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GEOCHEMISTRY AND ECONOMIC POTENTIAL OF MASSIVE SULFIDE DEPOSITS FROM THE EASTERN PACIFIC OCEAN

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ABSTRACT

Bulk chemical analyses were performed for major and minor elements using a variety of techniques on a suite of 9 samples of sea floor massive sulfide deposits from 21°N EPR, Juan de Fuca Ridge and Galapagos Rift. Results indicate that deposits at 21°N and Juan de Fuca are very similar despite a geographic separation of 2300 km and are composed primarily of Zn, Fe, and S, with important minor concentrations of Ag, As, Cd and Ge. The Galapagos Rift massive sulfide is primarily Fe, Cu and S and with important minor contents of only Co and Mo. Au is low, ranging from below detection up to 0.17 ppm. Pt group metals are very low, and average about 0.001 ppm. Consideration of enrichment factors and relative metal abundance suggests that MORB is a sufficient source for all the metals enriched in the sea floor deposits.

The economically important metals for the 21°N and Juan de Fuca deposits are primarily Zn and Ag, (97%) with potential by-products of Cu, Cd and possibly, Ge. For the Galapagos Rift, the primary value is with Cu (86%) with potential by-products of Co and Mo. The Galapagos Rift deposit is similar to, but contains about twice the Cu content, of typical ore from the Skouriotisa mine of the Troodos complex of Cyprus. The grade of the 21°N/Juan de Fuca deposits is 4 times greater than that of the Galapagos Rift and about twice that of prime deep-sea manganese nodules.

INTRODUCTION

Massive sulfide deposits are prominent features in many land-based ophiolite complexes of the world, and have produced large tonnages of copper. The suspicion that these massive sulfide deposits originally formed on the sea floor led to the discovery of massive sulfide mounds (Francheteau et al., 1979) and later to hydrothermal vents and actively growing mounds on the East Pacific Rise (EPR) at the mouth of the Gulf of California (Spiess et al., 1980). Observed by manned submersibles, hydrothermal vents with fluid temperatures exceeding 350°C were found to be actively forming massive-sulfide mounds, several meters high, composed of zinc, copper, and iron sulfides along with significant quantities of silver. Similar systems (Fig. 1) were later discovered in the Galapagos Rift, (Malahoff, 1981, 1982) the Guaymas Basin (Lonsdale et al., 1980), the East Pacific Rise at 13°N (Hekinian et al., 1981) and most recently along the Juan de Fuca Ridge off the coast of Oregon (Normark et al., 1982). Much optimism has been expressed concerning the economic potential of these deposits, spurred on by reports that the deposits may have high values of Zn, Cu, Ag, Au and Pt (Hekinian et al., 1980).

All of these deposits have been found at medium- to fast-rate spreading centers with a total separation rate of approximately $\geq$5 cm/yr). The presence of active hydrothermal vents at all these sites suggests that the phenomenon may occur over much of the vast length of medium-rate and faster spreading systems, which in the Pacific and Indian Ocean basins extend a total of approximately 40,000 km.

We report here the results of chemical analyses of major and minor components of bulk samples from 21°N EPR, Juan de Fuca Ridge and the Galapagos Rift. The results are discussed in terms of their economic implications and how they bear on the question of whether the mid-ocean ridge basalts (MORB) are a reasonable source of the massive sulfide deposits via sea-water leaching and transport.

THE DEPOSITS

The deposits at 21°N are the most extensively studied to date and details of their morphology structure, petrography, mineralogy and partial chemistry are given by Hekinian et al. (1980), Styrt et al. (1981) and Haymon and Kastner (1981), Oudin et al. (1981), Oudin (1981), and Zierenberg et al. (in press). These deposits are classified as chimney edifices and basal mounds. Chimneys appear to top the basal mounds; some are actively venting hydrothermal fluids (black and white smokers) while others are inactive. Inner linings of the highest temperature active chimneys are chalcopyrite or cubanite while the slightly cooler ones are lined by wurtzite (Styrt et al., 1981). The chimneys are composed of anhydrite and mixed sulfides. Basal mounds are composed primarily of zinc sulfides and make up the bulk of the deposits.

A portion of the basal mounds may have accreted from the physical and chemical degredation of the chimneys as the conduits progressively become plugged with precipitate, a process suggested by Haymon and Kastner (1981). However, most of the basal mounds do not have chimneys (W. Normark, personal communication), and therefore, were possibly formed in place by slow, but pervasive advection of hydrothermal fluid through the body of the mound.

The deposits described by Hekinian et al. (1980) (CYAMEX deposit) are all apparently older inactive mounds which constituted the original discovery on the East Pacific Rise at 21°N, and are located on somewhat older ocean floor 10 km NE of the active field.

Slabs of massive sulfides were recovered by transponder navigated dredges from the Juan de Fuca Ridge after vent sites had been located by bottom photography (Normark et al., 1982). On the basis of the morphology of the dredge samples the deposits are classified into two categories, types A & B (Koski et al., 1982). Type A are angular slabs of crudely layered, coarsely crystalline sulfide aggregates composed primarily of dark grey zinc sulfides with minor layers of pyrite. Type B are rounded fragments of hard but porous spongy-textured light grey zinc sulfides. Type A, is about twice as abundant as Type B (Koski et al., 1982). The mineralogy of both A and B resembles the basal mounds of 21°N, EPR.

At the Galapagos Rift, solid massive sulfide stacks 3 to 4 meters high in a 2 km long zone along a normal fault were observed and sampled from a manned submersible (Malahoff, 1981, 1982). Texturally and mineralogically the Galapagos material contrasts with that from 21°N EPR and Juan de Fuca, being composed in all the samples described of structureless and coarsely crystalline pyrite with important amounts of chalcopyrite.

SAMPLES

Samples were chosen to represent the typical mineralogy of the deposit as much as possible, and are described in Table 1.

A. 21°N EPR

Five samples were chosen for chemical analyses (Table 1); three from basal mounds (samples 1, 2 and 3), and two from black smoker chimneys (samples

4 and 5). Splits of these samples were taken for petrographic and isotopic analyses as reported by Zierenberg et al. (in press). Samples were kindly provided by R. Haymon and M. Kastner, and are described in their sample catalogue (Haymon and Kastner, 1979).

B. Juan de Fuca

Bulk samples of Type A (sample 8) and Type B (sample 6) were cut from slabs adjacent to petrographic samples as described in Koski et al. (in press). In addition a sample of a pyritic layer within sample 8 was taken, representing a minor but typical segretation. Samples were kindly provided by R. Koski.

C. Galapagos Rift

The sample made available for chemical analysis was brassy colored coarsely crystalline pyrite with minor chalcopyrite. The sample has neither layering nor biologic structures. This sample was kindly provided by A. Malahoff.

ANALYTICAL METHODS

A variety of techniques was applied to the samples, each chosen for its optimum reliability for a specific element or group of elements. Some of these techniques also provided duplicate analyses of other elements, which allowed a limited comparison between analytical techniques. Such overlap proved valuable in one case in which significant contamination for Au was identified in one split of samples. Lack of agreement between methods prompted re-sampling and analysis that confirmed the contamination. Without the overlap, the contamination might have been overlooked and an erroneous conclusion of an economically significant concentration of Au might otherwise have been reported.

Because samples became available at different times, they were not processed as a single batch, which complicates the intercomparison of results somewhat. Samples 1 through 8 were analyzed for Zn, Fe, Cu, Pb, Si, Al, Ca, Ag, Mo and Cd by quantitative optical emission spectroscopy using an inductively coupled plasma source (ICP, J. Crock, analyst). The samples were dissolved in $HCl-HNO_3-HF$ mixture using a teflon-lined autoclave at 110°C. After dissolution the samples were taken to dryness in the presence of perchloric acid to drive off all silica, and were then taken up in 1% HNO_3 for spectral analysis. Analyses were performed on a Jarrell-Ash model 1160 ICP emission spectrometer, calibrated against multielement artificial standard solutions.

