

## NOBLE METALS IN SEAFLOOR HYDROTHERMAL MINERALIZATION FROM THE JUAN DE FUCA AND MID-ATLANTIC RIDGES: A FRACTIONATION OF GOLD FROM PLATINUM METALS IN HYDROTHERMAL FLUIDS

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### ABSTRACT

Gold, Ir and Pd were determined by neutron activation in hydrothermal mineralization from two mid-ocean ridges, the Juan de Fuca and the Mid-Atlantic at 26°N. In the Juan de Fuca suites, Au ranges from 9.5 to 5403 ppb. Most samples with >1000 ppb are from Axial Seamount, a recently active volcano. Those with <218 ppb are from Middle Valley and the Endeavour segment at the northern extremity of the ridge and represent thermal regimes of <100°C. Palladium is <20 ppb in the Au-rich Axial Seamount samples, and probably about 2 ppb. Iridium in Middle Valley and Endeavour samples averages 0.024 ppb. The Mid-Atlantic Ridge suites are from a hot, hydrothermal mound and a nearby sediment field containing hydrothermal particulate matter indicative of high-temperature venting. Gold is >1000 ppb in sulfides from the hydrothermal mound area and in sediments high in hydrothermal vent precipitate. With one exception, Pd ranges from 2.6 to 136 ppb, and Ir averages 0.50 and 0.77 ppb in mound sulfides and sediments. The Mid-Atlantic suites are comparable to Axial Seamount in Au but higher in Pd and Ir. Metals are derived from a basalt rock column; Au/Ir values of rock-equilibrated fluids are probably comparable to MORB-hosted sulfide globules, or about 16. The Au/Ir ratio in Juan de Fuca and Mid-Atlantic Ridge sulfides ranges from 1700 to 41,000. In active systems, such fractionation likely occurs at the site of precipitation, usually within tens of meters of the seafloor.

**Keywords:** seafloor sulfides, noble metals, Mid-Atlantic ridge, Juan de Fuca ridge.

### SOMMAIRE

Les concentrations de Au, Ir et Pd dans les secteurs minéralisés de deux crêtes océaniques, Juan de Fuca et la ride médio-atlantique à 26°N, ont été déterminées par activation neutronique. Dans les suites à Juan de Fuca, les teneurs en Au varient entre 9.5 et 5403 ppb. La plupart des échantillons contenant plus de 1000 ppb proviennent du guyot Axial, édifice volcanique récemment en éruption. Ceux qui en contiennent moins de 218 ppb proviennent de Middle Valley et du secteur Endeavour, à l'extrémité nord de la crête, et représentent des régimes thermiques inférieurs à 100°C. Il y a moins de 20 ppb de Pd dans les échantillons aurifères du guyot Axial, et probablement même moins de 2 ppb. Les échantillons de Middle Valley et de Endeavour contiennent, en moyenne, 0.024 ppb d'Ir. Les suites de la crête médio-atlantique proviennent d'une structure hydrothermale formée à température relativement élevée et d'une séquence sédimentaire avoisinante contenant des débris hydrothermaux typiques d'événements de haute tempé-

rate. Les sulfures dans ces structures hydrothermales et ces sédiments contiennent plus de 1000 ppb d'Au. Avec une seule exception, le Pd varie entre 2.6 et 136 ppb; les sulfures des structures hydrothermales et des sédiments contiennent en moyenne 0.50 et 0.77 ppb d'Ir, respectivement. Les suites médio-atlantiques se comparent au guyot Axial dans leur teneur en Au, mais sont plus riches en Pd et Ir. Ces métaux sont dérivés du socle basaltique. Les fluides qui ont équilibré avec ces roches ont probablement un rapport Au/Ir proche de 16, valeur typique des globules dans les basaltes des fonds océaniques (MORB). Des valeurs du rapport Au/Ir allant de 1,700 à 41,000 caractérisent les sulfures de Juan de Fuca et de la crête médio-atlantique. Dans des systèmes actifs, ce genre de fractionnement serait typique au site de précipitation, généralement à des dizaines de mètres du fond de l'océan.

(Traduit par la Rédaction)

**Mots-clés:** sulfures des fonds marins, métaux nobles, crête médio-atlantique, crête de Juan de Fuca.

### INTRODUCTION

Studies of noble metals in seafloor hydrothermal sulfides have produced a useful data-base for gold and silver (see Hannington *et al.* 1986), but very few systematic data exist for the platinum-group elements (PGE). In the present work Au, Ir and Pd were determined on suites of sulfide-rich seafloor mineralization from the Juan de Fuca ridge (JFR) and the Mid-Atlantic Ridge (MAR) at the Trans-Atlantic Geotraverse or TAG area at ~26°N. The suites represent a spectrum of materials ranging from sulfides characteristic of hot (>300°C), active hydrothermal mound areas venting black smoke (pyrrhotite-rich particles) to cold, extinct, massive sulfide ridges formed by coalesced chimney blocks and fragments. Recovery techniques included dredging, sampling by submersible vehicle (ALVIN) and coring in sediments.

The solubilities of noble metals in hydrothermal fluids are highly relevant to the redistribution and possible concentration of these metals by the action of water-rich fluids on magmatic occurrences, and to an assessment of the potential of other types of mineralization, such as pyritic base-metal sulfides, for PGE concentration. Except for ophiolites, sulfide mineralization in mid-ocean ridge settings is not analogous to the great majority of on-land base-

metal deposits, but the basic physical and chemical processes that govern metal distribution in the MOR hydrothermal environment are undoubtedly comparable to those relevant in other environments (e.g., Kuroko-type deposits). In general, an absence of postdepositional deformation and deep burial permit modeling of some aspects of metal distribution and concentration in seafloor deposits far more readily than in ancient on-land analogues. The distinctive proportions of noble metals found in many samples in this study indicate that seafloor hydrothermal fluids and their associated sulfides strongly fractionate Au from the PGE.

### SAMPLE DESCRIPTION

#### *Juan de Fuca Ridge (JFR)*

Three regions of the JFR between the Blanco and Sovanco transform faults, including Axial Seamount, the Endeavour segment and the Middle Valley areas, were sampled (Fig. 1). The Axial Seamount suite includes one sample from a hydrothermal chimney-like spire, and two dredge samples recovered from Axial Seamount caldera. The spire has

been studied in detail by Hannington *et al.* (1986) and Hannington & Scott (1988). Fluid inclusions in wurtzite have an average temperature of homogenization of about 235°C. Hannington *et al.* (1986) viewed this as the temperature of the main pulse of mineralization. The two dredge samples are subsamples of a single fragment. They are sphalerite-rich and barite-poor compared to the spire sample.

