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Nickel-copper sulfides from the 1959 eruption of Kilauea Volcano, Hawaii: Contrasting compositions and phase relations in eruption pumice and Kilauea Iki lava lake

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ABSTRACT

Iron-nickel-copper sulfides in picritic eruption pumice from the 1959 eruption of Kilauea Volcano, Hawaii, and associated Kilauea Iki lava lake have been studied in detail. The sulfides occur as micrometer-sized subspherical blebs in glass inclusions within olivine phenocrysts and in glass within quenched groundmass. The proportion of blebs present within the volume of a thin section and within individual olivine grains is widely variable. Sulfide minerals present in the eruption pumice include monosulfide solid solution (mss), isocubanite, pentlandite, bornite, and an unidentified metal-excess iron-rich sulfide. Bulk sulfides in the eruption pumice are enriched in Ni relative to Cu. These minerals are also present in Kilauea Iki lava lake, along with chalcopyrite, but the bulk sulfides are markedly enriched in Cu relative to Ni.

In the eruption pumice, the high-temperature history of the sulfide liquid precursor to the blebs involved crystallization entirely to mss and subsequent exsolution of isocubanite on cooling or crystallization of mss and formation of residual Cu-rich sulfide liquid. In Kilauea Iki lava lake, the high-temperature history of the sulfide liquid precursor to the olivine-hosted blebs involved crystallization and subsequent unmixing of isocubanite, whereas that of the sulfide liquid precursor to groundmass glass-hosted blebs involved exsolution of bornite solid solution from cubic chalcopyrite ± isocubanite and chalcopyrite ± isocubanite from bornite solid solution. The presence of pentlandite + chalcopyrite and pentlandite + bornite solid solution suggests that the blebs have equilibrated internally below approximately 600 °C.

The Ni-rich bulk sulfide composition in the pumice reflects the higher temperature and rate of quenching. The Cu-rich bulk sulfide composition in Kilauea Iki reflects a lower temperature of quenching and more extensive annealing and crystallization history of the lava. The wide variability in bulk sulfide composition in the samples and lack of equilibration with coexisting olivine are inconsistent with an origin solely by early magmatic, sulfide liquid immiscibility. Instead, bulk sulfide compositions reflect late magmatic processes. Blebs in the eruption pumice and Kilauea Iki lava largely represent cooling- and quench-induced segregation of sulfides with metals scavenged from the silicate liquid.

INTRODUCTION

The origin of nickel-copper sulfide ore bodies has generally been interpreted as caused by either sulfide liquid immiscibility in silicate magma during the early magmatic stage (Naldrett, 1989; Lesher and Groves, 1986) or sulfidation of the host rocks during the late magmatic stage or high-temperature subsolidus stage (Fleet, 1979; Fleet and MacRae, 1983; Stone et al., 1989). Proponents of sulfide liquid immiscibility cite the association of nickel-copper sulfides with mafic and ultramafic rocks and bulk sulfide compositions in the mss phase field within the Cu-Fe-Ni-S system. Alternatively, those favoring sulfidation note that the bulk compositions of the sulfides are too variable for equilibration under magmatic conditions (Fleet, 1978, 1979; Fleet and MacRae, 1983, 1987, 1988) and that in unmetamorphosed to low-grade metamorphosed rocks, the NiO content of olivine is commonly too high and the NiS content of the associated sulfides is too low, relative to results of laboratory partitioning studies, for equilibration during magmatism (Fleet et al., 1977; Fleet, 1979; Fleet and MacRae, 1983; Fleet and Stone, 1990).

Iron-nickel-copper sulfide blebs have been described in ocean floor basalt (Czamanske and Moore, 1977), ocean island basalt (Skinner and Peck, 1969), olivine megacrysts from Mount Shasta, California (Stone et al., 1989), hydrothermally altered sediment (Missack et al., 1989),

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TABLE 1. Composition of glass in groundmass and inclusions (wt%)

	Eruption pumice				Kilauea Iki lava lake			
	Groundmass		Inclusion		Groundmass		Inclusion	
	1	2	3	4	5*	6**	7**	8**
SiO_2	49.90	49.72	55.65	49.25	61.68	55.57	52.46	52.35
TiO_2	2.51	2.76	1.64	2.66	2.19	3.63	2.77	1.70
Al_2O_3	12.32	13.73	10.81	12.81	13.63	13.21	13.93	13.54
Cr_2O_3	0.05	0.00	0.07	0.06	0.05	0.00	0.00	0.03
FeO	11.24	11.94	9.77	10.83	8.46	9.85	10.64	10.74
MnO	0.14	0.13	0.16	0.24	0.09	0.13	0.15	0.15
MgO	9.96	6.82	5.24	5.64	2.24	3.81	4.47	4.91
CaO	11.23	8.54	13.54	13.27	4.67	7.08	10.48	11.24
Na_2O	1.67	2.01	0.94	1.15	0.96	1.47	1.33	1.33
K_2O	0.44	2.84	0.01	0.81	1.72	1.57	0.50	0.30
NiO	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.01
CuO	0.01	0.03	0.00	0.02	0.00	0.05	0.02	0.00
S	0.00	0.18	0.14	0.15	0.00	0.00	0.07	0.10
Total	99.50	98.99	98.17	97.14	95.69	96.37	96.93	96.55

* Sample KI79-3-163.7.
** Sample KI81-1-306.7.

xenoliths and megacrysts in kimberlite (Bishop et al., 1978; Tsai et al., 1979; Boctor and Boyd, 1980), alkali basalt (Lorand and Conquere, 1983), and continental basalt (Andersen et al., 1987). These blebs have analogous mineral assemblages and equivalent host rock associations to nickel-copper sulfide ore bodies and may have formed by similar processes. The petrogenesis of sulfide blebs is, therefore, significant because of the potential for insight into the origin and cooling history of nickel-copper sulfide ore bodies.

In this paper, the petrography, composition, and phase relations of iron-nickel-copper sulfide blebs in samples of picritic basalts from the 1959 eruption of Kilauea Volcano, Hawaii, including quenched eruption pumice and quenched lava from Kilauea Iki lava lake, are documented, and their origin is discussed. These sulfides are distinctive because the bulk composition of the blebs ranged from extremely Ni rich and Cu poor to Ni poor and extremely Cu rich. The blebs are also generally devoid of evidence for low-temperature oxidation (Helz, 1987a), and the thermal history of the host rocks is well constrained (Helz and Thornber, 1987). Therefore, study of these blebs may allow comparison with the results of laboratory experimentation in the Cu-Fe-S and Cu-Fe-Ni-S systems (Yund and Kullerud, 1966; Kullerud et al., 1969; Craig and Kullerud, 1969) and could yield insight into the effects of cooling rate on bulk sulfide composition as well as the origin and cooling history of nickel-copper sulfide ore bodies. The extent of equilibration of their bulk sulfide compositions with coexisting olivine is discussed by Fleet and Stone (1990).

