SELENIUM, TELLURIUM, ARSENIC AND ANTIMONY CONTENTS OF PRIMARY MANTLE SULFIDES

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Abstract

Sulfide phases in peridotitic mantle xenoliths from Ichinomegata in Japan, Nunivak Island in Alaska, and southern Africa occur as globular grains within silicate minerals, and along grain boundaries of silicate and oxide minerals. The morphology of the sulfide grains suggests that the sulfide liquid was not interconnected in the mantle, even within single samples. This is supported by compositional variations of sulfides. Proton-induced X-ray excitation (PIXE) micro-analyses of 53 sulfide grains larger than 20 μm in diameter reveal a wide range of compositions: Se 21–280 ppm, S/Se 1120–18800; Te up to 103 ppm, S/Te 2,600–31,000; As up to 670 ppm, As/S up to 208×10^{-5}, and Sb, up to 146 ppm, Sb/S up to 37×10^{-5}. S/Se and Ni show an inverse correlation in the sub-arc xenoliths, suggesting preferential retention of Se in the mantle during partial melting. Sulfur is the most readily removed element, whereas Te is the most likely retained element in the residual mantle. This interpretation is consistent with low S/Se values for sulfides from refractory mantle wedges compared to values for the primitive mantle, generally high S/Se and Se/Te values in basalts, and low S/Se and Se/Te in boninites compared to mid-ocean-ridge basalts. The evidence implies that S/Se values of mantle-derived magmas may vary depending on the degree of partial melting and previous melting history in the source mantle. High concentrations of As and Sb in arc magmas are considered to be supplied from subducting slabs. Our data showing low levels of As and Sb in sulfides from sub-arc mantle suggest their fast removal from mantle wedges compared to the rate of supply of these elements from subducting slabs. Alternatively, these elements may be transported by a fluid phase from slabs to the site of partial melting without residing in the mantle.

Keywords: chalcophile elements, selenium, tellurium, arsenic, antimony, sulfides, mantle metasomatism, xenoliths, sub-arc mantle, subcontinental lithospheric mantle, subduction flux, recycling.

Sommaire

Les phases sulfurées des xénolithes péridotitiques du manteau provenant de Ichinomegata au Japon, l'île de Nunivak, en Alaska, et de l'Afrique du Sud se trouvent sous forme de grains globulaires piégés à l'intérieur de grains silicatés, et le long de bordures de grains de silicates et d'oxydes. La morphologie des grains de sulfures fait penser que le liquide sulfuré ne faisait pas partie d'un réseau interconnecté dans le manteau, même dans le cas d'échantillons individuels. C'est ce que semble aussi montrer les variations en composition des sulfures. Ces compositions, obtenues par micro-analyse PIXE (excitation de rayons X par faisceau de protons) de 53 grains de sulfures dépassant une taille de 20 μm en diamètre, définissent un intervalle important de variation: Se 21–280 ppm, S/Se 1120–18800; Te jusqu'à 103 ppm, S/Te 2,600–31,000; As jusqu'à 670 ppm, As/S atteignant 208×10^{-5}, et Sb, jusqu'à 146 ppm, Sb/S atteignant 37×10^{-5}. S/Se et Ni montrent une corrélation inverse dans les xénolithes provenant d'un milieu sub-arc, ce qui pourrait indiquer une conservation préférentielle du Se dans le manteau au cours d'une fusion partielle. Le soufre serait l'élément le plus facile à mobiliser, tandis que le Te serait le plus apte à demeurer dans le manteau résiduel. Cette interprétation concorde avec les faibles valeurs de S/Se dans les sulfures provenant des biseaux réfractaires du manteau, par rapport au manteau primitif, ainsi que des rapports S/Se et Se/Te généralement élevés dans les basaltes, et faibles dans les boninites par rapport aux basaltes des rides océaniques. Le rapport S/Se d'un magma dérivé du manteau varie donc en fonction du degré de fusion partielle et des événements de fusion antécédents de la source mantélique. Les concentrations élevées de As et Sb dans les magmas d'arcs insulaires résulteraient d'apports provenant de la croûte subductée. Nos données impliquant de faibles niveaux de As et Sb dans les sulfures du manteau en dessous d'arcs insulaires semblent indiquer une extraction rapide

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à partir des biseaux mantéliques par rapport au taux d'addition de ces éléments par contributions des plaques lithosphériques subductées. En revanche, il est possible que ces éléments soient transportés efficacement par une phase fluide d'une plaque lithosphérique subductée au site de fusion partielle sans période de résidence dans le manteau.

(Traduit par la Rédaction)

Mots-clés: éléments chalcophiles, sélénium, tellurium, arsenic, antimoine, sulfures, métasomatose du manteau, xénolithes, manteau sub-arc, manteau lithosphérique subcontinental, flux de subduction, recyclage.

INTRODUCTION

The distribution and composition of sulfides in the mantle are not well known, but such information is relevant to two fundamental questions. First, the concentrations of siderophile elements in the mantle are greater than expected from equilibrium separation of the mantle from the core by several orders of magnitude, and the cause for this "overabundance" has been long debated (*e.g.,* Sun 1985, Rama Murthy 1991, Palme 1999). Sulfides may contribute to this "overabundance" (Arculus & Delano 1981) since they are rich in siderophile and chalcophile elements. Second, the enrichment of chalcophile elements in the mantle may in turn be associated with the formation of gold and base-metal deposits. Such metallic ore deposits are abundant in volcanic arcs, and the metals in the deposits may have been derived from subducting slabs *via* metasomatized mantle wedges (Sillitoe 1972). The heterogeneous distribution of such metal deposits in volcanic arcs may be related to localized enrichment of chalcophile elements in mantle wedges.

Previous studies of the behavior of siderophile and chalcophile elements in the mantle have been based on bulk analyses of mantle rocks (*e.g.,* Jagoutz *et al*. 1979, Kurat *et al*. 1980, Jochum & Hofmann 1997). Here, we use a micro proton-induced X-ray excitation probe (PIXE) to provide the first documentation of the concentrations of As, Sb, Se, and Te in primary sulfides in xenoliths from mantle wedges, and in xenoliths in kimberlites derived from the subcontinental lithospheric mantle. Our data show a wide range of Se, Te, As, and Sb concentrations, as well as S/Se, S/Te, S/As, and S/Sb values in mantle sulfides. We relate these variations primarily to depletion by partial melting events in the mantle.