The Endeavour segment of the northern JFR is represented by five samples (Sampson 1986), which were recovered by the submersible ALVIN. Two samples (ALVIN dive 1417) are from an old, extinct ridge of massive sulfide 150 m in length consisting of coalesced, oxidized chimney fragments. A third sample (ALVIN dive 1418) is an old, filled chimney fragment recovered from an active black smoker area. The remaining two Endeavour samples (ALVIN dive 1419) are from an active low-temperature (white smoker) area and are pieces of oxidized, coalesced chimneys.

Middle Valley is at the extreme northern end of the JFR. Two suites from this area were analyzed, including a dredge suite of mainly massive sulfide material and a sulfide-rich sediment core, PAR 85-13. The dredge suite consists of samples from two hauls, DR02 and DR06, which are mainly polymetallic massive sulfides consisting mostly of pyrite, pyrrhotite and wurtzite. The sediment core penetrated 2.35 m of mainly alternating beds of coarse- and fine-grained clastic sulfides of variable thickness and clast size. The sedimentology and geochemistry of this core have been discussed in detail by Goodfellow & Blaise (1988). The sediments occur on the flank of a sulfide mound structure, and the analyzed samples, which consist of 3- to 5-cm intervals, probably represent debris flows. Where very coarse sulfide clasts are prominent, the sample taken consists of matrix only. The principal sulfide minerals are pyrite and pyrrhotite, accompanied by sphalerite, marcasite, isocubanite, chalcopyrite and galena. Talc, Mg-rich clays, silica and barite are widespread.

#### *TAG area, Mid-Atlantic Ridge*

The TAG area at 26°08' N (Fig. 2) contains both an active high-temperature (> 300°C) black smoker field and a hydrothermal sediment field, with substantial contributions of fallout precipitate from black smoker plumes, along with other manifestations of hydrothermal activity (Thompson *et al.* 1988, Nelson *et al.* 1986). The black smoker area is part of an elliptical compound mound, where chimneys of up to 10 m in height occur in the central part of the mound, over an area 30 to 40 m in diameter. Chimney fragments and blocks of sulfide and anhydrite make up the floor of the mound. The black smoke issues from cracks and fissures near the base of chimneys. The analyzed samples represent the

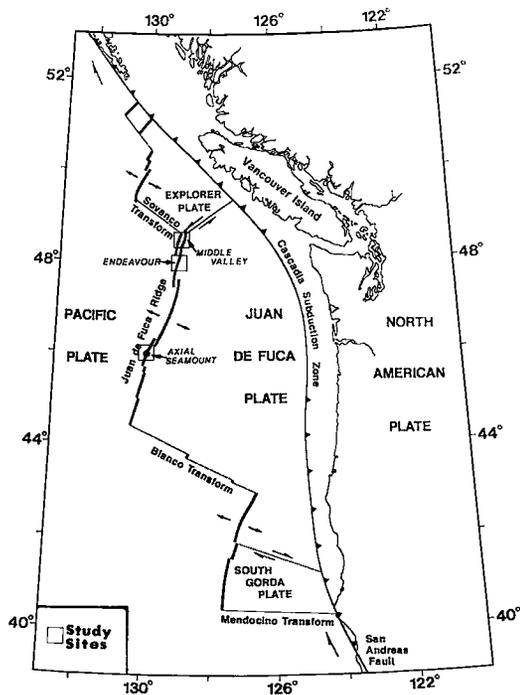


FIG. 1. Site locations sampled on the Juan de Fuca Ridge: Axial Seamount, Endeavour Segment (ALVIN suite) and Middle Valley, including dredge hauls DR02 and DR06 and sediment core PAR 85-13.

main sulfide assemblages found in blocks and chimney fragments and include pyrite-sphalerite [1-45(2)], sphalerite (1-9) and chalcopyrite-pyrite [1-46(1)] types, all of which are considered to represent fragments of chimney interiors. In addition, an iron oxide sample (1-17), which is probably oxidized sulfide, was analyzed. Bulk chemical compositions and mineralogical notes for samples 1-45(2) and 1-46(1), and for samples similar to 1-17, are given in Thompson *et al.* (1988).

The field of hydrothermal sediments is located approximately 2 km NNE of the active smokers and consists of material deposited by mass flow and grain-by-grain sedimentation. The latter sediment is probably fallout from plumes of black smoke, such as the plume currently circulating some 200 to 700 m above seafloor over about 10 km of the TAG area (Nelson *et al.* 1986, Trefry *et al.* 1986). The Cu-rich nature of much of this sediment is indicative of sustained high-temperature exhalations. The sediments were sampled by a 1.25-m core. The analyzed material includes three iron-rich samples from two beds, which probably are mainly vent-plume precipitates. Two other samples include a turbidite bed and a carbonate-rich bed that is a mixture of hydrothermal precipitate and pelagic carbonate.

#### ANALYTICAL METHODS

Noble metals, As, Sb, Se, Zn and Ba were determined by radiochemical (RNAA) and instrumental neutron-activation analyses (INAA) using the McMaster Nuclear Reactor. Concentrations of Pb and Cu were obtained by inductively coupled plasma-emission spectrometry from the Geological Survey of Canada laboratories (Table 1). Palladium and Ir concentrations were obtained by RNAA. The Au data for the Juan de Fuca ridge samples represent an average of results obtained by RNAA and INAA, the latter performed on 10-g samples. Gold was determined by RNAA only on the TAG suites. Silver, As, Sb, Se, Zn and Ba were determined on 10-g samples by INAA.

The high gold content, coupled with relatively low Pd and Ir, generated analytical problems in some cases. The method of tellurium coprecipitation (Stockman 1983), in which the three metals are counted in the same source, was generally unsuccessful where ppm levels of Au occur with low Pd and Ir contents (<10 ppb Pd, <0.01 ppb Ir). Separation and counting of individual metals as in the procedure of Crockett *et al.* (1968) proved satisfactory except for Pd in samples with a Au/Pd ratio in excess of  $10^3$ , where insufficient decontamination of Au from Pd apparently occurred. A number of Pd values (Table 1) are upper limits only.