SAMPLES AND ANALYSES

The three thin-section samples studied are of picritic pumice and lava from Kilauea Iki lava lake, Hawaii, effused during the 1959 eruption of Kilauea Volcano (Helz, 1987a, 1987b). The pumice sample, Iki-22, quenched on eruption at 1216 °C. The lava samples, KI79-3-163.7 and KI81-1-306.7 (hereafter referred to as KI79 and KI81), are of drill core recovered from olivine-phyric basalt in Kilauea Iki. KI79 and KI81 annealed at temperatures above 1053 °C and 1083 °C for 20 and 22 yr, respectively, before quenching during drilling (Helz, 1987b; Helz and Thornber, 1987).

Analyses of the olivine, glass (Table 1), and sulfides (Tables 2, 3) were made with a JEOL JXA-8600 automated superprobe at the University of Western Ontario, using natural silicate minerals, synthetic FeS and NiS, and natural chalcopyrite as standards. Analyses of olivine and glass were made at 15 kV, 10 nA, and with a beam diameter of 3 μm. The counting time for Ni in olivine was 50 s and that for Ni, Cu, and S in glass was 100 s.

Bulk sulfide compositions (Table 2) were calculated on the basis of modal proportion of phases present, as determined by point counting, or were determined by WDS electron microprobe analysis with a focused or slightly defocused beam at 20 kV, 20 nA cup current, 20 s or 20000 counts, and a beam diameter of 2 to 10 μm. Analyses of individual sulfide phases were made under the conditions used for bulk sulfide analysis, except that the cup current was 4 nA and the beam diameter was 1 μm. The sulfide phase compositions (Table 3) represent either a spot analysis or the average of up to five spot analyses. Analysis of the sulfide phases was complicated by the fine grain size. Analyses that were grossly contaminated by contributions from adjacent phases or had very low totals (less than 95 wt%) were rejected. Standard deviations for the averaged composition of the phases are less than 0.9 wt% for the elements present. Repeated analyses of the standards indicate a precision relative to absolute element concentrations of within 1 wt%.

PETROGRAPHY AND CHEMISTRY

The sulfide blebs occur in the eruption pumice and in Kilauea Iki lava as <1 to 40 μm subspherical multiphase

TABLE 2. Bulk composition of the sulfide blebs

Sample	Bleb	Host	Fe	Ni	Cu	S	Assemblage
			(wt%)				
Iki-22	1	ol	46.15	14.74	0.85	37.18	mss + icb + mt
Iki-22	2	ol	45.61	14.52	1.15	36.76	mss + icb + mt
Iki-22	3	ol	42.20	15.89	4.18	37.26	mss + icb
Iki-22	4	ol	37.78	8.26	17.62	34.91	mss + icb
Iki-22	5	ol	37.32	9.45	16.43	34.83	mss + icb + mt?
Iki-22	6	ol	37.95	14.94	10.47	35.50	mss + icb + pn
Iki-22	7	ol	34.91	14.59	14.35	34.99	mss + pn
Iki-22	8	ol	37.71	15.58	10.33	35.56	mss + icb
Iki-22	9	gls	29.01	31.81	5.00	32.01	mss + icb
Iki-22	10	gls	54.70	3.40	6.07	33.79	UMIS + iss
Iki-22	11	gls	34.06	27.40	6.07	32.74	pn + icb + bn
KI81	1	ol	37.89	4.44	22.11	33.84	icb + pn
KI81	2	ol	47.91	7.73	6.43	35.47	mss + icb
KI81	3	ol	38.70	4.23	22.70	33.68	icb + pn
KI81	7	ol	36.84	6.11	21.50	33.66	icb
KI81	10	ol	40.64	3.67	20.12	33.76	mss + icb
KI81	11	ol	46.99	8.80	7.08	34.67	mss + icb
KI81	12	ol	41.83	7.80	14.75	33.42	mss + icb
KI81	16	ol	25.27	2.90	37.45	31.40	icb + pn? + bn?
KI81	17	ol	32.80	5.49	24.83	33.28	icb
KI81	18	ol	32.16	3.24	29.32	33.86	icb + cp
KI81	19	ol	27.02	5.56	34.77	31.38	icb + bn + pn
KI81	21	ol	17.81	0.25	52.35	27.41	bn
KI79	1	ol	32.23	5.31	27.33	34.74	cp + pn + po?
KI79	2	gls	18.57	0.06	50.74	30.68	bn ± cp ± icb ± mt
KI79	3	gls	19.21	0.10	49.39	30.55	bn ± cp ± icb ± mt
KI79	4	gls	18.66	0.04	49.08	30.73	bn ± cp ± icb ± mt
KI79	5	gls	19.66	0.11	48.32	30.49	bn ± cp ± icb ± mt
KI79	6	gls	21.28	0.11	45.35	32.04	bn ± cp ± icb ± mt
KI79	7	gls	17.29	0.20	52.88	29.13	bn ± cp ± icb ± mt
KI79	8	gls	19.86	0.08	49.75	30.68	bn ± cp ± icb ± mt
KI79	9	gls	17.64	0.07	51.98	29.93	bn ± cp ± icb ± mt
KI79	10	gls	22.61	0.27	44.00	32.10	bn ± cp ± icb ± mt
KI79	11	gls	18.55	0.06	50.22	30.32	bn ± cp ± icb ± mt
KI79	12	gls	19.53	0.02	48.06	31.14	bn ± cp ± icb ± mt
KI79	13	gls	18.52	0.20	51.87	30.11	bn ± cp ± icb ± mt
KI79	14	gls	17.69	0.15	51.54	30.25	bn ± cp ± icb ± mt
KI79	15	gls	16.96	0.12	52.80	30.56	bn ± cp ± icb ± mt
KI79	16	gls	17.05	0.05	50.96	31.25	bn ± cp ± icb ± mt
KI79	17	gls	15.47	0.03	57.93	27.54	bn ± cp ± icb ± mt
KI79	18	gls	19.55	0.25	47.55	31.64	bn ± cp ± icb ± mt
KI79	19	gls	22.50	0.05	45.07	31.70	bn ± cp ± icb ± mt
KI79	20	gls	18.06	0.08	50.38	30.52	bn ± cp ± icb ± mt
KI79	21	gls	19.12	0.04	49.03	30.84	bn ± cp ± icb ± mt

Note: Abbreviations: ol, olivine phenocryst; gls, groundmass glass; mss, monosulfide solid solution; icb, isocubanite; pn, pentlandite; UMIS, unidentified metal-excess iron-rich sulfide; bn, bornite; cp, chalcopyrite; mt, magnetite.

