

29. PALLADIUM, PLATINUM, AND GOLD DISTRIBUTION IN SERPENTINITE SEAMOUNTS IN THE MARIANA AND IZU-BONIN FOREARCS: EVIDENCE FROM LEG 125 FLUIDS AND SERPENTINITES¹

I. J. Parkinson,² G.E.M. Hall,³ and J. A. Pearce²

ABSTRACT

Palladium, platinum, and gold were analyzed for 20 interstitial water samples from Leg 125. No Pd or Pt was detected in fluids from serpentinite muds from Conical Seamount in the Mariana forearc, indicating that low-temperature seawater-peridotite interaction does not mobilize these elements into the serpentinizing fluids to levels above 0.10 parts per billion (ppb) in solution. However, Au may be mobilized in high pH solutions. In contrast, fluids from vitric-rich clays on the flanks of the Torishima Seamount in the Izu-Bonin forearc have Pd values of between 4.0 and 11.8 nmol/L, Pt values between 2.3 and 5.0 nmol/L and Au values between 126.9 and 1116.9 pmol/L. The precious metals are mobilized, and possibly adsorbed onto clay mineral surfaces, during diagenesis and burial of the volcanic-rich clays. Desorption during squeezing of the sediments may produce the enhanced precious metal concentrations in the analyzed fluids. The metals are mobilized in the fluids probably as neutral hydroxide, bisulfide, and ammonia complexes. Pt/Pd ratios are between 0.42 and 2.33, which is much lower than many of the potential sources for Pt and Pd but is consistent with the greater solubility of Pd compared with Pt in most natural low-temperature fluids.

INTRODUCTION

During dredging and submersible studies of the Mariana forearc, scientists discovered a series of serpentinite seamounts in the outer-half of the forearc terrane (Fryer et al., 1985; Ishii, 1985; Fryer and Fryer, 1987). Detailed *Alvin* submersible studies of Conical Seamount in 1987 found that the seamount was made up of serpentinite flows, and was actively venting cold, dense fluids through aragonite chimneys from its summit (Fryer et al., unpubl. data). The fluids sampled had high pH and were depleted in chloride, calcium, and magnesium and enriched in silica, methane and sulfide relative to the ambient seawater (Fryer et al., unpubl. data). Experimental work by Seyfried and Dibble (1980) and Janecky and Seyfried (1987) produced fluids of similar chemistry during serpentinization of harzburgite. Moreover, the fluids are similar to some of the present-day serpentinizing fluids analyzed from the Coastal Ranges ophiolites of the western United States (Barnes et al., 1970; 1972).

During Ocean Drilling Program (ODP) Leg 125, five sites were drilled on two of these serpentinite seamounts (Fig. 1): two flank sites (778 and 779) and one summit site (780) on Conical Seamount in the Mariana forearc; and one upper flank (783) and one lower flank (784) site on Torishima Forearc Seamount in the Izu-Bonin forearc. Conical Seamount was shown predominantly to comprise serpentinite-rich muds in which serpentinized ultramafic and metabasalt clasts were entrained. In contrast, Torishima Forearc Seamount was found to be made up predominantly of vitric rich muds and sands overlying a lower serpentinite mud section. The thick sediment cover and the lack of recent serpentinite flows suggest that Torishima forearc Seamount is no longer actively venting fluids. Detailed lithologic sections of the holes samples are shown in Figure 2.

Shipboard and post-cruise studies of the interstitial waters squeezed from the sediments revealed a similar chemistry to that of fluids sampled by the *Alvin* dives, with low chloride, high pH (up to 12.6), and high concentrations of carbonate, bicarbonate, sulfate ions, and the light hydrocarbons, methane, ethane, and propane (Mottl and Haggerty, this volume). Preliminary work by shipboard scientists suggested that three different sources contributed to the unusual

chemistry of these fluids. Seawater reaction with harzburgites and metabasics, diagenetic pore fluids, and a possible deep-sourced fluid from the downgoing Pacific slab (Leg 125 Shipboard Party, 1989). A detailed discussion of the fluid geochemistry is presented by Mottl and Haggerty (this volume).