Samples 6 through 9 were analyzed for Zn, Fe, Cu, Pb, Ag, and Cd by conventional atomic absorption spectroscopy, using the same dissolution technique as employed for ICP (AA, R. Rosenbauer, analyst). Analyses were performed on a Perkin-Elmer 370 atomic absorption spectrometer calibrated against multielement artificial standard solutions in a matrix matched to that of the samples.

Total sulfur was analyzed for all samples by the conventional total combustion technique (LECO, J. Seeley, analyst). All 9 samples were analyzed by instrumental neutron activation analysis (INAA, described in Baedecker, 1979; P. Baedecker, analyst). The gamma-ray spectrum of the irradiated sulfide samples is dominated by the single gamma-ray line at 1115 keV from ^{65}Zn and its associated compton continuum, which limits the sensitivity for the determination of many of the other elements. Interference-free lines for the determination of about 15 elements could be observed in at least some of the sample spectra, but Ba, Cr, Cs, Sr, U, and W were near or at the detection limit in most samples, and the results for those elements should be considered as semiquantitative. The INAA technique appears to be best suited to the determination of the following subset of elements in polymetallic sulfides: Fe, Zn, As, Co, Sb, Se, Ag, Au. The elements Fe, Co, and Sb all have gamma-ray lines of higher energy than the ^{65}Zn 1115 keV line, and the sensitivity for their determination is not limited by the Zn content of the samples. The detection limits for the determination of Ag and Au are roughly 30 ppm and 80 ppb respectively for samples with Zn contents near 50%, while contents as low as 10 ppm Ag and 20 ppb Au could be measured with Zn contents near 1%. Mo was determined in several samples and the results agreed well with those obtained by semiquantitative spectrographic analysis. The determination of Mo can be subject to interference from Fe unless the Ge(Li) detector used for counting has adequate resolution.

All samples were analyzed for Au, Pt, Pd, and Rh by atomic absorption spectroscopy after pre-concentration by fire assay techniques (fire assay AA, F. Brown, P. Aruscavage, analysts). The procedure used for the determination of Au was that described by Huffman et al. (1967). The powdered sample is roasted at 700°C to remove sulfide sulfur and then reductively fused with a mixture of PbO, Na_2CO_3, Borax glass, and flour. The Au is collected in the reduced lead button containing a 2 milligram silver inquart. The lead is re-oxidized (cupelled) leaving the Au in the silver bead. The bead is then dissolved in HNO_3 followed by aqua-regia and the Au is then further purified by extraction into methyl isobutyl ketone (MIBK). The absorbance of the organic phase is determined by flame atomic absorption spectrometry and compared to standards treated (extracted) similarly.

The procedure used for the determination of the Pt metals also employs a fire-assay reductive fusion similar to that described above for Au, however the silver inquart is replaced by a Au inquart because Au collects the Pt metals more efficiently. After separation of the Au bead from the fire assay cupellation, the bead is dissolved in aqua-regia, the volume adjusted to 1 ml and the absorbance determined by graphite furnace atomic absorption spectrophotometry, the absorbance being compared to standards carried through the entire procedure.

All samples were analyzed for Ag, As, B, Ba, Bi, Cd, Co, Cr, Ga, Ge, Hg, Mn, Ni, Sb, Sc, Se, Te, Tl, Sr, Y, Zr, Na, K, Ti, P, Be, Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Li, Nb, Sn, Ta, and Th by several conventional semiquantitative optical emission spectroscopy techniques (SQS, SWR, analysts C. Heropoulis, P. Briggs, J. Crock, L. Mei and J. Harris).

DATA

A. Intercomparison of techniques

Results for those elements analyzed by more than one technique are shown in Table 2. In general, agreement is quite good, particularly for replicates within a single batch. Important discrepancies are mostly between batches (see, for example Ag and As, Table 2) and can, therefore be attributed to inhomogeneity of the sample. An additional point is that with few exceptions, the semiquantitative optical spectroscopy results are consistent with the more quantitative techniques. A composite composition was compiled for each sample (Table 3). For most samples, the composite concentration reflected agreement among two or more redundant analyses for many elements. In other cases only a single quantitative analysis was available. Where there was disagreement, the result for the method considered optimum for that element was used. Asterisks are shown by those entries for which only semiquantitative analyses are available.

B. Major components

Results indicate that Fe, Zn, Cu, SiO_2, CaO, and MgO, S and SO_3 are the only major components (>1%) for all samples, and the summations of close to 100% indicate no major component was missed and that the quality of the analyses is good (Table 3). These components reflect the mineralogical composition very well; the 21°N samples of the three basal mounds (1, 2, and 3) are composed of Fe, Zn and S and correspond to the bulk mineralogy of Zn and Fe sulfides, while the samples of the two black smokers (4 and 5) are composed of primarily of CaO and SO_3 with important MgO corresponding to anhydrite and minor magnesium hydroxysulfate (MHSH) (compare Tables 1 and 3). A significant SiO_2 content (19%) is found only in the mound sample, 1. Mineralogical analysis of this sample detected no crystalline silicates except for a trace of opaline silica; all the silica, therefore, must be amorphous. Cu and Pb are present in the inactive chimney and basal mound samples, but only at a few tenths of a percent, and these low values are consistent with the trace amounts of chalcopyrite and galena detected in the mineralogical analysis (Table 1).

Both Type A and Type B samples of the Juan de Fuca deposits (samples 6 and 8) are primarily Zn and S, which corresponds to their sphalerite-wurtzite mineralogy and they almost totally lack CaO and SO_3. They are chemically very similar, therefore, to the basal mounds of 21°N (samples 1, 2, and 3). The sample of the pyritic lense (sample 7) is almost pure Fe and S with a little SiO_2. The Galapagos sample, 9, is also primarily Fe and S, but contains almost 5% Cu, consistent with its mineralogy and in marked contrast to all the other samples.

C. Minor components

The Zn-rich samples from 21°N and Juan de Fuca (1, 2, 3, 6 and 8) share high concentrations of the chalcophile elements Ag, As, Cd, Tl and Ge (Table 3). Ag is particularly rich, exceeding 200 ppm in samples 1, 3, 6 and 8, in agreement with comparable values reported by Hekinian et al. (1980) for 21°N samples and by Koski et al. (1982) for Juan de Fuca samples. The two groups contrast only in Sb for which 21°N is enriched and Juan de Fuca depleted.

The Galapagos sample, in contrast, is particularly depleted in the minor components except for Co and Mo, in which it is the only sample so enriched. Its Co content of 482 ppm contrasts with the low values for all the other samples. Ni is strikingly low for all 9 samples, and ranges from <1.5 to only 5 ppm. Sr clearly follows anhydrite, being enriched in the two black smokers (samples 4 and 5). Ba is highest in the basal mound (sample 1) and occurs to varying degrees in all samples, presumably as barite.

The precious metals (Au and platinum group) are of particular interest because high concentrations were reported by Hekinian et al. (1980) for Au (up to 3.5%), and for Pt (up to 1%) from 21°N. These concentrations were obtained by electron microprobe analysis and referred only to small micron-sized areas on the polished sections. Hekinian et al. (1980) made no claims that these spot concentrations were representative of the bulk samples. The highly sensitive bulk analyses of the present study are conclusive. Bulk Au, analyzed by three independent techniques, is less than 0.2 ppm for all massive sulfide samples from 21°N Juan de Fuca and Galapagos Rift, the highest concentrations are 0.17 ppm for sample 2 and 0.13 ppm for sample 8 (Table 3). The platinum group (Pt, Pd, and Rh) ranged from less than 1 ppb up to only 3 ppb for any sample (Table 3), amounts significantly below any economic importance.