For INAA analyses the sensitivity limits are: Au, 5 ppb; Sb, 0.2 ppm; As, 2 ppm; Ag and Se, 5 ppm;

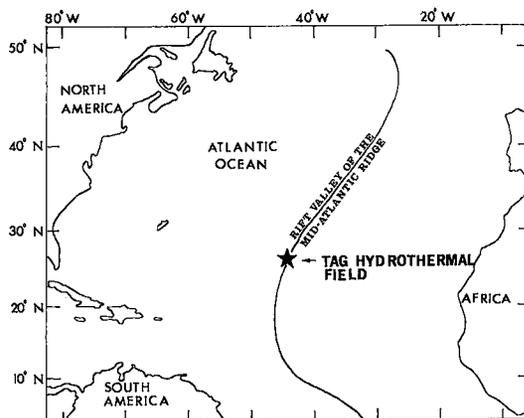


FIG. 2. Trans-Atlantic Geotraverse (TAG) hydrothermal field at 26°08' N, 44°49' W on the Mid-Atlantic Ridge, where two suites of samples are located, one from an active smoker mound and one from a field of hydrothermal vent sediments.

Zn, 50 ppm and Ba, 100 ppm. All Au, As, Sb and Zn values exceed their respective limits of sensitivity, whereas at least 60% of the analyses of remaining elements exceed the sensitivity limits. This level of discrimination allows recognition of several distinctive elemental groupings among the JFR suites.

#### RESULTS

The JFR and TAG data bases are presented in Tables 1, 2 and 3, respectively, and the Au, Pd and Ir values are displayed in Figures 3 and 4. Where replicate analyses were carried out, a standard deviation is included and the number of samples noted in parentheses. Various group averages are noted by vertical arrows in Figures 3 and 4, and values that are upper limits only are capped with horizontal arrows. The TAG sulfide samples (filled squares) are distinguished by compositional type, with the labels Cu, Zn and ZnFe for chalcopyrite-pyrite, sphalerite and pyrite-sphalerite, respectively.

Two different aliquots of the Cu-rich sample 1-46(1) were analyzed in separate irradiations. One aliquot analyzed in duplicate yielded Au values of 6500 and 5700 ppb, whereas the second aliquot returned a value of 18,900 ppb. The sample probably has a heterogeneous distribution of Au owing to the presence of discrete gold-rich minerals (see Discussion). The difference between the two aliquots is thought to reflect this heterogeneity. The result for each aliquot is recorded as a subsample, 1-46(1)a and 1-46(1)b.

In the case of JFR samples in which adequate material was available, data on a suite of additional

TABLE 1. NOBLE METALS, TRACE AND MAJOR ELEMENTS, JUAN DE FUCA RIDGE

Sample	Description	Au	Pd	Ir	Ag	As	Sb
		ppb					
Axial Seamount, central Juan de Fuca Ridge							
XL1720-2A		2905	<4.1	-	180	430	98
XL1720-2B		1900	<1.9	-	150	550	89
Axial seamount spire		5403	<2.6	<0.1	440	510	600
Middle Valley, northern Juan de Fuca Ridge							
Massive sulfide dredge suite							
DR02-01	po, wz	1138	1.9	0.0076	57	210	240
DR02-05	po, py	645	-	0.024	47	100	36
DR02-18	clay-rich	711	-	-	37	190	130
DR06-03	massive sulfide	300	-	0.019	52	35	91
DR06-04	po, py	71	-	0.056	<7	67	11
DR06-08		84	-	0.015	12	95	15
DR06-10	py	51	-	0.014	<9	300	5.2
Middle Valley, northern Juan de Fuca Ridge							
Sulfidic sediment core PAR 85-13							
Core depth, cm							
102-106	Mainly sulfide	85	-	-	<5	225	14
132-135	matrix only if	218	-	-	<5	170	21
197-202	clasts are coarse;						
	po,py,mar,sp,ccp,	102	-	-	<5	140	13
	iso,co,gn;						
	brt,si,talc	132	-	-	<5	130	15
Endeavour segment, northern Juan de Fuca Ridge							
Massive sulfides, Alvin suite							
14171B-B2	py, m.ccp; old	9.5	-	-	13	190	0.6
	sulfide ridge						
14171E-B4	py, m.ccp; old	34	-	-	11	230	2.1
	sulfide ridge						
14186B-B9	wz,mar,py	180	-	0.043	180	580	64
	black smoker area						
14191C-B2	brt,si,m.sp,mar	40	-	0.026	35	51	58
	white smoker area						
14191D-B3	brt,si,m,wz	65	-	0.007	29	130	21
	white smoker area						
Axial Seamount, central Juan de Fuca Ridge							
Sample		Se	Pb	Cu	Zn	Ba	
		ppm		wt. %			
XL1720-2A		<9	-	-	32.0	0.43	
XL1720-2B		<12	-	-	29.0	0.48	
Axial seamount spire		<14	3700	0.41	12	5.5	
Middle Valley, northern Juan de Fuca Ridge							
Massive sulfide dredge suite,							
DR02-01		<11	-	-	25.0	0.14	
DR02-05		250	-	-	0.06	3.5	
DR02-18		<6	-	-	2.0	0.14	
DR06-03		48	-	-	7.6	<0.02	
DR06-04		160	-	-	2.6	<0.04	
DR06-08		49	-	-	5.6	<0.02	
DR06-10		180	-	-	3.7	<0.02	
Middle Valley, northern Juan de Fuca Ridge'							
Sulfidic sediment core PAR 85-13							
Core depth, cm							
102-106		72	-150	-0.4	2.55	0.65	
132-135		71	-500	-0.3	2.4	2.3	
197-202		92	-200	-0.25	2.1	1.1	
218-222		39	-200	-0.25	1.2	2.45	
Endeavour segment, northern Juan de Fuca Ridge'							
Massive sulfides, Alvin suite							
14171B-B2		160	130	4.4	0.26	0.05	
14171E-B4		61	21	1.55	0.34	0.02	
14186B-B9		<11	2500	0.71	25	1.15	
14191C-B2		<18	1450	0.03	0.63	34	
14191D-B3		34	680	0.05	0.72	37	

1. This sample was studied in detail by Hannington *et al.* (1986) and Hannington & Scott (1988). The Cu and Pb values are the average of 13 analyses reported by Hannington *et al.* (1986). The remainder are analyses carried out in this study on one sample provided by Dr. I. Jonasson, Geological Survey of Canada. 2. Cu and Pb are estimates from Fig. 11 in Goodfellow & Blaise (1988). 3. The Endeavour suite samples were recovered by the submersible ALVIN and are designated by the Alvin dive numbers 1417-1419 and the sample site 1B-1D. Cu and Pb values are from Sampson (1986). Mineral abbreviations: brt barite, ccp chalcopyrite, iso isocubanite, mar marcasite, py pyrite, si silica (amorphous), sp sphalerite, wz wurtzite; m minor.

elements (Ag, As, Sb, Se, Zn and Ba) were obtained to further characterize suites from different areas and settings (Table 1).