The mobility of platinum-group elements (PGE) in hydrothermal solutions has only recently received attention by geologists. This was mainly because of the beliefs (1) that PGEs are inert under most geological environments, (2) that PGE deposits can be explained by magmatic processes, and (3) the scarcity of proven hydrothermal PGE deposits. However, recent studies of classic magmatic PGE sulfide deposits in the Bushveld and Stillwater complexes suggest that late-stage chloride-rich fluids may be important in the redistribution of Pt and Pd (Boudreau et al., 1986). Also, several stratiform sediment-hosted base metal deposits, such as the Kupferschiefer (Kucha, 1982), have elevated Pt and Pd values, which are thought to be related to hydrothermal mobilization of these elements. Work on laterites by Bowles (1988) suggested that PGEs were mobile in the surficial environment, a conclusion also reached by Wood and Vlassopoulos (1990). In contrast, many Au deposits are hydrothermal in origin and a considerable body of work exists about the transport and deposition of Au in hydrothermal systems (Seward, 1984).

Recent research on the mantle sections of ophiolites has shown some rocks to have high PGE values. The highest values are from ultramafic rocks in the Unst ophiolite in the Shetland Isles, which has been suggested to have a supra-subduction zone (SSZ) origin (Prichard and Lord, 1988). The peridotites drilled during Leg 125 are petrographically similar to SSZ ophiolite peridotites (Ishii and Robinson, this volume). Serpentinization has long been suggested as a potential process for mobilizing precious metals (e.g., Stumpfl, 1974), and both serpentinized peridotites and fluids from Leg 125 have been analyzed for this study.

The interstitial pore fluids collected during Leg 125 have allowed us to undertake a preliminary study of the concentration of Pd, Pt, and Au in serpentinizing and diagenetic fluids. Fluids from the actively venting Conical Seamount and the "extinct" Torishima forearc Seamount have been analyzed to study the effects of fluid composition and source rock on the solubility of Pd, Pt, and Au. This research allows us to study (1) the absolute concentrations of Pd, Pt, and Au in the fluids, (2) how these elements are mobilized in solution in comparison to the thermodynamic models of Mountain and Wood (1988a,b), Wood et al (1989), Vlassopoulos and Wood (1990), and Vlassopoulos et al. (1990), and (3) the source of the precious metals.

¹Fryer, P., Pearce, J. A., Stokking, L. B., et al., 1992. *Proc. ODP, Sci. Results*, 125: College Station, Texas (Ocean Drilling Program).

²Department of Geological Sciences, Science Laboratories, South Road, Durham, DH1 3LE, U.K.

³Geological Survey of Canada Sector, 601 Booth Street, Ottawa, K1A 0E8, Canada.

