17. CHEMICAL COMPOSITION AND FORMATION OF A MASSIVE SULFIDE DEPOSIT, MIDDLE VALLEY, NORTHERN JUAN DE FUCA RIDGE (SITE 856)¹

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ABSTRACT

Studies of sulfide cores from Site 856, Middle Valley, northern Juan de Fuca Ridge, established the vertical zonation of a large inactive oceanic massive sulfide deposit. Zone 1 consists mainly of pyritic massive sulfide with minor sphalerite and magnetite (0 to 28 mbsf in Hole 856H and 0 to 40 mbsf in Hole 856G). Compared with the rest of the deposit, this zone is strongly enriched in Zn and a large number of trace metals (in particular Cd, Mn, Sn, and Sb), and in elements contained in gangue minerals (Si, Al, Mg, and Ba). Most of these elements reach their maximum concentrations in the upper part of the zone; the lower part is enriched in Cu, Se, and Ca. Zone 2 consists dominantly of pyrrhotite-rich massive sulfide with minor pyrite and magnetite (28 to 48 mbsf in Hole 856H) and is depleted in minor elements. Zone 3 is almost pure pyritic massive sulfide (48 to 75 mbsf in Hole 856H and 40 to 65 mbsf in Hole 856G) and is relatively enriched in Ge, As, Sb, Pb, and Tl. Zone 4 consists of dominant pyrrhotite with minor chalcopyrite (75 to 95 mbsf in Hole 856H) and shows a maximum enrichment in Cu, Co, and Bi.

Correlation analysis shows that elements enriched in zone 1 are associated with different ore-forming and gangue minerals: sphalerite (Cd and Pb), talc and/or chlorite (Sc, Th, and REE), silica (Hg and Ta), dolomite (V), and barite (Sr, Zr, and Hf). Sb, As, Sn, Au, Ag, Mn, Mo, and Tl form a separate association, presumably related to sulfosalt minerals.

Enrichment of Zn and minor elements in the upper part of the deposit, which is typical of ancient massive sulfide deposits, is attributed to the zone-refining process of progressive upward replacement of lower temperature minerals by higher temperature minerals during growth of the sulfide body, with the concomitant hydrothermal leaching of trace metals.

Later, the deposit was hydrothermally altered, probably due to lateral flow of evolved seawater along turbidite layers. The alteration produced replacement of primary pyrrhotite by pyrite in zone 3 and by pyrite + magnetite assemblages in the upper zones. In the upper levels of the deposit, sulfate-rich water acted as a strong oxidant. At lower levels a hotter and more evolved sulfur-enriched pyritizing solution also introduced additional Pb, Sb, As, and other sediment-derived elements into zone 3. The absence of light rare earth element enrichment and the existence of a positive Eu anomaly in the massive sulfides of this zone is connected with the alteration of plagioclase in the associated turbidites.

The secondary convection system that caused alteration of the massive sulfides could have been driven by one of the sills emplaced into Middle Valley sediments subsequent to sulfide formation.

INTRODUCTION

During Leg 139 of the Ocean Drilling Program (ODP) a large body of massive sulfides was drilled in the rift valley (Middle Valley) of the Endeavour Segment, northern Juan de Fuca Ridge. With the exception of several relatively shallow holes drilled during Leg 106 wi^{1/L} in the Snake Pit Hydrothermal Field in the Atlantic (Honnorez et al., 1990), this was the first opportunity to core an oceanic sulfide deposit and study its inner structure.

Similar massive sulfides within sedimentary-volcanic sequences, genetically related to mafic volcanic rocks, are commonly referred to as Besshi-type deposits (Franklin et al., 1981). These deposits comprise an important group of ancient volcanogenic massive sulfides, which have been actively studied and mined on land. Therefore, information on the structure of these modern equivalents is of primary importance for understanding the genesis of economically significant base-metal deposits.

The aim of this paper is to describe the chemical compositions of the recovered massive sulfides, compare them to those of other oceanic sulfide deposits, and discuss possible genetic implications.

GEOLOGIC SETTING

Hydrothermal vents and massive sulfide deposits of the northern Juan de Fuca Ridge are situated in Middle Valley, a 15-km-wide, sediment-filled abandoned rift valley. Heat-flow anomalies in excess of 1 W/m² were discovered in the eastern part of the valley between $48^{\circ}20'N$ and $48^{\circ}30'N$ (Davis et al., 1987). A hydrothermal origin has been suggested for a number of mounds in Middle Valley, each several hundred meters across and up to 60 m high, which were found by SeaMARC-I acoustic imagery in this area (Davis et al., 1987). A shallow core, taken at the base of one of the mounds during the 1985 cruise of *C.H.S. Parizeau*, contained 2.4 m of sediments rich in disseminated sulfides and massive sulfide clasts (Goodfellow and Blaise, 1988).

Later photographic and video studies and subsequent sampling documented the presence of extensive massive sulfide outcrops along the margins of the mounds, which confirmed the large scale of the deposits. Little hydrothermal venting was discovered in the area, and the sulfide deposits are mostly relict. However, another area with numerous high-temperature vents of the black and white smoker type was found about 3 km to the northwest, closer to the axis of the valley (Kappel and Franklin, 1989).

During ODP Leg 139, eight holes were drilled at Site 856 in the mound area, near where the Middle Valley sulfides were first sampled in 1985 (Shipboard Scientific Party, 1992). Two holes (856A and 856B) were drilled into Bent Hill, a large mound typical of several in the area. This mound appeared to be covered by more than 100 m of undisturbed sediments that were uplifted by sill intrusion. In Hole 856B, at the southern edge of Bent Hill, massive sulfide clasts were recovered in the sediment column at a depth of about 30 m. Six more holes were drilled at Site 856 (856C to 856H) within a sulfide mound that is up to 100 m in diameter and 20 m high, lying immediately to the south of Bent Hill. These holes are distributed over a distance of 60 m across the southern flank of the sulfide mound, but none reached the base of the deposit. Drilling of the deepest hole (856H) was terminated for technical reasons at 94 m below seafloor (mbsf), or

¹ Mottl, M.J., Davis, E.E., Fisher, A.T., and Slack, J.F. (Eds.), 1994. Proc. ODP, Sci. Results, 139: College Station, TX (Ocean Drilling Program).

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		Element co	oncentrations, me	easured (top) and	l certified (bottom)	0	
Standard	Fe	Mn	Cu	Zn	Cd	Ca	Mg
SNK-1	18.67 ± 0.13 19.09						
SNK-2	$\frac{4.01 \pm 0.00}{4.07}$	$\frac{0.173 \pm 0.007}{0.16}$	$\underbrace{\begin{array}{c} 0.40 \pm 0.00 \\ \hline 0.39 \end{array}}$	$\frac{0.038 \pm 0.001}{0.039}$			
#3031	$\frac{10.15 \pm 0.24}{10.24}$	$\frac{0.21 \pm 0.00}{0.21}$	$\frac{3.38\pm0.08}{3.37}$			20.00	$\frac{0.86 \pm 0.002}{0.80}$
#708	16.26 ± 0.54 16.38			$\frac{10.40 \pm 0.10}{10.39}$	Ξ.		
#681				$\frac{1.18 \pm 0.02}{1.23}$			
#710			$\frac{12.62 \pm 0.12}{12.50}$	$\frac{6.43 \pm 0.07}{6.55}$			
RUS-3					$\frac{0.0037 \pm 0.0003}{0.0035}$		
#2891					$\frac{0.0028 \pm 0.0001}{0.0029}$	20	
ST 1						7.29	3.43 ± 0.07
51-1						7.29	3.44

Table 1. Comparison between certified and measured element concentrations (%) in the standard samples, used in atomic absorption analyses at VNIIoceangeologia.

Note: Certified concentrations are from Chernyakhovskaya and Osyko (1983). Measured concentrations are average values of two to three individual determinations.

2518 m below sea level (mbsl). This is much deeper than the level of the seafloor near the mound.

ANALYTICAL METHODS

All chemical analyses were carried out in St. Petersburg. SiO_2 and Al_2O_3 were analyzed by photometry at the Institute for Geology and Mineral Resources of the Ocean (VNIIoceangeologia) by N. Luneva. The samples were decomposed by melting with sodium carbonate and borax. Silica was determined by the reduction product of yellow silica molybdenum heteropolyacid complex, with ascorbic acid used as a reducer. Aluminum oxide was determined using alumocreson, an ammonia salt of dioxytricarbonic acid of triphenylmethane row. Sulfur was determined gravimetrically, by means of precipitation with barium chloride.

Fe, Mn, Cu, Cd, Ca, and Mg were also analyzed at VNIIoceangeologia by N. Luneva, using atomic absorption spectrometry (C-115 spectrophotometer with flame atomization), with preliminary acidic treatment. Certified standards were used for control (Table 1).

Zn, Pb, Mo, and Ti were determined by the same method, by S. Shishkova and Ye. Chikhacheva at the Russian Geological Institute (VSEGEI). A Perkin Elmer M 305 spectrophotometer with flame atomization was used for the determination of Zn and Pb. A Perkin Elmer M 603 with electrothermic atomization was used for Mo analyses, and an AAS-3 spectrophotometer with electrothermic atomization was used for Ti determination. Comparison between certified and measured concentrations in the standards, analyzed by atomic absorption at VSEGEI, is given in Table 2.

Sr, Sn, Bi, V, Ge, and Tl were analyzed by Ye. Khitric (VNIIoceangeologia) by quantitative optical emission spectrometry, using a DFS-13 spectrograph with a flat grating (600 lines/mm). The working range was 200–1000 nm, relative aperture 1:40, and linear dispersion 0.4 nm/mm. Certified and measured element concentrations in the standards used are given in Table 3.

A wide range of minor elements was determined by I. Shtangeeva (St. Petersburg State University) by instrumental neutron activation analysis (INAA): Ag, Au, As, Sb, Co, Ni, Sc, Cr, Zr, Cs, Rb, Ba, Hf, Ta, Th, U, Se, Hg, La, Ce, Sm, Eu, Tb, and Yb. The samples and standTable 2. Comparison between certified and measured element concentrations in the standard samples, used in atomic absorption analyses at VSEGEI.

	Element concen	trations, meas (bottom	ured (top) and	certified
Standard	Zn (%)	Pb (ppm)	Mo (ppm)	Ti (ppm)
DIIS 1	3.39 ± 0.04			
K03-1	3.49			
ST 2	0.0112 ± 0.0012			
51-2	0.0112			
SDPS-3		$\frac{253 \pm 23}{250}$		
BM		12.3 ± 0.7		
Din		13		
SKR-3			$\frac{10.7 \pm 0.7}{13}$	
SG-1A			15	436±26
				430

Note: Certified concentrations are from Chernyakhovskaya and Osyko (1983). Measured concentrations are average values of two to four individual determinations.

ards were irradiated with epithermal neutrons at a flux density of $5 \times 10 \text{ n/cm}^2\text{s}$ for two days. Measurements were carried out by means of a Ge(Li) detector (resolution 2.1 keV for line 13332 keV). Results of INAA for the standard samples are given in Table 4. The method of inner standard (Vaganov, 1975) was used for Au, Ag, As, Hg, Ni, and Se determinations.

X-ray diffraction was conducted by M. Ostroumov (St. Petersburg Mining Institute), using DRON-2 (V = 30 kV, I = 10 ma) and URS-50-IM (V = 15–20 kV, I = 3–4 ma) diffractometers. Electron microprobe analyses were conducted by O. Yakovleva (VSEGEI), using a Cameca MS-46 instrument. The detection limit was 0.01%, with the relative analytical error of 2% for major elements. The ZAF correction method was used in data processing.

Table 3. Comparison between certified and measured element concentrations (ppm) in the standard samples, used in quantitiative optical emission spectrometry.

	Elen	nent concentr	ations, measu	ired (top) and	certified (bo	ttom)
Standard	Bi	Ge	Sr	Sn	TI	v
SC 14	1.7 ± 0.4	3.5 ± 0.1	<100	8.6 ± 2.5	6.7 ± 0.7	5 ± 0
30-1A	2.0	3.3	20	3.3	7.0	5
ST 14			268 ± 18	3.8 ± 0.5		322 ± 12
31-1A			270	3.5		320
SCD 1			232 ± 18	3.8 ± 0.6		240 ± 10
500*1			230	3.7		240

Note: Certified element concentrations are from Chernyakhovskaya and Osyko (1983). Measured concentrations are average values of three to four individual determinations.

MINERAL COMPOSITION AND STRUCTURE OF THE MASSIVE SULFIDE DEPOSIT

Results of detailed ore petrology studies of the massive sulfide deposits are given by Duckworth et al. (this volume). We studied and consider here mainly the distribution of the major minerals, which directly determine the chemical composition of the ores, across the drilled section of the massive sulfide deposit.