TABLE 3. Composition of minerals in sulfide blebs

Sample	Bleb	Phase	Host	Fe	Ni	Cu	S	Fe	Ni	Cu	S
				(wt%)				(at.%)			
Iki-22	1	mss	ol	46.07	14.77	0.77	37.81	36.37	11.09	0.53	52.01
Iki-22	2	mss	ol	45.79	14.52	0.67	36.92	36.53	11.70	0.47	51.30
Iki-22	10	UMIS	gls	56.81	3.78	3.56	33.95	46.21	2.93	2.55	48.21
Iki-22	10	icb	gls	42.76	1.25	20.26	32.84	35.95	0.99	14.97	48.09
Iki-22	11	pn	gls	34.21	32.15	1.28	32.83	27.79	24.85	0.91	46.45
Iki-22	11	icb	gls	34.37	4.27	27.85	32.55	28.73	3.39	20.47	47.41
Iki-22	11	bn + icb	gls	25.33	4.05	41.27	30.63	21.32	3.24	30.53	44.91
KI81	2	icb	ol	39.52	1.83	22.44	35.49	32.17	1.45	16.05	50.33
KI81	2	mss	ol	50.70	9.69	1.09	35.47	41.33	7.52	0.78	50.37
KI81	1	icb	ol	38.99	2.28	23.87	33.93	32.16	1.79	17.30	48.75
KI81	1	pn + icb	ol	38.17	10.83	15.10	34.23	31.44	8.49	10.93	49.14
KI81	18	icb	ol	33.17	2.80	28.29	34.05	27.64	2.22	20.72	49.42
KI81	18	cp	ol	25.66	4.72	35.38	33.44	21.47	3.76	26.02	48.75
KI81	19	icb	ol	30.51	1.75	31.66	33.40	25.82	1.41	23.54	49.23
KI81	19	pn + icb	ol	31.68	17.18	16.13	31.51	27.06	13.96	12.11	46.87
KI81	19	bn	ol	18.49	0.34	49.12	27.62	16.80	0.29	39.21	43.70

Note: Abbreviations: mss, monosulfide solid solution; UMIS, unidentified metal-excess iron-rich sulfide; icb, isocubanite; pn, pentlandite; bn, bornite; cp, chalcopyrite; ol, olivine phenocryst; gls, groundmass glass.

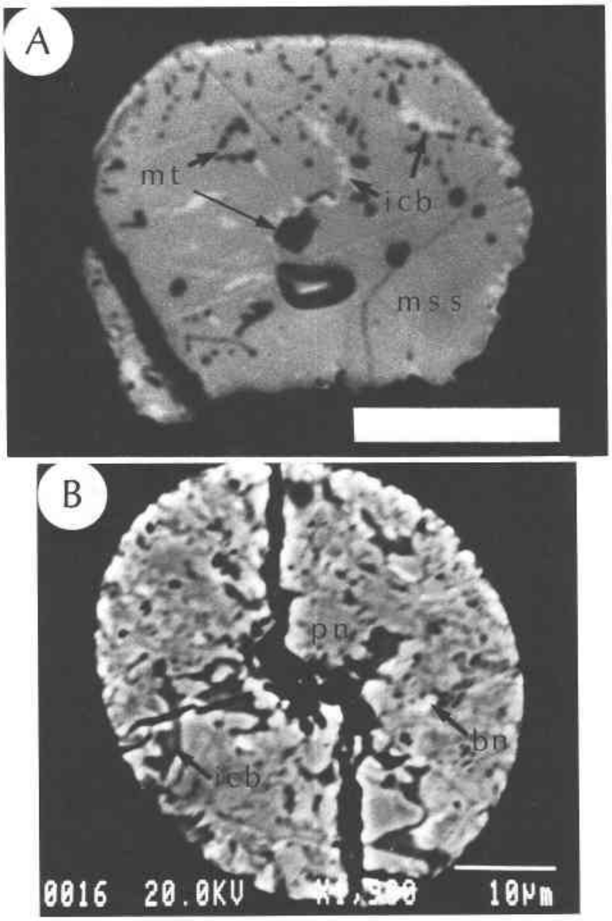

Fig. 1. Sulfides in eruption pumice. (A) Olivine phenocryst-hosted bleb of mss (gray) and lamellar isocubanite (icb, bright) and magnetite (mt, dark). Polished section, reflected light, oil; scale bar represents 100 μm. (B) Backscattered-electron image of a pumice glass-hosted bleb of pentlandite (pn, gray), isocubanite (icb, dark), and bornite (bn, bright).

blebs in glass inclusions within olivine phenocrysts and as inclusions in the olivine phenocrysts, groundmass glass, and segregation veins (Figs. 1, 2). The blebs are very limited in distribution and are present at much less than 0.01 modal% of a sample. The sulfide minerals observed include monosulfide solid solution (mss), isocubanite (previously intermediate solid solution or iss; Caye et al., 1988), pentlandite, chalcopyrite, bornite, and an unidentified metal-rich iron sulfide.

The sulfide-bearing olivine crystals observed in the eruption pumice comprise a loose aggregate of three phenocrysts, the largest of which is 500 μm across. They are Fo_{87-88} in composition and contain 0.26 wt% NiO. The sulfide blebs in sample KI81 occur only within olivine, whereas those in sample KI79 occur primarily within groundmass glass. The sulfide-bearing Kilauea Iki lava olivines are singular phenocrysts more than 1 mm across. The olivines in KI81 are Fo_{74-75} in composition and have 0.26 wt% NiO. Those in KI79 are Fo_{81} and have 0.26 wt% NiO. Analyses of the olivine phenocrysts in the Hawaiian samples resemble those in the literature (Helz, 1987a, 1987b; Helz and Thornber, 1987) except that the NiO content is higher in the present study. The higher NiO content is supported by repeated analysis of the Ni standard (P140 olivine) and selected product olivines from Fleet and MacRae (1988). The discrepancy in NiO content of olivine is discussed further in Fleet and Stone (1990).