SAMPLES

Peridotitic xenoliths from Ichinomegata, Japan, were brought to the surface by explosive volcanic eruptions of tholeiitic basalt and calc-alkaline andesite ~10,000 years ago (Abe & Arai 1993). The samples are predominantly lherzolite with minor harzburgite, and show equigranular to porphyroclastic textures. They represent a metasomatized, refractory mantle that provided calc-alkaline magmas for construction of the Japanese arc (Kuno 1967, Takahashi 1986). Olivine is Mg-rich,

Fo$_{88-91}$ in anhydrous samples and Fo$_{83-86}$ in pargasite-rich (10 vol.%) samples. Spinel (0.1–5.6 modal %) has a value (atomic basis) of Cr/(Cr + Al) ranging from 0.1 to 0.5 (Abe & Arai 1993). Hydrous metasomatism is expressed by the occurrence of pargasite (up to 20 vol.%) and phlogopite. Pargasite is characterized by low Ti (<1.6 wt.% TiO$_2$) and commonly replaces subsolidus minerals such as pyroxene of symplectitic intergrowths and clinopyroxene lamellae in orthopyroxene (Arai 1986, Abe *et al*. 1992). Phlogopite occurs as clotted aggregates with pargasite-rich veinlets. Samples used for this study consist of harzburgite, pargasite spinel lherzolite, and phlogopite – pargasite spinel lherzolite (Table 1), and their mineral chemistry and textures are described in Abe *et al* (1992, 1998) and Abe & Arai (1993).

Nunivak Island, ~50 km west of the Alaskan coast, consists of olivine tholeiite flows and overlying alkali olivine basalts (Roden *et al*. 1984). The spatter cones and maars of alkali basalts contain abundant megacrysts of clinopyroxene, kaersutite, and anorthoclase, as well as peridotitic xenoliths. The peridotitic xenoliths show coarse-equant, coarse-tabular, and granuloblastic-equant textures and include lherzolite and minor dunite, harzburgite, and pargasite-bearing pyroxenite (Francis 1976, 1978, Roden *et al.* 1984). The peridotitic xenoliths used for this study occur in basanites less than 1 million years old and include pargasite-bearing spinel lherzolite, with or without phlogopite veinlets, and a garnet pyroxenite (Table 1). The xenoliths sampled commonly contain abundant fluid inclusions and also show evidence of incipient melting (Francis 1976). A lherzolite sample (10001) contains "glass" that replaces hornblende and now consists of relict pargasite and fine aggregates of clinopyroxene and phlogopite. Garnet pyroxenite (sample 13008) is different from the rest of the samples. It represents a cumulate formed from a melt that solidified in the mantle, as pyroxenites in obducted mantle rocks (Kumar *et al*. 1996). Peterson & Francis (1977) described a megacryst of chromian diopside containing immiscible sulfide spherules of a mixture of pyrrhotite and chalcopyrite, and fluid inclusions along growth planes of the host diopside. Unfortunately, these sulfide grains are too small, less than 10 μm across, for PIXE analysis, so were not used for this study. Overall, the Nunivak samples are similar to those from Ichinomegata in that they appear to represent rocks from a refractory mantle wedge that has undergone hydrous

TABLE 1. LIST OF SAMPLES SELECTED FOR A STUDY OF PRIMARY MANTLE SULFIDES

	Location		Primary minerals and their composition**	Fo	Cr#
014	Ichinomegata	Phl Prg harzburgite	Ol (51.1), Opx (32.4), Cpx (0.8), Spl (0.9), Prg (14.1), Phl (0.3)	83.7	0.27
015	Ichinomegata	Spl Prg lherzolite	Ol (51.5), Opx (26.6), Cpx (14.5), Spl (2.1), Prg (4.0)	88.5	0.13
538	Ichinomegata	Prg Spl lherzolite	Ol (50) Opx (20), Cpx (15), Spl (5), Prg (10)	88.8	0.11
638	Ichinomegata	Harzburgite, rare Prg	Ol (51.8), Opx (26.6), Spl (1.8), Cpx (10.0), Prg (0.9), Symp(Pl–Px) (8.0)	90.0	0.14
10001	Nunivak	Coarse equant spinel lherzolite containing devitri- fied "glass"*	Ol (35), Cpx (35), Opx (15), Spl (8), Prg (5), Phl (2) $0.90 < Mg\#(Cpx) < 0.93$, Mg(Opx) 0.90	89–91	
10057	Nunivak	Coarse, weakly foliated spinel lherzolite	Ol (50), Cpx (25), Opx (20), Spl (4), Prg (1), Mg#(Cpx) 0.91, Mg#(Opx) 0.90	90	
13008	Nunivak	Grt pyroxenite	Cpx (85), Ol (8), Grt (5), Spl (1), Prg (1), sulfides (3), Mg#(Cpx) 0.73		
FS	Frank Smith	Cpx megacryst with oriented inclusions	Cpx (84), lamellae of Ilm (15), sulfide blebs (1; Po, Pn, Djr) Cpx $(Mg_{0.859}Fe_{0.057}Cr_{0.013}Si_{1.97}Al_{0.093}O_6)$		
DBC-47	Kimberley	Grt harzburgite containing Cr-rich (1.9 wt% Cr_2O_3) Di	Ol + Opx (85), Cpx (<5), Grt (5–10), Phl (1); Mg# (Opx) 0.940, Mg# (Phl) 0.95, Grt (73.4% Prp, 11.2% Uvr, 8% Alm, 6.1% Adr, 0.6% Sps)	92–93	
PTH516	Lesotho	Phl lherzolite containing Cr-rich (2.6–3.2 wt% Cr_2O_3) Di	Ol + Opx (75), Cpx (10), Phl (14), Spl (1); Mg# (Opx): 0.931; Mg# (Phl): 0.944	92–93	0.86 – 0.89
DBC-L	Lesotho	Grt harzburgite containing Cr-rich Di (~ 1.8 wt% Cr_2O_3)	Ol + Opx (90), Cpx (5), Grt (5); Mg# (Opx) 0.929, Mg# (Cpx) 0.952, Grt (67.2% Prp, 15.1% Uvr, 12.8% Alm, 4.1% Adr, 0.8% Sps)	92–93	

Symbols: Cpx: clinopyroxene, Djr: djerfisherite, Grt: garnet, Ilm: ilmenite, Ol: olivine, Opx: orthopyroxene, Phl: phlogopite, Pn: pentlandite, Po: pyrrhotite, Prg: pargasite, Spl: spinel, Symp(Pl–Px) = symplectite of spinel + pyroxene. Components of garnet: Adr: andradite, Alm: almandine, Prp: pyrope, Sps: spessartine, Uvr: uvarovite.
* Glass is now composed of fine aggregates of clinopyroxene and relict pargasite.
** Cr# = atomic Cr/(Cr + Al) in chromian spinel, Mg# = atomic Mg/(Mg + Fe^{2+}).
The modal proportion of the primary minerals is reported in parentheses.

metasomatism. The samples from Nunivak appear to have undergone more advanced degrees of hydrous alteration.

The samples from kimberlites in southern Africa include: a diopside megacryst (sample DBC–FS) from the Frank Smith mine, South Africa (Clarke *et al.* 1977), containing exsolution lamellae of magnesian (~10 wt% MgO) ilmenite and blebs of sulfide, including pyrrhotite, pentlandite, and djerfisherite, $K_6(Cu,Fe, Ni)_{25}S_{26}Cl$; a coarse-grained, granular, pyrope garnet harzburgite nodule from the Bultfontein Floors, Kimberley, South Africa (sample DBC–47); a coarse-grained, granular, pyrope harzburgite with minor chromian diopside (< 5 vol.%), and wide, fine-grained kelyphitic rims on the garnet from Pipe 200, Lesotho (sample DBC–L) (Carswell *et al.* 1979, Mitchell *et al.* 1980), and a medium-grained, granular lherzolite (sample PTH–516) from Pipe 200, Lesotho, that appears to be the metasomatized equivalent of a garnet lherzolite

in which coarse-grained clusters of chromian diopside, phlogopite, and magnesian chromite have replaced garnet (Schandl 1980). Olivine in all samples is Mg-rich, ranging from $Fo_{91.9}$ to $Fo_{93.2}$, and Ni-rich, ranging from 2000 to 4500 ppm Ni, confirming the highly refractory nature of the source, subcontinental lithospheric mantle underlying the Kaapvaal craton.