DISCUSSION

A. Normative mineralogy

The bulk chemical analysis allows a calculation of the normative mineralogical composition because all the identified minerals have relatively simple and constant stoichiometries. The calculation is made as follows: all Cu and an equivalent amount of Fe and S is assigned to chalcopyrite. All the remaining Fe and equivalent S is assigned to pyrite, all Zn and equivalent S to wurtzite plus sphalerite (this assumes no Fe in the wurtzite), all Ba and equivalent SO_4 to barite, all Ca and equivalent SO_4 to anydrite and all MgO with equivalent SO_4 and H_2O to MHSH. Results (Table 4) are entirely consistent with mineralogical analysis (Table 1) and indicate that the 21°N basal mounds and Juan de Fuca samples are composed of 30 to 90% wurtzite plus sphalerite and the remainder largely pyrite. The black smokers (samples 4 and 5) are almost entirely anhydrite with one (sample 5) containing 8.5% MHSH. Sums close to 100% demonstrate the consistency of the chemical analyses.

B. Similarity between deposits at 21°N EPR and Juan de Fuca

Bulk composition and mineralogy of the basal mounds at 21°N are very

Q (C27): PLACE PEN ON LOWER RIGHT CONTROL POINT:

R: Place graphics tablet pen on the lower right control point and press down to enter the location.

Q (C28): PLACE PEN SAMPLE LOCATION:

R: Place graphics tablet pen on the sample location and press down to enter the location.

For the subsequent samples you enter this session you will be asked:

Q (C29): IS THIS SAMPLE ON THE SAME QUADRANGLE SECTION AS THE LAST ONE?

R: Enter Y for yes or N for no.

Q (C30): DO YOU WANT ANY MORE INPUTING NOW (Y OR N)?

R: Enter Y for yes or N for no.

2) Editing Field Information

This program allows you to edit the field information that you have entered. You will be asked if you want to page through the data set or if you have a specific record that you want to edit. The record number must be known, which is simply the sequence number for the sample.

Editing is done by entering the number beside the item you wish to change. You will be asked the appropriate question for the item you want to change. The editing program does not check your answers to determine whether or not they are suitable, except for the proper length. If you want to change the free-coding space, you must enter all 14 spaces.

A warning must be made here. After making a change to an item, you will be asked if you have any other changes to make. If you answer yes (Y), the corrected record will be displayed. If you enter a zero for no change at this time, the record will not be updated on the disk with the changes you have just made. If you feel that you may have made an error in correcting the information and want to display the record again, then re-enter one of the single-character data items and answer the question about more changes with no

(N). This will update the record to disk.

The procedure to enter the editing program is as follows:

1. Enter the MIRA System (see Chapter II): Start-Up Procedures).'
2. Enter a "1" for the category "ENTRY AND EDITING OF RASS DATA."
3. Enter a "4" for the task "EDIT FIELD INFORMATION."
4. The program now begins.

follows Mg in magmatic processes of the ocean crust (Clague et al., 1981) and it seems, therefore, that both are strongly lithophilic during hydrothermal interaction with sea water. In experimental alteration of basalt by sea water dissolved Mg is quickly lost from heated sea water, and basaltic Ni appears to remain locked in the solids (Seyfried, 1977). Co, however, is enriched in the Galapagos Rift sample and locally in the Cyprus Ores (Constantinou and Govett, 1973) so Co must be transported under some hydrothermal conditions.

The most strongly enriched elements are Zn, Ag, Pb, and Cd, and all are enriched to almost the same degree (Fig. 2). This suggests that MORB is an adequate and likely source for these elements, because their relative abundances are similar in the basalt and sulfides. Moreover, their fractionation from the basalt during sea water leaching must have been homogeneous or complete, as was their bulk precipitation from the vent waters. The relative mass of MORB needed to provide this suite of metals is not large. Using Ag as an example, the enrichment factor for the sulfides with respect to MORB is calculated to be approximately 7500. This means that deposition of the Ag in 1 gram of massive sulfide required the quantitative leaching of Ag from 7500 grams of basalt. The size of typical massive sulfide ore bodies on Cyprus is about 3 million tons (Cann, 1980). If the modern deposits are this large then at least 2.3×10^{10} tons of basalt are required as source rock. This translates to 7.67×10^9 m^3 of basalt (density = 3.0 g/cc) or a cube of basalt with sides of about 2 km. Leaching by sea water is certainly not quantitative nor all pervasive, so much larger blocks of crustal basalt are likely involved for each sizable deposit of massive sulfide. Nevertheless, this calculation illustrates that both the relative and the absolute amounts of metals in the deposits could be derived from local leaching of reasonable amounts of basalt by sea water.

The ratio, Ag/Zn is virtually identical for 21°N and Juan de Fuca. Ag usually follows Pb, and most of the Ag produced in the world is from galena-rich ores. Although the association of Ag with Zn is unusual it is not unknown. Taylor and Radtke (1969) describe such an association in Zn-rich ores of the Mississippi Valley, in which sphalerites contain up to 2000 ppm Ag.

Au and a second group of chalcophilic elements, Cu, As, Hg, Mo, Ge and Tl is also strongly enriched in both sets of sulfides, all to approximately the same degree, but much less so than for the first group (Fig. 2). The much smaller enrichment for this group can be due to several causes. One is that these elements are not mobilized from the rock to the same degree as the Zn group. Another is that they are comparably mobilized but they are being fractionated from the concentrated fluid in another part of the system, possibly at depth under hotter conditions. Such a fractionation is suggested for Cu by the observation that chalcopyrite lines the inner walls of only the higher temperature chimneys (Styrt et al., 1981). Alternatively, some of these elements particularly As, Hg and Tl may remain in solution, dispersing and mixing into the bottom waters above the vents.

The mobility of Au in these systems is of interest. At Cyprus Au is enriched in some of the gossans, locally called "Devil's Mud", from which it has been mined profitably (Bear, 1963). Devil's Mud typically contains 17 ppm Au and has an acid insoluble residue of about 50% (Bear 1963) presumably as SiO_2. In contrast, Cyprus primary massive sulfide ore typically contains only about 0.5% SiO_2, and Au is below unspecified detection limits (Bear, 1963). Comparing these figures and assuming approximate conservation of SiO_2 during formation of the gossan, it is calculated that the gossan is a residue of about 100 times its mass of primary massive sulfide. This would suggest that the Au content of the primary ore is about 0.17 ppm, a value within the range of the Au analyses of the present study.

The enrichment of Pt or Rh cannot be directly calculated because, as far as we have been able to discern, no analyses of these elements exist for MORB. Analyses do exist for Pd, however, (Hertogen et al., 1980; Table 5), and an enrichment factor of only 0.6 is determined for the massive sulfide. If Pt or Rh behave similarly, then this implies the platinum group is not concentrated in the sea floor massive sulfide deposits.

ECONOMIC FACTORS

Much of the interest in sea floor massive sulfide deposits stems from the content of valuable heavy metals and their potential exploitability. In bulk composition, mineralogy, and texture, the Galapagos Rift sample is very typical of ophiolite massive sulfide deposits, e.g. those found in the Skouriotisa Mine of Cyprus, composed of pyrite and chalcopyrite. Moreover, at 5% Cu, the Galapagos sample is of higher grade than the more typical 2.5-3% Cu ore from this mine (Bear, 1963). Although small parts of some ore bodies in Cyprus are zinc-rich, e.g., the Agrokipia Mine (Bear, 1963, Koski, et al., in press), they are relatively rare compared to the more common pyrite-chalcopyrite ores. Thus the high Zn content of the 21°N and Juan de Fuca samples, while represented in, are not typical of ophiolite massive sulfide deposits. They are compositionally (but not texturally) more comparable to the metalliferous muds of the Red Sea brine deposits (Shanks and Bischoff, 1980).

The exploitability of the sea floor deposits, as with any kind of mineral resource, depends on several factors. The more important of these factors are grade (metal value per ton), size of reserves (total tonnage), accessibility, metallurgical "winability" of the metals from the ore, ease of exploration and discovery, and legal ownership. At present too little is known concerning many of these factors to project their economic significance beyond some limited generalizations. In the context of these factors, however, the exploitability of the sea floor massive sulfides can be compared with the deep-sea manganese nodules, the economics of which have been reviewed in some detail (see, for example, Archer, 1975; McKelvey et al., 1979).