Vertical changes in the mineralogy of the core from the deepest (95 mbsf) and most extensively sampled hole (856H; Fig. 1) are described herein. The percentage of core recovery and quantity of massive sulfide samples do not allow us to describe these changes in detail. However, certain trends in mineral distribution can be traced that make it possible to divide the deposit into several zones.

Zone 1

Massive sulfides from the upper part of the deposit, to about 28 mbsf, are the most complex in composition. They consist of pyrite as the dominant mineral, together with pyrrhotite, sphalerite, and magnetite in different proportions, and with minor quantities of marcasite, chalcopyrite, and isocubanite. Chlorite, talc, dolomite, and amorphous silica are the main gangue minerals; barite occurs in minor amounts. The uppermost part of the deposit (Core 139-856H-1R) was destroyed in the course of drilling. The resultant disintegrated mass was sorted by grain size during drilling, from fine-grained clayey sand in the upper part to coarse-grained sand with gravel and separate clay lumps in the lower part. The sands contain clasts of massive, cavernous, partly oxidized sulfides up to 4 cm in size. The 15-cm-long lowermost interval of Core 139-856H-1R consists almost totally of this massive sulfide debris, which resembles clasts recovered from conventional black smoker chimneys (e.g., Krasnov et al., 1992).

The pyrite from Core 139-856H-1R typically forms round, roselike aggregates, intergrown with gangue minerals. Traces of primary pyrrhotite, most of which is replaced by pyrite, occur locally. Subhedral sphalerite is interstitial and dispersed in the matrix of gangue minerals. The sphalerite contains tiny chalcopyrite inclusions oriented in one direction. Chalcopyrite (locally with isocubanite) and pyrrhotite also occur as isolated grains. Marcasite is intergrown with pyrite, replacing pyrrhotite. Rhombic barite crystals and crystal aggregates, and dark-brown grains of hydroxides, are also present. Talc and silica locally replace the clayey sediment matrix.

The largest sulfide clasts are composed of tabular pyrrhotite crystals up to 0.1 mm in size, forming a framework with interstitial sphalerite. In some of the clasts pyrrhotite is totally replaced by pyrite (Fig. 2). Clasts are commonly semioxidized. Table 4. Comparison between certified and measured element concentrations (ppm) in the standard samples AGV-1, used in neutron-activation analyses.

Element	Certified concentrations	Measured concentrations				
Ba	1221.0	1240 ± 60				
Co	15.2	15.0 ± 0.8				
Cr	12.0	9.5 ± 0.5				
Cs	1.26	1.50 ± 0.08				
Hf	5.1	5.4 ± 0.3				
Rb	67.0	65 ± 3				
Sb	4.4	5.0 ± 0.2				
Se	12.1	13.4 ± 0.7				
Ta	0.91	0.90 ± 0.04				
Th	6.5	6.4 ± 0.3				
U	1.89	1.75 ± 0.09				
Zr	225.0	240 ± 12				
La	35.9	37.0 ± 1.8				
Ce	64.9	65.0 ± 3.0				
Sm	6.1	6.1 ± 0.3				
Eu	1.71	1.76 ± 0.09				
Tb	0.79	0.80 ± 0.04				
Yb	1.73	1.75 ± 0.09				

Note: Certified concentrations are from Baedecker and McKown (1970). Measured concentrations are averages of five individual determinations, using the BCR-1 standard.

The sulfides of zone 1 in Core 139-856H-2R and the following cores are massive. Major minerals are pyrite, magnetite, and sphalerite with a variable pyrrhotite content, and small amounts of chalcopyrite. Abundant gangue minerals (dolomite, local silica, and traces of talc) form veins and are characteristic of the zone. Two generations of pyrite can be recognized: anhedral pyrite that is intergrown with tiny, oriented magnetite grains, and a subhedral variety that lacks magnetite intergrowths. Another form of magnetite occurrence is thin spongy intergrowths with gangue minerals. Sphalerite forms subhedral crystals that vary in size from 0.05 to 1 mm and are partly dispersed in massive sulfide and partly grouped in blebs. The largest grains occur in veins, together with pyrite and dolomite. Traces of pyrrhotite replacement by pyrite are evident in zone 1. The two pyrite generations reflect successive stages of the replacement process. The paragenetically earlier generation involved the pseudomorphic replacement of tabular crystals of pyrrhotite by pyrite, intergrown with magnetite. Pyrite of the younger generation, associated with sphalerite, replaces both pyrrhotite relicts and early pyrite-magnetite aggregates. Only general outlines of the replaced pyrrhotite crystals are seen in the resultant structure (Fig. 3).

The upper meter of Core 139-856H-4R (at about 27 mbsf) is a sedimentary layer heavily veined with sulfide minerals and magnetite. The altered sediment consists of chlorite with minor talc and traces of siderite and dolomite rimming pyrite veins. Crystals of hexagonal pyrrhotite form sheaflike aggregates between pyrite crystals in veins and are dispersed in the sediment, along with minor sphalerite and chalcopyrite. Sporadic large sphalerite crystals (up to 0.2 mm) occur in veins. The spongy magnetite is mostly intergrown with dolomite.

Zone 2

Massive sulfides of zone 2 (to about 48 mbsf) are characterized by the dominance of pyrrhotite, which forms a framework of elongated plates up to 3 mm in length. Based on X-ray diffraction data, pyrrhotite is mostly hexagonal, and partly monoclinic. The crystals of pyrrhotite are overgrown and partly replaced by pyrite (Fig. 4), the second most abundant mineral. Pyrite also fills interstitial spaces, forming large (up to 1.5 mm) anhedral grains, and occurs in thin ramifying veins. Marcasite is locally present together with pyrite, forming rims and overgrowths on pyrrhotite. Anhedral sphalerite grains, up to 1 mm in size, fill the interstitial spaces. Small, mostly anhedral chalcopyrite grains fill the interstices and form tiny (up to 0.1 mm) inclusions in pyrrhotite and sphalerite.



Figure 1. Mineral composition (percentage of total ore minerals) and zonation of sulfide cores from Holes 856G and 856H. Py = pyrite, Po = pyrrhotite, Mt = magnetite, Sp = sphalerite, Cp = chalcopyrite, Ic = isocubanite, Mc = marcasite, and Hm = hematite.

Magnetite occurrences in zone 2 are different from those in zone 1. The intergrowth of magnetite with pyrite is atypical, and more commonly it forms subhedral crystals in pyrrhotite and spongy, mossy aggregates of skeletal crystals in cavities (Fig. 5). Gangue minerals, represented mostly by chlorite, with minor carbonates and local silica and barite, are less abundant than in zone 1. The lower part of zone 2 (Core 139-856H-7R) forms a transition to zone 3. Typical of this transition is Sample 139-856H-7R-1, 80–82 cm, where fine-grained pyrite forms boxwork textures including overgrowths and partial replacements of pyrrhotite. Magnetite and hematite are associated with the newly formed pyrite, and occur in thin veinlets. Abundant fine anhedral grains of marcasite, intergrown with pyrite in its finest aggregates, are also characteristic of this core. Sphalerite and chalcopyrite are rare. Carbonate content is higher than that in the upper part of zone 2.

Zone 3

To about 75 mbsf, the core from Hole 856H consists of almost pure pyrite. Different types of pyrite aggregates in this zone form a thick megascopic framework (on the scale of several millimeters), and cells are either void or filled with gangue minerals, mostly amorphous silica and talc. Colloform, banded, and embayed pyrite textures are common. Structures that display local pyrrhotite replacement can also be seen, although pyrite is mainly recrystallized (Fig. 6). Small quantities of sphalerite and chalcopyrite are dispersed in pyrite.

Strong enrichment in barite is seen in Sample 139-856H-8R-1, 124–126 cm. Barite crystals are overgrown by euhedral pyrite and radial aggregates of hematite (Fig. 7). A talc aggregate, partly replaced by pyrite and magnetite, occurs in the lower part of zone 3



0.2 mm

Figure 2. Boxwork texture of pyrite, growing over dissolved pyrrhotite crystals. Photomicrograph in reflected light, Sample 139-856H-16R-1, 108-110 cm.



0.1 mm

Figure 3. Outlines of tabular crystals of pyrrhotite, totally replaced by pyrite (Py), sphalerite (Sp), and magnetite (Mt). Photomicrograph in reflected light, Sample 139-856H-3R-2, 67–70 cm.



0.2 mm

Figure 4. A large tabular crystal of pyrrhotite (Po), replaced and overgrown by pyrite (Py), with interstitial sphalerite (Sp). Photomicrograph in reflected light, Sample 139-856H-5R-1, 52–53 cm.











30 µm

Figure 5. SEM photomicrographs of magnetite aggregates from cavities in massive sulfides. A. Mossy magnetite with a crystal of chalcopyrite (Cp), Sample 139-856H-5R-1, 52–53 cm; area in box is shown in (B). B. Skeletal magnetite crystal, shown enlarged from (A). C. Skeletal magnetite, Sample 139-856H-4R-1, 144–146 cm.

(Sample 139-856H-13R-1, 48-49 cm). Pyrite and magnetite cement the sediment or form network structures within it.

Zone 4

Below 75 mbsf, homogeneous fine-grained pyrrhotite defines zone 4 (Fig. 8). The pyrrhotite is mainly monoclinic, with traces of the hexagonal variety. Aggregates of anhedral grains and interpenetrating



0.1 mm

Figure 6. Recrystallized pyrite (Py1), with chalcopyrite (Cp) and sphalerite (Sp), overgrown by euhedral Pyrite (Py2). Photomicrograph in reflected light, Sample 139-856H-10R-1, 13–15 cm.



300 µm

Figure 7. Overgrowth of a rhombic crystal of barite by cubic pyrite with hematite spherulites. SEM photomicrographs, Sample 139-856H-8R-1, 124–126 cm. The scale bar refers to the left, general view; box shows area of detail enlarged in right photomicrograph. Close-up (right) is enlarged 5.5×).

plates are most common. Pyrite forms rare euhedral crystals, up to 4 mm in size. Small (0.1 to 0.3 mm) anhedral chalcopyrite grains are dispersed in the massive sulfide. Magnetite is scarce in the ore matrix, although it occurs locally, together with pyrite, in thin (0.5 mm) veinlets.

At the bottom of Hole 856H, at about 90 mbsf, two pieces of brecciated sulfide were recovered. This sulfide differs in composition from that typical of zone 4, in that pyrrhotite is partly recrystallized and replaced by pyrite containing fine-grained dispersed magnetite. Pyrite and minor marcasite also overgrow pyrrhotite. Chalcopyrite emulsion textures occur in coarse-grained, recrystallized pyrrhotite. Aragonite, the main gangue mineral, is dispersed in the sulfide and forms, along with calcite, dolomite, and chlorite, thin ramifying veinlets.

Hole 856G

The massive sulfides recovered from the second deepest hole (Hole 856G, to 64 mbsf), differ mainly from those of Hole 856H by the almost complete absence of pyrrhotite. Evidence of the former existence of pyrrhotite is clearest in the upper part of the core, where thin boxwork textures of pyrite, overgrowing and partly replacing dissolved pyrrhotite crystals, can be seen. Two generations of pyrite



Figure 8. Fine-grained pyrrhotite aggregate. Photomicrograph in reflected light, Sample 139-856H-16R-1, 79-81 cm, under crossed nicols.

also are present, similar to those observed in Hole 856H (Fig. 9). Sulfides from the upper part of Hole 856G differ from the corresponding deposits of zone 1 in Hole 856H by containing skeletal magnetite crystals and small quantities (up to 5%) of hematite. Morphologically similar magnetite is present in zone 2 of Hole 856H, which is absent in Hole 856G. Voids and pores between pyrite grains in the lower part of Hole 856G locally contain aggregates of spherulitic talc (Fig. 10). Sphalerite and magnetite are less evenly distributed in the upper part of Hole 856G than in zone 1 of Hole 856H.

In spite of these differences, massive sulfides in the upper part of Hole 856G to about 40 mbsf share the most characteristic feature of zone 1 in Hole 856H, the presence of pyrite with tiny oriented magnetite intergrowths. This distinctive feature makes correlation between the two holes possible. Massive sulfides from the lower part of Hole 856G therefore clearly correlate with those of zone 3 in Hole 856H.

Holes 856C through 856F

Massive sulfides from the shallower Holes 856C, 856D, 856E, and 856F were completely destroyed during drilling. On the whole they correspond to the upper part of zone 1 in Hole 856H. Two sulfide varieties can be distinguished: silica-rich (more than 20% SiO₂), and relatively silica-poor. The silica-rich sulfides contain round, roseshaped pyrite aggregates that are generally similar to those in the sands of Hole 856H, and are evenly dispersed in the siliceous matrix. The relatively silica-poor ores are similar to those in large clasts from the upper part of Hole 856H, where pyrite replaces tabular crystals of pyrrhotite, forming boxwork textures.

