The Canadian Mineralogist
Vol. 35, pp. 1453-1463 (1997)

ORIGIN OF SULFIDE BLEBS IN VARIABLY METASOMATIZED MANTLE XENOLITHS, QUATERNARY WEST EIFEL VOLCANIC FIELD, GERMANY

CLIFF S.J. SHAW[1]

Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7

ABSTRACT

Twenty-eight samples of mantle-derived xenoliths from the West Eifel volcanic field, in Germany, were examined in detail; of these, seven are anhydrous peridotite, 12 are metasomatized (with either disseminated pargasitic amphibole and phlogopite, phlogopite–pargasite veins or olivine clinopyroxenite veins), and the remaining nine are aluminian augite (group II) clinopyroxenite. Sulfide abundance in the xenoliths varies by rock type. Anhydrous peridotites are sulfide-free. Metasomatized peridotites contain between 0.01 and 0.05 vol.% sulfide. Group-II clinopyroxenites contain up to 0.15 vol.% sulfide. There are three textural types of sulfide inclusion. Type-I sulfide occurs as spherical inclusions following healed fractures and trails of fluid inclusions in primary olivine, clinopyroxene and spinel. Type-II inclusions also are associated with fluid inclusions, but are hosted in metasomatic minerals, *i.e.*, phlogopite, pargasite and clinopyroxene. Type-III inclusions are restricted to glass-rich zones in pargasitic amphibole and phlogopite. The mineralogy of the type-I and type-II sulfides varies with rock type. Monosulfide solid-solution (*mss*), with locally exsolved patches of Cu-rich sulfide, is the dominant phase in the metasomatized xenoliths. In contrast, the main sulfide in group-II clinopyroxenite is pyrrhotite, and only minor Cu-rich sulfide is present. Type-III sulfide grains consist of pentlandite, and are considered to have formed by inclusion of earlier-formed type-I or type-II inclusions in partly melted pargasite and phlogopite. Each type of xenolith has a distinct bulk-sulfide composition (*BSC*), suggesting the existence of several distinct events of sulfide deposition. The association of sulfides with healed fractures in primary minerals and with metasomatic minerals, added to the disequilibrium illustrated by Fe–Ni partition coefficients for *BSC* – olivine, and the lack of sulfides in the anhydrous peridotites interpreted to have been affected by partial melting, suggest that the sulfides formed from metasomatic processes in the mantle rather than from *in situ* partial melting.

Keywords: sulfides, mantle metasomatism, xenoliths, West Eifel, Germany.

SOMMAIRE

Vingt-huit échantillons de xénolites mantelliques, prélevés dans le champ volcanique de l'Eifel de l'Ouest, en Allemagne, ont fait l'objet d'une étude approfondie. Parmi ces xénolites, sept sont anhydres, douze ont subi une métasomatose (avec disséminations d'amphibole pargasitique et phlogopite, des veines à phlogopite + pargasite ou de clinopyroxénite à olivine), et les neuf autres sont faits de clinopyroxénite à augite alumineuse (groupe II). La teneur en sulfures de ces xénolites varie selon la sorte de roche. Les péridotites anhydres sont sans sulfure. Les péridotites métasomatisées contiennent entre 0.01 et 0.05% par volume de sulfures. Les clinopyroxénites du groupe II en contiennent jusqu'à 0.15%. Il y a trois types d'inclusions de sulfures, selon leur texture. Les grains de sulfures de type I sont des inclusions sphériques qui suivent des fissures cicatrisées et des lignées d'inclusions fluides dans l'olivine, le clinopyroxène et le spinelle primaires. Les inclusions de type II sont aussi associées avec des inclusions fluides, mais se trouvent dans les minéraux métasomatiques, par exemple phlogopite, pargasite et clinopyroxène. Les inclusions de type III sont limitées aux zones riches en verre dans l'amphibole pargasitique et la phlogopite. L'assemblage de minéraux sulfurés de types I et II varie selon la sorte de roche. Une solution solide monosulfurée (*mss*) montrant localement des taches d'exsolution d'un sulfure cuprifère est dominante dans les xénolites métasomatisés. En revanche, le sulfure principal dans les clinopyroxénites du groupe II est la pyrrhotite, avec un sulfure cuprifère très accessoire. Le sulfure prédominant dans les inclusions de type III est la pentlandite, qui se serait formée par inclusion de sulfures précoces de type I ou de type II dans la pargasite et la phlogopite passées à l'état partiellement fondu. Chaque type de xénolite possède une composition globale des sulfures distincte, ce qui fait penser que plusieurs événements de déposition distincts ont eu lieu. L'association des sulfures avec des fissures cicatrisées dans les minéraux primaires et avec les minéraux d'origine métasomatique, ainsi que le déséquilibre illustré par le coeffiient de partage Fe–Ni entre la fraction sulfurée et l'olivine, ainsi que l'absence de sulfures dans les péridotites anhydres qui auraient subi une fusion partielle, font penser que les sulfures se sont formés par processus de métasomatose du manteau, et non par fusion partielle *in situ*.

(Traduit par la Rédaction)

Mots-clés: sulfures, métasomatose du manteau, Eifel de l'Ouest, Allemagne.

---

[1] Current address: Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany.
E-mail address: cliff.shaw@uni-bayreuth.de

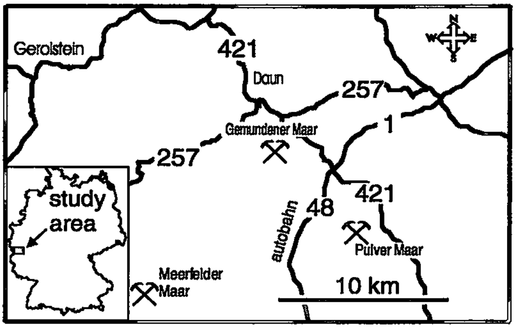

FIG. 1. Location map showing the quarries in which the xenolith samples were collected.

INTRODUCTION

Mantle-derived xenoliths in alkaline mafic and ultramafic volcanic rocks are an important source of information on the composition of the upper mantle and the processes that affect it. Investigations of silicate mineral assemblages in mantle xenoliths suggest that in some areas, the upper mantle was depleted in its low-temperature components by partial melting and later enriched by metasomatism (Stosch & Seck 1980, Bailey 1982, Stosch & Lugmair 1986, Lloyd 1987, Harte 1987). Although most studies of mantle-derived xenoliths focus on the silicate assemblages, Szabó & Bodnar (1995) showed that sulfide minerals also are useful in understanding the processes of partial melting and metasomatic enrichment. The available data on the petrographic and chemical characteristics of sulfide minerals in xenoliths or peridotite massifs suggest that they developed as an immiscible phase during partial melting (Bishop *et al.* 1975, De Waal & Calk 1975, Dromgoole & Pasteris 1987). However, since S, Fe, Ni, Cu and Co may be added to the mantle during metasomatism (Bailey 1982, 1987, Lorand 1989a, b), sulfides may also develop during metasomatic enrichment events or movement of a basaltic melt through the mantle (Irving 1980, Andersen *et al.* 1987, Lorand 1987, 1989a, Szabó & Bodnar 1995).