ANALYTICAL METHODS

Major compositions of minerals were determined using a JEOL 6400 digital SEM equipped with a 40° take-off angle and a Link X-ray analyzer. Analytical conditions included a beam size 0.25 μm in diameter, an accelerating potential of 20 kV, a current of 0.8 nA and a counting time of 140 to 200 s. The following standards were used for the analysis of sulfides; pyrite (Fe, S), chalcopyrite (Cu), Ni metal (Ni), Co metal (Co), and ZnS (Zn); oxide standards were used: SiO_2 (Si),

Al_2O_3 (Al), MgO (Mg), chromite (Cr), $MnTiO_3$(Mn, Ti), and hematite (Fe). Detection limits are ~ 0.05 wt%. The levels of selected trace elements in the sulfides were determined using a micro proton-induced X-ray excitation probe (PIXE) at the University of Guelph. Operating conditions were: a proton energy of 3 MeV, a specimen current of ~4 to 8 nA, a counting time of 1,000 to 1,200 s, and a beam size of 4×5 µm. The proton beam has an angle of 45° to the specimen and excites elements up to a depth of ~20 µm. The detection limit of each element is equal to three standard deviations on the mean background measured on both sides of the peak of the element, and the background values vary depending on the composition. Accordingly, detection limits of a given element are different among different grains. Detailed operating conditions and analytical procedures were described by Cabri *et al.* (1984) and Campbell & Czamanske (1998). To monitor the quality of the analysis, Mg, Al, Si, and S were simultaneously determined. Data with totals of (FeS + NiS + CuS + CoS) greater than 90 wt% were used, and subsequently normalized to 100 wt%. Typical analytical precision and accuracy are believed to be better than 10% for most elements, based on replicate analyses of a natural pyrrhotite standard.

Sulfide grains are minor constituents in our samples and rarely exceed more than 1 vol.%, except in the case of a garnet clinopyroxenite from Nunivak Island. Furthermore, most sulfide grains are very small (< 10 µm). To obtain reliable trace-element data using the PIXE, we chose sulfide grains greater than 20 µm in diameter because the proton beam excites elements up to ~20 µm below the surface. This size restriction may have resulted in a potential bias in the data, although there are no apparent differences between large and small grains.

RESULTS

Sulfide occurrences

Most sulfide inclusions in ultramafic rocks are globular in shape, reflecting their former liquid state at mantle temperatures (> 1000°C). On cooling, they probably first crystallized as sulfide solid-solutions, and at a lower temperature, unmixed to form various proportions of pyrrhotite, pentlandite, chalcopyrite, heazlewoodite and magnetite (Table 2). These exsolution products form blebs, lamellae (less than several µm), and irregularly shaped phases. We have classified our samples into four types, based on the morphology of the sulfides, and the occurrences are tabulated in Table 2.

Type 1. Isolated spherical grains enclosed within silicate minerals (Figs. 1a, 1b).

Type 2. Isolated globular grains [up to ~ 100 µm in diameter (Fig. 1c)] not hosted by silicates or oxides, but most commonly occurring at triple junctions of silicate minerals.

Type 3. Rare isolated angular grains along grain boundaries of silicate minerals.

Type 4. Discontinuous veinlets of sulfides along grain boundaries of silicate minerals. This type of sulfide is not common and occurs only in spinel lherzolite from Nunivak Island (sample 10057; Fig. 1d). The veinlets, 20–30 µm wide, along silicate grain-boundaries, consist of a pyrrhotite matrix with exsolved chalcopyrite, pentlandite, and magnetite (Fig. 1d). The occurrence of exsolved sulfide phases (Fig. 1e) suggests that the veinlets are a high-temperature product. Magnetite can be an exsolution product because natural sulfide liquids can contain significant concentrations of oxygen (up to 14 wt% O; Francis 1990, Roy-Barman *et al.* 1998, Rose & Brenan 2001). The composition of the veinlets (Table 2, grain F, anal. 127) is similar to that of the sulfide grains enclosed in olivine and clinopyroxene in the sample, supporting the idea that these veinlets represent rare channeled sulfide liquid in the mantle, as has been postulated by Gaetani & Grove (1999).

Serpentinized samples show destabilization of primary sulfides and the formation of secondary sulfides. Altered sulfides have low reflectivity caused by the formation of fine-grained hematite and Fe hydroxides. The secondary pyrrhotite forms narrow films, less than 10 µm wide, along grain boundaries of silicates. The compositions of such secondary sulfides are not included in the results.

Selenium and tellurium

All analyzed grains contain detectable amounts of Se (Table 2), and the weight ratios of S to Se range from 1,120 to 18,800 (Fig. 2a). The ratios from individual samples are clustered, approximating chemical equilibrium, except for sample 10001. The low S/Se values, ~ 1,500, occur in sulfides in a spinel harzburgite (sample 638) from Ichinomegata, which represents the most refractory sample judging from the lithology and high level of Mg in olivine (Fo_{90}). The values of S/Se, ~ 1500, are low compared to those of primitive mantle (3,300; McDonough & Sun 1995) and CI chondritic meteorites (~2,540; Dreibus *et al.* 1995). Sulfides from the metasomatized kimberlite nodules have S/Se values lower than the primitive mantle, the Frank Smith discrete nodule matches primitive mantle, and the garnet lherzolite from Kimberley has S/Se greater than primitive mantle.

Only five sulfide grains from mantle wedges, and four sulfide grains from the subcontinental lithosphere, contain concentrations of Te above the detection limit (~20 ppm).