The sulfide-bearing glass inclusions within olivine are up to 100 μm in diameter. They are subspherical in outline, commonly contain a chromite grain, and lack crystalline silicate phases. Results from analysis of sulfide bleb-bearing inclusion glass show that composition varies widely within a single olivine crystal and between the eruption pumice and Kilauea Iki lava (Table 1). The inclusion glass varies from basaltic to andesitic in range of composition. It is devoid of Ni and Cu to the detection limits of the analysis (0.05 and 0.02 wt%, respectively). Inclusion glass in the eruption pumice contains more S (up to 0.2 wt% S) than that in Kilauea Iki lava (0.1 wt% S). Analyses of pumice glass (basalt) and groundmass glass (andesite to dacite) from Kilauea Iki (Table 1) resemble those of Helz (1987a, 1987b).

Bulk sulfides

Although the sulfide blebs are generally multiphase (Figs. 1, 2), few are large enough for analysis of the individual phases. Therefore, they are best characterized in terms of their bulk composition. The bulk sulfide compositions from the eruption pumice and Kilauea Iki lava range from Ni rich and Cu poor to extremely Ni poor and Cu rich (Fig. 3 of Fleet and Stone, 1990; Fig. 3; Table 2). This extremely wide range in bulk sulfide composition exceeds that reported for sulfide blebs in other Hawaiian lavas (Desborough et al., 1968; Skinner and Peck, 1969). The sulfides in the eruption pumice are more nickeliferous and larger, whereas those in Kilauea Iki lava are more cupriferous and more abundant.

The bulk compositions of sulfide in the eruption pumice plot in the mss field or in the two-phase field between isocubanite and mss in the Cu-(Fe + Ni)-S system at 600 °C (Fig. 3). The bulk composition of these blebs varies widely, both for blebs within olivine and those within the pumice glass (Table 2). Among the eight olivine-hosted blebs analyzed, the bulk Ni/Cu ratio is 20.0 and 14.3 in two of the blebs (e.g., Fig. 1A) and it ranges from 1.6 to 0.5 in the remaining six. The variability among the Ni-rich compositions may be within analytical error. Much of that among the more Ni-poor compositions may reflect sampling bias because the phases in some of these blebs are more coarsely segregated. However, the extreme compositional disparity is real and significant.

The sulfide blebs in the pumice glass are larger than those in the olivine (Fig. 1) and they are metal rich. Among the three pumice glass-hosted blebs analyzed, the Ni content of two (blebs 9 and 11, Table 2) exceeds that of the

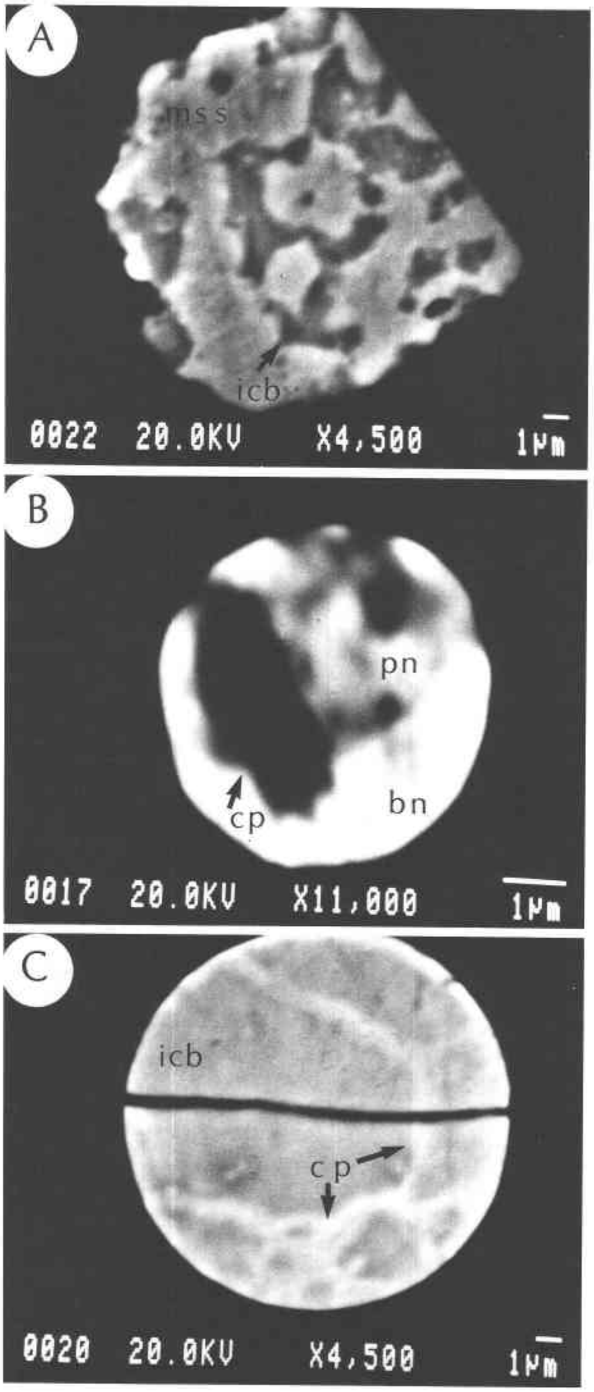

Fig. 2. Sulfides in quenched Kilauea Iki lava. (**A**) Backscattered-electron image of an olivine phenocryst-hosted bleb of intergrown mss (light gray) and isocubanite (icb, dark gray). (**B**) Backscattered-electron image of an olivine phenocryst-hosted bleb of pentlandite (pn, gray), chalcopyrite (cp, dark), and bornite (bn, bright). (**C**) Backscattered-electron image of an olivine phenocryst-hosted bleb of isocubanite (icb, light gray) and lamellar chalcopyrite (cp, bright).

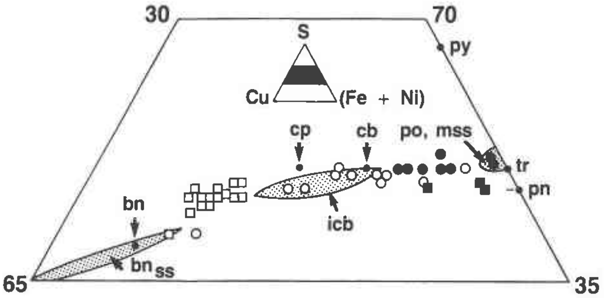

Fig. 3. Bulk sulfide compositions (at.%). Full symbols are eruption pumice; open symbols are Kilauea Iki lava; circles are olivine phenocryst-hosted blebs; squares are rock matrix glass-hosted blebs. Phase fields for 600 °C are from Craig and Scott (1974) and Hill (1983).

most Ni-rich olivine-hosted blebs. The bulk composition of the third bleb (bleb 10, Table 2) is Fe rich and richer in Cu than Ni.