This study provides petrographic and chemical data for sulfides in a variety of mantle xenoliths from the West Eifel volcanic field, Germany (Fig. 1). Five distinct rock-types were examined: anhydrous spinel lherzolite, modally metasomatized pargasite- and phlogopite-bearing lherzolite, discrete pargasite and phlogopite veins in lherzolite, chromian-diopside-bearing olivine clino-

TABLE 1. PETROGRAPHY OF SULFIDE-BEARING XENOLITHS

Group*	Rock Type	Sample #	Description	T °C[1]	Interpretation
Anhydrous Peridotite					
Ib	Spinel lherzolite	TO7, TO9, TO10, TO11, TO17, TO20, TO21	Igneous texture. Dominated by deformed olivine. Minor to significant glass present along fractures.	ca. 1125	Derived from mantle that has undergone various degrees of partial melting
Hydrous Peridotite					
Ia	Amphibole-bearing spinel lherzolite	TO2, TO4, TO5, TO12, TO16	Igneous texture. Dominated by deformed olivine with interstitial amphibole, some of which is broken down to glass + microlites. Sulfides are included in olivine, spinel and cpx.	ca. 900	Open-system equilibration of type-Ib mantle with a metasomatic fluid or melt enriched in incompatible elements
Ia	Phlogopite-bearing spinel lherzolite	TO 15	Igneous texture. Olivine shows 120° triple junctions. Phlogopite is associated with infiltrated glass. Sulfides are mainly enclosed in olivine.	ca. 900	
Chromian-diopside-bearing clinopyroxenite					
Ib	Olivine websterite	TO 6	Igneous texture. Dominated by anhedral cpx crystals rich in inclusions of olivine. Sulfides are rare, found in both olivine and cpx.	ca. 1160	Enriched by reaction with Ca- and alkali-rich metasomatic melt or fluid
Ib	Olivine clinopyroxenite	TO8, M17	Igneous texture. Olivine occurs as inclusions in clinopyroxene. All of the sulfides occur as inclusions in clinopyroxene.	ca. 1160	
Hydrous veins in type-Ia peridotite					
Ia	Phlogopite-bearing pargasite veins	M4, M9, MFJ-1	Pargasite + phlogopite veins cross-cutting amphibole- and phlogopite-bearing spinel lherzolites. Sulfides occur in both pargasite and phlogopite	ca 1000 - 1050 (reheating)	Intrusion and crystallization of SiO_2-undersaturated alkaline magma
Clinopyroxenite					
II	Pargasite - phlogopite clinopyroxenite	M2, M12, GM2, GM3, GM5, GM7 P1, P2, P11	Coarse-grained pargasite- and phlogopite-bearing clinopyroxenite. Hydrous minerals are commonly broken down to glass + microlites. Sulfides occur as inclusions in cpx, spinel, amphibole and rarely in apatite.	??	Either high-pressure cumulates from W. Eifel magmas or result of reaction between melts and peridotitic wallrocks

* - groups according to Frey & Prinz (1978) and Stosch & Seck (1980). [1] - Temperatures from Witt-Eickschen *et al.* (1993). Symbols: Meerfelder Maar (prefixed TO & M), Gemündener Maar (GM), Pulver Maar (P).

pyroxenite and aluminian-augite-rich clinopyroxenite. The aim of this study is to determine the relationship between sulfide inclusions and their host silicates and to identify the process(es) by which sulfide minerals formed in the mantle beneath the West Eifel region.

GEOLOGICAL SETTING AND PREVIOUS STUDIES

The West Eifel volcanic field consists of a cluster of 240 Quaternary (*ca.* 0.7 Ma) volcanic centers that erupted approximately 1.7 km^3 of mantle-derived, mafic alkaline lava and pyroclastic rock (Mertes & Schmincke 1985). Group-I and group-II (Frey & Prinz 1978) mantle-derived xenoliths are present in at least ten of the eruptive centers (Frechen 1948, 1963). Many detailed studies of the mineralogical and geochemical characteristics of these xenoliths have been done [see Witt-Eickschen *et al.* (1993), O'Connor *et al.* (1996) and references therein]. In addition, several studies on the composition and origin of glass inclusions in the xenoliths suggest the presence of a quenched melt responsible for metasomatism (Edgar *et al.* 1989, Zinngrebe & Foley 1995, O'Connor *et al.* 1996). Witt-Eickschen *et al.* (1993) related each of the main types of xenoliths to partial melting or to an episode of metasomatism. The following sequence of events may be inferred:

1) The depletion of light-rare-earth elements (*LREE*) in anhydrous (Group-Ib) peridotite xenoliths equilibrated at *ca.* 1125°C suggests that partial melting affected at least part of the mantle (Stosch & Lugmair 1987).

2) Enrichment of the *LREE* in peridotites accompanied by formation of Ti-poor pargasitic amphiboles at low temperatures (*ca.* 900 – 950°C: Kempton *et al.* 1988).

3) Enrichment in high-field-strength elements (Hf, Ti, Zr) was associated with the formation of phlogopite – pargasite veins and reheating of the mantle to temperatures between 900 – 1050°C.

4) An episode of *LREE* enrichment of peridotitic mantle without amphibole formation was associated with high-temperature (*ca.* 1125°C) olivine clinopyroxenite veins that cut peridotite.

Stosch & Lugmair (1986) and Witt-Eickschen *et al.* (1993) proposed a common origin for metasomatism and volcanism, based on isotopic and chemical similarities between metasomatized peridotites and the West Eifel lavas. The relationship of Group-II clinopyroxenites (Table 1) to the metasomatic events described by Witt-Eickschen *et al.* (1993) is unclear. Becker (1977) and Duda & Schmincke (1985) have suggested that the clinopyroxenites represent cumulates that crystallized from a nephelinitic magma under variable pressures. As an alternative, Lloyd (1987) suggested that many clinopyroxenites represent an originally lherzolitic mantle transformed *in situ* to clinopyroxenite by metasomatic reaction with either a volatile-rich silicate melt or a solute-rich fluid.

TABLE 2. ABUNDANCE AND MODAL PROPORTIONS OF SULFIDES

Sample	Abundance[1]	mss	iss	pn	po
Anhydrous lherzolites (Group 1b)					
See Table 1	Zero				
Hydrous lherzolites (Group 1a)					
TO5	L	100	0	0	0
TO2	L	100	0	0	0
TO16	L	100	0	0	0
TO12	L	100	0	0	0
TO4	L	95	5	0	0
TO15	L	92	6	2*	0
Chromian-diopside-bearing clinopyroxenites (Group 1b)					
M17	L	92	8	0	0
TO6	L	95	5	0	0
TO8	L	100	0	0	0
Hydrous veins (Group 1a)					
M4	M	100	0	0	0
MFJ1	M	100	0	0	0
M9	M	98	0	2*	0
Clinopyroxenites (Group 2)					
GM2	H	0	0	0	100
GM3	H	0	0	0	100
GM5	M	0	5	0	95
GM7	H	0	0	0	100
M12	M	0	0	0	100
M2	M	0	0	0	100
P1	H	0	0	0	100
P11	L	0	0	0	100
P2	H	0	5	0	95

[1] - determined by counting at least 4500 points
L < 0.01 vol.%, M 0.01 - 0.05 vol%, H 0.05 - 0.15 vol%
mss - monosulfide solid-solution, iss - intermediate solid-solution
pn - pentlandite, po - pyrrhotite
* associated with glass

SAMPLES AND ANALYTICAL METHODS

Twenty-eight samples from three localities (Meerfelder Maar, Gemündener Maar and Pulver Maar, Fig. 1) were selected for detailed study. Seven of the samples are anhydrous, glass-bearing peridotite, and twelve are variably metasomatized, with veins or interstitial accumulations of phlogopite or metasomatic clinopyroxene. The remaining nine xenoliths are group-II clinopyroxenite (Table 1).