Arsenic and antimony

Many sulfide grains in our samples show detectable amounts of As. High As contents occur in sulfides from peridotite nodules in kimberlites, with several grains containing more than 200 ppm (Fig. 3). Similarly, high

TABLE 2. TRACE-ELEMENT CONCENTRATIONS IN PRIMARY MANTLE SULFIDES

section	13008	13008	13008	13008	13008	13008 -Z	13008	13008	13008	13008	13008	13008	13008	13008
loc. (α)	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI
grain	BA	BC	AB	CA	CB	Z	Y	X	J	F	K	L	X	H
anal.	5	7	11	13	14	16	17	18	40	41	44	45	47	48
phase (β)	Po	Po	Po	Po	Po	Po	Po	Po	Po	Po	Po	Po	Po	Po
occurrence (χ)	Spl–Cpx	Cpx	i.Sp	Cpx	i.Cpx	Cpx–Ol	Ol	i.Cpx	i.Ol	i.Cpx	Spl–Cpx	Cpx	Spl–Cpx	i.Ol
shape (δ)	S	A–R	S	S	S	S	S	S	S	A	R	R	R	S
Ni wt%	1.13	2.12	2.09	2.29	1.72	1.45	1.82	2.13	2.63	2.13	2.06	2.01	2.09	2.28
As ppm	24	<4	44	6	<9	14	?4	9	0	<4	?6	<5	<5	<6
Se	21	60	27	32	21	30	23	24	24	23	24	33	40	43
Sb	?9	<9	<10	11	<10	<8	<9	<8	<16	<18	<16	<15	<17	<16
Te	?9	12	?9	<11	<11	<11	?20	<10	<20	<22	<21	<21	<20	<20

section	10001	10001	10001	1001	1001	10001	10057	10057	10057	014	15	015	015	538
loc. (α)	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	NunI	Ichi	Ichi	Ichi	Ichi	Ichi
grain	CA	CB	EA	EB	F	A	EA	EB	F	D	AA	AB	AC	B
anal.	23	24	26	64	63	25	125	126	127	19	20	61	62	49
phase (β)	Po	Po	Po	Po	Po	Po	Pn	Pn	Pn	Pn	Pn	Pn	Pn	Pn
occurrence (χ)	i.Cpx	i.Cpx	i.Opx	i.Opx	Ol	Ol–M	Ol	Ol–Cpx	Ol	i.Ol	Ol–Cpx	Opx	Opx	i.Cpx
shape (δ)	S	S	S	R	A	A	R–A	R	A	S	R–A	R	R	S
Ni wt%	2.86	2.39	3.30	8.73	11.9	3.31	19.2	11.6	21.8	10.4	14.3	14.14	14.3	16.1
As ppm	<3	?4	<3	<4	0	<2	<9	14	<8	10	35	<6	51	<6
Se	116	117	59	240	182	99	129	90	138	145	170	158	172	280
Sb	<9	<10	7	<23	<17	9	<14	30	<13	<13	146	<17	<16	<18
Te	20	<12	<10	103	<23	<14	24	14	30	18	20	<23	<20	<21

section	538	538	538	538	538	538	638	638	FC	FC	FC	FC	FC	FC
loc. (α)	Ichi	Ichi	Ichi	Ichi	Ichi	Ichi	Ichi	Ichi	Frank	Frank	Frank	Frank	Frank	Frank
grain	F	B–E	EA	EB	HA	HB	A	B	A	A	A	A	A	C
anal.	50	51	52	53	54	55	65	66	33	34	35	36	38	39
phase (β)	Pn	Pn	Pn	Pn	Pn	Pn	Pn	Pn	Pn	Djr	Pn	Po	Po+Pn	Pn
occurrence (χ)	Ol–Cpx	Ol–Cpx	Ol	Ol–Cpx	Ol	Ol	Opx	i.Opx	i.Cpx	i.Cpx	i.Cpx	i.Cpx	i.Cpx	i.Cpx
shape (δ)	S	R	R	R	R	R	R	S	R	R	R	R	R	A
Ni wt%	18.92	15.06	15.17	15.87	14.86	15.23	13.84	21.01	27.95	15.78	13.66	0.14	0.39	19.17
As ppm	7	6	6	<5	<6	28	25	<5	8	11	13	15	<6	<7
Se	189	217	200	229	222	216	194	255	103	113	129	111	101	111
Sb	<15	<17	<17	<14	<18	<16	<17	<16	<18	<18	<16	<16	<15	<18
Te	<21	<25	38	35	<21	<20	<22	<24	<18	<24	<23	<22	<21	<22

section	PTH 516	PTH 516	PTH 516	PTH 516	PTH 516	DBC 47	DBC 47	DBC 47	DBC -L	DBC -L	DBC -L
loc. (α)	Les.	Les.	Les.	Les.	Les.	Kimb.	Kimb.	Kimb.	Les.	Les.	Les.
grain	B	CA	CB	D	E	A	B	C	A	A	A
anal.	106	108	109	110	112	116	117	119	120	121	122
phase (β)	Pn	Pn	Pn	Pn	Pn–Ccp	Hz–Pn	Hz–Pn	Hz–Pn	Pn	Ccp–Po	Pn
occurrence (χ)	i.Ol	Ol	Ol	Ol	Ol	Ol	Ol	Ol	i.Ol	i.Ol	i.Ol
shape (δ)	A	A	A	R	R	A	R	R	S	S	S
Ni wt%	27.31	35.3	39.2	28.8	35.9	47.1	55.9	56.7	18.7	7.1	17.0
As ppm	12	480	670	34	240	29	54	52	<9	<9	14
Se	130	120	110	32	180	26	34	52	180	160	170
Sb	<11	28	73	?12	29	<14	<12	<13	<14	<14	<15
Te	<16	44	24	<15	<21	<15	<14	16	<19	<20	55

The PIXE beam excites a large area, and the results represent the weighted average of the area of the analysis. Therefore, the data likely represent the composition of the whole grain.

α: loc.: location; Ichi: Ichinomegata, NunI: Nunivak Island, Frank: Frank Smith kimberlite, Les.: Lesotho, Kimb.: Kimberley.

β: dominant sulfide phases: Ccp: chalcopyrite, Djr: djerfisherite, Hz: heazlewoodite, Pn: pendlandite, Po: pyrrhotite.

χ: i.: enclosed in mineral followed by "i", Cpx: clinopyroxene, M: melt (aggregate of Cpx), Ol: olivine, Opx: orthopyroxene, Spl: chromian spinel.