The bulk compositions of sulfide blebs from Kilauea Iki lava (Fig. 3) span the range from the pyrrhotite-mss phase field to the bornite solid solution field in the system Cu-(Fe + Ni)-S (Fig. 3). The bulk composition of the olivine-hosted blebs varies widely and is distinct from that of blebs in the groundmass. Analysis of the olivine-hosted blebs indicates a range in Ni/Cu ratio from <0.01 to 1.3 (Table 2). Most of the blebs are Cu rich (Fig. 3) and contain significant amounts of Ni. The bulk composition of the groundmass-hosted blebs is relatively uniform: extremely Ni poor and Cu rich, with an average Ni/Cu ratio of <0.01. The bleb with the highest bulk Cu content in the Hawaiian samples (KI81 bleb 21, 52.4 wt% Cu, Table 2) is actually olivine hosted. Although some of the variability in bulk composition of the sulfide blebs may reflect sampling bias, the extremely wide variability is considered to be real and significant because the blebs are primarily very fine grained, sulfide phases are intricately intergrown (see below), and a large number of blebs were analyzed (Table 2).

Sulfide phases

The blebs in the eruption pumice are of mss + isocubanite ± pentlandite ± magnetite, pyrrhotite + isocubanite, or pentlandite + isocubanite + bornite. The predominance of nickel sulfides is consistent with the nickeliferous bulk composition of the sulfides in the eruption pumice. The blebs in Kilauea Iki lava are of either isocubanite ± mss ± pentlandite ± chalcopyrite or bornite ± chalcopyrite ± isocubanite ± pentlandite ± magnetite. The predominance of copper sulfides in Kilauea Iki lava is distinctive from the eruption pumice and consistent with the cupriferous composition of the bulk sulfides.

In the eruption pumice, the mss + isocubanite blebs are the most common and occur in olivine and the pumice glass. They range in size from 5 to 40 μm across. The

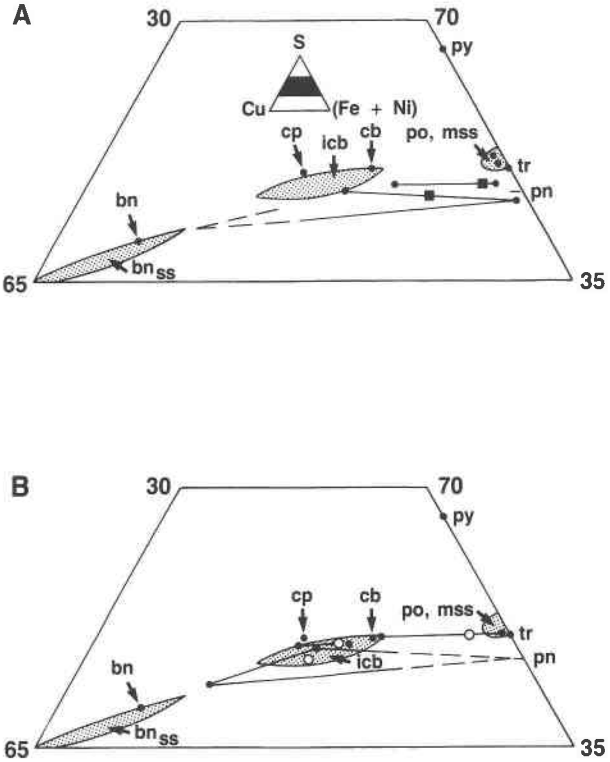

Fig. 4. Compositions of sulfide phases within the Cu-(Fe + Ni)-S system (at.%). (A) Eruption pumice and (B) Kilauea Iki lava. Dots represent averaged analyses of individual phases; full symbols represent bulk sulfide compositions in the eruption pumice; open symbols represent bulk sulfide compositions in Kilauea Iki. Dashed tie lines represent coexistence with an identified phase of a composition that was not determined quantitatively. Phase fields for 600 °C are from Craig and Scott (1974) and Hill (1983).

mss comprises from 50 to 90 modal% of the blebs and is the matrix phase. Composition of the mss (Table 3) plots in the mss(1) phase field (Misra and Fleet, 1973; Craig, 1973; Stone et al., 1989).

The isocubanite coexisting with the mss in these blebs is present in amounts up to 50 modal%, as either lamellae (Fig. 1A) or very tiny grains (0.1 μm). In the latter case, the isocubanite is concentrated in the bleb margins. Pentlandite comprises about 5 modal% of some of these blebs. It occurs as small specks within mss or along the contact between mss and isocubanite. One mss + isocubanite bleb has 3 modal% of very fine-grained (<1 μm) magnetite as isolated inclusions, inclusion trails, and lamellae (Fig. 1A). A second bleb within the same glass inclusion has a partial rim of Cr-bearing magnetite separating it from a chromite grain. Isocubanite, magnetite, and pentlandite present in the mss + isocubanite blebs are too fine grained for quantitative analysis.

The Fe-rich bleb in the eruption pumice consists of an unidentified metal-excess iron-rich sulfide (UMIS) + isocubanite. The bleb is within the pumice glass and is 30 by 20 μm in size. It resembles the mss + isocubanite blebs with lamellar isocubanite except that the isocubanite lamellae are up to 1 μm wide, more isocubanite is present (about 15 modal%), and magnetite is absent. The UMIS is metal rich (M/S = 1.07) and contains 2.9 at.% Ni and 2.6 at.% Cu (Table 3). Although similar in composition to mackinawite (cf. Clarke, 1970), the UMIS is isotropic and therefore quite distinct from that mineral. The composition of the coexisting isocubanite approximates that of cubanite (Fig. 4A).

One bleb with pentlandite + isocubanite + bornite was found in the eruption pumice (Fig. 1B). It occurs in the pumice glass and is 40 μm in diameter. The pentlandite is the matrix phase and it is Fe rich (bleb 11, Table 3). The isocubanite occurs as irregular interstitial areas within the pentlandite. It is metal rich and Cu rich relative to nominal $CuFe_2S_3$ (Table 3; Fig. 4A). The bornite is present as very fine-grained (<1 μm) spots within the isocubanite and along boundaries between the isocubanite and the pentlandite. The very fine grain size of the bornite precluded quantitative analysis.