All the samples were examined using reflected light microscopy to identify sulfide grains and examine their relationship to the enclosing minerals. Point counting with an eyepiece net micrometer allowed an estimate of the modal percent sulfide in each sample (Table 2). Estimates of the relative proportions of the sulfide phases (Table 2) were made on back-scattered electron micrographs.

Sulfide grains were analyzed with a JEOL 8600 Superprobe at the University of Western Ontario. All analyses were made by wavelength-dispersion spectrometry (WDS) using an accelerating voltage of 15 kV and a beam current of 10 nA. Peaks of Ni, Fe and S were counted for 20 seconds each; those of Cu

TABLE 3. REPRESENTATIVE RESULTS OF ELECTRON MICROPROBE ANALYSES OF SULFIDE GRAINS

Monosulfide solid-solution

Sample	TO5	TO5	TO12	TO6	M17	M17	MFJ-1	MFJ-1	MFJ-1	M4
Rock type	Hyd lherz	Hyd lherz	Hyd lherz	Ol cpxite	Ol cpxite	Ol cpxite	Vein	Vein	Vein	Vein
Host min.	Ol	Cpx	Ol	Cpx	Cpx	Cpx	Phl	Amp	Ol	Cpx
Fe wt%	44.99	41.79	42.67	48.83	50.36	45.91	55.24	52.46	51.87	52.56
Co wt %	0.30	0.36	0.27	0.32	0.31	0.30	0.32	0.23	0.20	0.18
Ni wt %	13.89	17.83	14.21	12.44	8.82	12.09	5.83	7.07	10.55	7.90
Cu wt %	0.33	0.44	4.97	0.23	0.19	2.97	1.29	1.33	0.38	0.52
S wt %	38.13	39.53	38.21	37.87	38.88	35.79	37.23	38.94	37.83	38.64
Total[1]	97.64	99.95	100.33	99.69	98.56	97.06	99.91	100.03	100.83	99.80

Pyrrhotite

Sample	M2	M2	M12	M12	GM3	GM5	P1	P11	M4	M4
Rock type	Cpxite	Cpxite	Cpxite	Cpxite	Cpxite	Cpxite	Cpxite	Cpxite	Vein	Vein
Host min.	Amp	Amp	Cpx	Cpx	Cpx	Amp	Cpx	Amp	Phl	Amp
Fe wt%	60.36	61.47	61.93	60.24	61.29	61.25	59.79	58.39	55.15	55.09
Co wt %	0.25	0.22	0.23	0.24	0.09	0.09	0.22	0.28	0.24	0.22
Ni wt %	0.57	0.53	0.77	0.92	0.00	0.96	1.17	2.29	4.44	4.61
Cu wt %	1.40	0.74	0.61	0.71	0.01	0.07	0.28	0.00	0.33	0.09
S wt %	35.90	37.09	36.97	37.99	36.00	38.03	38.30	39.13	39.33	40.20
Total[1]	98.48	100.05	100.51	100.10	97.39	100.40	99.76	100.09	99.49	100.21

Intermediate Solid-Solution and Pentlandite

Sample	TO4	TO15	M17	TO6	GM5	P2	TO15	M9	M9	TO4
Rock type	Hyd lherz	Hyd lherz	Ol cpxite	Ol cpxite	Cpxite	Cpxite	Hyd lherz	Vein	Vein	Hyd lherz
Host min.	Opx	Cpx	Cpx	Cpx	Amp	Cpx	Glass	Glass	Glass	Glass
Fe wt%	34.68	36.09	39.45	39.02	45.20	49.83	31.65	31.32	29.27	28.12
Co wt %	0.02	0.09	0.12	0.11	0.13	0.21	0.47	0.46	0.53	0.28
Ni wt %	0.58	0.73	1.81	2.34	0.11	0.92	33.05	34.27	35.03	36.68
Cu wt %	29.54	26.80	21.87	23.03	18.26	13.57	0.48	0.77	0.53	0.77
S wt %	35.45	34.50	35.45	35.10	35.59	34.93	33.44	33.67	33.51	33.4
Total[1]	100.27	98.21	98.70	99.60	99.29	99.46	99.09	100.49	98.86	99.25

[1] - grains with low totals are < 5 - 10 μm (see text for explanation)

Hyd lherz - hydrous lherzolite, Ol cpxite - olivine clinopyroxenite, Cpxite - group 2 clinopyroxenite

Ol - olivine, Cpx - clinopyroxene, Phl - phlogopite, Amp - amphibole

and Co were counted for 30 seconds each. Natural troilite was used as a standard for Fe and S, millerite for Ni, chalcopyrite for Cu, and pure cobalt wire for Co. Analytical uncertainty in wt% is estimated at: Fe 0.15, Co 0.15, Ni 0.2, Cu 0.2, S 0.2, on the basis of multiple analyses of standards.

About 20% of the grains analyzed gave low totals with WDS analysis (Table 3). No other major elements were detected, nor was there evidence that these grains were oxidized. Since the grains that yield low totals are less than 5–10 μm across, the suggestion of Dromgoole & Pasteris (1987), that the silicate matrix is excited during analysis of such small grains, may account for the low totals.

PETROGRAPHY OF SULFIDE INCLUSIONS

The abundance of sulfide inclusions varies according to rock type. Sulfides are not present in any of the nine anhydrous lherzolite samples studied. The metasomatically enriched lherzolite and olivine clinopyroxenite samples contain less than 0.01% sulfide by volume. Hydrous veins that cut lherzolite may contain up to 0.05 vol.% sulfide minerals. Samples of group-II clinopyroxenite contain the most abundant sulfides, with as much as 0.15 vol.% (Table 2). Three textural types of sulfide inclusion are present in the samples studied.

Type-I inclusions

Type-I sulfide inclusions are concentrated along healed fractures in primary olivine, clinopyroxene and, locally, spinel (Fig. 2a). This type of inclusion is common in hydrous lherzolite and olivine clinopyroxenite. The sulfide grains are spherical and attain 40 μm in diameter. Usually, type-I sulfides occur in association with dense trails of secondary fluid inclusions. Both sulfide and fluid inclusions occur in the same healed fractures; to suggest a genetic link between them seems reasonable.