Data from the present study allow some generalization concerning grade, although the analyses reported here do not constitute an adequate data base for precise estimates of grade of the deposits. However, the close similarity between the basal mounds of 21°N, the CYAMEX samples at 21°N, and the samples from Juan de Fuca (deposits separated by 2300 km) imply that the sea floor massive sulfides have considerable regional homogeneity. Therefore, the composite composition of the basal mounds presented here may well be representative of the bulk of the deposits along medium and fast spreading centers. To a first approximation we assume this to be so. Table 6 lists the metal values of typical massive sulfides and average deep-sea manganese nodules from the prime Clarion-Clipperton region (McKelvey et al., 1979). Values per ton are calculated for each deposit type by applying metal prices established at the time of writing (Metals Week, 6 Dec 1982). Such prices fluctuate as a function of the worldwide economy and are at present at historic lows compared to prevailing prices of the five years prior to 1981. Therefore, they provide only a basis for comparison. It is emphasized they do not reflect absolute realizable value of each ore, because they consider neither efficiency nor the relative costs of recovery. Only those metals presumed to be profitably extractable are listed. The major value for deep-sea manganese nodules has classically been with the metals Ni, Cu and Co, the sum of which along with Zn and Mo, is currently approximately \$192/ton. Including manganese (as ferromanganese) in these figures would add an additional \$115/ton making a total of \$307/ton. Manganese is usually not considered, however, because projected demand for manganese is signficantly less than projected production if manganese nodules were to be mined on a large scale (Archer, 1975). Therefore, a much lower but unquantifiable figure for manganese would apply.

In comparison the 21°N and Juan de Fuca massive sulfides have a value of about \$348/ton with 75% of the value due to zinc and the rest mostly to Ag, and less to Cd (Table 6). Ge at 100 ppm has an apparent value of \$106/ton. Ge appears to substitute for Zn in sphalerite, and it is commonly produced as a byproduct of Zn when it is present at about 500 ppm. At 100 ppm, the cost of extraction is close to its value (Adams, 1981; Adams, pers. comm.), so it is not included in the summation.

The value of the Galapagos-type massive sulfide is primarly Cu, which accounts for 86% of the total per ton value of \$85. Note that this is considerably higher grade than the \$38/ton of similar ores being presently mined in Cyprus (Table 6).

The other economic factors can be addressed only qualitatively. Size and abundance of the massive sulfide deposits remain one of the most important unknowns. Potential mine sites on land must have an ore deposit of sufficient size to pay back the cost of stationary capital equipment that must be constructed at the mine site and allow for profit. The minimum size of the deposit is usually quantifiable and depends on many local conditions. This concept, however, does not directly translate to mining at sea, because the sea floor mining equipment will presumably be from mobile ships which can be moved from deposit to deposit. A single deposit, therefore, may not have to repay capitalization costs. The question becomes more of distribution and abundance of the deposits than of individual size.

Dimensions of the Galapagos Rift massive-sulfide based on visual observations of the ALVIN traverses (Malahoff, 1982) imply about 20 million tons of deposit. Were such a deposit found on land both its grade and reserves are sufficient to make the deposit mineable, in comparison with existing Cu mines in the western U.S. (Cox et al., 1973).

Cann (1980) has estimated the occurrence of massive sulfide deposits presently exposed on the sea floor to be approximately one for every 100 km of active ridge crest. This estimate was based on the distribution of deposits within the Troodos ophiolite of Cyprus, and and an estimate of the amount of time each might have been exposed on the sea floor, assuming a spreading rate of 1 cm/yr.

The occurrence of newly formed deposits on the EPR might be much more frequent than this, for two reasons. First, much of the EPR is spreading at a much greater rate than the 1 cm/yr estimated for Troodos, which is considered analogous to the Reykjanes Ridge of the Mid-Atlantic Ridge (Cann, 1980). Faster spreading generates more heat output and therefore, more intensive and more closely spaced geothermal systems.

Secondly, all newly-formed deposits will not necessarily be preserved for the geologic record. Rather, only those deposits that are soon covered by lava or sediments to prevent oxidation to gossans will survive. The numerous "ochres" of Troodos (Robertson, 1976) may in fact be the residue of massive sulfide deposits which were not covered by lava before sea-floor alteration was complete. Thus, the abundance of massive sulfides on Cyprus may be only a fraction of those that originally formed on the sea floor. The Zn-rich sea-floor deposits that are so different from the typical ophiolite massive sulfide may also be due in part to this process. If the Zn-rich deposits are the outer-portions of the sea floor deposits they will be first to be altered on the sea-floor and thus, the least likely to be preserved. Moreover, the grade of these Zn-rich deposits appear to be considerably more attractive than the typical ophiolite ores (Table 6). In this regard it should be noted that to date sea floor hydrothermal systems have been found in every place on the moderate to fast spreading ridge crests where they have been sought by manned submersible or detailed photography.

Because massive sulfide deposits are currently being mined and processed throughout the world neither new metallurgical procedures nor construction of new kinds of smelters would be required to process the sea floor massive sulfide deposits. Metallurgical procedures for manganese nodules are not standard, but are experimental, and research into this question by the major industrial consortia has been highly proprietary. It is clear, however, that processing of the exotic matrix of manganese nodules would require construction of major new facilities.

It is too early to more than speculate on the relative accessability of the massive-sulfide deposits compared to manganese nodules. The massive sulfides are located in shallower water than the nodules (2500 m vs. 5000 m) but this positive factor, is counter-balanced by their occurrence within irregular "hard" volcanic terrane.

One of the most attractive advantages of the massive sulfides, however, is ease of exploration. The ridge crests are linear features and the active vents appear to be confined within the innermost 2 km. Exploration can be readily carried out by relatively inexpensive bottom-towed camera/TV systems navigated by bottom transponders, and the deposits located by the highly visible biological communities associated with the vents. This was, in fact, the way Normark et al. (1982) discovered the Juan de Fuca deposits. Sea floor massive sulfide deposits are probably most abundant along the fastest spreading portions of the spreading centers, which occurs in international waters south of the equator (i.e. from 0° to 50° S).

Probably the greatest barrier to eventual exploitation of the massive sulfide deposits and the deep sea manganese nodules is the lack of a favorable international legal agreement regarding the mining of deep sea mineral resources and, most importantly, the recognition of exclusive mining claims. Where the spreading centers occur within 200 nautical miles of a coastline, however, ownership will likely be claimed by the adjacent country, such as the Galapagos Rift by Ecuador, 21°N by Mexico, and Juan de Fuca Ridge by the U.S. and Canada, and the respective national mining laws will apply.

Thus, it would appear that the major unanswered question concerning the exploitability of the sea floor massive sulfides is the size and distribution of the deposits, a question that will likely be answered in the near future as the ambitious exploration plans for the next decade are carried out.

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REFERENCES

Adams, J., 1980. Germanium and Germanium Compounds. In: Encyclopedia of Chemical Technology, v. 11, 3rd ed., John Wiley and Sons, Inc., pp. 791-801.

Archer, A., 1975. Prospects for the Exploitation of Manganese Nodules: The Main Technical, Economic and Legal Problems. In: Glasby, G. and Katz, H., eds., Committee Coordination of Offshore Prospecting, Technical Bull. No. 2, U.N. Econ. and Soc. Comm. for Asia and Pacific, pp. 21-38.

Baedecker, P., 1979. The INAA Program of the U.S. Geological Survey (Reston, Virginia). In: Carpenter, B., Agostino, M., and Yule, H., eds., Computers in Activation Analysis and Gamma Ray Spectroscopy, D.O.E. Symp. Ser. 49, pp. 373-385.

Bear, L. M., 1963. The Mineral Resources and Mining Industry of Cyprus. Bulletin No. 1, Ministry of Commerce and Industry, Geological Survey Dept., Republic of Cyprus, 208 p.