TABLE 2. NOBLE METALS IN THE TAG HYDROTHERMAL AREA, 26°N, MID-ATLANTIC RIDGE

Black smoker central mound complex, mainly massive sulfide blocks				
Sample	Description	Au, ppb	Ir, ppb	Pd, ppb
1-9 <sup>1</sup>	Zn sulfide	2690±10(2) <sup>2</sup>	1.01±0.57(3)	1000
1-45	Zn, Fe sulfide	3290	0.22±0.08	3.5
1-46(a) <sup>3</sup>	Cu, Fe sulfide	6100±566(2)	7.6±1.4(2)	3.2
1-46(b)	Cu, Fe sulfide	18900		
1-17	Fe oxide	120	0.28	68
Average sulfide <sup>4</sup>		4027	2.28	-
Preferred average sulfide <sup>5</sup>		2990	0.50	
Hydrothermal sediment field				
Core Depth, cm	Description	Au, ppb	Ir, ppb	Pd, ppb
15-16	top Fe-rich bed, upper portion	1450±230(3)	1.46±0.54(2)	70
32-33	top Fe-rich bed, middle portion	1430±670(3)	0.56±0.01(2)	27
41.5	turbidite bed	700	0.41	136
80-81	carbonate/iron mix zone	170±40(2)	0.51±0.17(2)	2.6
117	bottom Fe-rich bed	1090±0.0(2)	0.30	26
Average, Fe-rich beds		1320	0.77	41

1. Number of replicate analyses noted in parentheses. 2. Sample numbers as in Thompson *et al.* (1988). 3. Samples 1-46(a) and 1-46(b) are two aliquots of sample 1-46 and are entered as individual subsamples because of their very different gold contents (see text). 4. The gold average omits sample 1-17, and uses a value of 6100 ppb for sample 1-46(a). 5. Average sulfide omitting sample 1-46 (and 1-17 in the case of gold).

TABLE 3. AVERAGE TRACE ELEMENT CHARACTERISTICS OF HIGH- AND LOW-AU SUITES FROM JUAN DE FUCA

Suite	Au	Ag	As	Sb	Se	Au/Ag	As/Sb	Au/Se
		ppb		ppm				
Axial Seamount								
3403	257	497	262	<12	13	1.9	>284	
Middle Valley, DR02 + DR06-03								
699	48	134	124	<14	15	1.1	>50	
Endeavour 37								
	22	150	20	68	1.7	7.5	0.5	
Middle Valley, DR06-04, 08, 10								
69	<9.3	154	10	130	>7.4	15	0.53	
Middle Valley, PAR 85-13 core								
134	<5	166	15.5	68.5	>27	11	2.0	
Average all low-Au suites <sup>2</sup>								
80	-	157	15	89	-	11	1.0	

1. The Endeavour averages omit sample 1418-6B, and the Middle Valley dredge suite DR06 omits sample DR06-03. 2. Averages are based on equal weighting of area averages, and are omitted if area averages are upper or lower limits only.

## DISCUSSION

The distribution of noble metals in seafloor sulfides, as reflected in the JFR and TAG suites, differs in some respects from that in magmatic sulfides associated with mafic and ultramafic rocks. Most striking is the very high content of gold in proportion to Pd and Ir. For example, from Table 4 of Chyi & Crocket (1976), the average Au/Ir values for magmatic pyrrhotite and chalcopyrite of the Strathcona mine, Sudbury are 11 and 3, respectively (see also Barnes *et al.* 1985 or Naldrett 1981). For the seafloor sulfides in the present study, the Au/Ir values of various groups range from 1700 to 41,000 (Table 4).

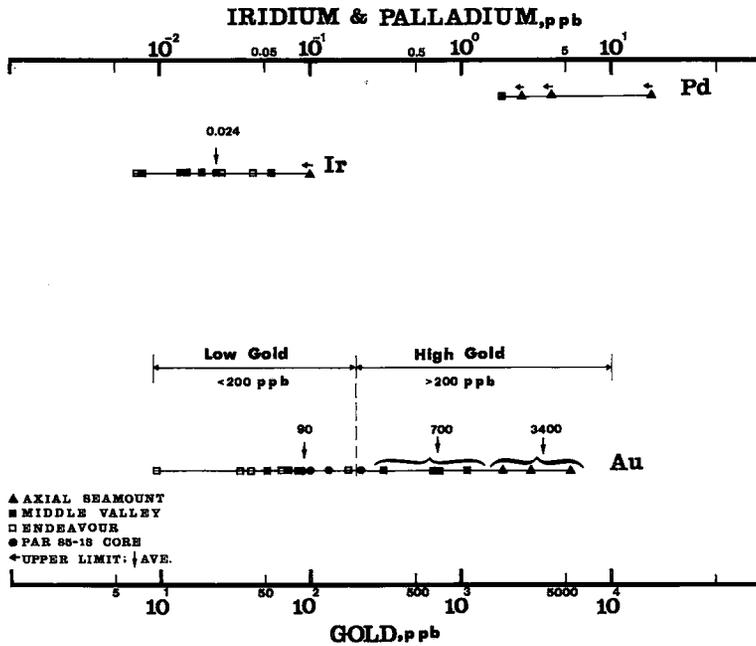


FIG. 3. Distribution of Au, Ir and Pd from Juan de Fuca Ridge sites. Data are listed in Table 1.

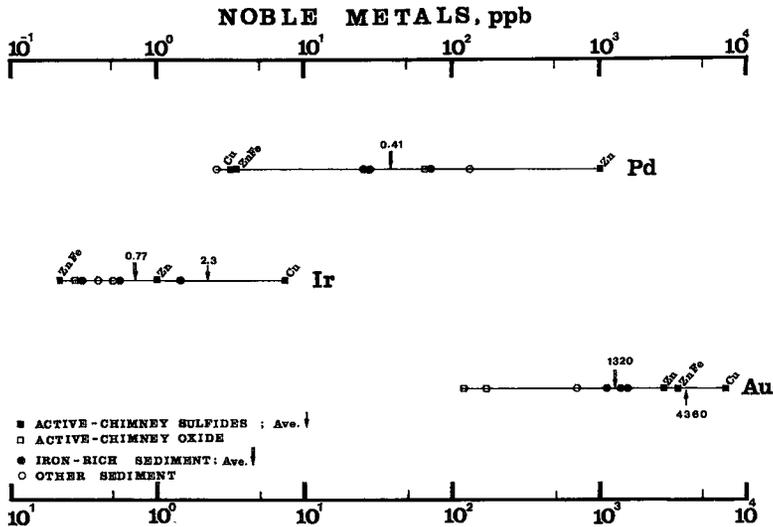


FIG. 4. Distribution of Au, Ir and Pd from the TAG field sites, 26°N, MAR. Data are listed in Table 2.