Sulfide clasts, discovered in sediments from Hole 856B between 18.4 and 24.2 mbsf, consist almost entirely of pyrite. Colloform, banded, and network structures are typical.

ANALYTICAL RESULTS

Chemical Composition of the Cores

Table 5 gives the results of bulk chemical analyses of sulfides from Site 856, and Table 6 gives summary statistics, along with comparative data from other locations. The two elements that dominate the composition of the sulfide deposit, Fe and S, are distributed normally; other elements are distributed log-normally. In plotting element distribution with depth (Fig. 11), we have to consider drilling disturbances in the uppermost parts of the holes. The evident sorting of sulfides according to grain size along the length of cores may have influenced the distribution of elements. Therefore, in Figure 11 we plot average element concentrations between pairs of samples representing the bottom and



0.1 mm

Figure 9. Two generations of pyrite (Py): early anhedral pyrite, totally replacing pyrrhotite, with tiny magnetite (Mt) intergrowths (gray) on the right, and later subhedral pyrite, without magnetite, on the left. Photomicrograph in reflected light, Sample 139-856G-4R-1, 75–77 cm.

top parts of the disturbed cores, instead of data from each of these samples. Analytical values corresponding to the middle parts of the disturbed cores are plotted individually for each sample. We presume that this method of data presentation gives a more realistic trend of element distribution in massive sulfides that were disintegrated and sorted during the course of drilling.

The vertical profile of the deepest hole (856H) is characterized by a nonuniform distribution of most elements. Only several of the elements show general trends throughout the cored section. Concentrations of Fe, Co, and Bi tend to increase downhole; Zn, Mn, Cd, Sn, Ta, and Mg increase uphole. Zn, Sn, and Ta concentrations increase abruptly in the uppermost part of the deposit. All of the other elements reveal a more complex behavior with depth in the sulfide deposit (Fig. 11, Table 5).

Changes in elemental concentrations from zone to zone, compared to average values, are described as follows.

Zone 1 is distinguished, along with relatively low Fe values in the sulfides, by variably high concentrations of many elements. In most samples throughout the zone, Zn, Cd, Mn, Se, Sn, and Al contents are high. Some samples from the zone are rich in Si, Cr, Cs, and Ni, and several are significantly enriched in V and Sc.

On the basis of the geochemical data, we divided zone 1 into two parts: the upper 1A and the lower 1B (Fig. 1). Many elements have distinctly different concentrations in the upper and lower parts of zone 1. In the upper part, to approximately 18 mbsf, Fe values are the lowest of the entire hole. Cu content is also low. Concentrations of Zn, Al, Mg, Si, Au, Ba, Sb, Sn, Sr, Ta, Tl, La, Sm, and Tb are at a maximum here. Ag, As, Mn, Mo, and Ni concentrations are highly variable, but in individual samples they also reach maximum values for the entire hole. The lower part of zone 1 is marked by increased concentrations of Cu and Se and low Au, As, and Sb. The peak in Cu concentration in the lower part of zone 1 is based on only three analyses (Fig. 11), but its existence is confirmed by the results of study aboard ship (Shipboard Scientific Party, 1992). Ca and Mg are enriched, due to the abundance of dolomite.

Zone 2 is characterized by relatively high Fe concentrations. Cu is low, and Zn is enriched in one sample from the upper part of the zone. Also relatively high in most samples are Mn and Se, whereas Pb, Bi, Co, Ge, Sn, and U contents are low compared to the average values for the deposit. Of the main gangue mineral elements, Al and Mg concentrations are higher than those in lower zone 3 due to the presence of chlorite.

Zone 3, which is dominated by pyrite, contains more S than any other zone. Its most characteristic features are very high concentra-



Figure 10. Talc spherulites from a cavity in massive sulfides. SEM photomicrograph, Sample 139-856G-6R-3, 95–97 cm.

tions of Pb, As, Sb, Ge, and Tl relative to those in the adjacent zone 2 and especially in zone 4. Concentrations of Pb and Ge are maxima for the entire hole. Co content increases downward within zone 3. Au shows relatively high, though variable, concentrations compared to adjacent zones. All gangue mineral elements are low, except for enrichment of Si and Mg in the lowermost sample, which contains significant amounts of talc, and of Ba in the uppermost sample. At the lower boundary of zone 3, Sb, As, Ge, and Tl concentrations decrease abruptly.

Zone 4 is characterized by relatively low S and high Fe contents, owing to the dominance of pyrrhotite. Of the other elements, only Cu, Co, and Bi show high concentrations. As, Au, Sb, Ag, Hg, and Pb values are low. The concentrations of all gangue mineral elements except Al are also low.

Not all features of the element distribution in Hole 856G are repeated in Hole 856H. Although enrichment of the upper cores in Ba, As, Au, Mn, Sb, Se, Sn, and Ta relative to the rest of the cores is evident (Fig. 11), no enrichment in Zn, Cd, Si, and Al can be seen. This may be attributed to the aforementioned uneven distribution of sphalerite, as well as that of the gangue minerals, in the upper part of Hole 856G. Element concentrations in the shallower Holes 856C, 856D, 856E, and 856F also display maximum enrichment of the uppermost part of the deposit (corresponding to subzone 1A) in Zn and most of the minor elements.

Based on the average data of Davis et al. (1987) and Goodfellow and Blaise (1988), the surficial part of the same deposit that was sampled before drilling by conventional methods (Table 6) corresponds in chemical composition to that shown by the uppermost part of the cores (subzone 1A).

REE Distribution

Figure 12 shows chondrite-normalized patterns for rare earth elements (REE), averaged for each of the four compositional zones recognized in Hole 856H. For comparison, similar patterns for massive sulfides from of the East Pacific Rise (EPR) and Mid-Atlantic Ridge (MAR), based on previous data of the authors (Krasnov et al., 1992), are also shown. In the upper part of the sulfide deposit, in zones 1 and 2, light rare earth elements (LREE) and intermediate REEs are enriched slightly over heavy rare earth elements (HREE). There are no Eu anomalies. The average Eu/Sm ratio is 0.95. Lower in Hole 856H, in pyrite ores of zone 3, abundances of LREEs do not exceed those of HREEs, and there is a well-pronounced positive Eu anomaly. The average Eu/Sm ratio is 1.72. Pyrrhotite-rich massive sulfide in the lowermost part of Hole 856H (zone 4) also lacks a Eu anomaly. The Eu/Sm ratio is 0.78. Table 5. Element concentrations in bulk sulfide samples from Site 856.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Core, section,	Depth (mbsf)	Description	Fe (%)	Zn	Cu (ppm)	CaO	MgO (ppm)	Mn (nom)	S (%)	SiO ₂	Al ₂ O ₃	Cd (npm)	Au (pph)	Ag (nnm)	As (ppm)	Sb (nom)	Co (ppm)
139-550- 394-5,110-113 18.40 Sulfide clasts from sedimens 45.55 0.76 0.12 0.13 0.53 70 50.94 1.12 0.16 27 170 50 180 6.0 139-550C- 11H-1, 48-50 0.48 Sulfide-clasts 41.48 5.60 0.50 0.10 0.13 460 39.68 3.80 0.62 67 145 2.0 40 17.0 4.0 11H-1, 99-100 11H-1, 99-102 0.99 Sulfide-silicac clasts 23.38 3.53 0.27 0.11 5.01 20 7.47 3.00 0.45 48 64 160 2.0 40 17.0 4.0 11H-4, 62-64 2.14 Sulfide-silicac clasts 22.33 2.23 3.32 0.21 0.16 0.06 0.04 94 n.a.	interval (em)	(most)	Description	(70)	(ppm)	(ppm)	(ppm)	(ppin)	(ppm)	(70)	(10)	(70)	(ppm)	(ppu)	(ppm)	(ppin)	(ppin)	(ppm)
$\begin{array}{c} 1375, 1107-15 10805 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	139-856B- 3H-5_110_113	18/40	Sulfide claste from codimente	15 55	0.76	0.12	0.12	0.52	70	50.04	1.12	0.16	27	170	5.0	180	13.0	60
	511-5, 110-115	10.40	Sumue clasis from sediments	45.55	0.70	0.12	0.15	0.55	/0	50.94	1.12	0.10	21	170	5.0	100	1.5.0	0.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	139-856C-	0.49	Sulfida elaste	41.49	5.60	0.50	0.10	0.12	160	20.68	2.80	0.62	67	145	20	33	40	21
$ \begin{array}{ 199-102 \\ 141, 99-102 \\ 142, 94-60 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-67 \\ 142, 64-87 \\ 142,$	111-1, 40-50	0.40	Sumue clasis	41.40	5.00	0.50	0.10	0.15	400	39.00	3.00	0.02	07	145	2.0	55	4.0	2.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	139-856D-	0.00	Culfide alliente electe	22.08	4.05	0.21	0.00	10.05	220	20.12	24.00	0.26	64	160	2.0	40	17.0	4.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1H-1, 99-102 1H-2 64-67	2 14	Sulfide-silicate clasts	23.98	4.05	0.21	0.09	5 01	220	28.13	24.00	0.36	54	160	3.0	30	13.0	4.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1H-4, 62-64	5.12	Sulfide-silica clasts	16.28	3.11	0.16	0.10	4.07	120	18.70	47.80	< 0.01	30	15	<1.0	5	2.0	3.6
	1H-5, 113-116	7.13	Sulfide-silicate clasts	24.32	3.32	0.25	0.11	7.01	180	27.69	30.50	0.26	44	175	<1.0	28	3.2	8.0
	139-856E-																	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1H-1, 106-108	1.06	Sulfide clasts	32.20	17.40	0.91	0.15	0.17	1000	37.61	0.06	0.04	954	n.a.	n.a.	n.a.	n.a.	n.a.
	1H-2, 84-86	2.34	Sulfide clasts	44.80	1.11	0.18	0.15	0.21	730	50.21	0.36	n.a.	34	82	5.0	52	6.8	1.0
$ \begin{array}{c} 2X-CC, 1-3 & 11.7 \\ Suffide-silica clasts & 17.50 & 1.09 & 0.10 & 0.20 & 0.72 & 33 & 21.20 \\ SLGC, 3-24 & 12.02 \\ SUffide clasts & 34.30 & 1.15 & 0.22 \\ ILS & 7.35 & 330 & 28.20 & 9.44 & 0.14 \\ ST & 1.45 & 14.7 \\ IR-1, 145-147 & 1.45 \\ Suffide-silicat clast & 43.40 & 0.10 & 0.48 \\ IR-4, 42.44 & 4.22 \\ Suffide-silicat clast & 19.78 \\ IR-4, 42.44 & 4.22 \\ Suffide-silicat clast & 19.78 \\ IR-4, 15.7 & 9.7 \\ Suffide-silicat clast & 19.78 \\ IR-4, 15.7 & 11.89 \\ Suffide-silicat clast & 19.78 \\ IR-4, 15.7 & 11.89 \\ Suffide-silicat clast & 19.78 \\ IR-4, 15.7 & 11.89 \\ Suffide-silicat clast & 19.78 \\ IR-4, 15.7 & 11.89 \\ Suffide-silicat clast & 19.78 \\ IR-4, 12.44 \\ IR-4, 12.47 \\ I$	139-856F-		1970291 min - 5	12-20-						1000			221	12212	1.00		1418	12.12
$\begin{array}{c} 2A-C, 32-3 & 12.02 \\ 139-856C \\ 1100 $	2X-CC, 1-3	11.71	Sulfide-silica clasts	17.50	1.09	0.10	0.20	0.72	30	21.20	55.16	0.10	30	110	2.0	34	3.6	3.2
$ \begin{array}{l} 139:856G-\\ 184:145-147 & 1.45 \\ 147:42-44 & 4.92 \\ 184:142-44 & 4.92 \\ 184:142-44 & 4.92 \\ 184:142-44 & 4.92 \\ 184:142-148 & 4.92 \\ 184:142-148 & 4.92 \\ 184:142-148 & 4.92 \\ 184:142-148 & 4.92 \\ 184:142-148 & 4.92 \\ 184:142-148 & 5.92 \\ 184:142-148 & 5.94 \\ 184:142-144 & 5.94 \\ 184:144-144 & 5.94 \\ 184:144-144 & 5.$	2A-CC, 32-34	12.02	Suinde clasts	34.30	1.15	0.22	1.15	1.35	330	28.20	9.44	0.14	37	108	4.0	<1	0.0	9.0
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	139-856G-				220022			Sectors 1	100-00			140-1508-01			-			-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	IR-1, 145–147	1.45	Sulfide clasts	43.40	0.10	0.48	0.09	0.24	680	50.61	1.00	0.42	<10	44	7.0	110	13.0	14.0
$\begin{array}{c} 2R+3, (29-3) \\ 2R+3, (29-3) \\ 2R+3, (29-3) \\ 11.89 \\ 3R+1, (61-64) \\ 15.24 \\ Sulfide sand \\ 23.80 \\ 0.82 \\ 0.23 \\ 0.82 \\ 0.23 \\ 0.25 \\ 0.23 \\ 0.25 \\ 0.23 \\ 0.25 \\ 0.28 \\ $	1R-4, 42-44 2P 1 67 60	4.92	Sulfide sand	41.93	0.30	0.40	0.09	0.55	630	50.35	1.80	0.44	13	120	8.0	98	10.0	10.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2R-3, 29-31	11.89	Sulfide clasts	41 50	0.92	0.25	0.22	0.22	1600	52 63	0.40	< 0.01	<10	290	18.0	35	11.0	3.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2R-5, 64-66	15.24	Sulfide sand	23.80	0.82	0.23	0.25	9.88	530	28.90	4.60	0.26	19	260	3.0	165	13.0	5.8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3R-1, 61-64	18.21	Massive sulfide	45.55	0.50	0.71	0.35	2.90	540	35.11	3.32	0.26	<10	23	3.9	7	1.7	9.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4R-1, 49-51	27.49	Massive sulfide	42.70	1.53	0.74	0.25	2.27	130	40.57	5.26	0.06	37	60	4.3	48	3.2	8.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4R-1, 75-77	27.75	Massive sulfide	46.20	0.29	0.29	0.35	3.25	290	35.40	1.80	0.14	<10	35	1.5	9	0.8	24.0
$\begin{array}{c} 6r.3, 95-7 \\ 50.25 \\ 7R-1, 38-40 \\ 56.18 \\ Porous massive sulfide \\ 43.40 \\ 1.08 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.20 \\ 2.50 \\ 60 \\ 50.09 \\ 3.10 \\ 0.16 \\ 1.0 $	5R-1, 47-49	37.17	Massive sulfide	36.40	0.06	0.22	0.20	9.20	90	35.07	7.70	0.04	<10	12	1.0	93	0.3	6.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6R-2, 101-103	48.81	Porous massive sulfide	43.40	1.08	0.06	0.20	1.12	170	50.49	2.38	0.12	-10	50	2.0	20	0.5	2.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7R-1 38-40	56.18	Porous massive sulfide	44.00	0.04	0.02	0.20	2.50	50	50.00	3.10	0.16	13	44	5.5	60	14	83.0
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	7R-4, 67-69	60.77	Porous massive sulfide	43.40	0.08	0.41	0.10	1.97	<20	49.11	2.64	0.16	<10	64	4.7	140	1.6	23.0
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	139-856H-																	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1R-1, 108-110	1.08	Sulfide-silicate clasts	31.70	0.65	0.41	0.66	1.04	2000	28.83	14.40	20.00	46	110	3.0	280	13.0	20.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1R-2, 4-7	1.54	Sulfide sand	28.60	2.31	0.18	0.64	7.18	350	34.30	18.90	< 0.01	32	156	4.0	50	7.8	5.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1R-3, 59-62	3.59	Sulfide sand	29.57	2.04	0.16	0.41	6.41	330	37.22	17.50	0.26	27	130	3.0	74	8.6	6.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	IR-CC, 3-5	3.96	Sulfide clasts	35.52	10.00	0.40	0.10	0.73	1400	45.90	1.60	0.58	71	250	10.0	66	13.0	5.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2R-1, 8-10 3P-1 34 37	22.44	Massive sulfide	29.40	4.02	0.23	4.20	9.40	010	24.52	8.02	0.30	98	13	<1.0	<1	0.7	3.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3R-2, 67-70	23.93	Massive sulfide	39.90	1.51	1.48	4.30	6.20	210	28.15	4 26	1.08	44	42	3.0	<1	0.7	54.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3R-3, 14-16	24.85	Massive sulfide	43.75	3.21	0.65	1.25	2.23	150	35.66	1.68	0.64	108	8	5.5	7	0.4	24.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4R-1, 18-20	26.78	Sulfide in altered sediment	38.50	0.77	0.28	3.60	6.20	400	28.68	7.24	1.88	24	22	1.7	4	0.7	14.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4R-2, 144-146	29.54	Massive sulfide	58.10	0.54	0.34	0.20	0.13	30	35.85	0.10	0.16	17	8	2.6	<1	0.1	84.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5R-1, 52-53	32.92	Massive sulfide	49.35	4.28	0.21	0.50	0.62	260	38.55	0.62	0.16	129	11	3.2	6	0.5	7.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6R-1, 24-26	37.64	Massive sulfide	46.55	0.27	0.13	0.25	2.92	260	33.14	8.12	0.36	20	32	1.0	74	5.5	14.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	/R-1, 80-82 8D 1 124 126	43.90	Massive sulfide	38.85	0.12	0.10	5.55	3.77	230	39.84	1.80	0.12	<10	52	2.8	12	0.5	13.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9R-1 80_82	53 30	Porous massive sulfide	41.50	0.42	0.51	0.25	0.54	20	52 56	0.70	0.02	<10	24	2.8	53	30	40.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10R-1, 13-15	57.13	Porous massive sulfide	44.45	0.25	0.58	0.10	0.17	50	51.14	1.50	0.08	<10	36	3.9	67	3.6	56.0
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	11R-1, 49-51	61.79	Porous massive sulfide	44.80	0.08	0.40	0.10	1.52	n.a.	52.97	1.68	0.04	<10	99	3.4	94	3.7	130.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13R-1, 48-49	71.38	Sulfide-talcose aggregate	33.60	0.04	0.91	0.20	10.00	140	30.81	20.06	0.02	<10	36	2.5	80	4.1	380.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	14R-1, 4-6	75.74	Massive sulfide	52.15	0.41	0.91	0.10	0.83	20	35.12	0.84	0.08	<10	22	2.7	2	0.2	210.0
108 + 1, 7 - 51 = 52.59 massive summe $52.50 = 0.09 = 1.74 = 0.13 = 0.29 < 20 = 37.41 = 0.30 = 0.12 < 10 = 14 = 2.7 < 1 = 0.2 = 190.0 = 178.13 = 3.36 = 9.045 Sufficient between 23.36 = 0.045 Sufficient betw$	15R-1, 60-62	81.10	Massive sulfide	52.85	0.23	0.43	0.75	1.95	90	35.18	2.14	0.58	<10	7	2.0	<1	0.2	60.0
	17R-1, 79-81	90.45	Sulfide breccia	29.40	0.09	0.21	5.00	2.87	<20	31.41	4.24	1.24	<10	12	1.6	<1	0.2	100.0