In Kilauea Iki lava, the blebs consist of either isocubanite ± mss ± pentlandite ± chalcopyrite or bornite ± chalcopyrite ± pentlandite. The isocubanite-bearing blebs are most common within olivine. One such bleb consists of 25 modal% isocubanite in lamellar intergrowth with mss (Fig. 2A). The isocubanite is close to stoichiometric $CuFe_2S_3$ (KI81 bleb 2, Table 3; Fig. 4B). The composition of the mss corresponds to mss(1) (Misra and Fleet, 1973; Stone et al., 1989).

The blebs of isocubanite ± pentlandite ± chalcopyrite in Kilauea Iki lava are of isocubanite as matrix and 5 to 15 modal% lamellar pentlandite or chalcopyrite. The pentlandite in these blebs is too fine grained (<1 μm) for quantitative analysis. In one bleb where isocubanite and lamellar chalcopyrite coexist (Fig. 2B), the former is Cu rich relative to ideal $CuFe_2S_3$ (KI81 bleb 1, Table 3). The coexisting chalcopyrite is metal rich and Cu rich relative to ideal $CuFeS_2$ (Table 3; Fig. 4B).

The bornite-bearing blebs occur mostly in the groundmass glass of sample KI79. These blebs are the smallest (<2 μm) and most abundant in the samples studied. Many consist of a core with intricately intergrown lamellar bornite ± chalcopyrite ± isocubanite and a margin of more discrete chalcopyrite ± isocubanite. Others have bornite in the margin that is more coarsely intergrown with discrete isocubanite ± chalcopyrite in the core. Blebs entirely of bornite are apparently present. The small size of the bornite-bearing blebs precluded quantitative analysis of the phases. Magnetite is present in the margin of a very few of these blebs.

Three bornite-bearing blebs were observed within a small olivine phenocryst in KI81. One of the blebs contains a small core of intergrown isocubanite and pentlandite and a margin composed partly of discrete isocubanite and partly of intricately intergrown isocubanite and bornite (Fig. 2C). The discrete chalcopyrite is S poor relative to ideal $CuFeS_2$ (bleb 19, Table 3), whereas the bornite appears to be Cu poor and S rich relative to ideal Cu_5FeS_4 (Fig. 4B). The pentlandite is too fine grained for quantitative analysis. The deviations from stoichiometry of the chalcopyrite and the bornite probably reflect beam overlap onto adjacent sulfides during analysis.

PHASE RELATIONS

The sulfide blebs of the 1959 eruption pumice and Kilauea Iki lava are extremely variable in bulk composition. Solidification of the blebs probably occurred between 1200 and 850 °C because this interval includes the liquidus temperatures of the three common sulfide minerals that crystallize from Fe-Ni-Cu-S liquid: mss (1191–1100 °C; Naldrett et al., 1967; Kullerud et al., 1969), bornite solid solution (1129–1059 °C; Craig and Kullerud, 1969; Kullerud et al., 1969), and isocubanite (970–850 °C; Craig and Kullerud, 1969; Craig and Scott, 1974). Cooling of sulfide liquid to the range of 1192 to 1000 °C results in crystallization of mss, which removes much of the available Ni and up to 5 wt% Cu in solid solution (Kullerud et al., 1969). Any sulfide liquid residual of mss crystallization would therefore be more Cu rich. However, the solubility of Cu in mss increases with decreasing temperature and may attain a maximum of 7.5 wt% at 940 °C (Kullerud et al., 1969). Isocubanite exsolves from mss below 940 °C.

In the eruption pumice and Kilauea Iki lava, the blebs of lamellar isocubanite within mss or UMIS are interpreted to represent an unmixing during cooling of a high-temperature, more Cu-rich mss precursor. The original high-temperature mss appears to have contained all of the Ni and Cu in these blebs. This apparent congruent crystallization of complex mss is apparent in sulfide blebs described in the literature (Stone et al., 1989; Boctor and Boyd, 1980).

The present of a Cu-rich margin about a more Ni-rich core in most of the olivine-hosted blebs suggests that in the eruption pumice and Kilauea Iki lava, Cu-rich sulfide liquid was residual from mss crystallization. Isocubanite crystallized from the Cu-rich residual liquid between about 970 and 850 °C (Craig and Kullerud, 1969). This crystallization history has been inferred for many sulfide blebs in the literature (Lorand, 1989a, 1989b; Stone et al., 1989; Stone and Fleet, 1990).

Although the UMIS + isocubanite bleb encountered is depleted in Ni relative to Cu and is metal rich, the sulfide liquid precursor appears to have initially crystallized entirely to high-temperature UMIS. At high temperature, pyrrhotite can accommodate 5 wt% Ni and 5 wt% Cu (Yund and Kullerud, 1966; Kullerud et al., 1969; Craig and Kullerud, 1969). Sulfide liquid enriched in Fe relative to Ni and Cu and containing less than 10 wt% Ni + Cu would crystallize as hexagonal pyrrhotite rather than mss. Therefore, the metal-enriched bulk composition of the UMIS + isocubanite bleb is a curiosity. The metal enrichment is consistent with the composition of the UMIS and isocubanite. The contents of Fe, Ni, and Cu in the UMIS resemble those of high-temperature pyrrhotite (Craig and Kullerud, 1969; Craig, 1973), but the UMIS appears to be isotropic and S poor. Admittedly, the averaged analysis of the UMIS totals only to 98.1 wt%. If the S content of this analysis were 2 wt% higher, then the composition would plot on the S-poor mss boundary. Metal-rich analyses of mss are reported from MORB samples (Kanehira et al., 1973; Czamanske and Moore, 1977) and in experimental samples (Misra and Fleet, 1973), but these also remain to be explained.

Although the eruption pumice and Kilauea Iki lava samples were quenched from the range of 1216 to 1053 °C, the sulfide phases in the blebs continued to reequilibrate in the sulfide subsolidus. The exsolution of isocubanite of cubanite composition from the UMIS is consistent with the observation that isocubanite in equilibrium with pyrrhotite has a smaller Cu/Fe ratio than that in equilibrium with chalcopyrite (Yund and Kullerud, 1966). Theoretically, tie lines formed between isocubanite and pyrite at 743 °C persist during cooling to 590 °C and prevent the coexistence of isocubanite and pyrrhotite (Craig and Kullerud, 1969). In the eruption pumice, the coexistence of isocubanite and UMIS reflects the S-poor bulk composition, which precluded pyrite formation.