Cann, J., 1980. Availability of Sulphide Ores in the Oceanic Crust: J. Geol. Soc. London, v. 137, p. 381-384.

Church, S. E., and Tatsumoto, M., 1975. Lead isotope relations in oceanic ridge basalts from the Juan de Fuca-Gorda area, N.E. Pacific Ocean: Contributions to Mineralogy and Petrology, v. 53, p. 253-279.

Clague, D. A., Frey, F. A., Thompson, G., and Rindge, S., 1981. Minor and trace element geochemistry of volcanic rocks dredged from the Galapagos spreading center: Role of crystal fractionation and mantle heterogeneity: Jour. Geophys. Res., v. 86, no. B10, p. 9469-9482.

Constantinou, G., and Govett, G. J. S., 1973. Geology, geochemistry, and genesis of Cyprus sulfide deposits: Econ. Geol., v. 68, p. 843-858.

Cox, D., Schmidt, R., Vine, J., Kirkemo, H., Tourtelot, E., and Fleisher, M., 1973. Copper. In: Brobst, D. and Pratt, W., eds., U.S. Mineral Resources U.S. Geol. Survey Prof. Paper 820, p. 163-190.

Francheteau, J., Needham, H., Choukroune, P., Juteau, T., Seguret, B., Ballard, R. D., Fox, P., Normark, W., Carranza, A., Cordoba, D., Guerrero, J., Rangin, C., Bougault, H., Cambon, P., and Hekinian, R., 1979. Massive Deep-Sea Sulphide Ore Deposits Discovered on the East Pacific Rise: Nature, v. 277, p. 523-528.

Haymon, R., and Kastner, M., 1979. Descriptive Catalogue of RISE Sulfide Samples from the East Pacific Rise, 21°N: Scripps Inst. Oceanography Reference 79-28, 11 p.

Haymon, R. M. and Kastner, M., 1981. Hot spring deposits on the East Pacific Rise at 21°N: preliminary description of mineralogy and genesis: Earth Planet. Sci. Lett., v. 53, pp. 363-381.

Hekinian, R., Fevrier, M., Bischoff, J., Picot, P., and Shanks, W., 1980. Sulfide deposits from the East Pacific Rise near 21°N: A mineralogical and geochemical study: Science, v. 207, p. 1433-1444.

Hekinian, R., Fevrier, M., Needham, H. D., Avedik, F., and Cambon, P., 1981. Sulfide deposits: East Pacific Rise near 13°N [abs.]: Eos, v. 62, no. 45, p. 913.

Hertogen, J., Janssens, M. J., and Palme, H., 1980. Trace elements in ocean ridge basalt glasses: implications for fractionation during mantle evolution and petrogenesis: Geochim. Cosmochim. Acta, v. 44, pp. 2125-2143.

Huffman C., Mensik, J. D., and Riley, L. B., 1967. Determination of gold in geologic materials by solvent extraction and atomic absorption spectrometry. Geological Survey Circular 544, 6 pages.

Koski, R. A., Goodfellow, R., and Bouse, R. M., 1982. Preliminary description of massive sulfide samples from the southern Juan de Fuca Ridge: U.S. Geological Survey Open-File Report, 82-200B, 11 p.

Koski, R., Clague, D., and Oudin, E., in press. Mineralogy and chemistry of massive sulfide deposits from the Juan de Fuca Ridge: Bull. Geol. Soc. Amer.

Lonsdale, P. F., Bischoff, J. L., Burns, V. M., Kastner, M., and Sweeney, R. E., 1980. A high temperature hydrothermal deposit on the sea bed at a Gulf of California Spreading Center: Earth Planet. Sci. Lett., v. 49, p. 8-20.

Malahoff, A., 1981. Comparison between Galapagos and Gorda Spreading Centers: 13th Ann. Offshore Tech. Conf., no. 4129, May 1981, pp. 115-121.

Malahoff, A., 1982. A comparison of the massive submarine polymetallic sulfides of the Galapagos Rift with some continental deposits: Marine Technology Society Journal, v. 16, no. 3, p. 39-45.

McKelvey, V., Wright, N., and Rowland, R., 1979. Manganese nodule resource in the northeastern equatorial Pacific, In: Bischoff, J. and Piper, D., eds., Marine geology and oceanography of the Pacific Manganese Nodule Province. Plenum Press, N.Y., pp. 747-762.

Normark, W. R., Lupton, J. E., Murray, J. W., Koski, R. A., Clague, D. A., Morton, J. L., Delaney, J. R., and Johnson, H. P., 1982. Polymetallic sulfide deposits and water column tracers of active hydrothermal vents on the southern Juan de Fuca Ridge: Marine Technology Society Journal, v. 16, no. 3, p. 46-53.

Oudin, E., 1981. Etudes mineralogique et geochimiques des depots sulfures sous-marin actuels de la ride est-pacifique (21°N). Docum. Bur. Rech. Geol. Min., no. 25, 241 p.

Oudin, E., Picot, P., and Povit, G., 1981. Comparison of Sulfide Deposits from the East Pacific Rise and Cyprus. Nature, v. 291, pp. 404-407.

Seyfried, W., 1977. Seawater-basalt interaction from 25°C to 350°C and 1-500 bars: Unpub. Ph.D. thesis, Univ. Southern California, 242 p.

Shanks, W., and Bischoff, J., 1980. Geochemistry, sulfur isotope composition, and accumulation rates of Red Sea geothermal deposits: Econ. Geol., v. 75, pp. 445-459.

Spiess, F. N., Macdonald, K., Atwater, T., Ballard, R., Carranza, A., Cordoba, D., Cox, C., Diaz Garcia, V., Francheteau, J., Guerrero, J., Hawkins, J., Haymon, R., Hessler, R., Juteau, T., Kastner, M., Larson, R., Luyendyk, B. Macdougall, J. D., Miller, S., Normark, W., Orcutt, J., and Rangin, C., 1980. East Pacific Rise: Hot springs and geophysical experiments: Science, v. 207, p. 1421-1432.

Styrt, M. M., Brackmann, A. J., Holland, H. D., Clark, B. C., Pusutha-Arnond, V. Elridge, C. S., and Ohmoto, H., 1981. The mineralogy and the isotopic composition of sulfur in hydrothermal sulfide/sulfate deposits on the East Pacific Rise, 21°N latitude: Earth Planet. Sci. Letts., v. 53, p. 382-390.

Taylor, C., and Radtke, A., 1969. Micromineralogy of silver-bearing sphalerite from Flat River, Missouri: Econ. Geol., v. 64, pp. 306-318.

Turekian, K. and Wedephol, K., 1961. Distribution of the elements in some major units of the Earth's crust: Bull. Geol. Soc. Amer., v. 72, pp. 175-192.

Zierenberg, R., Shanks, W. C., and Bischoff, J., in press. Massive sulfide deposits at 21°N, EPR: chemical composition, stable isotopes, and phase equilibria: Bull. Geol. Soc. America.

FIGURE CAPTIONS

Figure 1. Location of Pacific Ocean spreading segments where hydrothermal activity and associated massive sulfide deposits have been found (from Koski et al., 1982).

Figure 2. Enrichment factors over MORB of various metals in sea floor massive sulfide deposits from 21°N EPR and Juan de Fuca Ridge.