Element Associations in Sulfides

Linear correlation analysis was used to study the relations among elements in massive sulfide samples. The results are given in Table 7. Figure 13A shows the main positive correlations. For comparison, a similar scheme is also given, based on geochemical data (Krasnov et al., 1992) for samples of massive sulfides from several sites at sediment-free mid-oceanic ridges (Fig. 13B).

Massive sulfides from the studied cores show rather weak correlations among the elements. The main ore-forming metals have few significant correlations. Fe correlates only with S (group 1, Fig. 13A) and slightly with Cu. Cu forms a separate group (2) with two strongly correlated metals that enrich the pyrrhotite ores of the lowermost part of Hole 856H (zone 4): Co and Bi.

Zn shows the strongest correlations with Cd and Pb (group 3), typical of all oceanic massive sulfides. Zn, however, differs in its behavior in the sulfides at Site 856 relative to those of sediment-free ridges because it is not correlated with Ag nor with elements such as Ba and As that are characteristic of low-temperature surficial facies of oceanic sulfide bodies.

Ba and Sr tend to form their own small element group (4). This group is associated through the usual Ba-Sb correlation with the most

dense association of elements (group 5), including Sb, Sn, Mn, Ag, Au, As, Mo, and Tl. All of these elements are enriched in the surficial part of the deposit. They are, however, neither directly related to zinc sulfides nor to the main gangue minerals.

Three additional geochemical groups (6, 7, and 8) are associated with different gangue minerals that are also enriched in the upper part of the ore body. The Al-related group (6), including most of the lithophile elements, is the largest and most tightly associated through the Mn-Al correlation with group 5. Si (with Ta and Hg) and Ca (with V) form separate groups (7 and 8, respectively).

MINERAL CHEMISTRY

Microprobe Analyses

Results of microprobe analyses of minerals are shown in Tables 8 through 10. Iron concentrations in sphalerites (Table 8) are mostly in the range of 11 to 16 wt% Fe. The only sphalerite grain analyzed from almost pure pyritic massive sulfide of zone 3 (Sample 139-856G-6R-2, 101–103 cm) has a much lower Fe content (4.8 wt%) than sphalerites from the other zones. Among the analyzed pyrites (Table 9), varieties from magnetite-bearing zones are mostly Fe-deficient in comparison to their theoretical compositions. Iron concentrations are

Table 5 (continued).