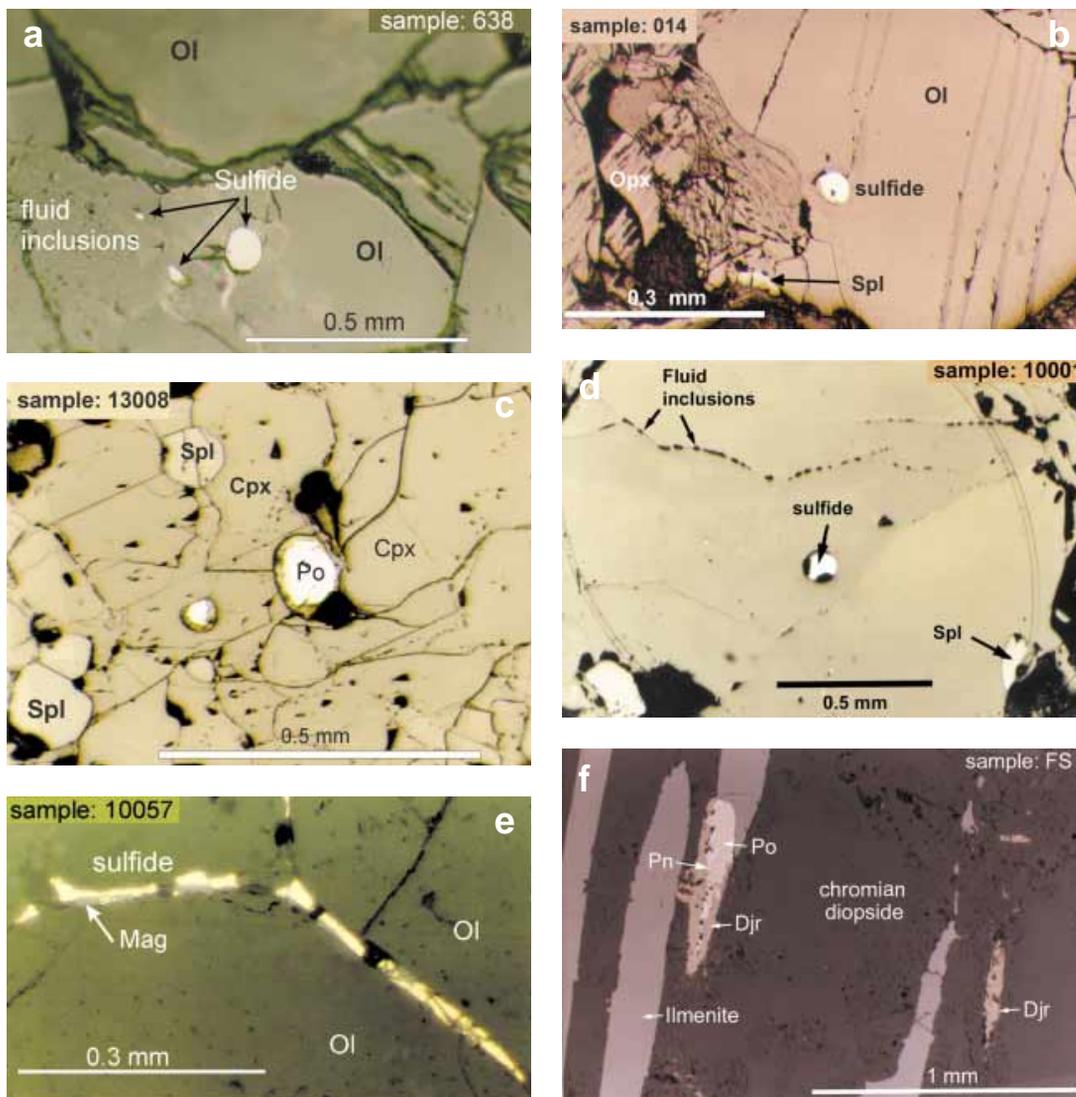δ: shape; A: portion of outer shape is angular, R: well rounded, but not spherical, S: spherical.

FIG. 1. Photomicrographs showing the mode of occurrence of sulfide grains, taken under reflected light. a. Spherical sulfide grain enclosed in olivine (Ol) in harzburgite (sample 638) from Ichinomegata, Japan. The sulfide is predominantly pentlandite. The olivine ($Fo_{90.0}$) contains abundant fluid inclusions. b. Sulfide grain enclosed in olivine ($Fo_{83.4}$) in spinel lherzolite (sample 014) from Ichinomegata, Japan. The sulfide is pentlandite and pyrrhotite. Ol: olivine, Opx: orthopyroxene, Spl: chromian spinel c. Globular sulfide grain along grain boundaries of clinopyroxene (Cpx) and olivine (Ol) in spinel pyroxenite (13008) from Nunivak Island, Alaska. Cpx: clinopyroxene, Spl: spinel. d. Spherical grain of sulfide in orthopyroxene in lherzolite (sample 10001) from Nunivak Island, Alaska. The large circle is engraved for analytical purposes. e. Veinlets containing primary sulfide along grain boundaries of olivine (Ol) in spinel lherzolite (sample 10057) from Nunivak Island, Alaska. The veinlet contains pyrrhotite and exsolution products of pentlandite and magnetite (Mag). f. Sulfide phases and ilmenite inclusions oriented within diopside megacryst in kimberlite from Frank Smith mine, South Africa (sample FS). Djr: djerfisherite, Po: pyrrhotite, Pn: pentlandite. Pentlandite, a product of exsolution of monosulfide solid-solution, rims the sulfide phase. The diopside host contains high Mg [atomic Mg/(Mg + Fe) = 0.87], Na (1.68–1.78 wt% Na_2O), Cr (0.33–0.56 wt% Cr_2O_3) and Ni (390–890 ppm).
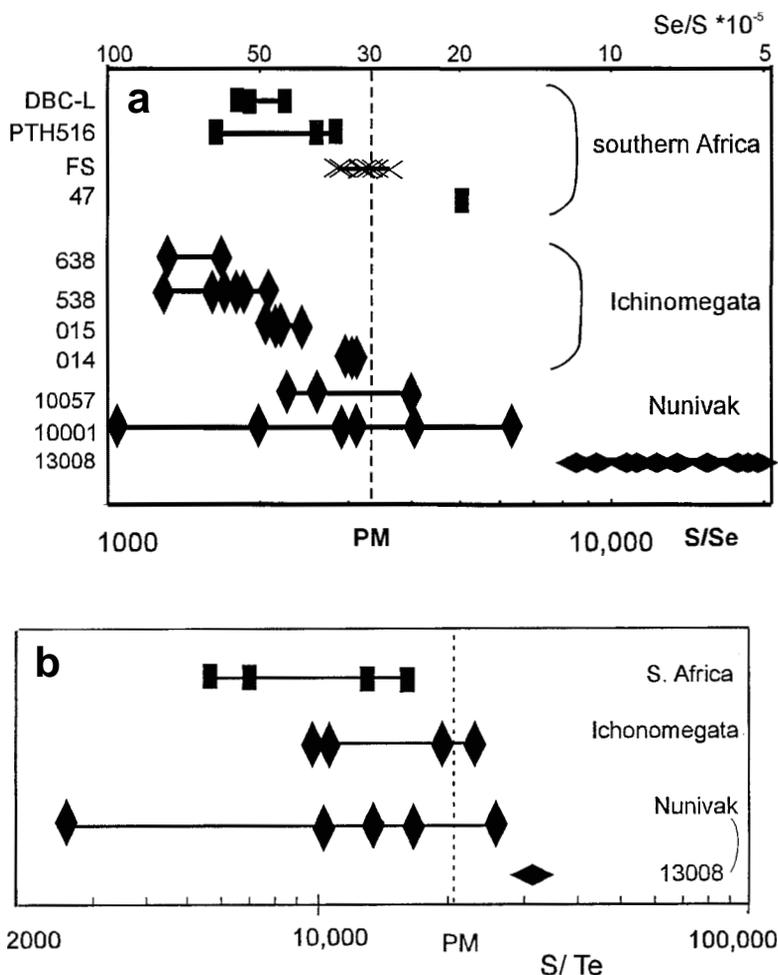
FIG. 2. a. Range of S/Se values in all samples. The ratio of primitive mantle (PM) calculated from the values given by McDonough & Sun (1995) is shown by the dashed line. b. Range of S/Te values in all samples. Solid diamonds: samples from mantle wedges at Nunivak and Ichinomegata. Tall diamonds represent residues (lherzolite and harzburgite) and short tabular diamonds represent garnet clinopyroxenite (solidified melt in the mantle) from Nunivak Island. × : Sulfide associated with potassium sulfides in diopside megacryst in kimberlite. Squares: peridotite nodules in kimberlite.