The occurrence of isocubanite in pentlandite within one bleb (Fig. 1B) suggests that the former exsolved from a high-temperature mss precursor during cooling rather than crystallized from residual Cu-rich sulfide liquid. The paucity of mss and pyrrhotite in this bleb suggests that the precursor mss decomposed entirely to pentlandite and isocubanite rather than to pentlandite and pyrrhotite. This is consistent with the Fe-rich composition of the pentlandite (Misra and Fleet, 1973; Stone et al., 1989) and the isocubanite and with the S-poor bulk composition of the bleb. The exsolution of bornite rather than chalcopyrite from the isocubanite probably reflects the Cu-rich and S-poor composition of the latter (e.g., Yund and Kullerud, 1966). The coexistence of pentlandite and bornite solid solution implies that this bleb equilibrated internally during cooling below 590 °C (Craig and Kullerud, 1969; Craig and Scott, 1974).

The predominance of Cu over Ni in the bulk composition of the blebs in Kilauea Iki lava suggests that the crystallization history of these sulfides reflects more the decomposition of isocubanite than mss. Given that isocubanite at 600 °C may contain as much as 15 wt% Ni (Craig and Kullerud, 1969), the pentlandite in the Cu-rich blebs could have exsolved from isocubanite. Pentlandite in Ni-rich masses of chalcopyrite within spinel peridotite massifs in France has been attributed to exsolution from Ni-rich isocubanite (Lorand, 1989c). Indeed, the presence of pentlandite as a discrete phase intergrown with chalcopyrite in the core of isocubanite-dominated blebs (e.g., Fig. 2C) and as lamellae in isocubanite suggests that the exsolution of pentlandite from isocubanite can predate that of chalcopyrite.

The single bleb with lamellar chalcopyrite in isocubanite (Fig. 2C) is interpreted to represent an unmixing of high-temperature isocubanite into chalcopyrite and more Fe-rich isocubanite. Isocubanite crystallizes from sulfide liquid during cooling between 970 and 850 °C (Craig and Kullerud, 1969). It subsequently unmixes into cubic chalcopyrite and isocubanite of about $CuFe_2S_3$ composition at approximately 590 °C (Yund and Kullerud, 1966; Cabri, 1973). During unmixing, most of the Ni in the isocubanite is partitioned into the chalcopyrite, which in turn is exsolved as pentlandite at about 550 °C (Craig and Kullerud, 1969).

The bulk sulfide compositions of the extremely Ni-poor and Cu-rich bornite-bearing blebs from Kilauea Iki lava span the miscibility gap between bornite solid solution and chalcopyrite or, in one case, isocubanite at 600 °C. At temperatures above 840 °C, this miscibility gap is much narrower. During cooling below 840 °C, bornite exsolves from Cu-rich isocubanite, and chalcopyrite with or without isocubanite exsolves from S- and Fe-rich bornite solid solution (Yund and Kullerud, 1966; Craig and Kullerud, 1969; Sugaki et al., 1975). By analogy, the crystallization history of the extremely Ni-poor and Cu-rich blebs in Kilauea Iki lava involved exsolution of chalcopyrite ± isocubanite from bornite solid solution and exsolution of bornite solid solution from chalcopyrite ± isocubanite during cooling below about 840 °C.

The lamellar and inclusion trail magnetite in sulfide blebs within the eruption pumice reflects exsolution from precursor high-temperature mss, perhaps during the exsolution of isocubanite. The bleb margin of magnetite in the Kilauea eruption pumice is attributable to late-stage oxidation of the sulfide.

SULFIDE PETROLOGY

Features of the sulfide blebs from Hawaii, such as their rounded shape and the fact that many of the bulk sulfide compositions would plot in the mss phase field of the Ni-Fe-S system, appear to be consistent with an early magmatic origin. However, the extreme variation in composition of the sulfide blebs (Fig. 2 of Fleet and Stone, 1990; Table 2; Fig. 3) is of fundamental significance to hypotheses of their origin.

Variation in the bulk composition of sulfide blebs and nickel-copper sulfide ore bodies has been attributed variously to fractionation of immiscible sulfide liquid (Craig and Kullerud, 1969; MacLean and Shimazaki, 1976; Rajamani and Naldrett, 1978), filter pressing and mechanical dispersion of Cu-rich liquid residual of mss crystallization (Lorand, 1989a, 1989b), loss of Fe from sulfide inclusions to chromite hosts during subsolidus cooling (Naldrett and von Gruenewaldt, 1989), and to the effects of low-temperature alteration such as serpentinization (Abrajano and Pasteris, 1989; Lorand, 1989d). According to the fractionation hypothesis, during olivine crystallization, the immiscible iron-nickel-copper sulfide liquid fractionates to a more Cu-rich composition as crystallization of the silicate liquid proceeds. The bulk composition of olivine-hosted blebs within the volume of a hand specimen should be nearly identical and more Ni rich than those in later crystallized minerals or in the groundmass.

In the eruption pumice, the variability of the Ni/Cu ratio of the olivine-hosted blebs and presence of the most Ni-rich blebs in the pumice glass are inconsistent with an origin by fractionation of immiscible sulfide liquid. Conversely, in Kilauea Iki lava, the presence of the more nickeliferous blebs within the olivines and the extremely Ni-depleted and Cu-rich blebs in dacite glass within the groundmass appears to be consistent with nonequilibrium fractionation. However, here, the restriction of the occurrence of the sulfide blebs to the olivine in one sample and to the groundmass in the other is unexplained by this model. Furthermore, the Cu-rich sulfide bleb inclusions cannot be in equilibrium with the host olivine or basalt liquid.

Wide variation in the modal percentages of chalcopyrite and pyrrhotite in the mantle pyroxenite vein-hosted sulfide blebs from the Lherz and Freychinède spinel-peridotite massifs in France has been attributed to mechanical dispersion of Cu-rich liquid residual to mss crystallization (Lorand, 1989a, 1989b). The mechanical dispersion is said to have been induced by plastic deformation of the host rock in the range of 750 to 950 °C. Evidence for pervasive plastic deformation in the Hawaiian samples is lacking. It is difficult to envisage how the variable bulk sulfide compositions of the olivine-hosted blebs might be explained by this model. Furthermore, mechanical dispersion of liquid is unlikely to have occurred in the eruption pumice.