interval (cm) (ppm) (ppm	(ppm) (j <1.0 <1.0 12.0 <1.0 270.0 20.0	ppm) 17.0 30.0 70.0 58.0
139-856B- 3H-5, 110-113 27 n.a. 85.0 <100 0.55 290 0.23 <0.05 0.3 2.6 <10.0 100 <0.5 n.a. 0.62 0.23 n.a. 0.27 5.1 139-856C-	<1.0 <1.0 12.0 <1.0 270.0 20.0	17.0 30.0 70.0 58.0
3H-5, 110-113 27 n.a. 85.0 <100 0.55 290 0.23 <0.05 0.3 2.6 <10.0 100 <0.5 n.a. 0.62 0.23 n.a. 0.27 5.139-856C-	<1.0 <1.0 12.0 <1.0 270.0 20.0	17.0 30.0 70.0 58.0
139-856C-	<1.0 12.0 <1.0 270.0 20.0	30.0 70.0 58.0
	<1.0 <1.0 270.0 20.0	70.0 58.0
1H-1, 48-50 10 0.82 12.0 130 0.30 250 0.48 0.32 0.2 3.0 13.0 300 3.1 n.a. 0.25 0.14 0.26 1.00 160.0	12.0 <1.0 270.0 20.0	70.0 58.0
139-856D- 181-192-102 66 0.54 200 460 0.82 1000 1.60 110 0.2 100 210 100 20 27 3.40 0.07 0.13 0.55 27	<1.0 270.0 20.0	58.0
11+2, 6+67 60 0.19 19.0 620 0.56 21000 1.60 1.0 0.3 10.0 51.0 100 2.9 5.7 5.40 0.97 0.15 0.53 2.71 11+2.64-67 60 0.19 19.0 620 0.56 21000 2.60 2.00 0.2 19.0 40.0 840 1.7 0.8 2.70 0.68 0.90 1.10 3.8	270.0 20.0	
1H-4, 62-64 10 0.17 10.0 150 0.12 <50 0.52 3.60 0.1 1.3 <10.0 300 3.6 0.6 0.45 0.45 0.20 0.43 1154	20.0	9.0
1H-5, 113-116 20 0.32 36.0 330 0.20 510 0.35 0.92 0.2 5.0 <10.0 200 2.4 3.0 1.30 0.15 0.10 0.38 58.0		1.0
139-856	101	04.0
11+1,100-108 n.a. n.a. n.a. n.a. n.a. 50 n.a. n.a. n.a. n.a. n.a. 100 n.a. n.a. n.a. n.a. n.a. n.a. n.a. n.	n.a. 7.0	13.6
130.956E		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.0	26.0
2X-CC, 32-34 <6 0.52 18.0 100 0.27 <50 0.83 0.16 <0.1 4.5 14.0 200 1.5 n.a. 1.50 0.22 n.a. n.a. 68.0	<1.0	13.0
139-856G-		
1R-1,145-147 30 0.20 28.0 250 0.20 2200 1.10 0.62 0.2 2.3 20.0 <100 1.3 5.9 2.30 0.37 n.a. 0.13 94.0 12 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.	<1.0	62.0
$10^{-4}, 42^{-4+4}$ 24 <0.10 5.10 4.50 0.55 0.200 0.80 1.50 0.2 20.0 <10.0 3.00 5.4 n.a. n.a. 0.21 0.20 n.a. n.a. n.a. 1.2 21 0.20 n.a. n.a. 1.a. 1.2 21 0.20 n.a. n.a. 1.2 22 $= 12^{-1}, 62^{-5},$	13.0	62.0
2R-3, 29-31 28 0.16 35.0 100 0.34 180 0.60 1.00 0.2 7.0 <10.0 100 1.2 n.a. 0.82 0.06 0.10 0.23 18.0	n.a.	4.6
2R-5, 64-66 <6 <0.10 14.0 220 0.22 7700 n.a. 0.74 0.2 26.0 22.0 200 2.7 n.a. n.a. 0.44 0.12 0.14 42.4	2.0	42.0
3R-1, 61-64 10 0.80 30.0 190 0.40 290 0.90 <0.05 0.4 8.2 16.0 200 2.0 n.a. 1.70 0.40 0.45 1.20 390	n.a.	27.0
$4R_{-1}, 49=31$ < < < < 10 < 10.0 < 13.0 < 44 < 0.00 < 200 < 0.70 < 0.00 < 0.2 < 3.5 < 10.0 < 200 < 0.5 < 3.0 < 0.40 < n.a. n.a. 30.0 (3.0 < 13.0 (3.0) 15.0 (9.0 0.41) 18.0 (5.0 (5.0) 10.5 (5.0) 10.0 (5.0) 13.0 (3.0) 13.0 (3.0) 15.0 (3.0) 15.0 (3.0) 15.0 (4.1) 18.0 (5.0) 10.5 (3.0) 10.0 (3.0) 10.0 (3.0) 10.0 (3.0) 10.0 (4.1) 10.0 (5.0) 10.0 (4.1) 10.0 (5.0) 10.0 (5.	14.0	19.0
5R-1,47-49 80 0.50 <5.0 210 0.23 260 1.50 0.12 0.3 3.8 22.0 200 0.7 4.0 0.90 0.90 0.36 0.70 17.4	49.0	7.6
6R-2, 101-103 24 0.50 15.0 80 0.30 205 0.80 <0.05 0.7 1.2 n.a. 200 0.9 14.0 n.a. 0.60 0.40 2.40 3.4	n.a.	17.0
6R-3,95-97 28 1.00 30.0 340 0.60 120 2.20 0.50 0.9 1.6 43.0 200 2.1 20.0 n.a. 0.70 0.30 3.40 3.	20.0	48.0
78-4, 67-69 17 0.20 10.0 90 0.60 37 0.00 0.05 0.5 5.5 43.0 200 1.2 17.0 0.90 1.20 1.20 1.20 1.20 1.20 1.20 1.20 1.2	8.0	12.0
130-856H-		
1R-1, 108-110 110 3.10 63.0 120 0.94 2970 0.90 0.66 1.1 4.3 18.0 300 7.4 5.0 3.60 0.86 0.67 1.50 58.4	n.a.	7.0
1R-2, 4-7 <6 0.18 36.0 260 0.80 10000 0.90 1.20 0.4 8.2 18.0 500 2.1 5.9 0.51 0.24 0.14 0.43 50.0	7.0	28.0
1R-3,59-62 32 0.13 80.0 260 0.39 7800 2.90 1.50 0.5 5.0 23.0 400 0.5 3.9 1.30 0.10 0.58 1.50 48.	n.a.	30.0
16 - 0.5 = 58 0.55 50.0 150 0.78 5100 1.10 0.82 <0.1 6.0 <10.0 500 5.7 9.0 2.50 0.44 0.50 0.70 154 28-18 10 30 0.80 200 210 110 550 140 0.05 0.4 40 pp 200 0.8 140 0.90 0.20 0.18 0.80 300	18.0	12.0
3R-1,34-37 13 0.30 28.0 320 0.20 n.a. 2.20 0.05 0.3 2.0 2.40 200 2.0 8.0 0.50 0.30 n.a. 0.70 91.0	39.0	6.8
3R-2,67-70 80 1.90 <5.0 n.a. 0.28 <50 0.92 0.12 0.2 2.0 <10.0 300 <0.5 6.5 0.79 0.20 n.a. 0.34 100.0	37.0	10.0
3R-3, 14-16 83 1.10 57.0 400 1.10 610 1.40 0.14 0.5 5.5 28.0 200 1.6 13.0 1.70 0.60 0.49 1.30 53.0 40 1.40 1.40 0.44 0.5 5.5 28.0 200 1.6 13.0 1.70 0.60 0.49 1.30 53.0 53.0 53.0 55.0 55.0 55.0 55.0 5	n.a.	12.0
$4R_{-1}$ $16-20$ 17 1.90 20.0 150 <0.10 210 1.50 0.11 1.1 2.0 25.0 200 0.9 14.0 0.70 0.30 0.21 0.80 50.4 4R-2 142-146 37 0.90 360 69 0.30 220 <0.10 0.05 0.5 40 470 100 ns 50 0.20 0.30 ns ns 32	28.0	17.0
5R-1,52-53 14 0.70 <5.0 120 0.20 300 2.40 0.07 0.2 2.5 2.00 200 1.7 9.0 0.70 0.30 1.12 n.a. 49.0	26.0	6.8
6R-1, 24-26 33 0.60 30.0 140 0.50 2000 <0.10 0.08 0.5 9.0 33.0 200 1.2 44.0 n.a. 0.80 n.a. 1.00 67.	n.a.	46.0
78-1,80-82 17 <0.10 17.0 300 0.25 270 0.90 0.08 0.2 2.5 18.0 200 5.4 4.0 1.40 0.30 0.30 0.40 177	48.0	12.0
36-1, 12-120 51 0.00 19.0 120 0.30 16000 0.90 0.10 0.4 3.8 25.0 440 1.3 9.0 1.40 0.60 n.a. 1.70 11.0 9.0 19.0 9.0 19.0 19.0 19.0 19.0	n.a.	46.0
10R-1, 13-15 17 <0.10 17.0 n.a. 0.58 500 0.80 <0.05 0.4 3.0 44.0 200 0.9 6.0 0.70 0.80 0.20 0.90 13.0	n.a. 1	20.0
11R-1, 49-51 24 0.40 20.0 140 0.20 350 0.80 0.12 0.4 10.0 13.0 100 1.5 2.0 0.90 0.70 0.15 0.40 28.0	37.0	12.0
13B-1, 48-49 25 0.30 <5.0 140 0.56 400 1.20 0.07 0.3 4.8 30.0 100 <0.5 3.0 0.90 0.40 0.40 0.30 46.	n.a.	39.0
148 + 1, 4 - 0 52 0.40 10.0 130 < 0.10 140 1.10 0.07 0.2 2.1 22.0 200 0.9 3.0 0.50 0.50 0.25 0.50 3.1 158 160-62 22 0.60 0.20 0.0 140 1.00 0.08 c.0.1 80 450 200 0.9 2.20 0.00 0.00 0.25 0.50 3.1	0.0	19.0
16R-1, 79-81 51 0.60 28.0 28.0 1.20 210 0.40 <0.05 0.5 9.0 38.0 100 2.0 5.0 1.00 0.40 0.20 0.80 300	n.a.	10.0
17R-1, 35-36 12 1.20 26.0 100 0.18 370 1.80 0.08 0.4 6.0 23.0 300 0.8 n.a. 1.40 0.30 0.18 1.00 96.0	n.a.	42.0

higher in the cores of pyrite grains than in the rims of the same grains. Cu-Fe sulfides are deficient in Cu (Table 10).

Neutron Activation Analyses

Table 11 presents the results of neutron activation analyses of sulfide minerals hand-picked from samples of massive sulfide. Comparative data on the chemical composition of minerals from oceanic sulfide deposits of other regions (EPR and MAR) are also included. It was possible to separate only pyrite without visible contamination from most of the samples. We also managed to pick sphalerite and pyrrhotite out of one of the samples from zone 2 in Hole 856H.

Sphalerite is richer in minor elements relative to other minerals of the sulfide deposit. In Sample 139-856H-5R-1, 52–53 cm, from which different minerals were analyzed, most of the elements reach their maximum concentrations in sphalerite. One exception is Co, which is preferentially enriched in pyrrhotite. This is consistent with Co enrichment in bulk samples of pyrrhotitic sulfide from zone 4 in Hole 856H. Also enriched in pyrrhotite, compared to other minerals, are Cs, Se, Hg, and Yb. Pyrite is characterized by maximum concentrations of U and Sm, relative to other sulfides.

DISCUSSION

Comparison of Chemical Composition with Other Seafloor Sulfide Deposits

The average chemical data from Site 856 cannot be directly compared with data for other oceanic massive sulfide deposits that were sampled only from the surface. The sharp downward decrease in concentrations of most elements in the Middle Valley cores is the main reason that the averages for Zn, Cu, and most of the minor elements are low (Table 6). Most of the gangue-related elements have the same range of concentrations as those of other seafloor deposits. Mg and Ca are higher than in most of the deposits, however. Guaymas Basin in the Gulf of California, where massive sulfides also overlie sedimentary cover, is the only site for which the published data on these elements are comparable to those for the cores from Middle Valley.

The absence of any significant enrichment of the Middle Valley deposit in elements common to oceanic massive sulfides from sedimentary environments, such as Pb, As, and Sb, is especially noteworthy. This absence of sediment-derived elements holds true even for the surficial part of the deposit, where element concentrations increase.

Table 5 (continued).

Core, section,	Ti	Pb	Sn	Bi	Ge	TI	v	Li
interval (cm)	(ppm)							
139-856B-								
3H-5, 110-113	22	120	20.0	< 0.5	15.0	5.1	<5	<30
139-856C-								
1H-1, 48-50	43	534	5.4	0.9	<1.0	1.0	<5	<30
139-856D-								
1H-1, 99-102	12	132	53.0	1.2	4.0	3.1	<5	40
1H-2, 64-67	17	74	46.0	1.1	4.0	3.7	<5	<30
1H-4, 62-64	34	34	14.0	1.1	<1.0	1.6	<5	30
1H-5, 113–116	8	60	7.8	2.0	<1.0	4.0	<5	40
139-856-								
1H-1, 106-108	83	98	100.0	< 0.5	9.0	9.2	11	<30
1H-2, 84-86	22	170	27.0	< 0.5	9.0	5.5	14	<30
139-856F-								
2X-CC, 1-3	36	<10	15.0	0.7	1.0	3.0	<5	<30
2X-CC, 32-34	42	54	5.6	1.0	2.5	2.0	<5	<30
139-856G-								
1R-1, 145-147	30	136	48.0	1.5	1.0	7.3	<5	<30
IR-4, 42-44	16	210	28.0	< 0.5	<1.0	4.9	<5	<30
2R-1, 67-69	9	100	22.0	1.2	3.0	5.0	<5	40
2R-3, 29–31	<1	20	45.0	< 0.5	<1.0	4.0	<5	<30
2R-5, 64-66	11	118	26.0	1.6	2.0	9.2	<5	40
3R-1, 61-64	46	66	12.0	1.8	3.4	2.2	10	<30
4R-1, 49-51	44	92	23.0	2.2	<1.0	<1.0	<5	<30
4R-1, 75-77	75	61	6.0	1.0	<1.0	<1.0	<5	<30
5R-1, 47-49	350	<10	5.0	0.5	<1.0	<1.0	<5	<30
6R-2, 101-103	40	120	5.8	<0.5	20.0	7.9	<>	<30
0R-3, 95-97	44	15	3.0	<0.5	8.2	14.0	0	<30
7R-1, 38-40 7R-4, 67-69	180	130	5.0	2.0	9.3	4.5	<0	<30
100 0000	100		0.0		10.0			
139-856H-	102	20	25.0	0.5		10.0	2	20
IR-1, 108-110	103	30	26.0	<0.5	1.0	10.0	<>	<30
IR-2, 4-1	8	620	20.0	1.9	5.0	0.1	<0	<30
IR-5, 59-62	20	154	14.0	<0.5	<1.0	0./	<0	<30
2P 1 8 10	29	5400	21.0	1.1	5.0	0.0	5	<30
2R-1, 0-10 3P 1 34 37	22	37	15.0	1.0	<1.0	<1.0	5	<30
3P-2 67-70	110	12	15.0	1.0	<1.0	<1.0	19	<30
3R-2, 07-70	56	25	10.0	2.2	<1.0	<1.0	11	<30
4R-1 18-20	120	-10	0.1	31	<1.0	<1.0	14	<30
4R-7 144-146	32	<10	4.0	2.5	<1.0	<1.0	-5	<30
5R-1 52-53	46	<10	4.0	1.0	<1.0	<1.0	-5	<30
6R-1. 24-26	50	<10	5.5	0.8	<1.0	2.8	<5	<30
7R-1 80-82	50	26	5.0	13	<1.0	43	<5	<30
8R-1, 124-126	16	110	6.5	23	16.0	5.5	5	<30
9R-1, 80-82	120	130	5.9	<0.5	12.0	7.4	<5	<30
10R-1, 13-15	24	100	6.0	<0.5	11.0	6.7	<5	<30
11R-1, 49-51	120	58	8.3	6.2	14.0	5.5	<5	<30
13R-1, 48-49	42	100	10.0	12.0	9.0	<1.0	<5	<30
14R-1, 4-6	48	29	7.6	12.0	<1.0	<1.0	<5	<30
15R-1, 60-62	140	58	5.5	5.5	<1.0	<1.0	12	<30
16R-1, 79-81	22	<10	5.7	9.5	<1.0	<1.0	<5	<30
17R-1, 35-36	100	<10	5.0	10.0	3.0	<1.0	11	<30

Note: n.a. = not analyzed.