As contents, 51 and 120 ppm, are reported from magnetic fractions of xenoliths, assumed to be sulfides, from Kilbourne Hole, New Mexico, and Dreiser Weiher, Germany (Jagoutz *et al.* 1979). High values are also noted in sulfide grains enclosed in diamond from samples showing of a peridotitic mineral assemblage (Bulanova *et al.* 1996).

With the analytical techniques used, antimony has high detection-limits (7 to 40 ppm). Furthermore, mantle sulfides are not expected to contain high concentrations of Sb because sulfides in the primitive mantle contain only 7 ppm Sb (Table 3). Thus only four grains from

mantle wedges yielded detectable amounts of Sb, ranging from 9 to 146 ppm, and three grains from the subcontinental lithospheric mantle have Sb concentrations, ranging from 28 to 73 ppm.

DISCUSSION

*Sulfide morphology, and the occurrence
of sulfide liquid in the mantle*

Sulfides in our samples are considered to have been liquid in the mantle, as sulfides of relevant composi-
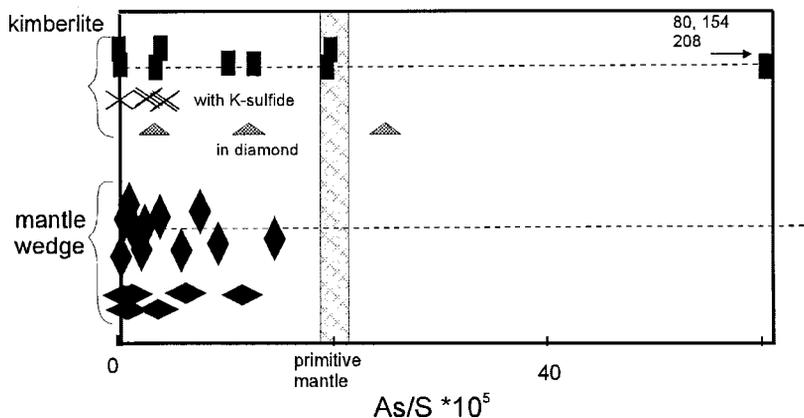
FIG. 3.   Range of As/S values in sulfide grains. Symbols same as in Figure 2. Three sulfides
          grains with high As/S plot outside the range of the diagram and are indicated by an
          arrow.

tions are liquid even in the shallow crust, in magmas that are much cooler than the mantle (Czamanske & Moore 1977, Francis 1990, Hattori 1993). The morphology of the sulfides in our samples is similar to that of sulfides in megacrysts at San Carlos, Arizona (Andersen *et al.* 1987) and Kilbourne Hole in New Mexico (Andersen *et al.* 1987, Dromgoole & Pasteris 1987) and peridotitic mantle xenoliths in Hawaiian volcanic rocks (De Waal & Calk 1974).

Experiments by Shannon & Agee (1996) and Ballhaus & Ellis (1996) suggest that the surface tension is large between sulfide liquid and silicates, whereas recent experiments by Gaetani & Grove (1999) produced angular sulfides wetting the surface of olivine grains, leading them to suggest the presence of interconnected channels of sulfide liquid in the upper mantle. Secondary pyrrhotite forms veinlets along grain boundaries in silicates in serpentinized xenoliths, but such veinlets are very rare in unaltered xenoliths.

TABLE 3. CONCENTRATION OF Se, Te, As AND Sb
IN PRIMITIVE MANTLE SULFIDE*

	Bulk primitive mantle (ppm)	Partition between sulfide liquid and silicate melt	Primitive mantle sulfide
S	250 (1)		36.4%
Se	0.075 (1)	100,000 (2)	109 ppm
Te	0.012 (1)	100,000 (2)	17 ppm
As	0.05 (1)	1000 (3)	30 ppm
Sb	0.011 (4)	1250 (3)	7.4 ppm

Primitive mantle sulfide is defined as an immiscible sulfide liquid in the primitive mantle. References are given in parentheses; 1: McDonough & Sun (1995), 2: Value of 100,000 assigned for strongly chalcophile elements, 3: Klöch & Palme (1988), 4: Jochum & Hofmann (1997).
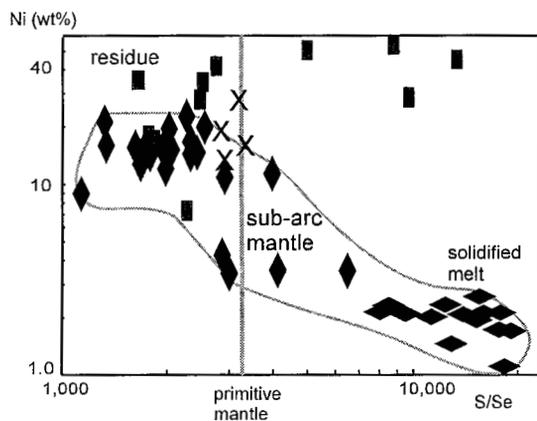
The rounded shapes of sulfide grains in our samples suggest that the interfacial energy between sulfide liquid and silicates in the mantle is large, and that sulfide liquid does not form interconnected thin films on the surfaces of silicate minerals there. First, the sulfide grains are commonly small, <10 μm, but grains less than 1 μm are not observed. Even grains along growth planes of diopside megacrysts are mostly greater than 1 μm (Peterson & Francis 1977). Second, a globular shape of sulfide grains is common along grain boundaries of silicate minerals. Angular sulfides thinly spread along silicate surfaces occur in only one sample. This morphological evidence suggests that sulfide liquids in the mantle do not wet silicate minerals to a significant degree. Sulfides are not connected to each other in the mantle. In addition, the compositional variation of sulfides, both within and between our samples, supports our petrographic observation, because interconnected sulfides would have a similar composition.

S/Se and Se/Te values of the mantle

Nickel is a compatible element in olivine, and is enriched in the mantle during partial melting. It is likely that Ni contents in sulfides in the mantle increased in response to increasing Ni in silicate minerals, judging from rapid equilibration between silicate minerals and sulfide liquid in the short-duration experiments (Gaetani & Grove 1997). Therefore, the inverse relationship between Ni and S/Se in the sub-arc mantle rocks (Fig. 4) suggests that Se is preferentially retained in the mantle during partial melting. Our data confirm this intuitive interpretation (Fig. 4). Except for the "melt" sample (13008) from Nunivak Island, the S/Se values are significantly lower than that of primitive mantle and those from mid-oceanic ridge basalts (MORB; Peach *et al.* 1990) (Fig. 4).