Type-II inclusions

This type of sulfide is enclosed in metasomatically introduced clinopyroxene, phlogopite, and pargasite that occur in veins, group-II clinopyroxenite and hydrous lherzolite (Fig. 2b). The grains are spherical to

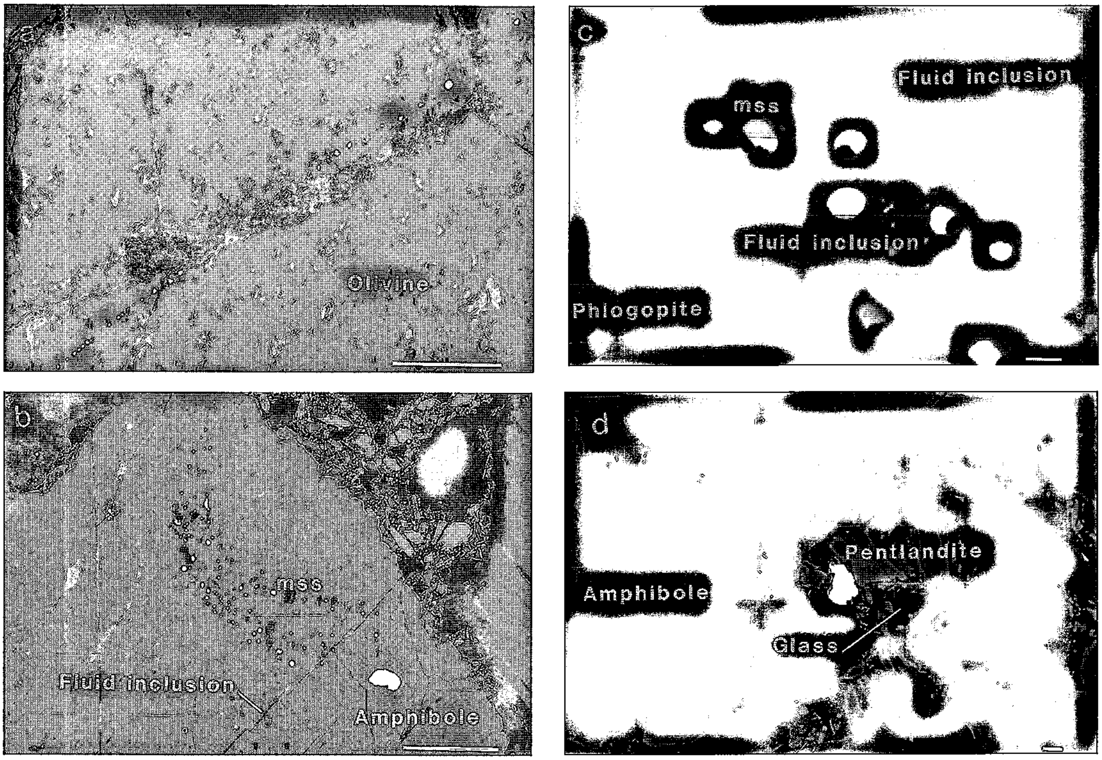

FIG. 2. a. Trail of type-I Ni-rich *mss* blebs following a healed fracture in olivine. b. Cluster of type-II *mss* grains in pargasite from a vein. Note the association of the *mss* with large fluid inclusions. c.Type-II *mss* grains in phlogopite associated with fluid inclusions. d. Type-III pentlandite in glass associated with clinopyroxene microlites in a partially melted pargasite. The scale bar corresponds to 100 μm in a and b, and to 10 μm in c and d.

cylindrical, and vary from less than 1 μm to more than 75 μm in diameter. Sulfide grains of this type occur in clusters (Fig. 2b), and many grains have a "tail" of smaller inclusions that may result from secondary ovulation (Andersen *et al.* 1987) of a larger grain. Type-II inclusions, particularly those enclosed in pargasite and phlogopite, are commonly associated with patches of apparently primary fluid inclusions (Fig. 2c). The texture of both the sulfide grains and the fluid inclusions suggests that they formed during growth of the enclosing crystals.

Type-III inclusions

Type-III sulfide blebs are enclosed in glass-rich zones in pargasite and phlogopite crystals (Fig. 2d). In these zones, ragged grains of pentlandite up to ~40 μm in diameter are surrounded by alkaline, variably SiO_2-rich glass similar in composition to that reported by O'Connor *et al.* (1996). Type-III sulfide inclusions form as much as 8 vol.% of these glass-rich zones. Given this abundance, it is unlikely that the sulfides were formed during partial melting of phlogopite or pargasite, since the S content of these minerals is extremely low. It is most likely that they represent early-formed type-I or type-II inclusions accidentally caught up in the glass-rich zones.

MINERALOGY OF SULFIDE INCLUSIONS

The sulfide assemblages in the West Eifel xenoliths consist of monosulfide solid-solution (*mss*), pyrrhotite and a Cu-rich phase optically similar to chalcopyrite. Pentlandite occurs only in glass-rich zones in pargasite and phlogopite (type III). Grains close to the outer edge of xenoliths are oxidized to a porous iron hydroxide. Table 2 summarizes the assemblages observed and the relative proportions of each phase. Monosulfide solid-solution is the dominant phase in lherzolite and olivine clinopyroxenite xenoliths. Up to 8% Cu-rich sulfide occurs as small exsolved blebs and, less commonly, as a rim around *mss* grains. There is no apparent difference in mineralogy between type-I and type-II sulfide inclusions.

Sulfide inclusions in phlogopite – pargasite veins that cut lherzolite consist of a single, optically homogeneous *mss*. In the group-II clinopyroxenites, *mss* is absent, and pyrrhotite dominates the assemblage, with up to 5% Cu-rich sulfide as exsolved blebs in the samples from Gemündener Maar and Pulver Maar. Sulfide blebs in Group-II clinopyroxenites from Meerfelder Maar do not contain an exsolved Cu-rich phase.

SULFIDE MINERAL CHEMISTRY

Monosulfide solid-solution (mss)

$(Fe, Ni)_{1-x}S$ monosulfide solid-solution is the principal phase in the lherzolite and chromian-diopside-bearing xenoliths and in the phlogopite – pargasite veins. Most of the *mss* observed falls within the Fe-rich field (Fig. 3a). Monosulfide solid-solution with less than 5 wt% Ni is referred to as pyrrhotite and is described later. Sulfur contents of *mss* show that both Fe_9S_{10}-type and Fe_7S_8-type compositions are present (Table 3). In lherzolite xenoliths, *mss* contains between 13.8 and 27.7 wt% Ni and up to 5 wt% Cu in grains that do not have an exsolved Cu-rich phase. Although they are optically homogeneous, electron-microprobe analyses of large grains reveal internal variations with coexisting Ni-rich and relatively Ni-poor *mss* (Table 3).