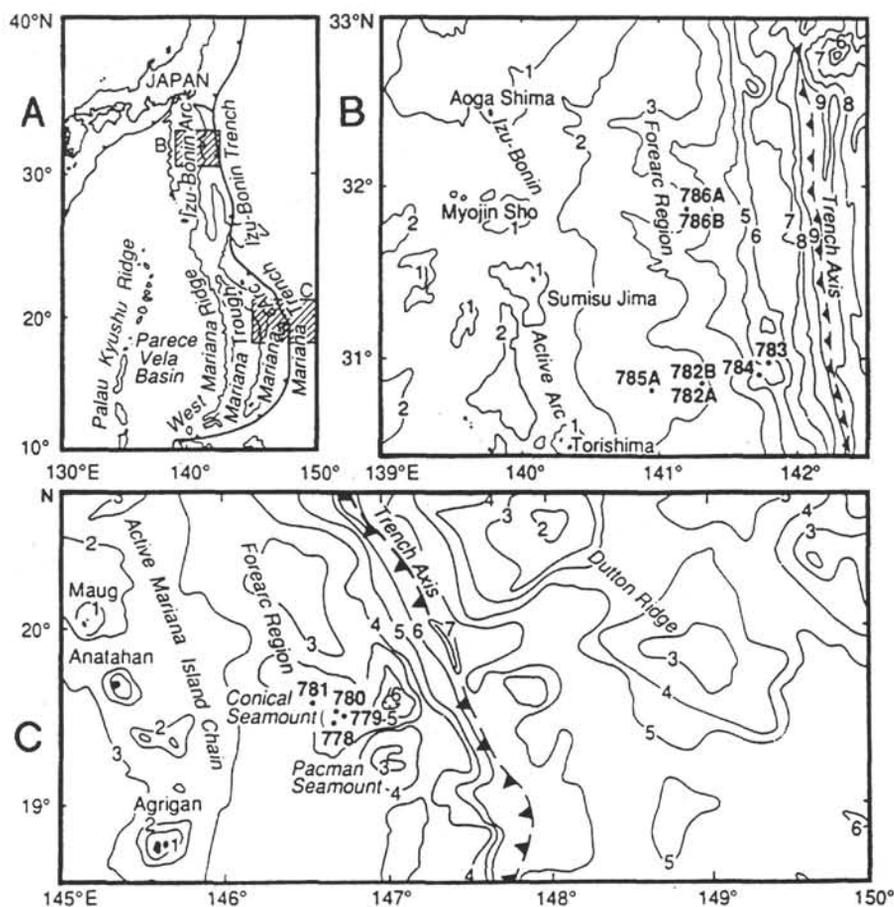


Figure 1. Location of Leg 125 sites: (A) the regional setting of the Izu-Bonin and Mariana forearcs; (B) the precise setting of the Izu-Bonin drill sites (Sites 782 through 786); and (C) the precise setting of the Mariana drill sites (Sites 778 through 781). (Contours in kilometers below sea level).

ANALYTICAL TECHNIQUES

Recent analytical developments at the Geological Survey of Canada at Ottawa have enabled the measurement of extremely low concentrations of Au, Pd, and Pt in natural waters by graphite furnace atomic absorption spectrometry (GFAAS) and isotope dilution-electrothermal vaporization inductively coupled plasma mass spectrometry (ID-ETV-ICP-MS), permitting direct studies of the mobilization of precious metals. Because of the initial small volumes of the fluids and the expected low concentrations of these elements, pre-concentration of Pd, Pt, and Au was undertaken before analysis. Beta-autoradiography coupled with reflected light-microscopy of five of the Leg 125 peridotites were undertaken to try to detect any precious metal phases as the peridotites are one possible source for the precious metals. The beta-autoradiography techniques used are the same as those described by Potts (1984, 1988). A detailed description of the analytical techniques are given below.

Pre-concentration Measurements

An accurate measurement of the initial volume of fluid was undertaken ($3-12 \pm 1$ mL) and a 1-mL aliquot removed for backup studies. The solutions were emptied into Teflon beakers and evaporated to dryness. An HF-aqua regia (5- to 8-ml) mixture was added to dissolve the precipitate, and the solutions were again evaporated to dryness. A total of 8 mL of aqua regia was added, and the solutions heated for 1 hr until no precipitate was seen.

To precipitate quantitatively the precious metals, a Te solution was used. Five mL of HCl and 45 mL of distilled water were added, and the solutions warmed. To this, 5 mL of a 1000-ppm Te solution was added, and the solution continued to be warmed (not boiled). To promote precipitation of Te metal (with the precious metals), 5 mL of SnCl_2 (20 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 17 mL HCl up to 100 mL with H_2O) was added and the solutions heated. An extra 2 mL of SnCl_2 solution was added, and the Te precipitate allowed to coagulate. The precipitate was filtered through 0.45- μm filter paper, rinsed with 1 M HCl and placed into a beaker containing 4 mL of aqua regia. After warming for 1 min., the filter papers were removed with plastic tweezers and rinsed with 1 M HCl. The resultant solution (A) was evaporated to 0.5 mL, transferred to a test tube, and made up to 5 mL with H_2O .

Extraction of Elements From Vial Walls

Because the solutions were analyzed over 1 yr after having been collected on board the ship, it was thought that many of the elements might have been adsorbed onto the walls of the plastic vials, especially as the solutions had not been acidified. After the solutions were removed all the vials were therefore subjected to an extraction process. A 5% Br_2 -95% HCl solution was added and the resulting solution left to stand for 24 hr. The solutions were then poured into beakers, and the vials rinsed with HCl and then water. The resulting solutions (B) were then evaporated to 0.5 mL, transferred to a test tube, and distilled H_2O added to make 3 mL.