Table 1 Location and Sample Particulars of Sea-Floor Massive Sulfide Deposits used for Chemical Analyses

	Designation	Description	Sample Weight	Mineralogy	Notes
21°N, East Pacific Rise (20°50'N, 109°05'W, 2600 m)					
1	914-R1A	Inactive basal mound; massive grey-black aggregate honey-combed with unfilled worm-tubes	75g	wurtzite, pyrite, marcasite chalcopyrite, barite, amorphous silica	1
2	923-R7	Inactive basal mound; filled worm tubes	161g	pyrite, marcasite, wurtzite, anhydrite chalcopyrite.	1
3	914-R7A	Inactive chimney, honey-combed by partially filled worm tubes	134g	wurtzite, pyrite, chalcopyrite	1
4	914-R8A-5-3	Active black-smoker chimney, grey-black, smooth and massive outer portion	78g	anhydrite, wurtzite, pyrite	1
5	917-R4	Active black-smoker chimney greenish-grey, with patches of white, massive outer portion.	116g	anhydrite, MHSH, chalcopyrite	1
Juan de Fuca Ridge (44°40'N, 130°22'W, 2200 m)					
6	WF-22D-3	Medium-grey massive sulfide, honey-combed with filled worm tubes (Type B)	35g	sphalerite	2
7	WF-22D-6C	2 cm pyrite layer taken from the layered dark grey massive sulfide of sample 8 below	35g	pyrite, amorphous silica	2
8	WF-22D-6D	Dark grey, coarsely crystalline, massive sulfide, crudely layered - no worm tubes (Type A)	40g	sphalerite, wurtzite	2
Galapagoes Rift (0°45'N, 85°50'W, 2600 m)					
9	--	Brassy, coarsely crystalline massive sulfide	15g	pyrite, chalcopyrite	3

Notes:

1) Samples collected during RISE expedition: Spiess et al. (1980), Sample description in Haymon & Kastner (1979), mineralogy from Zierenberg et. al. (in press).

2) Samples collected during cruise L11-81-WF of the S.P. Lee, Normark et. al. (1982), Sample description and mineralogy from Koski et. al. 1982, and Koski et. al. (in press).

3) Samples collected during ALVIN dive 1001 described in Malahoff (1982).

Table 2

Comparative analyses of selected elements of massive sulfide samples from 21°N, EPR, Juan de Fuca, and Galapagoes spreading centers. Sample numbers are explained in Table 1. INAA = instrumental neutron activation analysis, ICP = inductive coupled plasma arc optical emission spectroscopy, AA = conventional atomic absorption spectroscopy, fire assay = fire assay preconcentration followed by atomic absorption spectroscopy, SWR = short wave radiation optical spectroscopy (semi-quantitative), SQ = conventional semi-quantitative optical emission spectroscopy. Number in parenthesis after analytical method refers to one of two sample batches. (1) = job number BB56, (2) = job number KV97. The two batches were seperated without prior homogenization and, therefore, are not exact aliquots.

	SAMPLE NUMBER								
	1	2	3	4	5	6	7	8	9
Fe %									
SQ (1)	10	>24	17	2.8	2.5	-	-	-	-
INAA (1)	-	37.1	15.7	5.4	-	-	-	-	-
INAA (2)	-	26.1	-	3.83	2.19	-	41.2	7.26	44.1
ICP (2)	14.7	27.2	16.7	3.98	0.61	1.8	41.4	15.6	-
AA (2)	-	-	-	-	-	1.8	50.5	8.0	44.4
SQ (2)	-	-	-	-	-	1.7	>24	7.2	>24
Zn %									
ICP (2)	-	20.3	-	17.5	-	61.0	2.27	46.9	-
AA (2)	-	-	-	-	-	59.2	0.63	54.0	0.14
INAA (2)	-	20.4	-	17.3	-	60.0	0.21	54.4	0.14
SQ (2)	-	-	-	-	-	>10	1.2	>10	0.13
PB %									
Fire Assay (1)	0.14	0.017	0.22	0.007	<0.0005	-	-	-	-
SQ (1)	>0.10	0.018	>0.10	0.006	<0.0007	-	-	-	-
ICP (2)	0.61	0.07	0.29	0.006	<0.004	0.20	0.27	0.30	-
AA (2)	-	-	-	-	-	0.25	0.18	0.06	-
SQ (2)	-	-	-	-	-	0.06	0.10	0.09	-
Cu %									
SQ (1)	0.077	>0.32	>0.32	0.11	>0.32	-	-	-	-
ICP (2)	0.23	1.27	0.89	0.13	0.35	0.08	0.004	0.35	-
AA (2)	-	-	-	-	-	0.07	<0.0003	0.32	-
SQ (2)	-	-	-	-	-	0.08	<0.003	0.32	-
Ag (ppm)									
Fire Assay (1)	200	14	170	5.4	1.6	-	-	-	-
SQ (1)	340	260	260	<150	<150	-	-	-	-
INAA (1)	241	25	202	9.6	1.6	-	-	-	-
INAA (2)	-	34.7	-	<20	-	225	15.5	169	<20
AA (2)	-	-	-	-	-	230	<3	290	<10
ICP (2)	510	30	240	<20	<20	240	<20	150	-
SQ (2)	-	-	-	-	-	220	11	150	8
Cd (ppm)									
SQ (1)	78	430	810	120	<32	-	-	-	-
ICP (2)	120	890	790	60	<20	1260	<20	750	-
AA (2)	-	-	-	-	-	1060	8	490	-
SWR (2)	4	10	7	10	0.5	1000	0.5	500	-
SQ (2)	-	-	-	-	-	1300	<32	950	-
Mo (ppm)									
INAA (1)	17	77	13	3	<1	-	-	-	-
SQ (1)	14	86	12	5.4	1.9	-	-	-	-
ICP (2)	30	160	20	<20	<20	<20	20	<20	-
SQ (2)	-	-	-	-	-	<1	36	3	-
Au (ppm)									
Fire Assay (1)	-	<0.2	-	<0.2	-	<0.1	<0.1	<0.1	-
SWR (2)	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	-
INAA (2)	-	0.17	-	0.025	-	-	-	0.13	.05
Hg (ppm)									
SQ (1)	<7	<7	<7	<7	-	-	-	-	
SWR (2)	2	<1	<1	2	2	-	-	-	
AS (ppm)									
SQ (1)	340	260	260	<150	<150	-	-	-	-
INAA (1)	483	260	215	13	1	-	-	-	-
INAA (2)	-	770	-	15.2	-	238	433	412	125
SWR (2)	700	500	300	<1	<1	700	300	500	-
SQ (2)	690	610	270	<20	<20	250	330	240	<150

Table 3: Chemical Composition of Massive sulfide deposits from the sea floor at 21°N, EPR, Juan de Fuca and Galapagoes Spreading Centers.

	21°N, EPR					Juan de Fuca			Galapagoes Rift
Percent	1	2	3	4	5	6	7	8	9
Fe	14.7	26.2	16.7	4.0	0.61	2.19	41.4	15.6	44.1
Zn	34.9	20.3	41.8	1.7	0.12	61.0	2.27	46.9	0.14
Cu	0.23	1.3	0.89	0.13	0.35	0.08	0.04	0.35	4.98
Pb	0.61	0.07	0.29	0.06	<0.04	0.20	0.27	0.30	<0.07
S	31.3	39.7	34.9	4.3	0.74	32.6	48.3	36.8	52.2
SO_3	<0.01	7.6	<0.01	49.4	58.4	0.15	<0.05	<0.03	<0.03
SiO_2	19.0	<0.5	4.3	2.8	1.7	2.6	11.3	1.5	<0.1
Al_2O_3	0.3	0.11	0.77	0.04	0.08	0.06	0.15	0.15	<0.06
MgO	<0.03	0.07	0.02	0.03	3.15	<0.05	<0.05	<0.05	<0.05
CaO	<0.01	5.42	<0.01	35.1	37.9	0.15	<0.03	<0.03	<0.03
Sum	101.04	100.77	99.67	97.53	103.05	99.03	103.73	101.60	101.42
PPM									
Ag	241	34	202	9.6	1.6	230	15	290	<10
As	483	770	215	13.2	1.2	235	430	411	125
Au	-	0.17	<0.2	0.025	<0.2	<0.1	<0.1	0.13	0.05
B	<7*	<7*	<7*	<7*	<7*	90*	40*	40*	<7*
Ba	6030	65	850	225	225	1200	465	19*	16*
Bi	<0.2*	2*	<0.2*	2*	1*	<0.2*	<0.2*	<0.2*	<10*
Cd	120	890	790	60	<20	1060	8	490	<32*
Co	<2.0	2.5	6	37	20	6.4	1.2	24	482
Cr	8	16	<30	<6	13	<8*	12	<8*	55
Cs	6.7	<5.0	6.6	<2	<0.7	<5	<3	<9	<3
Ga	3.3*	18*	21*	1.5*	<1.5*	<20*	<20*	<20*	15*
Ge	96*	<1.5*	100*	<1.5*	<1.5*	120*	27*	270*	<1*
Hg	2*	<1*	<1*	2*	2*	5*	<1*	<1*	-
Mn	570*	91*	500*	52*	19*	90*	2100*	720*	140*
Mo	16	78	13	2	0.6	<1*	36*	3*	170*
Ni	2*	5*	2*	<1.5*	2*	<8*	<8*	-	3.1*
Pd	0.001	0.001	0.001	0.001	0.001	<0.002	<0.002	<0.002	<0.002
Pt	0.002	0.002	<0.001	0.003	0.001	<0.005	<0.005	<0.005	<0.005
Rh	0.002	0.0010	0.0022	0.0007	0.0010	0.003	0.002	0.003	<0.001
Sb	45.0	13	52.9	3.2	1.4	19	0.7	34	1.8
Sc	<0.4	0.2	0.25	<0.3	0.02	2	0.1	<1	<0.3
Se	7*	172	10*	5	<5*	<5*	<5*	29	100
Te	<1*	2*	<1*	2*	<1*	<1*	5*	<1*	-
Tl	40*	20*	<1*	2*	<1*	20*	40*	10*	<5*
Sr	220	9	19	3965	2870	120*	30*	<10*	<1*
U	6.0	1.3	3.1	<2.0	1.3	<7	2.7	10	1.0
Y	4*	<1.5*	3*	2*	<1.5*	<2*	<2*	<2*	<2*
W	1.0	<2.0	<3.0	<1.0	<2.0	<10*	<10*	<10*	<10*
Zr	9*	<3*	43*	14*	<3*	<11*	<3*	28*	<3*