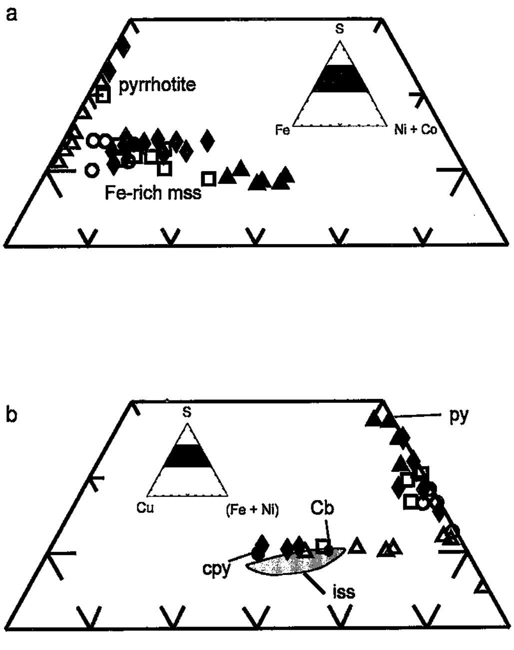

FIG. 3. a. Sulfide compositions in the system Fe – (Ni + Co) – S (in atomic %) showing the wide range of Ni contents observed in the sulfide inclusions. Symbols: filled diamond: hydrous lherzolite, open square: olivine clinopyroxenite, filled circle: vein, filled triangle: glass, open triangle: group-II clinopyroxenite. b. Sulfide compositions in the system Cu – (Fe + Ni) – S (in atomic %) showing the Cu-rich phases and the location of the intermediate solid-solution (*iss*) field at 600°C (after Cabri 1973). Symbols as in Figure 3a.

Monosulfide solid-solution in the olivine clinopyroxenites is similar in composition to that in the lherzolites, with a larger range of Ni contents (Fig. 3a). In the hydrous veins that cut lherzolite, the *mss* is Ni-poor compared with that in olivine clinopyroxenites and the host lherzolites. In one sample, compositions extend into the pyrrhotite field (Fig. 3a). As before there is some internal variation in composition in optically homogeneous grains.

Pyrrhotite

Pyrrhotite occurs as a few isolated grains in the hydrous veins, but is most common in the group-I clinopyroxenites (Fig. 3a). Pyrrhotite has a very wide range of Ni contents (0 to 4.6 wt.%), and most of the grains have compositions consistent with Fe_9S_{10}-type pyrrhotite (Table 3). Although pyrrhotite grains are homogeneous in reflected light, close examination using back-scattered electron imaging reveals complex internal compositional variations from Cu-rich to Cu-poor varieties (Fig. 4).

Cu-rich sulfide

Copper-rich sulfide occurs as exsolved blebs and as rims on larger Cu-poor sulfide grains. It varies in composition between cubanite and chalcopyrite (Table 3, Fig. 3b). There are distinct compositional variations with rock type. Chalcopyrite-like sulfide is the main Cu-bearing phase in the lherzolites. In the olivine clinopyroxenites a cubanite-like phase dominates, and in the group-II clinopyroxenites, the Cu-rich phase is intermediate in composition between cubanite and pyrrhotite (Fig. 3b). All the compositions, except the Cu-sulfide in the samples of group-II clinopyroxenite, are within the intermediate solid-solution (*iss*) field in the Cu–Fe–S system at 600°C (Fig. 3b).

Pentlandite

Pentlandite occurs only in type-III assemblages, associated with pools of glass in phlogopite and pargasite. It shows no systematic variation in composition with rock type or the host glass (Table 3).

BULK SULFIDE COMPOSITIONS

The bulk composition of the various sulfides before exsolution of *iss* can be calculated using the modal proportions of the sulfides (Table 2) and their compo-

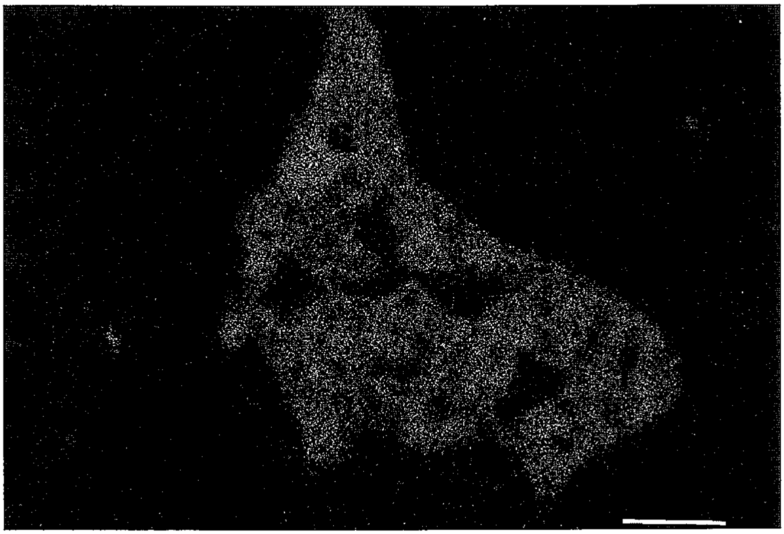

FIG. 4. X-ray map for Cu showing the distribution of Cu-rich zones (light) and low-Cu zones (dark) in an optically homogeneous grain of pyrrhotite in a group-II clinopyroxenite. Scale bar corresponds to 10 μm.

sitions (Table 3). There are, however, limitations to this technique. Derivation of accurate measurements of the relative abundance of sulfides in the xenoliths is difficult because of their small size and the compositional zonation described earlier. Sulfides associated with glass-rich zones in phlogopite and pargasite were not included in these calculations, since they may have been affected by secondary enrichment of Ni. Despite these uncertainties, bulk sulfide composition (*BSC*) estimates (Table 4) can be used, at least qualitatively, to assess original sulfide compositions for each sample.

As shown in Table 4, there are four distinct bulk compositions of sulfide, and these show a close relationship to the olivine content of the host rock. The most Ni-rich compositions pertain to the hydrous lherzolites and olivine clinopyroxenites. Although phlogopite and pargasite veins are olivine-poor, they contain sulfide with appreciable amounts of Ni. This Ni may be primary, or it may have been derived by diffusion of Ni from the surrounding wallrocks. Finally, the olivine-free group-II clinopyroxenites are Ni-poor. The variation in *BSC* with xenolith type is similar to that noted by Dromgoole & Pasteris (1987)

TABLE 4. CALCULATED BULK SULFIDE COMPOSITIONS FOR WEST EIFEL XENOLITHS (WT. %)

