog. Mitt.* **34**, 183–209.

Marchetto, C.M.L. (1990): Platinum-group minerals in the O'Toole (Ni-Cu-Co) deposit, Brazil. *Econ. Geol.* **85**, 921–927.

Misra, K.C. and Fleet, M.E. (1973): The chemical composition of synthetic and natural pentlandite assemblages. *Econ. Geol.* **68**, 518–539.

Misra, K.C. and Fleet, M. E. (1974): Chemical composition and stability of violarite. *Econ. Geol.* **69**, 391–403.

Mukherjee, A.D. and Sen, P.P. (1991): Compositional variations in mackinawite from the Chandmari mine of Khetri copper belt, Rajasthan. *J. Geol. Soc. India* **38**, 96–100.

Naldrett, A.J. (1966): Talc-carbonate alteration of serpentized ultramafic rocks from south of Timmins, Ontario. *J. Petrol.* **7**, 489–499.

Naldrett, A.J. and Kullerud, G. (1967): The Strathcona mine and nickel-copper ores, Sudbury district. *J. Petrol.* **8**, 493–529.

Nickel, E.H., Ross, J.R. and Thronber, M.R. (1974): The supergene alteration of pyrrhotite-pentlandite ore at Kambalda, western Australia. *Econ. Geol.* **69**, 93–107.

Papunen, H. (1970): Sulphide mineralogy of the Kotalahti and Hitura nickel-copper ores, Finland. *Acad. Sci. Fennicae Annales, Ser. A, III, Geologica-Geographica* **109**, 74 pp.

Schandl, E.S. and Naldrett, A.J. (1992):  $CO_2$  metasomatism of serpentinites, south of Timmins, Ontario. *Can. Mineral.* **30**, 93–108.

Searle, M.P. (1991): Geology and Tectonics of the Karakorum Mountains. Wiley, London, 358 pp.

Snee, L.W. and Kazmi, A.H. (1989): Origin and classification of emerald deposits. In: Kazmi, A.H. and Snee, L.W. (eds): *Emeralds of Pakistan*, Van Nostrand Reinhold, New York, 229–236.

Taylor, L.A. and Finger, L.W. (1971): Structure refinement and composition. *Carnegie Inst. Wash. Year Book* **69**, 319–323.

Vaughan, D.J., Burns, R.G. and Burns, V.M. (1971): Geochemistry and bonding of thiospinel minerals. *Geochim. Cosmochim. Acta* **35**, 365–381.

Yund, R.A. (1962): The system Ni–As–S: phase relations and mineralogical significance. *Am. J. Sci.* **260**, 761–782.

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