The evident diversity in geochemical associations between the drilled deposit and previously studied sulfide deposits of sediment-free ridge crests (Fig. 13) may be easily attributed to the change from the surface collection of samples to vertical coring. In oceanic sulfides from sediment-free ridges (Fig. 13B), sampled by conventional methods, the main gangue-mineral elements do not form separate groups, but enter, along with Zn, a single large association corresponding to relatively low-temperature surficial parts of deposits. Thus, in the Middle Valley sulfides, elements can be divided into more groups than in the sulfides of sediment-free ridges.

Ore aggregates belonging to the two main types commonly are sampled from the surficial parts of deposits in sediment-free environments. Cu-enriched aggregates come from high-temperature chimneys and from some central parts of mature sulfide mounds (Krasnov et al., 1992). In contrast, aggregates enriched in Zn and gangue minerals belong to moderate-temperature chimneys and to the peripheral parts of large mounds, such as in the TAG active mound in the Atlantic (Lisitzin et al., 1990). In the Middle Valley deposit, sampled by deep coring, we found a greater variety in the types of sulfide and gangue-mineral aggregates, even in the upper part of the cored holes, which produces the observed diversity of geochemical associations. REE patterns in the upper part of the Middle Valley deposit (Fig. 12) on the whole resemble those of the MAR sulfides from hydrothermal fields at 26°N and 24.5°N (Krasnov et al., 1992). In pyritic sulfides of zone 3 the REE pattern is more similar to those of deposits from the EPR at 13°N.

Iron concentrations in sphalerites from Site 856 (11 to 16 wt% Fe) are lower than the values reported by Koski et al. (1985) for sulfide deposits of Guaymas Basin (15 to 24 wt% Fe). Iron concentrations in sphalerites of massive sulfides sampled from the surface on sediment-free ridges are variable, even within individual deposits. At 44°N on the Juan de Fuca Ridge, the Fe concentrations are between 1 and 17 wt% in type A sulfides and <3 wt% in type B sulfides (Koski et al., 1984). At 13°N on the EPR, Fe concentrations in zinc sulfides vary over a wide range, from low values (2 to 6 mol% FeS) in surficial dendritic aggregates, to 35 mol% FeS in the Cu-enriched inner parts of chimneys (Fouquet et al., 1988). At 21°N on the EPR, the iron contents vary from 2 to 22 wt% Fe at different types of vents (Oudin, 1983).

Sphalerite is depleted in most minor elements relative to sphalerites from other oceanic massive sulfide deposits (Table 11). This tendency is most evident for Au, Ag, As, Sb, and Cr. It corresponds to the general depletion of the cores in minor elements in comparison with other deposits, as observed in the bulk samples (Table 5). The exceptions are U and Ni: their concentrations in sphalerite from the Middle Valley cores are higher than in those from other sites. The pyrites do not exhibit the same tendency, however, as their minor element concentrations are mostly at the same levels shown by pyrites from other regions.

Copper concentrations in Cu-Fe sulfides (32.6 to 34.1 wt% Cu in chalcopyrites and about 23 wt% Cu in isocubanites) are comparable to those in the same minerals from 21°N on the EPR (Oudin, 1983), 13°N on the EPR (Fouquet et al., 1988), and 44°N on the Juan de Fuca Ridge (Koski et al., 1984). Oudin (1983) reported copper concentrations of 31.6 to 33.4 wt% Cu in chalcopyrites and 21.39 to 22.95 wt% Cu in chalcopyrrhotites (isocubanites) from 21°N on the EPR.

Model of Massive Sulfide Formation

No significant amount of sediment was obtained in cores from the sulfide deposit at Site 856, although the core recovery at this site was relatively low (20% and 33% in the two deepest sulfide holes). The absence of sediment throughout the section was confirmed by logging (Shipboard Scientific Party, 1992). Thus, the sulfide body under investigation in this study, like all other sulfide deposits studied previously in the ocean (e.g., Krasnov et al., 1992), must have formed above the seafloor. In Middle Valley, the accumulation of Pleistocene sediments flanking the deposit was concurrent with its growth. However, sulfide deposition could have been interrupted during relatively short episodes. While sulfide formation was interrupted, the surface of the deposit was covered with sediments, represented now by thin, highly altered interlayers.

Evidence of pyrrhotite replacement by pyrite, described herein, shows that pyrrhotite was the main primary mineral of the cored massive sulfides. Duckworth et al. (this volume) arrived at the same conclusion, based on detailed mineralogical investigations. The formation of pyrrhotite instead of pyrite as the main sulfide mineral is typical of oceanic sites of massive sulfide deposition, where solutions pass through sedimentary cover in the course of convective circulation, as at Guaymas Basin in the Gulf of California (Koski et al., 1985), and at Escanaba Trough on the Gorda Ridge (Koski et al., 1988).

It is generally accepted that strongly reducing conditions, with low fO_2 and fS_2 , are needed for the crystallization of pyrrhotite in oceanic hydrothermal systems (Koski et al., 1985, 1988). In black smokers at sediment-free ridges, pyrrhotite appears in certain regions (e.g., at 21°N on the EPR) to be the main constituent of the "smoke," as a fine-grained precipitate formed by crystallization in the solutions within their sub-bottom pathways (Haymon and Kastner, 1981). On sedimented ridges, the additional reduction of hydrothermal solutions

through solution-sediment interaction causes the deposition of large pyrrhotite masses.

The sedimentary pile is usually a sink for the main ore metals and a source for Ca in these environments. In Guaymas Basin, these relationships result in a low percentage of precipitated sulfides, especially Cu and Zn sulfides, in hydrothermal deposits (Koski et al., 1985). In other oceanic sites, as in hydrothermal deposits of Gorda Ridge and the Okinawa Trough, Pb, As, Sb, and Sn are extracted from sediments and enriched in the massive sulfides (Table 6). Some of these metals may form discrete minerals in the sulfide deposits (Koski et al., 1988; Halbach et al., 1989). The structures and textures of pyrrhotite-rich massive sulfides of zone 4 in the lower part of Hole 856H are similar to those previously described from Guaymas Basin (Koski et al., 1985), Gorda Ridge (Koski et al., 1988), and the surficial part of the Middle Valley deposit (Goodfellow and Blaise, 1988). Therefore, the sulfides of zone 4 are interpreted to represent primary aggregates, which, for some reason, escaped the later alteration that affected the rest of the sulfide body.

The Middle Valley deposit differs greatly in its chemical composition from deposits of some other sediment-covered spreading centers, such as Gorda Ridge and the Okinawa Trough (Table 6). At Middle Valley, the sulfide deposits contain only traces of Pb, As, and Sb, which are believed to have been extracted from the sediments by hydrothermal solutions. Concentrations of As and Pb in sulfide deposits of Guaymas Basin are in the same range as those observed in the surficial part of the Middle Valley deposit. It is possible that the temperatures of the hydrothermal solutions that formed the deposit under study were never high enough in the shallow part of the convective system to extract significant amounts of metals from the sediments.

Prominent in the vertical element distribution of the drilled deposit is the enrichment of its upper part (zone 1) in Zn, Si, Al, Ca, Mg, and a wide range of trace metals. Most of these elements (Ag, As, Au, Ba, Mn, Mo, Ni, Sb, Sn, Sr, Ta, Tl, La, Sm, and Tb) reach their maximum values at the top of the deposit, corresponding to subzone 1A of Hole 856H. In contrast, a peak of Cu and Se enrichment is present in the lower part of zone 1 (Fig. 11).

Zn enrichment, characteristic of the uppermost parts of ancient massive sulfide deposits on land, is generally attributed to the zone refining process (Franklin et al., 1981; Eldridge et al., 1983). The inner structure of mature deposits is determined by the progressive upward replacement of lower temperature minerals, including Zn sulfides, by high-temperature Cu and Fe sulfides during growth of the sulfide bodies. In typical ancient deposits, Cu is enriched in the intermediate parts below zones of Zn enrichment; the central parts consist of the highest-temperature, coarse-grained Fe sulfides. Edmond (1980) was the first to discuss the zone refining process in connection with modern oceanic massive sulfide ore formation. Hannington et al. (1986) attributed gold enrichment in the surficial parts of large deposits on the Mid-Atlantic Ridge to the same process.

Zone refining is the most probable origin for Zn-enriched subzone 1A and Cu-enriched subzone 1B of the Middle Valley deposit. The second zone of Cu enrichment, in the lower part of Hole 856H (Fig. 11), may be the result of a decline of hydrothermal activity that led to crystallization of lower-temperature chalcopyrite in interstitial spaces of the earlier-formed, highest-temperature Fe sulfides.

The vertical distribution of trace elements in pyrites (Table 11) is basically similar to that in the bulk sulfides. Thus, the zone refining process was not confined to the low-temperature minerals, which contain most of the trace elements, from lower to upper levels of the deposit. Iron sulfides were also recrystallized, with the trace metals leached from them at lower levels.

Although sphalerite shows maximum enrichment in the majority of minor elements (Table 11), it is not the only (and for some elements, even the main) host. Considering the dominance of iron sulfides in the deposit, iron sulfides should be significant hosts for most of the minor elements. However, the probable existence of small inclusions in the mineral grains limits the use of INAA data to define the actual mineral phases that contain the minor elements.

Almost all of the geochemical correlation groups, shown on Figure 13A, include elements (Fe, Cu, Zn, Ba, Al, Si, and Ca) that evidently form the host minerals for minor elements of the same groups. Group 5, which contains the largest number of elements, including Sb and As, presumably is associated with sulfosalts. Hannington et al. (1986) discovered the important role of sulfosalt minerals in concentrating certain minor elements, including Au, in oceanic massive sulfide deposits.

Secondary Alteration of the Deposit

The main features of the distribution of metals in Hole 856H are repeated in Hole 856G, except for the enrichment of Zn and associated metals in the uppermost part (Fig. 11). The apparent differences between the two holes in the extent of replacement of primary pyrrhotite by pyrite did not influence the metal zoning. The vertical distribution of metals was determined by zone refining that took place during formation of the sulfide deposit, mostly in its later stages. The pervasive processes of pyrrhotite replacement occurred later, when the deposit had already formed, and did not affect the lowest part of the deposit that was reached by drilling (zone 4 in Hole 856H), and only partly affected zone 2.

In zone 3 (Holes 856G and 856H), pyrrhotite was replaced by almost pure pyrite. Such a replacement process requires an additional source of sulfur, and reflects more oxidizing conditions compared to those of primary pyrrhotite formation. In the overlying magnetitebearing zones, oxidation was much more intense.

A positive correlation is evident between pyrite and magnetite concentrations in magnetite-bearing zones from the studied cores (Shipboard Scientific Party, 1992). These two minerals presumably formed as a result of a single process, when sulfur and oxygen were added to the system. Additional sulfur was fixed in pyrite, while oxygen and excess iron gave rise to formation of magnetite.

According to Duckworth et al. (this volume), sulfur is isotopically heavier in pyrite from Middle Valley than in pyrrhotite because of the involvement of seawater sulfate in secondary pyrite formation. The talc found in massive sulfide at different levels (from zone 3 and upward) is considered in similar geologic environments as evidence for the involvement of seawater as a source for the Mg (Koski et al., 1985).

Sphalerite redeposition during secondary alteration may explain the uniform iron concentration (11 to 16 wt% Fe) in the analyzed sphalerites (Table 7). This contrasts strongly with the widely varying Fe concentrations in Zn sulfides from the surficial parts of most other oceanic sulfide deposits (see above). The low Fe concentration in the sample from zone 3 may indicate higher S2 fugacities of the solutions during alteration of this zone (e.g., Scott and Kissin, 1973).

Only preliminary assumptions can be made concerning the geometry of the secondary hydrothermal convection. Below we discuss the variety of indirect evidence that favors a shallow, sill-driven, secondary convective system.

The small but distinct, positive anomaly of sediment-derived metals (Pb, Sb, As, Ge, and Tl) in the sulfides of the most strongly altered zone 3 is significant (Fig. 11). Considering the mineral chemistry and element correlations, this anomaly cannot be attributed simply to the association of these metals with pyrite, particularly as pyritic subzone 1B lacks signs of their enrichment. Enrichment of zone 3 in sedimentderived metals during secondary alteration is therefore probable.