Rock type	Sample	Fe	Co	Ni	Cu	S	Fe/S	Fe/Ni	Bulk FeS	Bulk NiS	Kd$_3$[1]	Modal Olivine
Hydrous lherzolite	TO15	33.7	0.4	29.3	2.7	33.9	1.0	1.2	52.4	43.3	12	67
Hydrous lherzolite	TO2	43.4	0.3	17.7	0.8	37.8	1.1	2.5	70.9	27.5	9	55
Hydrous lherzolite	TO5	43.9	0.3	16.1	0.4	39.3	1.1	2.7	73.4	25.5	9	48
Ol. clinopyroxenite	TO6	48.5	0.3	12.0	1.4	37.9	1.3	4.1	79.0	18.6	5	9
Ol. clinopyroxenite	TO8	45.4	0.3	15.4	2.5	36.4	1.2	2.9	72.5	23.4	-	21
Phlogopite- and pargasite-bearing veins	M4	52.7	0.2	7.2	0.5	39.5	1.3	7.3	87.6	11.4	-	1.2
	M9	53.3	0.3	6.9	0.2	39.3	1.4	7.7	88.3	10.9	-	0
	MFJ1	53.1	0.3	8.2	0.9	37.6	1.4	6.5	85.7	12.6	-	1.3
Clinopyroxenite	GM3	58.5	0.3	2.0	0.8	38.5	1.5	28.7	95.3	3.2	-	0
Clinopyroxenite	GM5	56.8	0.2	3.6	2.1	37.3	1.5	15.8	91.2	5.5	-	0
Clinopyroxenite	M12	60.2	0.2	1.0	0.8	37.9	1.6	62.0	97.1	1.5	-	0
Clinopyroxenite	M2	60.7	0.2	0.6	1.3	37.2	1.6	110.4	97.0	0.8	-	0
Clinopyroxenite	P1	60.4	0.2	1.0	0.3	38.1	1.6	63.6	97.8	1.5	-	0
Clinopyroxenite	P2	59.5	0.2	0.6	1.5	38.2	1.6	99.2	96.6	0.9	-	0
Clinopyroxenite	P11	58.6	0.3	2.1	0.2	38.9	1.5	27.4	96.0	3.3	-	0

[1] - $Kd_3 = XNiS * XFeSiO_4 / XFeS * XNi_2SiO_4$ (Fleet & Stone 1990)

for the xenoliths from Kilbourne Hole. These authors suggested that since there were distinct values of *BSC*, each compositional group had a different origin. Given the evidence for multiple metasomatic events in the West Eifel region (Witt-Eickschen *et al.* 1993), this is a likely explanation for the range of *BSC* described here.

DISCUSSION

One of the most viable explanations for the origin of sulfides in mantle-derived xenoliths is that they formed as an immiscible melt during *in situ* partial melting of the mantle. In this case, the host xenolith should have major- and trace-element characteristics that reflect partial melting. None of the anhydrous lherzolites contains a sulfide phase. In addition, the clinopyroxene in these xenoliths has a range of compositions indicative of partial melting, *i.e.*, low Al and Na (O'Connor *et al.* 1996). This being so, it appears that partial melting cannot generate an immiscible sulfide melt. A second possible source for the sulfide minerals is the host lava. This too is considered unlikely, since no sulfides were observed in the samples of lava. Also, the range of sulfide compositions in the Meerfelder Maar samples suggests that the sulfides could not be derived from a single source. Thus, it is suggested that the sulfides in the West Eifel xenoliths are related to the passage of a noncogenetic, metasomatizing melt or fluid through the mantle. The following evidence favors this hypothesis.

1) Sulfide inclusions are closely associated with trains of fluid inclusions and are commonly hosted in healed fractures, indicating a secondary origin.

2) Sulfides are common in metasomatic minerals, *i.e.*, pargasite, phlogopite and, to a lesser extent, clinopyroxene.

3) Calculated partition-coefficients for Fe and Ni between the *BSC* and olivine (Table 4) do not suggest equilibrium, as might be expected if the sulfides were derived from *in situ* partial melts. Calculated Kd_3 (Table 4) values vary from 5 to 12, which is far from the equilibrium value of ~30 (Fleet & Stone 1990).

4) Finally, *mss* compositions similar to those described here have been shown to have a temperature of crystallization of approximately 1100 to 1197°C at one atmosphere from a Cu–Fe–Ni–S liquid (Kullerud *et al.* 1969). Extrapolation of the liquidus temperature to depth using the 7°C per kilobar increase in stability determined by Ryzhenko & Kennedy (1973) gives a temperature of crystallization of 1205 to 1296°C for *mss* at 15 kilobars. In all cases, the sulfides occur in rocks where the estimated maximum temperature is less than this (Table 1). This fact suggests that the sulfide grains did not form as an immiscible liquid from a silicate melt. The exception to this inference may be the sulfide in the group-II clinopyroxenites, for which there is no reliable estimate of temperature.

The balance of the evidence suggests that the sulfides in the West Eifel xenoliths were deposited during infiltration of a non-cogenetic melt or fluid. Witt-Eickschen *et al.* (1993) pointed out that there have been at least four metasomatic events that affected the sub-Eifel mantle. In the following discussion, *BSC* from the xenoliths are linked to these metasomatic events.

Hydrous lherzolites

Witt-Eickschen *et al.* (1993) suggested that the Ti-poor phlogopite and pargasite in hydrous lherzolite xenoliths formed during *LREE* enrichment of the mantle, possibly by a hydrous fluid (Kempton *et al.* 1988) at temperatures ~900°C, *i.e.*, below the *mss* liquidus. This, with the close association of sulfides and fluid inclusions, suggests that the sulfides in these xenoliths were deposited from a Ni- and S-bearing fluid. Anhydrous lherzolites that were not affected by this metasomatic event do not contain a sulfide phase.

Phlogopite – pargasite veins

These veins are interpreted to have formed by magma infiltration during a reheating event after the initial metasomatism that formed the hydrous lherzolites (Witt-Eickschen *et al.* 1993). Since the temperature estimates for this event (Table 1) lie below the temperature of crystallization of the bulk sulfide composition, it is likely that the sulfide grains were deposited from a vapor phase. This suggestion is supported by the association of sulfide and fluid inclusions.

The *BSC* for the vein sulfide is much less Ni-rich than that in the lherzolites. It is not known whether this *BSC* represents the original composition of the sulfides. Sulfides in the veins may have re-equilibrated in response to Ni influx from the peridotitic wallrocks (Lorand 1989a, b). However, such an influx is considered unlikely; if the vein sulfides had re-equilibrated, those in the lherzolites should also have re-equilibrated. This is not reflected in the Kd_3 values for sulfides in the peridotites, which are far from equilibrium with the coexisting olivine.

Olivine clinopyroxenite

The final metasomatic event discussed by Witt-Eickschen *et al.* (1993) led to the formation of bodies of high-temperature olivine clinopyroxenite cutting peridotite. The calculated bulk sulfide composition for these bodies is intermediate between that of the lherzolites and that of the veins. It is not clear whether the sulfides in the olivine clinopyroxenite were formed during a distinct event, or whether they represent a mixture of components from the lherzolites and the infiltrating fluid that formed the olivine clinopyroxenites.

Group-II clinopyroxenites

The *BSC* of the group-II clinopyroxenites is extremely poor in Ni compared with the other types of xenolith. The origin of group-II clinopyroxenite is controversial. Becker (1977) and Duda & Schmincke (1985) suggested that these xenoliths are cumulates formed by crystallization of the West Eifel magmas at various depths. An alternative suggestion by Lloyd (1987) is that at least some samples of group-II clinopyroxenite result from metasomatic replacement. Given the narrow range of sulfide compositions, it is likely that group-II clinopyroxenite formed by a single process; however, the data presented here cannot distinguish which one. Since sulfide inclusions in clinopyroxenite are intimately associated with trails of fluid inclusions, it is possible that they too were deposited from a S-rich fluid. However, it is impossible to rule out an origin *via* immiscibility from a silicate melt.