FIG. 4.   Concentrations of Ni and S/Se values in all samples.
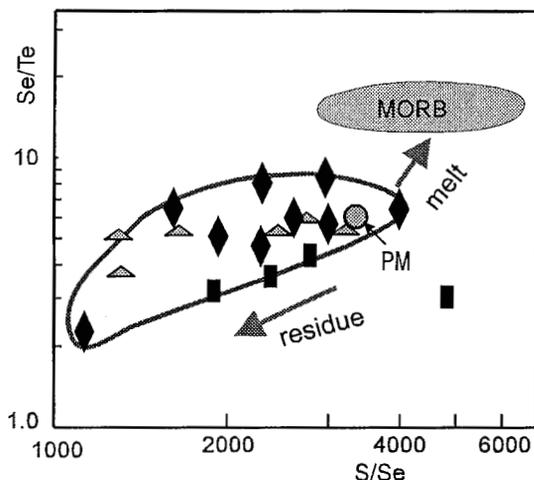Primitive mantle value is from McDonough & Sun (1995).

FIG. 5.   S/Se and Se/Te values of sulfides from mantle rocks.
Symbols same as those in Figure 2. The data on sulfides
enclosed by diamonds in peridotitic assemblages with no
apparent fractures (shown as solid triangles) are from
Bulanova *et al.* (1996). Data on mid-ocean-ridge basalts
(MORB) from Hertogen *et al.* (1980), Hamlyn & Keays
(1986) and Peach *et al.* (1990).

The Se/Te values range from 6 to 11 in the
Ichinomegata samples, 2.3 in the Nunivak sample, and
2.2 to 4.2 in the subcontinental lithosphere samples (Fig.
5). The Se/Te values of all sulfide samples are compa-
rable to the value for primitive mantle (6.3: McDonough
& Sun 1995), but are distinctly lower than the values
for MORB (Hertogen *et al.* 1980) and for Hawaiian and
Columbian River flood basalts (BHVO–1 and BCR–1;
Govindaraju 1994). The lower Se/Te values in the
mantle compared to basalt suggest that Te is probably
retained in the mantle.

Selenium and tellurium should behave coherently
with S in the generally reduced mantle, but our data in-
dicate considerable fractionation of these elements. Pos-
sible causes for the fractionation in the mantle include:

(1) Sulfate formation: Sulfate minerals contain low
concentrations of Se (Badalov *et al.* 1969), and oxida-
tion of sulfide to form soluble sulfate is the principal
cause for the variation in S/Se values in surface envi-
ronments (*e.g.,* Stanton 1972). The common occurrence
of anhydrite in arc magmas appears to support this pos-
sibility, but anhydrite in young volcanic rocks is a prod-
uct of degassing at crustal levels (Hattori 1993).
Although sub-arc mantle may be relatively oxidized
(Wood *et al.* 1990), there is no evidence for the forma-
tion of sulfate in sub-arc mantle. Therefore, we discount
this possibility.

(2) Addition of S from subducting slabs: Dehydra-
tion of subducting slabs discharge volatile elements into
overlying mantle wedges, among which is S (*e.g.,* Alt
et al. 1993). The variation in S/Se in our samples may
be attributed to a contribution of crustal S through sub-
duction. Ocean sulfate contains low Se (Measures *et al.*
1980), and marine pelagic sediments are generally low
in Se, except for organic-matter-rich black shales
(Stanton 1972). Therefore, a contribution of S from sub-
ducting sediments to the mantle wedge would generally

increase the S/Se value. The overall low S/Se values of
most sulfides in our samples do not support a signifi-
cant contribution of marine S to mantle wedges *via* sub-
duction.

(3) Fractionation of S, Se and Te during partial
melting in the mantle: High Se/Te values in MORB
compared to mantle rocks suggest preferential enrich-
ment of Se in melt and retention of Te in the mantle
(Hertogen *et al.* 1980). High S/Se values in MORB glass
(Peach *et al.* 1990) compared to mantle rocks suggest
that S is preferentially enriched in melt during partial
melting. The low S/Se values (666–2500) in obducted
refractory mantle rocks (Garuti *et al.* 1984) seem to sup-
port this idea. These studies suggest that the relative
preferential removal of elements from the mantle is:
S > Se > Te.

This proposed interpretation is consistent with low
S/Se values in the most refractory spinel harzburgite
(sample 638) from Ichinomegata and harzburgite from
subcontinental lithospheric mantle (sample DBC–26–
31). It is also consistent with high concentrations of
Te (> 30 ppm) in sulfide grains in the spinel harzburgite
from Ichinomegata. Therefore, we conclude that partial
melting resulted in the fractionation of S, Se and Te in
the mantle.

Sulfides in peridotitic xenoliths from kimberlites
show a wide range in S/Se (1600 to 9750), but the val-
ues are mostly lower than the primitive mantle value
(Fig. 2), suggesting a previous episode of melting in the
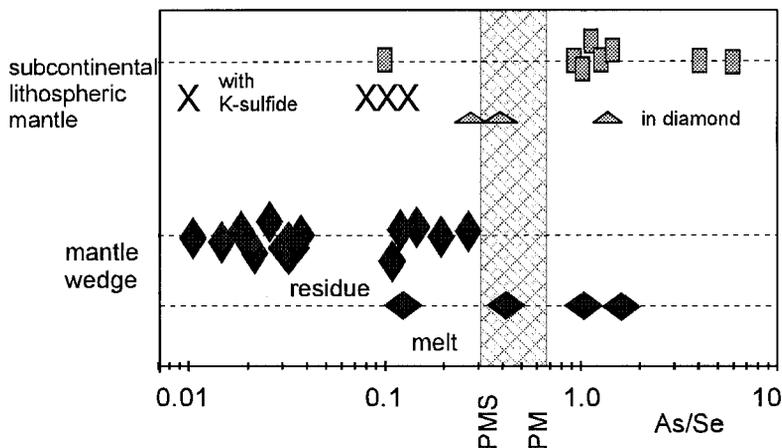subcontinental lithospheric mantle, from which the

FIG. 6.   Range of As/Se values of all sulfide grains sampled. Symbols same as in Figure 5.
The values of As/Se in primitive mantle (PM) and primitive mantle sulfide (PMS) are
listed in Table 3.

xenoliths were derived. Our data are consistent with numerous studies indicating the highly refractory nature of the subcontinental lithospheric mantle underlying the Kaapvaal craton (*e.g.*, Pearson *et al.* 1995).

Our data imply that the S/Se value of a mantle-derived magma may vary depending on that of the source. S/Se values of approximately 3,000 have been used as mantle signatures of S for magmatic Ni sulfide deposits (*e.g.*, Eckstrand *et al.* 1989, Maier & Barnes 1999). Sedimentary rocks generally contain low Se (Stanton 1972) and S may be preferentially lost from the rocks during thermal events. Thus, departure from the "mantle value" of S/Se is considered to indicate assimilation of sedimentary rocks (*e.g.*, Ripley 1990) or later modification of sulfides through a variety of mechanisms, such as loss of S during solidification (Brügmann *et al.* 1990), modification of Se/S value during sulfide formation (Maier & Barnes 1999), subsolidus alteration (Peck & Keays 1990), or loss of S during regional metamorphism (Maier & Barnes 1996). However, the compilation of data from a variety of "pristine" magmatic sulfide ores by Eckstrand *et al.* (1989) shows considerable variation in S/Se values. Our work suggests that at least some of the variation in S/Se in sulfide ores likely reflects the source mantle. Magmas derived from refractory mantle would have low S/Se values. Our proposed interpretation is supported by high levels of Se compared to S, S/Se < 400, in many boninite rocks (*e.g.*, Hamlyn *et al.* 1985, Peck & Keays 1990, Peck *et al.* 1992), which form by high degrees of melting of a refractory mantle in a supra-subduction-zone environment.