Zone 3 is also the only part of the sulfide deposit that shows a positive Eu anomaly and no dominance of LREEs over HREEs (Fig. 12). Europium is the only rare earth element subject to reduction to the 2+ form. In this valence it preferentially fractionates into plagioclase during magmatic processes, replacing Ca. Plagioclase phenocrysts that form in magmatic systems also preferentially concentrate



Figure 11. Element distribution vs. depth for massive sulfide samples from Site 856. Solid circles connected by heavy lines correspond to samples from Hole 856H, open circles connected with thin lines are from Hole 856G, right-pointing triangles are from Hole 856B, left-pointing triangles from Hole 856C, asterisks from Hole 856D, squares from Hole 856E, and crosses from Hole 856F.

heavy REEs (Graf, 1977). Thus, the supply of additional Eu and HREEs into hydrothermal solutions, concentrated in the massive sulfides, is usually explained by alteration of plagioclase.

Hole 856B, drilled in sediments immediately adjacent to the sulfide deposit, shows intense plagioclase alteration at a depth of more than 70 mbsf (Shipboard Scientific Party, 1992). The high Ca concentration in pore waters in this hole also supports the existence of this process. Thus, plagioclase in the sediments flanking the sulfide deposit is the most probable source for the additional Eu and HREE enrichment noted in our massive sulfide samples.

It is difficult to determine whether the two types of sulfide alteration, namely in zone 3 and in the upper part of the deposit, resulted from a single process. At elevated temperatures, heated seawater evolved to form a hydrothermal solution due to interaction with sediments. Most probably, this solution entered the sulfide deposit at different stratigraphic levels, passing through permeable turbidite lay-





ers. Such layers readily channelize solution flow in the Middle Valley hydrothermal systems (ODP Leg 139 Scientific Drilling Party, 1992). Notably, the negative sulfate anomaly at 78 mbsf in Hole 856B, which corresponds to the base of zone 3 in Hole 856H, may be evidence for lateral flow (Shipboard Scientific Party, 1992). The ascending flow of these secondary solutions passed through the pores and cracks in the sulfide deposit.

At higher levels, under mild geothermal conditions, the seawater that entered the sulfide deposit must have been less geochemically evolved. It probably retained part of its original sulfate, which caused strong oxidation of the sulfides. The more evolved solutions of the deeper, higher-temperature part of the sedimentary column are responsible for the alteration seen in zone 3. In these latter solutions, the retained seawater sulfur was reduced to S^- from interaction with the sediments. The solutions also are likely to have retained some seawater Mg, which was fixed in the talc of zone 3 and in the upper part of the deposit.

The scale of the alteration suggests that secondary convection may have been driven by the intrusion of one of the sills common in the sedimentary sequence at Site 856. Sill intrusions, related to the formation of Bent Hill, occurred later than the formation of the sulfide deposit (Stakes and Franklin, this volume). In Hole 856B there is no sill at a depth corresponding to the base of sulfide reworking in Hole 856H. Yet this fact does not contradict the model, and the absence of a correlation of sills between Holes 856A and 856B (Shipboard Scientific Party, 1992) still permits a relatively small lateral continu-



Figure 12. Average chondrite-normalized REE patterns concentrations in bulk massive sulfide samples from four different zones of Hole 856H, and from the Mid-Atlantic Ridge (MAR) and East Pacific Rise (EPR). Chondrite values from Taylor and McLennan (1985).

ity of the sills in the subsurface. A sill intrusion could heat secondary hydrothermal solutions in its vicinity to higher temperatures than any distant magmatic source. This would explain the later mobility of sediment-derived metals that remained relatively immobile during the earlier formation of the main part of the sulfide deposit.

Secondary hydrothermal systems are also associated with the sills that penetrate the sedimentary cover in Guaymas Basin, Gulf of California (Gieskes et al., 1982). These sill intrusions caused expulsion of the pore waters that formed special types of hydrothermal precipitates on the seafloor, such as talc-sulfide deposits (Lonsdale et al., 1980). The formation of larger carbonate-sulfate-sulfide chimneys associated with sill-derived mounds near the axis of Guaymas Basin has also been attributed by some authors to secondary silldriven hydrothermal systems (Lisitzin et al., 1990). Although the relative proportions of pore water and seawater participation in secondary hydrothermal activity may be different, on the whole we believe that the Guaymas Basin model is applicable to Middle Valley.

A schematic reconstruction of the cored massive sulfide deposit is shown in Figure 14. It presents the formation of the deposit by an upflow of hydrothermal solutions, genetically related to a relatively deep-seated magmatic body, and its subsequent partial alteration by lateral flow of secondary solutions, related to a sill. In reality the process was undoubtedly not that simple, and the differences between the cores from Holes 856G and 856H suggest a complex threedimensional geometry of secondary alteration of the deposit.

SUMMARY AND CONCLUSIONS

Primary pyrrhotite in a large, inactive massive sulfide deposit, drilled at Site 856 in Middle Valley, formed above the sedimentary cover, probably from hydrothermal solutions with low fO_2 and fS_2 , which are typical of sedimented ridges. The sediments, however, did not contribute significant quantities of Pb, Sb, and As to the hydrothermal solutions or to sulfide minerals, as at hydrothermal systems on Gorda Ridge and the Okinawa Trough. One possible reason for this lack of sedimentary contribution is that the temperature of the solutions in the upper part of the Middle Valley hydrothermal system was too low to extract metals from the sediments.

In terms of ore petrology, the drilled deposit has a complex inner structure. The correlation of sulfide facies between the two drilled deep holes, 856G and 856H, is not always possible. Essentially, Zn and almost all of the trace metals are scarce in the inner part of the sulfide deposit. Zn and trace metal concentrations increase in the outer part of the deposit (to about 28 mbsf in Hole 856H), as a result of zone refining.

The zone refining process of progressively upward replacement of comparatively low-temperature mineral phases by higher temperature minerals took place during later stages of the growth of the deposit. This process led to the mobilization of trace elements contained within the low-temperature phases. Apart from maximum Zn and trace metal enrichment in the surficial part of the deposit, the zone refining caused Cu enrichment in the subsurface (18 to 28 mbsf in Hole 856H). Similar vertical variations in Zn and Cu concentrations are typical of ancient massive sulfide deposits on land. Copper enrichment in the deepest drilled part of the deposit most likely formed during the waning stage of high-temperature hydrothermal activity.

Two types of alteration of primary pyrrhotite were connected with an intense post-depositional hydrothermal reworking process: (1) almost complete pyritization of pyrrhotite in the lower central part of the cored section (48 to 75 mbsf in Hole 856H) and (2) replacement of pyrrhotite by pyrite-magnetite aggregates in the upper part. Primary pyrrhotite is only preserved in the lowest drilled part of the deposit.

The presence of talc in secondary reworked sulfides shows that seawater, evolved to different extent, participated in both types of alteration. Seawater sulfate took part in the strongly oxidizing alteration in the upper part of the deposit. Below, under higher temperature conditions, more geochemically evolved seawater probably contained sulfur mainly in reduced form that caused pyritization.

The secondary convection systems could have been driven by heat from one of the sills that intruded the upper part of the sedimentary column following the main stage of sulfide formation. Evolved seawater entered the deposit laterally at different levels, possibly through permeable turbidite layers. A small but definite enrichment of secondary pyritic sulfide in sediment-derived elements such as Pb, Sb, and As, formed by lateral flow in the vicinity of the sill. The temperature here was sufficiently high for extracting metals from the sediments on the flanks of the sulfide deposit. The absence of LREE enrichment and the existence of a positive Eu anomaly in the pyritic sulfide may be due to release of additional Eu and HREE into secondary solutions from hydrothermally decomposed plagioclase in the turbidites.

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^{*} Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

Table 6. Comparison between bulk chemical composition of oceanic massive sulfides from Middle Valley and other locations.

Location	Fe	Cu	Zn	S	Mg	Al	Si	Ca	Ba	Mn	Pb	Cr	Со	Ni	As
Mid-Atlantic Ridge															
26°N	30.25	1.62	1.29	34.27	0.068	0.19	1.55	0.25	0.087	0.035	446	14.8	103.8	38.0	67.5
24°30'N	17.55	16.25	4.06						0.053	0.026	262	27.9	15.9	45.0	61.5
East Pacific Rise															
13°N	26.13	1.91	2.36		0.160	0.33	1.03	0.34	0.050	0.092	150		88.6		51.3
21°N	23.12	0.61	5.93	38.71	0.022	0.16	1.29		0.069	0.029	1161	15.7	44.1	2.7	430.5
9°40'N	33.02	3.59	1.99	38.00		0.19	0.96	0.16		0.010	102		22.3		
22°S	28.68	1.30	2.80	227											
Juan de Fuca															
Axial Seamount	5.03	0.61	28.84		20.72	0.17	10.25	0.17		0.039	2148	12.3	10.5	25.8	711.2
Cleft Segment	24.74	0.056	11.48	42.55		0.08	4.17		0.029	0.120	1820	12.0	5.4		420.7
Explorer Ridge	21.91	4.83	1.65	29.07			2.99		1.640		275				241.0
Galapagos Ridge	30.37	4.94	1.17	52.20		0.45	6.91	0.11		0.023	226	54.9	94.8	25.4	123.9
Guaymas Basin	35.61	0.55	1.19	26.37	0.36	0.07	3.81	2.66	0.170	0.155	711		67.0	29.7	476.4
Gorda Ridge	36.79	1.09	1.57	32.75					0.200	0.005	9120				4436.1
Okinawa Trougha	8.59	1.40	23.36		0.04	0.05	4.80	0.06	3.360	0.180	15.94%				3.08%
Middle Valley															
Surface samples ^b	30.30	0.40	2.47	26.00	2.92	1.56	8.13	0.32	1.97	0.092	400		25.0	95.0	227.0
Cores (this study)	2010/201	0000					3503	120 122							
Average	39.51	0.43	1.41	38.07	1.92	0.43	3.80	0.66	0.19	0.033	152	26.0	43.4	32.4	51.3
Median	42.08	0.32	0.53	35.75	1.26	0.08	1.24	0.14	0.03	0.019	56	20.0	11.1	27.5	34.5
Std. dev.	9.67	0.36	2.02	9.85	1.88	1.68	5.87	1.12	0.43	0.043	534	19.1	73.9	22.8	59.4

Table 7. Correlation coefficients for the elements of the Middle Valley massive sulfides calculated using the data on the 40 bulk samples analyzed (Table 5).

Mo
Mn
0.38 0.38 As 0.42 0.65 0.59 0.40
0.40
0.32 0.53
0.44 0.44 0.42 0.38
0.39
0.37
0.41
0.35

Note: Only coefficients significant at the 95% confidence level are shown.

						Table (6 (continu	ed).								
Location	Se	Sr	Мо	Cd	Sb	Hg	Ti	Sn	Bi	Ge	Tl	Ag	Au	U	Sc	Rb
Mid-Atlantic Ridges		222.4										10.7				
26°N		323.6	115.1	52.0	11.6	0.05	0.027	10.0				48.6	1.03		1.3	52.6
24°30 N					8.9	0.05	0.012					42.1	10.40		1.5	45.8
East Pacific Rise	7.0		20.1	10.7			0.010	10.0		10.0		20.4	0.00		1.0	26.1
13"N	1.8	22 6	20.1	48.7	21.4		0.010	10.0		10.0		38.0	0.20		1.9	35.1
21 N 0940/N	22.9	33.5	110.7	493.2	31.4		0.002	10.0			0.7	1/2.0	0.18		0.5	3.20
9-40 IN			110.7	20.2			0.002	10.0			9.1	9.4	0.00		0.0	24.9
Juan de Fuca						0.5			0.15			30.0	0.15		0.9	24.0
Avial Seamount	23	668 3	35 7	540.5	267.2	0.5			0.15			165.2	4 42		15	60.0
Cleft Segment	28.9	30.0	10.4	134.0	40							63.1	0.13		1.5	00.0
Explorer Ridge	53.7	108.4	119.4	70.1	15.0				33		36.8	0.55	0.15			
Galapagos Ridge	100.0	100.4	169.8	32.0	7.2				2.2		50.0	37.5	0.20			23.5
Guaymas Basin	10010		10210	114.8	112							15.1	0.07		1.8	70.0
Gorda Ridge				54.8	255.3			12.5		10.0	2.5	85.9	1.40		125473	1017270
Okinawa Trougha		1200.0		600.0							-	2500.0	5.50			
Middle Valley																
Surface samples ^b Cores (this study):	87.7		108.0	39.5	26.9		0.006		0.64			8.70	0.14			
Average	41.81	213.6	23.7	30.1	4.2	18.2	0.006	14.9	2.35	4.3	3.39	3.54	0.007	5.97	0.59	22.03
Median	34.00	200.0	17.0	18.5	1.9	6.0	0.004	8.7	1.10		2.90	3.00	0.004	4.00	0.43	22.00
Std. dev.	34.15	129.5	18.1	31.7	4.7	43.8	0.006	13.6	3.17	5.4	2.95	2.98	0.007	5.72	0.60	12.76

Table 7 (continued).