Notes: 1) See Table 1 for sample numbers.
2) - = not analyzed
3) * = Semi-quantitative optical emission spectroscopy
4) Following elements are below their respective detection limits (ppm) for all samples: (by semi-quantitative emission spectroscopy)
Na (500), K (700), Ti (30), P (500), Be (1), Ce (40), La (10), Pr (20), Nd (10), Sm (20), Eu (8), Gd (20), Tb (100), Dy (10), Ho (8), Er (10), Yb (10), Li (20) Nb (3), Sn (1), Ta (400), Th (20).

Table 4. Bulk normative mineralogical composition of sea floor massive sulfide deposits.

	21°N, EPR					Juan de Fuca			Galapagos Rift
	1	2	3	4	5	6	7	8	9
Wtz + Sp	52.0	30.3	62.3	2.3	0.2	90.9	3.4	69.9	0.2
Py + Mc	30.3	56.0	34.2	8.4	0.7	3.7	89.0	32.9	85.8
Cp	0.7	3.8	2.6	0.4	1.0	0.2	0.1	1.0	14.3
An	-	13.2	-	85.2	92.0	0.4	-	-	-
Ba	1.0	-	0.1	-	-	0.4	-	-	-
MHSH	-	-	-	0.1	8.5	-	-	-	-
OP	19.0	-	4.3	2.8	1.7	2.6	11.3	1.5	-
Sum	103.0	103.3	103.5	99.0	104.1	98.2	103.8	105.3	100.3

Notes: - = <0.1%
Wtz + Sp = wurtzite + sphalerite = ZnS
Py + Mc = pyrite + marcasite = FeS_2
Cp = chalcopyrite = $CuFeS_2$
An = anhydrite = $CaSO_4$
BA = barite = $BaSO_4$
MHSH = magnesium hydroxysulfate = $MgSO_4 \cdot 1/3\ Mg(OH)_2 \cdot 1/3\ H_2O$
OP = opaline silica = SiO_2

Table 5

Generalized content of selected elements in massive sulfide deposits of 21°N (basal mounds), Juan de Fuca (Types A & B) and in mid-ocean ridge basalts (MORB).

	21°N (basal mound)[1]	21°N (CYAMEX)[2]	Juan de Fuca (Type A/B)[3]	MORB[4]
	Percent			
Zn	32.3	40.76	53.95	0.0100
Cu	0.81	0.61	0.22	0.0060
Pb	0.32	0.05	0.25	0.00075
	Parts per million			
Ag	156	380	260	0.027
As	489	-	323	2.0
Au	0.17	-	0.13	0.00116
Cd	560	500	775	0.128
Co	3	100	15	65
Hg	1.5	-	2.5	0.09
Mo	36	-	25	1.5
Ni	3	-	<8	121
Pd	.001	-	<.002	0.0016
Se	63	-	17	0.20
Tl	20	-	15	0.21
Ge	65		195	1.5

Notes

1. Average of samples 1, 2 and 3, Table 3
2. Average of 3 samples reported by Hekinian et al. (1980)
3. Average of samples 6 and 8, Table 3
4. Typical values for Zn, Cu, Co, and Ni of MORB are from Clague et al. (1981); Pb for MORB from Church and Tatsumoto (1975); Ag, Au, Cd, Pd, Se, and Ge for MORB from Hertogen et al. (1980); As, Hs, Mo, and Tl for average basalt from Turekian and Wedepohl (1961).

Table 6

Estimates of typical grade and values per ton of contained metals for sea floor massive sulfide deposits, compared with typical ore from ophiolite massive sulfide deposits, and deep sea manganese nodules.

		Sulfides, 21°N & Juan de Fuca		Sulfides , Galapagos Rift		Sulfide ore, Cyprus[4]		Deep Sea manganese nodules	
	Metal values[1] ($/kg)	Typical[2] grade (%)	Value ($) per ton	Typical[3] grade (%)	Value ($) per ton	Typical[4] grade (%)	Value ($) per ton	Typical[5] grade (%)	Value ($) per ton
Zn	0.89	30	267.0	0.2	1.78	0.2	1.78	0.13	1.16
Cu	1.46	0.5	7.30	5.0	73.0	2.5	36.50	0.99	14.45
Ni	7.1	-	-	-	-	-	-	1.22	86.62
Co	35.08	-	-	0.02	7.01	-	-	0.23	80.69
Cd	2.22	0.07	1.55	-	-	-	-	-	-
Mo	18.87	-	-	0.017	3.20	-	-	0.018	9.05
Ag	355.28	0.02	71.06	-	-	-	-	-	-
Pb	0.44	0.30	1.32	-	-	-	-	-	-
Mn	0.40	-	-	-	-	-	-	28.8	(115.20)
Ge	1060.0	0.01	(106.0)	-	-	-	-	-	-
Sum			348.23[6]		85.0		38.28		191.97