Fe loss from sulfide inclusions to chromite hosts is an unlikely explanation because many of the blebs are not associated with chromite and the enrichment of Cu relative to Fe, Ni, and S is unexplained. Although olivine has, to varying degrees, lost Mg and gained Fe as a result of reequilibration during the annealing (Helz, 1987b), the similarity in NiO content of these grains suggests that Ni has not been significantly redistributed. The lack of opportunity for low-temperature alteration in the Hawaiian samples precludes this explanation as well.

In addition to the wide variability in bulk composition of the Hawaiian sulfide blebs even within individual olivine crystals, the NiO content of olivine is too high and the NiS content of the included and associated sulfides is too low, relative to laboratory partitioning data, for equilibration during magmatism (Fleet and Stone, 1990). The rounded shape of the sulfide blebs is not unequivocal evidence for sulfide liquid immiscibility (e.g., Skinner and Peck, 1969). Bulk sulfide compositions that plot in the mss phase field could reflect the composition of the host in which the sulfides occur. Therefore, origin of the Hawaiian sulfide blebs cannot be attributed solely, if at all, to sulfide liquid immiscibility in the early magmatic stage. Indeed, origin of the most Cu-rich bleb in the 1955 basalts from Kilauea Volcano by sulfide liquid immiscibility has been questioned (Desborough et al., 1968).

Alternatively, the sulfide blebs may have been present in the early magmatic stage of these rocks and were subsequently modified by late magmatic processes on cooling, particularly during quenching. Fleet and Stone (1990) surmised that all the sulfide inclusions from Kilauea Iki lava with less than equilibrium proportions of NiS have gained Fe, Cu, and S during cooling and quenching. The S capacity of basalt melts decreases during cooling and abruptly on quenching. Excess S could segregate as sulfides of metals locally abundant in the melt and may preferentially nucleate on existing sulfide blebs or be lost to the gas phase (e.g., Anderson, 1974). Wide variation of bulk-sulfide compositions would result. The observed tendency of increase in Cu_2S content with decrease in bleb size and lack of equilibrium between olivine hosts and included and associated sulfides is certainly consistent with sulfidation during late-stage magmatic processes.

The bulk compositions of the groundmass sulfides in both the eruption pumice and Kilauea Iki lava lake are certainly consistent with an origin by quench- and cooling-induced sulfidation, as reflected in their disparity in composition and their correlation with the composition of the immediate host material. The melt phase in Kilauea Iki lava lake evolved further by continued crystallization at a lower temperature than the eruption melt, producing extreme Cu enrichment of the sulfide blebs. Ample opportunity was available (about 20 yr) for both dissolved and segregated sulfides in Kilauea Iki lava lake to be modified, through degassing and sulfidation, before quenching. Indeed, blebs from Alae appear to have equilibrated with fractionated silicate liquid (MacLean and Shimazaki, 1976).

The nickeliferous sulfides in the olivine-hosted glass inclusions may represent early magmatic nickel sulfides, possibly formerly in equilibrium with the coexisting olivine, that have been diluted during cooling and quenching. The inclusion glass contains abundant S, and the size of the sulfide blebs decreases with decrease in area of the inclusion. However, many of the sulfide blebs appear to account for 20 or more modal% of some glass inclusions. This may reflect the level of section, but the large sulfide blebs appear to be relatively too large to have been significantly diluted by quench sulfide unless sulfur and metal were derived from a much larger volume of melt.

Recent study of the products of sulfide-silicate experiments indicates late introduction of sulfide blebs and silicate melt in olivine rather than entrapment during crystal growth. Inclusions of sulfide blebs and glass are commonly present within residual unmelted olivine grains in experiments involving equilibration of immiscible sulfide liquid and olivine basalt melt (Fig. 5). The sulfide liquid and silicate melt are apparently introduced by preferential dissolution along cleavage intersections and defects. The sulfide blebs illustrated in Figure 5A are Fe rich and Ni poor relative to the principal mass of immiscible sulfide in the charge. Stone et al. (1990) attributed this disparity in composition to incomplete sulfidation of the olivine basalt, but given the low quench rate of these experiments, dilution by iron sulfide during quenching cannot be excluded.

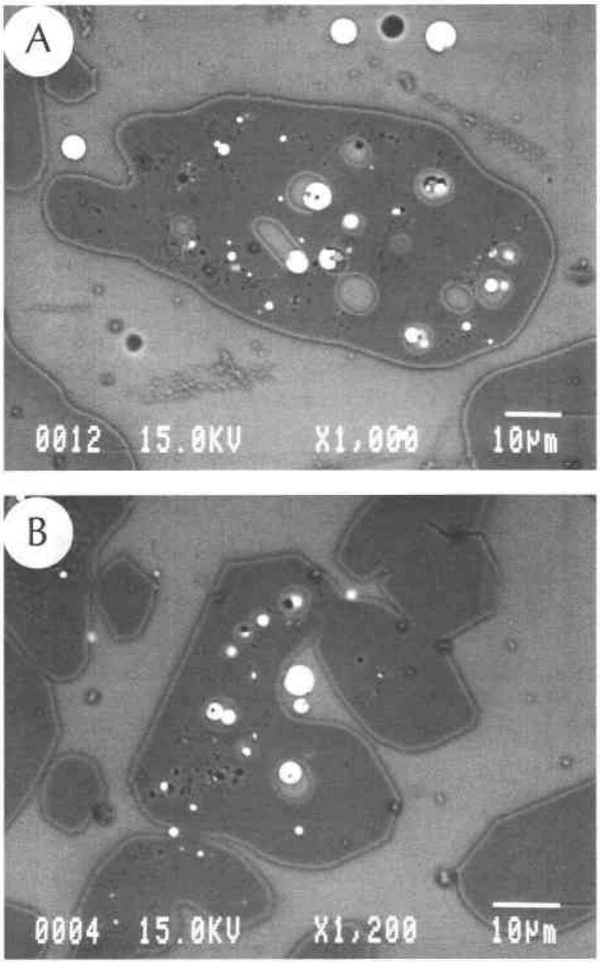

Fig. 5. Backscattered electron images of iron nickel sulfide blebs (bright) and glass (pale gray) introduced into residual unmelted olivine grains (gray). Experiments were conducted on the equilibration of Pt-group elements between immiscible sulfide liquid and olivine basalt melt (Stone et al., 1990). (**A**) is experiment PG31; (**B**) is experiment PG32.

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