Furthermore, although a minimum of 9.5 ppb Au is recorded, most samples from hot, active, hydrothermal areas have in excess of 1000 ppb Au, but as little as 2 or 3 ppb Pd and rarely exceed 100

ppb Pd. In the TAG area, with one exception, sulfides from high-temperature environments average 0.50 to 0.77 ppb Ir; in the JFR area, sulfides taken from low-temperature settings, with an average Au

TABLE 4. COMPARISON OF AVERAGE Au AND Ir CONTENTS OF MORB AND SEAFLOOR HYDROTHERMAL SULFIDES

Sample Type	Au		Ir		Au/Ir
	ppb		ppb		
MORB <sup>1</sup>	1.2		0.04		30
MORB sulfide globules <sup>2</sup>	19,000		1,200		16
TAG area <sup>3</sup>					
Massive sulfides, hydrothermal mound area	2,990		0.50		6,000
Vent particulate sediment	1,320		0.77		1,700
Juan de Fuca <sup>4</sup>					
Low-Au suite	80		0.027		2,960
Medium-Au suite	699		0.017		41,000

1. Au: literature average of 210 analyses (Crocket 1990). Ir: literature average; Keays & Scott (1976), Hertogen *et al.* (1980). 2. Peach *et al.* (1989). 3. Table 2, this study. 4. Table 1, this study; the low-Au suite includes samples with Au <218 ppb, and the medium-Au suite consists of dredge series DR02 and sample DR06-03.

content of 80 ppb, have an average Ir content of 0.027 ppb Ir (range 0.007 – 0.056), a level comparable with unmineralized MORB (Crocket 1981). These characteristics are considered to reflect mainly the influence of hydrothermal processes.

### Gold

The JFR suites are from areas where some high-temperature hydrothermal emission is currently active, such as Axial Seamount, and others, such as Middle Valley and the Endeavour segment, where low-temperature hydrothermal activity predominates or where hydrothermal activity has ceased (ALVIN dive 1416). In the area sampled in Middle Valley, the basalt rock column is buried beneath ~100 m of sediment having a maximum temperature of ~100°C (Goodfellow & Blaise 1988). The Axial Seamount suite is Au-enriched (>1000 ppb), but the majority of other samples are much lower, generally containing >200 ppb. A few samples from Middle Valley dredge hauls, including DR02 and sample DR06-03, have gold contents of 300 to 1138 ppb. The Axial Seamount samples are referred to as the high-Au suite (>1900 ppb), the Middle Valley dredge samples as the medium-Au suite (>200 – 1138 ppb), and the remainder, as the low-Au suite (<218 ppb).

The high- and low-Au suites are characterized by distinctive minor-element abundances, as noted in Table 3. The high-Au Axial Seamount samples are generally characterized by higher Ag, Sb and As, and lower Se than the low-gold suite. Metal ratios also differentiate the high- and low-Au groups, with higher Au/Ag and Au/Se values and a lower As/Sb value characteristic of the high-Au suite. The sediment core PAR 85-13 is an exception in that its Au/Ag value, greater than 27, is the highest of any JFR suite and apparently a reflection of very low Ag content in these sediments. The average Au content is  $134 \pm 59$  ppb. These relatively low metal contents

may reflect loss of precious metal as hydrothermal fluids rise through the sediment column (Goodfellow & Blaise 1988).

A systematic variation of Au with Zn, a major constituent of some samples, is evident; for example, those with >1000 ppb Au have Zn contents between 12 and 32 wt.%, whereas samples with <1000 ppb generally range from 7.6 to 0.056 wt.% Zn. However, relatively Au-poor samples may have high Zn (*e.g.*, sample 1418-6b-B9, with 180 ppb Au and 25 wt.% Zn), and moderately Au-rich samples are low in Zn (*e.g.*, DR02-05, with 645 ppb Au and 0.056 wt.% Zn). Barium content is only weakly correlated with Au (*e.g.*, Endeavour suite, Table 1).

TAG samples are mainly sulfides precipitated in an active, high-temperature hydrothermal mound environment or are sediments with a significant contribution of hydrothermal vent precipitate. Most carry in excess of 1000 ppb Au. The three exceptions include a sample rich in iron oxide, 1-17, from the central mound, which probably represents oxidized chimney sulfide (Thompson *et al.* 1988), with 120 ppb Au. This distinctly lower Au content suggests that significant loss of Au may accompany sulfide oxidation in cold seawater. The other two Au-poor samples are sediments, one carbonate-rich with 170 ppb Au, and the other a turbidite with a relatively high Au content of 700 ppb. The turbidite probably represents a debris flow of mainly hydrothermal sediment. The carbonate sample is a mixture of hydrothermal vent precipitate and pelagic carbonate (Nelson *et al.* 1986), in which the latter component represents a Au-poor dilutant. This sample also carries the lowest Pd content, 2.6 ppb, of the sediment suite. Thus for the TAG occurrence, a Au content of 1000 ppb seems characteristic of sulfides precipitated from high-temperature hydrothermal fluids. The Au content of the iron-rich sediments is very consistent, the upper bed yielding values of 1450 and 1430 ppb, and the lower bed, 1090 ppb Au. These precipitates are Cu-rich and Zn-poor (Thompson *et al.* 1988), which suggests a sustained period of high-temperature venting.

The generation of relatively high Au concentrations in seafloor sulfides has been discussed by Hannington & Scott (1988) and Hannington *et al.* (1986). One sample in the TAG suite, 1-46, a Cu-rich massive sulfide from the central mound region, yielded 18,900 ppb Au on one aliquot and 5700 and 6500 ppb on duplicate analyses of a second aliquot. These are the highest Au values obtained in the study and are indicative of heterogeneous distribution of the metal. In addition, the highest Ir value, 7.6 ppb, also was found in this sample. The above authors argued that buildup of Au in seafloor sulfides arises mainly by upgrading lower Au contents of a few hundreds of ppb from earlier, high-temperature stages of growth of chimneys during medium- to low-

temperature stages of chimney maturation. A variety of processes, including dissolution of early high-temperature minerals, prolonged fluid-rock reactions as chimney vents clog, and localized dissolution, transport and reprecipitation of auriferous phases are involved in an overall zone-refining process (Hannington *et al.* 1986).