Low As and Sb in the mantle wedge

The relatively high abundance of As in sulfides reflects a high concentration of As (~30 ppm) in the hypothetical primitive mantle sulfide (Table 3). The composition of this primitive mantle sulfide was calculated using the concentration of elements in the primitive mantle (McDonough & Sun 1995), and partition coefficients of the elements between silicate and sulfide melt (Table 3), assuming that S in the primitive mantle was present as sulfide.

Arc magmas are commonly enriched in As and Sb (Noll *et al.* 1996) and many metallic deposits in arcs contain high As and Sb (*e.g.,* Stanton 1972). The enrichment has been explained by the supply of these elements from subducting slabs to sub-arc mantle through mantle metasomatism. We, therefore, anticipated high As and Sb in sulfides from mantle wedges, but most grains contain low As (Figs. 5, 6). Our results are consistent with low contents of the two elements in bulk-rock samples of spinel lherzolite xenoliths (Jagoutz *et al.* 1979, Kurat *et al.* 1980).

If these elements are indeed supplied to arc magmas from subducting slabs (Noll *et al.* 1996), our low concentrations of As and Sb in mantle sulfides suggest that these elements have short residence-times in mantle wedges, or that scavenging of these elements by hydrous partial melt in mantle wedges is effective. It is also possible that these elements were directly transferred from fluids to partial melt without residing in the mantle wedges.

Fractionation of As and Sb

Antimony and As are expected to behave coherently in the mantle because these two elements have the same charge (+5; Hertogen *et al.* 1980) and similar ionic radii. Therefore, partial melting and solidification of the melt should not fractionate the two elements. However, our data show a large range in Sb/As values. The sulfide grain in olivine from the garnet lherzolite in kimberlite from Pipe 200, Lesotho (sample DBC26–31) has an Sb/As value of 0.12, the same as is expected for primitive mantle sulfide (Table 3). Grains from Ichinomegata and Nunivak show much higher Sb/As values, 4.1 and 2.4, respectively. High values suggest either an enrichment of Sb or a depletion of As. These Sb-bearing grains have low As/S values, 8 and 4×10^{-5}, compared with the primitive mantle value of 20×10^{-5} (McDonough & Sun 1995) to 33×10^{-5} (Taylor & McLennan 1985). Their Sb/S values are high, 37 and 8×10^{-5}, compared with 2.2×10^{-5} in the primitive mantle (McDonough & Sun 1995). These data suggest that the two sub-arc samples underwent As depletion and Sb enrichment.

Because As and Sb behave coherently in magmatic processes, we attribute the separation of the two elements to fluid transport. Both As and Sb are soluble in high-temperature aqueous fluids, and Sb is particularly mobile (Jochum & Verma 1996). The proposed interpretation, fluid transport of As and Sb in the sub-arc mantle, is supported by the composition of Sb-bearing sulfides. The high-Sb (146 ppm) sulfide in pargasite lherzolite from Ichinomegata contains 8 ppm Ag and 16 ppm Re, and other sulfide grains in the same section contain Sb below detection limits, although the morphology and textures of these Sb-bearing and Sb-poor sulfides are very similar. The Sb-bearing (30 ppm) sulfide from Nunivak Island also is rich in Ag (14 ppm).

Our data suggest that Sb-bearing fluids did not interact with all sulfide grains. The evidence is in accord with vein-like occurrences of phlogopite and pargasite in mantle xenoliths and compositional variation of amphibole, a product of hydration, in sub-arc mantle (Abe *et al.* 1992, 1998, Francis 1976).

Residual sulfide in refractory mantle?

Refractory mantle rocks contain low concentrations of incompatible elements in silicate minerals because these elements are preferentially removed by partial melts. Sulfur, one such element, is believed to be low in the mantle residue because S has a high solubility in mafic melts (*e.g.*, Wendlandt 1982). Essential absence of S in the residual mantle is supported by consistent Ce/Pb (Newsom *et al.* 1986) and Sb/Pr values (Jochum & Hofmann 1997) in oceanic basalts. Where S is not present, Pb and Sb behave like ordinary lithophile incompatible elements during igneous processes. Therefore, these pairs, Ce/Pb and Sb/Pr, are similar among igneous rocks. If S is present in the mantle, Pb and Sb would be retained in the mantle sulfide, and values of these ratios would change. These geochemical data for volcanic rocks suggest that essentially no sulfur should remain in the refractory mantle.

However, abundant petrographic evidence suggests that sulfur is still present in the residual mantle. MORBs are saturated with S, producing sulfide droplets in quenched glass (*e.g.*, Czamanske & Moore 1977, Francis 1990). Arc magmas derived from highly refractory mantle wedges are saturated with S (*e.g.*, Hattori 1993). Many arc volcanoes discharge enormous amounts of S gases (*e.g.*, Bluth *et al.* 1992). This apparently contradictory evidence may be attributed to the retention of sulfides protected by refractory silicate minerals during partial melting (Hart & Ravizza 1996), or by the replenishment of S from external sources such as slabs (*e.g.*, Alt *et al.* 1993) and the deep mantle. Sulfur may be replenished from deep mantle to sulfur-poor areas through interconnected sulfide liquid (*e.g.*, Gaetani & Grove 1999). The latter two possibilities are rejected by our limited data because S from slabs is characterized by high S/Se and because S from a deep fertile mantle should have a chondritic S/Se value. Therefore, S replenished by subducting slabs and from a deep fertile mantle should have a high S/Se value. This mechanism is not consistent with our data. Sulfide samples from sub-arc mantle show low S/Se and Se/Te values.

Sulfur in arc magmas may be efficiently scavenged from mantle wedges or supplied directly from subducting slabs without residing in mantle wedges.

Conclusions

Sulfur, Se and Te are fractionated in the mantle, *i.e.,* they do not behave coherently. Se/Te and S/Se values of sulfide grains from mantle wedges beneath arcs are generally lower than the inferred value of primitive mantle sulfide. Sulfides in the subcontinental lithospheric mantle also are depleted in S, similar to those in mantle wedges, reflecting a previous extraction of melt. Values of S/Se close to 3,300 are commonly viewed as being typical of mantle-derived magmas, but these may show a variation in the values reflecting the previous melting history of the mantle.

Arsenic and Sb are removed from the mantle during partial melting, leading to low concentrations in sulfide in refractory mantle. Erratically high values in the mantle wedges and from peridotite nodules in kimberlites are attributed to fluid transport of these elements during mantle metasomatism.

Enrichment of As, Sb and S in arc magmas generally are believed to reflect their enrichment in mantle wedges. We did not find any evidence of such enrichment in mantle wedges. These elements may be efficiently removed from mantle wedges by hydrated arc magmas. Alternatively, these elements may have been

transferred by aqueous fluid from slabs to arc magmas without residing in the mantle.

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