			Table	6 (conti	nued).					
Location	Cs	Hf	Та	Th	La	Ce	Sm	Eu	Tb	Yb
Mid-Atlantic Ridges										
26°N	0.97	1.58	0.17	0.56	1.34	10.6	0.71	0.75	0.24	0.32
24°30'N	1.25	2.63	0.11	0.65	6.92	24.4	0.87	0.76	0.14	0.47
East Pacific Rise										
13°N	0.26	1.27	0.31	0.84	0.97	3.0	0.38	0.91	0.19	0.73
21°N										
9°40'N					0.85	0.5	0.26	0.01	0.05	0.50
22°S	0.32	1.12	0.09	0.56	1.82	13.0	0.58	0.51	0.22	0.60
Juan de Fuca										
Axial Seamount Cleft Segment	1.50	4.70	1.10	1.00	4.10	10.2	2.00	1.23	0.49	0.47
Explorer Ridge										
Galapagos Ridge	1.50	0.50			4.10	1.8				
Guaymas Basin	2.10	5.10	0.49	0.85	1.70	8.9	1.80	1.30	0.39	0.74
Okinawa Trough ^a										
Middle Valley										
Surface samples ^b Cores (this study):					6.10					
Average	0.44	1.11	0.38	0.36	1.67	7.2	1.19	0.46	0.23	0.78
Median	0.32	0.91	0.08	0.30	1.30	5.0	1.10	0.40	0.20	0.70
Std. dev.	0.29	0.68	0.69	0.29	1.45	8.2	0.81	0.25	0.19	0.68

Notes: Fe, Cu, Zn, S, Mg, Al, Si, Ca, and Ba in percent (%); all other elements in parts per million (ppm). Analytical results, except for those indicated by footnotes ^a or ^b, are represented by average values for Fe and S and median values for all other elements, from the review of Krasnov et al. (1992).

^a Averages from five samples (Halbach et al., 1989).

^b Averages from 10 samples for Au (Davis et al., 1987).



Figure 13. A. Positive geochemical correlations in bulk sulfide samples from Site 856. Correlation coefficients greater than 0.8 are shown by triple lines, those greater than 0.7 by double lines, those greater than 0.6 by thick lines, and those greater than 0.5 by thin lines. Coefficients lower than 0.4, significant at the 95% confidence level, are shown selectively by dashed lines. Groups of associated elements are numbered from 1 to 8 (see text). **B.** Geochemical correlation of massive sulfide samples from sediment-free ridges (Krasnov et al., 1992). Conventions are the same as for (A).

Table 8. Representative microprobe analyses (wt%) of sphalerite.

Core, section, interval (cm)	Fe	Zn	S	Cd	Cu	Total	Additional comments
139-856E-1H-1, 106-108	15.6	47.7	35.0	0.19	0.11	98.60	
139-856F-							
2X-CC, 1-3	14.4	49.8	33.8	0.20	0.00	98.20	Inclusion in pyrite
2X-CC, 1-3	14.7	48.1	35.8	0.20	0.00	98.80	Grain with chalcopyrite inclusion
139-856G-							
4R-1, 49-51	12.8	50.1	35.5	0.16	0.00	98.56	
6R-2, 101-103	4.8	62.5	33.1	0.13	0.00	100.53	
139-856H-							
3R-2, 67-70	13.8	50.8	34.4	0.16	0.01	99.17	Inclusion in pyrite
6R-1, 24-26	15.2	50.7	34.1	0.17	0.00	100.17	<i></i>
15R-1, 60-62	11.3	52.2	34.7	0.19	0.50	98.89	Grain with chalcopyrite inclusion

Table 9. Representative microprobe analyses (wt%) of pyrite.

Core, section,	Fe	\$	Cu	Ae	Total	Additional						
uncervai (citi)	re	3	Cu	As	Total	comments						
139-856E-1H-1, 106-108	46.30	53.30	0.08	0.00	99.68	Skeletal crystal						
139-856F-												
2X-CC, 1-3	46.80	53.50	0.01	0.00	100.31	Center of a large grain						
2X-CC, 1-3	46.80	53.00	0.00	0.00	99.80	Margin of the same grain						
2X-CC, 1-3	46.00	52.80	0.01	0.05	98.86	Skeletal crystal						
2X-CC, 1-3	46.10	53.60	0.00	0.07	99.77	Center of a euhedral crystal						
2X-CC, 1-3	46.00	52.80	0.00	0.00	98.80	Margin of the same crystal						
139-856G-												
4R-1, 49-51	46.00	53.40	0.07	0.00	99.47	Grain with magnetite intergrowth						
4R-1, 49-51	45.50	52.90	0.00	0.00	98.40	Pyrite without intergrowth						
6R-2, 101-103	45.70	53.00	0.00	0.01	98.71	Colloform pyrite						
6R-2, 101-103	46.30	53.00	0.01	0.10	99.41	Center of a rounded grain						
6R-2, 101-103	46.70	52.60	0.01	0.08	99.39	Margin of the same grain						
139-856H-												
3R-2, 67-70	46.40	53.20	0.01	0.00	99.61	Grain with magnetite, chalcopyrite, and sphalerite intergrowth						
6R-1, 24-26	47.00	52.60	0.01	0.00	99.61	Skeletal crystal with sphalerite						
9R-1, 80-82	47.00	53.00	0.02	0.05	100.07	Fine-grained aggregate						
15R-1, 60-62	46.90	52.40	0.02	0.00	99.32	Anhedral grain						
17R-1, 53-36	46.70	52.80	0.03	0.00	99.53	Anhedral grain						



Figure 14. Proposed mechanism of massive sulfide formation and secondary alteration. 1 = unaltered and moderately altered sediments, 2 = turbidite layers, 3 = stockwork zone, and 4 = sill emplaced after formation of the sulfide deposit. Zones inside the sulfide deposit: Po = primary pyrrhotitic sulfide, Py = secondary pyritic sulfide, and Py + Mt = aggregates containing pyrite and magnetite as the main secondary minerals. Paths of primary hydrothermal solutions are shown by open arrows; those of secondary solutions by solid arrows.

Table 10. Representative microprobe analyses (wt%) of Cu-Fe sulfides.

Core, section, interval (cm)	Fe	Cu	s	Total	Additional comments							
Chalcopyrite 139-856F-2X-CC, 1-3	30.6	33.2	36.2	100.0	Inclusion in pyrite							
139-856H- 3R-2, 67-70 9R-1, 80-82 15R-1, 60-62 17R-1, 35-36	30.0 30.8 30.2 30.6	32.6 33.0 33.2 34.1	36.5 36.8 35.3 34.8	99.1 100.6 98.7 99.5	Inclusion in pyrite Inclusion in pyrite Intergrown with pyrite Intergrown with pyrthotite							
Isocubanite 139-856E-1H-1, 106-108	41.4	23.4	36.1	100.9	Intergrown with pyrite and sphalerite							
139-856G-4R-1, 49-51	40.5	22.6	35.5	98.6	Intergrown with chalcopyrite							

Note: Zn, As, Co, and Cd are below detection limits (<0.01%).

interval (cm)	Mineral	Au	Ag	As	Sb	Co	Ni	Sc	Cr	Zr	Cs	Rb	Ва	Hf	Та	Th	U	Se	Hg	La	Ce	Sm	Eu	Tb	Yb
139-856G-																									
2R-3, 29-31	Cubic, pyrite	n.a.	2.0	n.a.	11.0	2.1	19	0.20	33	250	0.34	30	220	0.40	0.08	0.1	n.a.	6	17	n.a.	2.1	n.a.	1.00	0.28	0.39
3R-1, 61-64	Fine-grained pyrite	114	2.0	n.a.	4.7	11.0	12	0.93	36	170	0.50	16	360	1.20	0.14	0.3	12.0	33	5	4.6	n.a.	3.80	0.38	0.23	0.40
4R-1, 75-77	Fine-grained pyrite	50	5.5	16	2.7	26.0	43	1.20	20	n.a.	1.20	80	240	2.0	0.14	0.4	2.8	26	n.a.	2.4	7.0	1.00	1.40	n.a.	0.80
6R-3, 95-97	Cubic pyrite	18	6.1	17	1.2	1.7	46	0.80	17	160	0.16	27	340	1.1	0.10	0.5	0.9	2	9	1.0	17.0	п.а.	1.30	0.30	1.00
7R-1, 38-40	Fine-grained pyrite	110	4.7	130	1.0	66.0	41	0.60	56	90	0.20	36	310	0.8	0.09	0.3	2.6	16	21	< 0.5	14.0	0.70	1.50	0.40	n.a.
139-856H-																									
IR-2, 4-7	Cubic, pyrite	140	<1.0	150	7.4	2.7	35	0.33	68	100	0.33	<10	580	1.2	0.09	0.3	1.3	38	16	1.0	6.9	0.42	0.20	0.11	0.46
1R-2, 4-7	Rhombohedral, pyrite	230	4.0	60	6.0	2.3	12	0.30	37	<100	0.32	25	2500	0.18	0.11	0.4	1.0	47	4	<1.0	13.0	0.64	0.88	0.23	0.78
3R-1, 34-37	Fine-grained pyrite	12	4.8	4	0.4	9.6	<10	0.70	<5	n.a.	0.51	16	620	0.8	0.10	0.5	3.0	n.a.	n.a.	1.6	9.0	1.70	0.30	n.a.	1.50
3R-3, 14-16	Fine-grained pyrite	131	3.2	n.a.	0.3	33.0	67	1.60	35	300	0.40	47	650	1.9	0.17	2.5	2.5	79	42	6.2	15.0	n.a.	0.80	0.34	1.00
4R-1, 18-20	Fine-grained pyrite	37	3.5	10	0.8	15.0	30	1.50	12	160	0.80	21	500	0.8	0.20	0.6	1.7	36	n.a.	1.1	14.0	0.20	0.50	n.a.	0.70
5R-1, 52-53	Cubic, pyrite	4	2.4	2	0.3	10.0	16	0.60	29	110	0.50	31	480	n.a.	0.10	0.6	4.5	88	22	1.0	3.0	0.90	0.30	0.49	1.80
7R-1, 80-82	Fine-grained pyrite	30	3.1	3	0.4	11.0	15	0.70	<5	200	0.50	35	200	0.8	0.08	0.3	5.1	10	п.а.	1.2	20.0	1.60	0.60	0.30	1.30
8R-1, 124-126	Fine-grained pyrite	36	7.4	130	6.5	84.0	66	0.40	47	120	0.53	77	0.1%	0.9	0.30	0.8	2.8	16	20	1.0	n.a.	0.80	n.a.	n.a.	1.50
9R-1, 80-82	Fine-grained pyrite	60	1.5	78	3.8	20.0	20	0.40	19	82	0.34	32	660	2.1	< 0.05	< 0.1	1.2	8	10	0.7	24.0	0.40	n.a.	0.15	1.00
11R-1, 49-51	Fine-grained pyrite	90	1.7	66	3.7	59.0	18	0.50	15	60	0.30	39	180	0.5	0.06	0.3	3.0	12	15	1.0	n.a.	0.90	0.40	0.40	n.a.
14R-1, 4-6	Porphyroblastic pyrite	16	2.5	2	0.3	170.0	40	0.70	11	110	0.60	43	440	0,9	0.14	1.0	1.1	42	28	0.9	n.a.	0.40	0.40	0.51	n.a.
19 samples from sediment-free ridges	Pyrite	370	12.0	26	10.5	1910.9	86	2.80	85	820	1.32	151	976	4.0	0.27	1.8	0.8	26	n.a.	2.3	9.1	0.70	0.87	0.45	1.14
139-856H-5R-1, 52-53	Pyrrhotite	17	3.0	2	0.3	12.0	12	0.60	39	170	0.70	25	90	< 0.5	0.20	0.3	0.5	130	52	2.0	19.0	0.20	0.30	0.51	7.20
139-856H-5R-1, 52-53	Sphalerite	36	7.4	7	0.7	4.5	140	21.0	50	640	<0.10	85	820	3.6	0.30	0.7	43.0	40	16	2.7	12.0	0.50	0.70	n.a.	1.10
22 samples from sediment-free ridges	Zinc sulfides	470	129.0	146	27.7	113.0	174	4.20	127	2039	3.74	128	1777	7.0	0.62	2.3	1.0	42	n.a.	2.8	18.0	2.63	2.75	1.18	2.52

Table 11. Trace element concentrations (Au in ppb; all other elements in ppm) in sulfide minerals from massive sulfide samples, determined by INAA.

Note: n.a. = not analyzed. Data on sulfides from sediment-free ridges are median values from previous studies (Krasnov et al., 1992).