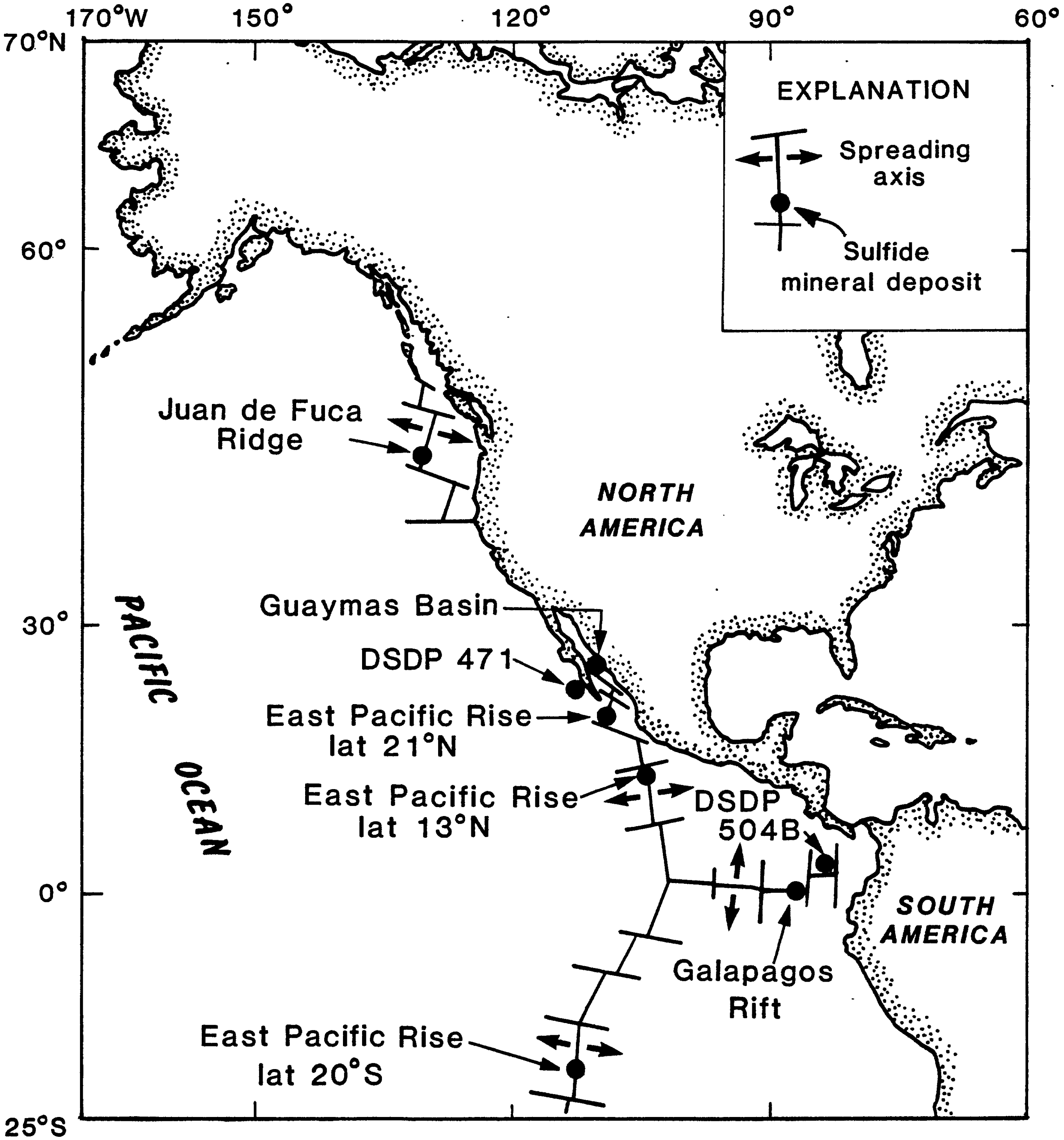
Notes:

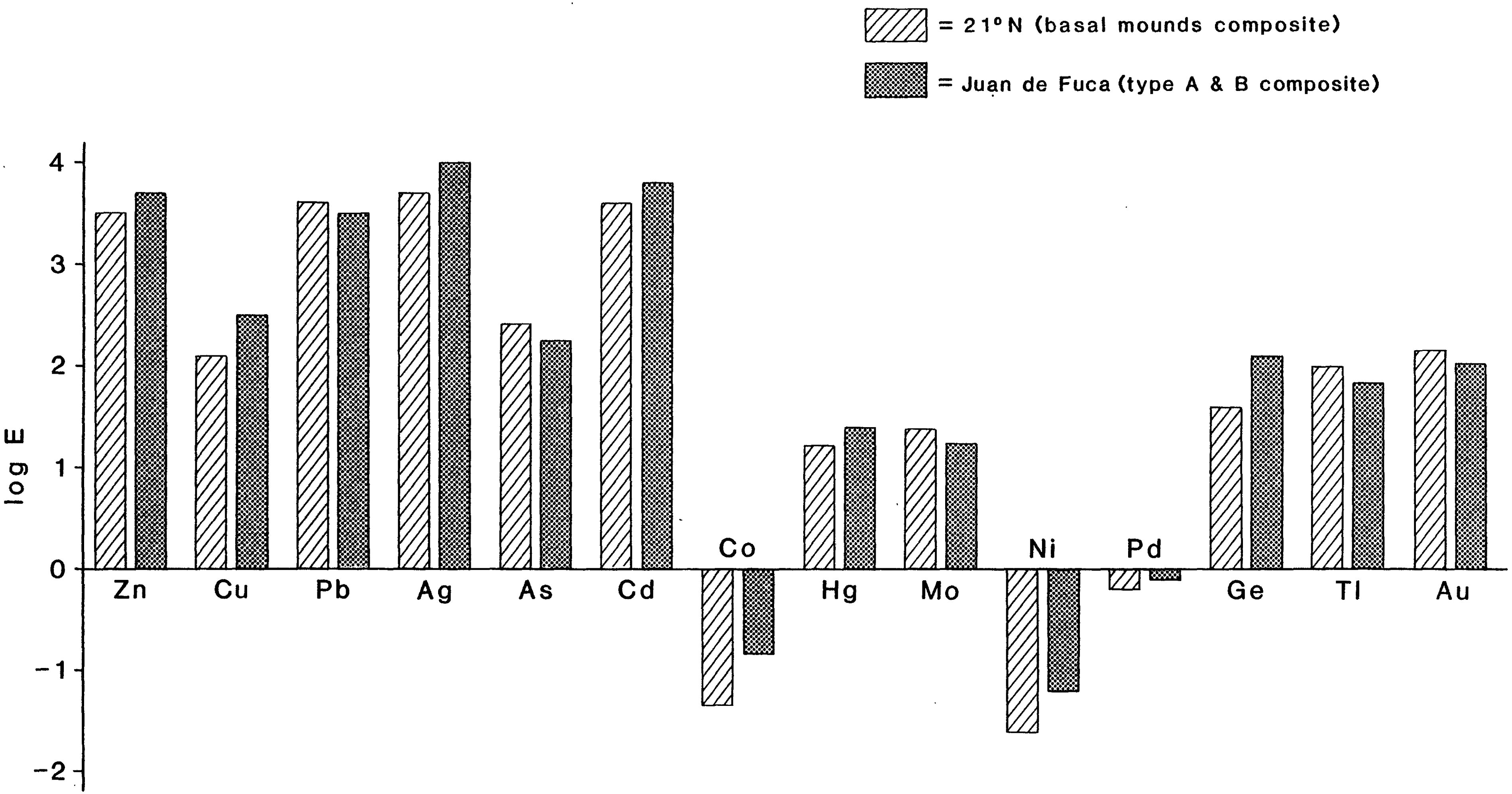
1. Prices from Metals Week, 6 Dec. 1982. Mn as ferromanganese, others as pure metals.
2. Approximate average from Table 5.
3. Taken from Table 3, sample 9.
4. Typical ore from Skouriotissa mine reported by Constantinou & Govett (1973).
5. Average for Clarion-Clipperton prime zone reported by McKelvey et al. 1979.
6. Excluding Ge.
7. Excluding Mn.

FIGURE CAPTIONS

Figure 1. Location of Pacific Ocean spreading segments where hydrothermal activity and associated massive sulfide deposits have been found (from Koski et al., 1982).

Figure 2. Enrichment factors over MORB of various metals in sea floor massive sulfide deposits from 21°N EPR and Juan de Fuca Ridge.


170°W
150°
120°
90°
60°
70°N
60°
30°
0°
25°S
EXPLANATION
Spreading axis
Sulfide mineral deposit
Juan de Fuca Ridge
NORTH AMERICA
PACIFIC OCEAN
Guaymas Basin
DSDP 471
East Pacific Rise lat 21°N
East Pacific Rise lat 13°N
DSDP 504B
SOUTH AMERICA
Galapagos Rift
East Pacific Rise lat 20°S


▨ = 21° N (basal mounds composite)
▩ = Juan de Fuca (type A & B composite)
log E
4
3
2
1
0
−1
−2
Zn
Cu
Pb
Ag
As
Cd
Co
Hg
Mo
Ni
Pd
Ge
Tl
Au