The initial level of Au achieved in the high-temperature stages of chimney growth suggested by TAG samples 1-9 and 1-45 is at least 1000 ppb. This level also is substantiated by the TAG sediment suite in that the hydrothermal precipitate-rich beds average approximately 1000 ppb Au. The zone-refining process characteristic of chimney maturation is unlikely to be relevant to these precipitates from high-temperature vent fluids. Thus the Au content of chimney sulfides inherited from early high-temperature stages of growth may be on the order of 1000 ppb.

### Iridium

The Ir content of TAG massive sulfides is some 25 times higher than the average of the JFR samples. The TAG massive sulfides, omitting sample 1-46, average 0.50 ppb Ir, and the Fe-rich sediments average 0.77 ppb compared with an average of 0.024 ppb Ir for the Middle Valley and Endeavour samples of the JFR. The omission of sample 1-46, which has the highest Ir content (7.6 ppb) of any sample in the study, is made on the grounds that it has been subject to zone refining and other fluid-rock reactions, which may have concentrated Ir in 1-46, as well as Au. Iridium will probably remain relatively immobile, and if early high-temperature phases are dissolved and removed, the initial Ir content of chimney assemblages should be increased.

The TAG samples probably provide a better estimate of the initial Ir content of high-temperature hydrothermal sulfides. This contention is supported by the similar average Ir contents of particulate-rich sediments and sulfides of the central mound. The low Ir in the JFR samples may reflect several factors. Thus extensive low-temperature submarine weathering may contribute to Ir loss in the case of Endeavour samples 1417, which were taken from a sulfide ridge lacking current hydrothermal activity. Also, the 1419 Endeavour samples were taken from a white smoker, or low-intensity, hydrothermal area. The Middle Valley dredge samples are sulfides precipitated from fluids that have traversed some 300 m of sediment, which may have depleted the fluids of metals at depth (Goodfellow & Blaise 1988). However, some Middle Valley samples, particularly those of dredge haul DR02, are relatively high in Au (711 - 1138 ppb) and very low in Ir (0.008 - 0.024 ppb). In this case, submarine weathering is unlikely to be a principal cause of low Ir in that low Au also would be expected.

### Palladium

As noted for Ir, the TAG area is characterized by higher Pd in sulfides than in the JFR region. The majority of TAG samples range from 136 to 2.6 ppb Pd, with one Zn-rich sulfide sample from the central mound area (1-9) recording the maximum Pd content of the study, 1000 ppb. The Pd content of Au-rich sulfides from Axial Seamount and Middle Valley indicates that Pd is less than 20 ppb in these samples, and probably as low as 2 ppb.

Both regions present good evidence that Pd is not concentrated in seafloor sulfides, as is the case for Au. Although one of three TAG massive sulfides from the mound area is Pd-rich, the other two, including the Au- and Ir-rich Cu sulfide sample, are low in Pd, with only 3.5 and 3.2 ppb. The Fe-rich hydrothermal sediments range from 26 to 70 ppb Pd, averaging 41 ppb. In view of the diverse Pd contents in the central mound suite and the likely influence of late-stage low-temperature processes in some of these samples, the average Pd concentration in hydrothermal sediments, 41 ppb Pd, probably is the best estimate of Pd levels reached during high-temperature precipitation of seafloor sulfides.

### Fractionation of noble metals in seafloor sulfides

A distinctive feature of noble metals in seafloor sulfides is a high Au content accompanied by low Ir and Pd. This fractionation is illustrated in Table 4 and Figure 5, in which average Au/Ir values for

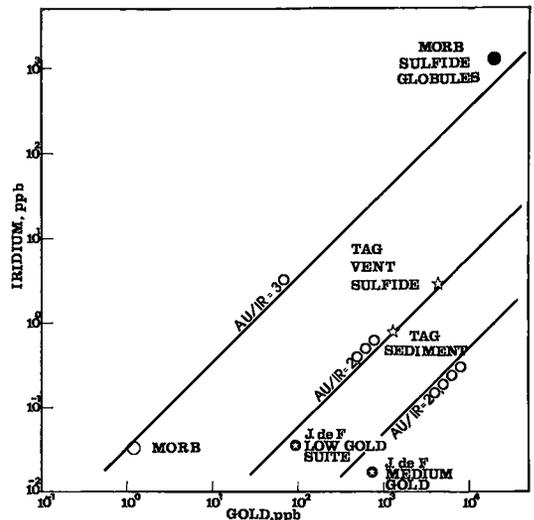


FIG. 5. Au/Ir values in seafloor hydrothermal sulfides compared with MORB and MORB-hosted magmatic sulfide globules.

various components of the seafloor hydrothermal environment are plotted. The Pd data base, particularly that for seafloor sulfides, is too limited to warrant detailed consideration.

As shown in Figure 5, average Au/Ir values for various types of seafloor sulfide range from roughly 1700 to 41,000. In contrast, in the MORB host rock the value is 16 to 30. In primary MORB-hosted Fe-Cu-Ni sulfide the Au/Ir ratio is 16, comparable to the MORB average. The most likely source of metal in seafloor hydrothermal fluids is the basalt wallrock of the fluid conduit (see subsequent discussion). Thus, relative to the MORB source, hydrothermal sulfides are richer in Au by some 100 times more than Ir (*i.e.*  $(\text{Au/Ir})_{\text{hydrothermal sulfide}}/(\text{Au/Ir})_{\text{MORB sulfide}} = 1700/16 = 106$ ). Whether this fractionation occurs in the source region, during ascent of the hydrothermal fluid, at the site of sulfide precipitation, or in all of these domains is difficult to quantify, but some constraints can be noted.

Much evidence points to a MORB-dominated rock column as the source of metals. Based on experimental and theoretical modeling of basalt-seawater reactions, Seyfried *et al.* (1988) and Morton (1984) concluded that pressures of 350 to 450 bars (1 to 3 km depth below seafloor) and temperatures of 350 to 400°C characterize the maximum *P-T* conditions applicable to seawater-generated hydrothermal fluids at mid-ocean ridges. Under these conditions, a variety of metasomatic reactions involving exchange of Mg, Ca and Na between the rock column and water-rich fluids convert a seawater-like fluid to a rock-equilibrated fluid. The latter is distinctly acid ( $4 < \text{pH} < 4.5$ ), reducing (probably buffered by pyrite + pyrrhotite  $\pm$  magnetite), enriched in reduced sulfur ( $\text{H}_2\text{S}$ ,  $10^{-1}$  to  $10^{-3}$  mole/kg), Cu, Zn, Fe and  $\text{SiO}_2$  and depleted in  $\text{SO}_4^{2-}$  ( $< 10^{-3}$  mole/kg) and Mg relative to seawater, with a prevailing water/rock ratio of  $\sim 1$  (Seyfried *et al.* 1988, Bowers *et al.* 1988, Von Damm 1988). Among the more persuasive lines of evidence that the rock column is the source of metals are lead isotopes (Hegner & Tatsumoto 1987) which, for the southern JFR, are virtually identical in MORB and seafloor sulfides. Furthermore, sulfur isotope models (Janecky & Shanks 1988, Shanks & Seyfried 1987) require a significant component of unfractionated sulfur ( $\delta^{34}\text{S} = 0\text{‰}$ ), with traces of rock-hosted magmatic sulfide comprising the most logical source.