Silicate glass inclusions

Silicate glass inclusions in the West Eifel xenoliths have been suggested to be quenched samples of a melt responsible for metasomatism (Edgar *et al.* 1989, Zinngrebe & Foley 1995, O'Connor *et al.* 1996). During this study, I examined a large number of these glass inclusions and pools in detail; however, no clearly primary sulfide phase was found. If this glass is the remains of a quenched metasomatic melt, this melt thus probably was not responsible for the formation of any of the major metasomatic rock-types described in this study, but reflects a later event, or it had lost all of its sulfide phase elsewhere before being quenched.

Phase relations and comparison with other sulfides in mantle xenoliths

Comparison of calculated bulk-sulfide compositions from West Eifel, Kilbourne Hole and northern Hungary shows that the estimated compositions of the primary sulfides before low-temperature re-equilibration were similar (Fig. 5a). In the system Fe – Ni – S, all the *BSC* fall within the stability field of *mss* at 1000°C. The restricted compositional range of *BSC* for the group-II clinopyroxenites indicates that these may have crystallized at approximately 1180°C, on the basis of new experimental data by Naldrett *et al.* (1997). The *BSC* in the group-II clinopyroxenites at West Eifel is much poorer in Ni + Co than those from the other localities; however, the *BSC* calculated for the olivine-bearing xenoliths and veins are similar to those from Kilbourne Hole and northern Hungary (Fig. 5a).

On a Fe–Ni–Cu projection of the Fe–Ni–Cu–S quaternary system (Fig. 5b), the West Eifel compositions again show close similarities with those from other localities. The exception to this generalization is the *BSC* of the Eifel clinopyroxenites, which are Ni- and Cu-poor relative to the *BSC* of the other localities and those in olivine-bearing xenoliths from the West Eifel.

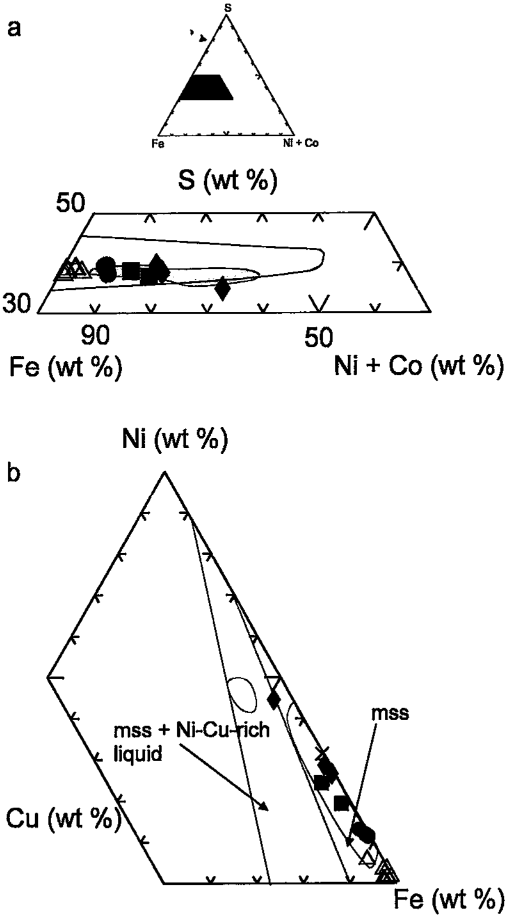

FIG. 5. a. Bulk compositions of sulfides in the West Eifel xenoliths in the system Fe–Ni–S (symbols as in Fig. 3). Also shown is the stability field of *mss* at 1000°C (Kullerud *et al.* 1969). The shaded region shows the range of compositions of sulfides in mantle xenoliths from Kilbourne Hole and northern Hungary (Dromgoole & Pasteris 1987, Szabó & Bodnar 1995). Symbols as in Figure 3a. b. Bulk compositions of sulfides in the West Eifel xenoliths in the Fe–Ni–Cu projection of the quaternary system Fe – Ni – Cu – S. The fields of *mss* and *mss* + Ni–Cu-rich liquid at 1000°C (Craig & Kullerud 1969) also are shown. The shaded region shows the compositional range of sulfides in xenoliths from Kilbourne Hole and northern Hungary. Symbols as in Figure 3a.

The presence of patches of relatively Ni-rich and Ni-poor *mss* suggests that homogeneous *mss* is unstable and is beginning to decompose to the equilibrium assemblage.

Most of the sulfides in the xenoliths from Kilbourne Hole and northern Hungary are considered to have originated as an immiscible melt from *in situ* partial melts of a lherzolitic mantle (Dromgoole & Pasteris 1987, Szabó & Bodnar 1995). In contrast, the data presented here suggest that the sulfides in the West Eifel xenoliths were deposited from a fluid phase during metasomatic enrichment of the mantle. The close similarity of compositions between those of the West Eifel and other regions shows that *BSC* alone is not a useful guide to the origin of the sulfides. Thus, to understand the origin of sulfides in xenoliths, it is necessary to know the paragenesis of the silicate minerals, and their relationship to metasomatism.

CONCLUSIONS

1) Sulfide inclusions from West Eifel xenoliths can be related to distinct metasomatic events.

2) The sulfides were deposited from either a fluid or vapor phase rather than from immiscible blebs of melt, since in all cases the estimated temperature of the metasomatic event is below that of the monosulfide solid-solution liquidus under mantle conditions.

3) Although sulfide compositions alone cannot be used to distinguish their process of formation, detailed study of the paragenesis of these minerals can be used to indicate the various metasomatic events.

ACKNOWLEDGEMENTS

This study was carried out while the author was a postdoctoral fellow at the University of Western Ontario. It was funded by NATO and NSERC grants to A.D. Edgar. T. O'Connor, L.A. Pizzolato and F.E. Lloyd provided me with additional samples from the West Eifel region. Y. Thibault assisted with the electron-microprobe analyses. Thanks to A.D. Edgar, F.E. Lloyd and R. Linnen for their comments on an earlier version of this manuscript, and the two anonymous referees for formal reviews.

REFERENCES

ANDERSEN, T., GRIFFIN, W.L., & O'REILLY, S.Y. (1987): Primary sulphide melt inclusions in mantle-derived megacrysts and pyroxenites. *Lithos* **20**, 279-294.

BAILEY, D.K. (1982): Mantle metasomatism – continuing chemical change within the earth. *Nature* **296**, 525-530.

________ (1987): Mantle metasomatism – perspective and prospect. *In* Alkaline Igneous Rocks (J.G. Fitton & B.G.J. Upton, eds.). *Geol. Soc., Spec. Publ.* **30**, 1-13.

BECKER, H.J. (1977): Pyroxenites and hornblendites from the maar-type volcanoes of the Westeifel, Federal Republic of Germany. *Contrib. Mineral. Petrol.* **65**, 45-52.