Peach *et al.* (1989) and Peach & Mathez (1988) have shown that MORB-hosted sulfide globules may carry ppm levels of noble metals (Table 4). Release of such metals to hydrothermal fluids is suggested by studies of Bowers *et al.* (1988) of fluids at several East Pacific Rise vents, in which approximate equilibrium with respect to pyrrhotite was demonstrated. As these fluids show very large variations in concentrations of dissolved iron and reduced sul-

fur, and yet are at approximate solubility equilibrium with pyrrhotite, dissolution of some rock-hosted pyrrhotite can be expected. It is significant that the average Au/Ir value of MORB (Crocket 1990) is within a factor of two of that in sulfide globules, suggesting that such sulfide must be a major sink for noble metals in MORB.

Depending on the extent of pyrrhotite dissolution by hydrothermal fluid, a release of noble metals to such fluids would seem inevitable. Provided an immiscible sulfide melt is the major MORB sink for noble metals, it is unlikely that any major fractionation will occur in the release of metals to hydrothermal fluids. Fractionation would be expected if various metals were hosted in different mineral phases. This possibility is unlikely in the case of a pyrrhotite-dominated immiscible sulfide host, in that the activity of reduced sulfur is probably much too high to permit the stable coexistence of non-sulfide phases, for example metals. Thus, high-temperature, rock-equilibrated hydrothermal fluids probably have Au/Ir values of approximately 16 to 30.

The solubility and speciation of noble metals in such fluids can be evaluated critically in the case of gold, but only very qualitatively for the *PGE*. Using the solubility data of Seward (1973) and thermodynamic data of Helgeson (1969) for bisulfides and chlorides, respectively, Hannington *et al.* (1986) showed that fluids modeled from the Axial Seamount vent could carry more than 20 ppb Au as  $\text{Au}(\text{HS})_2^-$  and that the solubility of Au as chloride complexes is insignificant in such fluids ( $250^\circ\text{C}$ ;  $5 < \text{pH} < 6$ ). Solubility data for Pd and Ir at relevant *P* and *T* are not available, but in the case of Pd, Mountain & Wood (1988) concluded, on a basis of extrapolation of low-temperature ( $25^\circ\text{C}$ ) thermodynamic data, that major solubility is generated by bisulfide complexes in mildly alkaline solutions. Chloride complexes are considered unlikely to contribute significantly to Pd solubility, except in strongly oxidizing, acidic solutions.

Transport of hydrothermal fluids to higher structural levels in the rock column is not considered a likely means of inducing fractionation. Of the critical intensive parameters including temperature, total pressure and various partial pressures such as  $P(\text{O}_2)$ , only total pressure is likely to change significantly in conjunction with fluid rise. Boiling has been advocated as a process relevant to seafloor hydrothermal fluids and would depress solubility of aqueous complexes, but positive evidence of boiling, as in fluid inclusions, has not been documented (Hannington & Scott 1988).

The zone of mixing of fluid with large volumes of seawater, roughly within the top 30 m of the rock column, is considered the major site of fractionation of the noble metals. The properties of seawater contrast sharply with those of the hydrothermal

fluid; seawater is cold, oxidizing, alkaline, sulfide- and metal-poor and sulfate-rich relative to rock-equilibrated hydrothermal fluids. Mixing of seawater and hydrothermal fluids should generate a lower temperature and a more oxidizing, alkaline, and sulfide-poor fluid compared to a pure hydrothermal end-member. Temperature drop would decrease the solubility of all noble metals, as can be verified for Au bisulfide solubility from Seward's (1973) experimental data. However, to account for the Au-Ir fractionation of 100 by temperature decrease alone would require large differences in stability constants of complex ions as a function of temperature, particularly if solubility for both metals is due to the same anionic complexes [e.g.,  $\text{Au}(\text{HS})_2^-$ ,  $\text{Ir}(\text{HS})_6^3-$ ]. If, however, the anion ligand is sensitive to oxidation state or pH, as is the case for reduced sulfur species such as bisulfide, then there is a greater potential for large solubility differences. In the case of the Au and Ir species used above for illustration, the Ir complex is more sensitive to changes in  $\text{HS}^-$  concentration. Another possibility is that PGE bisulfide complexes are kinetically more inert than Au bisulfide complexes, so that the latter persist beyond their thermodynamic fields owing to kinetic barriers. Thus the site of seawater mixing with hydrothermal fluid, that is, the deposition regime, is probably the most likely site of metal fractionation.

### CONCLUSIONS

A range of Au contents of about 2000 exists among seafloor accumulations of sulfide; the existence of a population of samples with Au contents in excess of 1000 ppb has been confirmed. The PGE, represented by Pd and Ir, are not strongly concentrated in seafloor sulfide mineralization. There is thus a major difference in proportions of the noble metals between these hydrothermal sulfides and, for example, magmatic sulfides.

In the TAG hydrothermal area, the presence of about 1000 ppb Au in a sediment field with substantial contribution from a high-temperature vent indicates that this level of Au must be generated in the TAG setting in high-temperature black smoke from hydrothermal fluids.

The degree of fractionation of Ir and Au can be estimated by comparison of Au/Ir values in MORB-hosted sulfides and hydrothermal sulfides. Arguments that MORB-hosted sulfide is the primary source of noble metals for hydrothermal fluids lead to the conclusion that high-temperature rock-equilibrated hydrothermal fluid will inherit a Au/Ir value of about 16 by dissolution of MORB sulfide. A fractionation of at least 100 times is implied by the Au/Ir values of 1700 or greater in hydrothermal sulfides.

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### REFERENCES

- BARNES, S.-J., NALDRETT, A.J. & GORTON, M.P. (1985): The origin of the fractionation of platinum group elements in terrestrial magmas. *Chem. Geol.* **53**, 303-323.
- BOWERS, T.S., CAMPBELL, A.C., MEASURES, C.I., SPIVACK, A.J., KHADEM, M. & EDMOND, J.M. (1988): Chemical controls on the composition of vent fluids at 13° - 11°N and 21°N, East Pacific Rise. *J. Geophys. Res.* **93**, 4522-4536.
- CHYI, L.L & CROCKET, J.H. (1976): Partition of platinum, palladium, iridium, and gold among coexisting minerals from the Deep Ore Zone, Strathcona mine, Sudbury, Ontario. *Econ. Geol.* **71**, 1196-1205.
- CROCKET, J.H. (1981): Geochemistry of platinum-group elements. In *Platinum-Group Elements: Mineralogy, Geology, Recovery* (L.J. Cabri, ed.). *Can. Inst. Min. Metall., Spec. Vol.* **23**, 47-64.
- \_\_\_\_\_ (1990): Distribution of gold in the earth's crust. In *Gold Metallogeny and Exploration* (R.P. Foster, ed.). Blackie & Son, London (in press).

- \_\_\_\_\_, KEAYS, R.R. & HSIEH, S. (1968): Determination of some precious metals by neutron activation analysis. *J. Radioanal. Chem.* **1**, 487-507.
- GOODFELLOW, W.D. & BLAISE, B. (1988): Sulfide formation and hydrothermal alteration of hemipelagic sediment in Middle Valley, northern Juan de Fuca Ridge. *Can. Mineral.* **26**, 675-696.
- HANNINGTON, M.D., PETER, J.M. & SCOTT, S.D. (1986): Gold in sea-floor polymetallic sulfide deposits. *Econ. Geol.* **81**, 1867-1883.
- \_\_\_\_\_, & SCOTT, S.D. (1988): Mineralogy and geochemistry of a hydrothermal silica-sulfide-sulfate spire in the caldera of Axial Seamount, Juan de Fuca Ridge. *Can. Mineral.* **26**, 603-625.
- HEGNER, E. & TATSUMOTO, M. (1987): Pb, Sr, and Nd isotopes in basalts and sulfides from the Juan de Fuca Ridge. *J. Geophys. Res.* **92**, 11,380-11,386.
- HELGESON, H.C. (1969): Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.* **267**, 729-804.
- HERTOGEN, J., JANSSENS, M.-J. & PALME, H. (1980): Trace elements in ocean ridge basalt glasses: implications for fractionations during mantle evolution and petrogenesis. *Geochim. Cosmochim. Acta* **44**, 2125-2143.
- JANECKY, D.R. & SHANKS, W.C., III (1988): Computational modelling of chemical and sulfur isotopic reaction processes in seafloor hydrothermal systems: chimneys, massive sulfides, and subjacent alteration zones. *Can. Mineral.* **26**, 805-825.
- KEYS, R.R. & SCOTT, R.B. (1976): Precious metals in ocean ridge basalts: implications for basalts as source rocks for gold mineralization. *Econ. Geol.* **71**, 705-720.
- MORTON, J.L. (1984): *Oceanic Spreading Centers: Axial Magma Chambers, Thermal Structure and Small Scale Ridge Jumps*. Ph.D. thesis, Stanford Univ., Stanford, California.
- MOUNTAIN, B.W. & WOOD, S.A. (1988): Chemical controls on the solubility, transport, and deposition of platinum and palladium in hydrothermal solutions: a thermodynamic approach. *Econ. Geol.* **83**, 492-510.
- NALDRETT, A.J. (1981): Platinum-group element deposits. In *Platinum-Group Elements: Mineralogy, Geology, Recovery* (L.J. Cabri, ed.). *Can. Inst. Min. Metall., Spec. Vol.* **23**, 197-231.
- NELSEN, T.A., METZ, S., TREFRY, J. & PIMMEL, A. (1986): Sedimentology and composition of sediment near a black smoker field on the Mid-Atlantic Ridge. *Trans. Am. Geophys. Union* **67**, 1022 (abstr.).
- PEACH, C.L. & MATHEZ, E.A. (1988): Gold and iridium in sulphides from submarine basalt glasses. In *Geo-Platinum 87* (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier Applied Science, London, U.K. (409-410).
- \_\_\_\_\_, \_\_\_\_\_ & KEAYS, R.R. (1989): Sulfide melt-silicate melt distribution coefficients for the noble metals as deduced from MORBs. In *Abstracts 5th International Platinum Symposium* (H. Papunen, ed.). *Bull. Geol. Soc. Finland* **61**(1), 58.
- SAMPSON, J. (1986): *A Petrological Study of Sea Floor Polymetallic Sulfides from the Endeavour Site, Juan de Fuca Ridge Northeast Pacific Ocean*. M.Sc. thesis, Univ. Ottawa, Ottawa, Ontario.
- SEWARD, T.M. (1973): Thio complexes of gold and the transport of gold in hydrothermal ore solutions. *Geochim. Cosmochim. Acta* **37**, 379-399.
- SEYFRIED, W.E., JR., BERNDT, M.E. & SEEWALD, J.S. (1988): Hydrothermal alteration processes at mid-ocean ridges: constraints from diabase alteration experiments, hot-spring fluids, and composition of the oceanic crust. *Can. Mineral.* **26**, 787-804.
- SHANKS, W.C., III & SEYFRIED, W.E., JR. (1987): Stable isotope studies of vent fluids and chimney minerals, southern Juan de Fuca Ridge: sodium metasomatism and seawater sulfate reduction. *J. Geophys. Res.* **92**, 11,387-11,399.
- STOCKMAN, H. W. (1983): Neutron activation determination of noble metals in rocks: a rapid radiochemical separation based on tellurium coprecipitation. *J. Radioanal. Chem.* **78**, 307-317.
- THOMPSON, G., HUMPHRIS, S.E., SCHROEDER, B., SULANOWSKA, M. & RONA, P.A. (1988): Active vents and massive sulfides at 26°N (TAG) and 23°N (Snakepit) on the Mid-Atlantic Ridge. *Can. Mineral.* **26**, 697-711.
- TREFRY, J.H., METZ, S., TROCINE, R.P. & NELSEN, T.A. (1986): Geochemistry and history of hydrothermal precipitates in a Mid-Atlantic Ridge vent field. *Trans. Am. Geophys. Union* **67**, 1022 (abstr.).
- VON DAMM, K.L. (1988): Systematics of and postulated controls on submarine hydrothermal solution chemistry. *J. Geophys. Res.* **93**, 4551-4561.

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