BISHOP, F.C., SMITH, J.V. & DAWSON, J.B. (1975): Pentlandite – magnetite intergrowth in DeBeers spinel lherzolite; review of sulphides in nodules. *Phys. Chem. Earth* **9**, 323-337.

CABRI, L.J. (1973): New data on phase relations in the Cu–Fe–S system. *Econ. Geol.* **68**, 443-454.

CRAIG, J.R. & KULLERUD, G. (1969): Phase relations in the Cu–Fe–Ni–S system and their application to magmatic ore deposits. *In* Magmatic Ore Deposits (H.D.B. Wilson, ed.). *Econ. Geol., Monogr.* **4**, 344-358.

DE WAAL, S.A. & CALK, L.C. (1975): The sulfides in garnet pyroxenite xenoliths from Salt Lake Crater, Oahu. *J. Petrol.* **16**, 134-153.

DROMGOOLE, E.L. & PASTERIS, J.D. (1987): Interpretation of the sulfide assemblages in a suite of xenoliths from Kilbourne Hole, New Mexico. *Geol. Soc. Am., Spec. Pap.* **215**, 25-46.

DUDA, A. & SCHMINCKE, H.-U. (1985): Polybaric differentiation of alkali basalt magmas: evidence from green-core clinopyroxenes (Eifel, FRG). *Contrib. Mineral. Petrol.* **91**, 340-353.

EDGAR, A.D., LLOYD, F.E., FORSYTH, D.M. & BARNETT, R.L. (1989): Origin of glass in upper mantle xenoliths from the Quaternary volcanics of Gees, West Eifel, Germany. *Contrib. Mineral. Petrol.* **103**, 277-286.

FLEET, M.E. & STONE, W.E. (1990): Nickeliferous sulfides in xenoliths, olivine megacrysts and basaltic glass. *Contrib. Mineral. Petrol.* **105**, 629-636.

FRECHEN, J. (1948): Die Genese der Olivineausscheidungen vom Dreiser Weiher (Eifel) und Finkenberg (Siebengebirge). *Neues Jahrb. Mineral., Abh.* **79A**, 317-406.

________ (1963): Kristallisation, Mineralbestand, Mineralchemismus und Förderfolge der Mafitite vom Dreiser Weiher in der Eifel. *Neues Jahrb. Mineral., Monatsh.*, 205-225.

FREY, F.A. & PRINZ, M. (1978): Ultramafic inclusions from San Carlos, Arizona: petrologic and geochemical data bearing on their petrogenesis. *Earth Planet. Sci. Lett.* **38**, 129-176.

HARTE, B. (1987): Metasomatic events recorded in mantle xenoliths: an overview: *In* Mantle Xenoliths (P.H. Nixon, ed.). John Wiley & Sons, London, U.K. (625-640).

IRVING, A.J. (1980): Petrology and geochemistry of composite ultramafic xenoliths in alkalic basalts and implications for magmatic processes within the mantle. *Am. J .Sci.* **280-A**, 389-426.

KEMPTON, P.D., HARMON, R.S., STOSCH, H.-G., HOEFS, J. & HAWKESWORTH, C.J. (1988): Open-system O-isotope behaviour and trace element enrichment in the sub-Eifel mantle. *Earth Planet. Sci. Lett.* **89**, 273-287.

KULLERUD, G., YUND, R.A. & MOH, G.H. (1969): Phase relations in the Cu–Fe–S, Cu–Ni–S and Fe–Ni–S system. *In* Magmatic Ore Deposits (H.D. Wilson, ed.). *Econ. Geol., Monogr.* **4**, 323-343.

LLOYD, F.E. (1987): Characterization of mantle metasomatic fluids in spinel lherzolite and alkali clinopyroxenites from the West Eifel and south west Uganda. *In* Mantle Metasomatism (M.A. Menzies & C.J. Hawkesworth, eds.). Academic Press, New York, N.Y. (91-123).

LORAND, J.P. (1987): Cu–Fe–Ni–S mineral assemblages in upper-mantle peridotites from the Table Mountain and Blow-Me-Down Mountain ophiolite massifs (Bay of Islands area, Newfoundland): their relationships with fluids and silicate melts. *Lithos* **20**, 59-76.

________ (1989a) The Cu–Fe–Ni sulfide component of the amphibole-rich veins from the Lherz and Freychinede spinel peridotite massifs (northeastern Pyrenees, France): a comparison with mantle derived megacrysts from alkali basalts. *Lithos* **23**, 281-298.

________ (1989b): Sulfide petrology of spinel and garnet pyroxenite layers from mantle-derived spinel lherzolite massifs of Ariège, northeastern Pyrenees, France. *J. Petrol.* **30**, 987-1015.

MERTES, H. & SCHMINCKE, H.-U. (1985): Mafic potassic lavas of the Quaternary West Eifel volcanic field. 1. Major and trace elements. *Contrib. Mineral. Petrol.* **89**, 330-345.

NALDRETT, A.J., EBEL, D.S., ASIF, M., MORRISON, G. & MOORE, C.M. (1997): Fractional crystallisation of sulfide melts as illustrated at Noril'sk and Sudbury. *Eur. J. Mineral.* **9**, 365-377.

O'CONNOR, T.K., EDGAR, A.D. & LLOYD, F.E. (1996): Origin of glass in Quaternary mantle xenoliths from Meerfeldermaar, West Eifel, Germany: implications for enrichment in the lithospheric mantle. *Can. Mineral.* **34**, 187-200.

RYZHENKO, B.N. & KENNEDY, G.C. (1973): The effect of pressure on the eutectic in the Fe–FeS system. *Am. J. Sci.* **273**, 803-810.

STOSCH, H.-G. & LUGMAIR, G.W. (1986): Trace element and Sr and Nd isotope geochemistry of peridotite xenoliths from the Eifel (West Germany) and their bearing on the evolution of the subcontinental lithosphere. *Earth Planet. Sci. Lett.* **80**, 281-298.

________ & SECK, H.A. (1980): Geochemistry and mineralogy of two spinel peridotite suites from Dreiser Weiher, West Germany. *Geochim. Cosmochim. Acta* **44**, 457-470.

SZABÓ, C. & BODNAR, R.J. (1995): Chemistry and origin of mantle sulfides in spinel peridotite xenoliths from alkaline basaltic lavas, Nógrád–Gömör volcanic field, northern Hungary and southern Slovakia. *Geochim. Cosmochim. Acta* **59**, 3917-3927.

WITT-EICKSCHEN, G., SECK, H.A. & REYS, C. (1993): Multiple enrichment processes and their relationships in the subcrustal lithosphere beneath the Eifel (Germany). *J. Petrol.* **34**, 1-22.

ZINNGREBE, E. & FOLEY, S.F. (1995): Metasomatism in mantle xenoliths from Gees, West Eifel, Germany: evidence of calc-alkaline glasses and metasomatic Ca-enrichment. *Contrib. Mineral. Petrol.* **122**, 79-96.

Received April 2, 1997, revised manuscript accepted September 14, 1997.