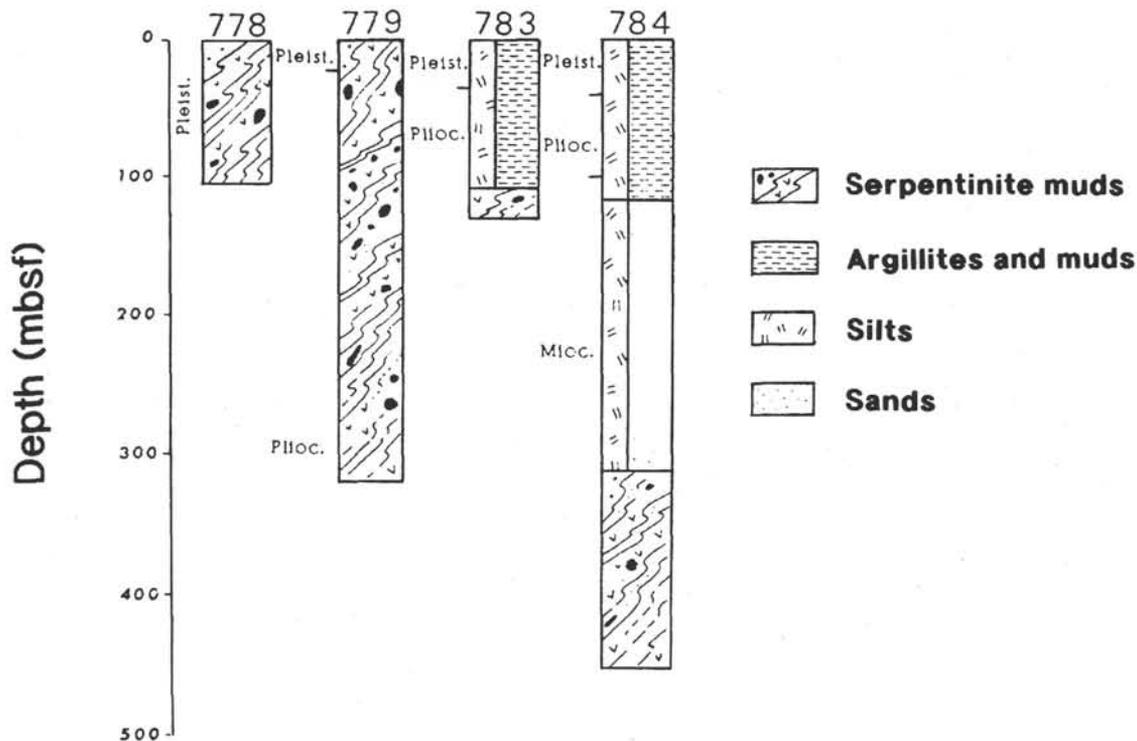


Figure 2. Lithologic sections of the holes from which the fluids were analyzed. Depth in meters below sea floor.

Gold Analysis

Analysis of Au was performed by GFAAS after extraction into MIBK (methyl isobutyl ketone). Three mL of solution A, was poured into a separating funnel and 7 mL of 4 M HCl + 0.8 mL of MIBK (saturated with 4 M HCl) was added. After 5 min. of shaking, the acid phase was removed and the remaining MIBK phase back-washed with 10 mL of 0.1 M HCl (saturated with MIBK). To 60 mL of the MIBK phase, 5 mL of 150 parts per million (ppm) Pd solution was added as a modifier (Hall and Vaive, 1987). This was then analyzed by GFAAS using a Perkin Elmer Model 500. Run conditions were the same as those in Hall et al., (1989) and are shown in Table 1. Exactly the same procedure was repeated for 1.5 mL of solution B.

Palladium and Platinum Analysis

Pd and Pt analyses were undertaken by a combination of standard nebulization isotope dilution ICP-MS and ID-ETV-ICP-MS. A 1-mL solution of A was spiked with 14.8 ng of ^{105}Pd and 19.8 ng of ^{194}Pt (as Cl^-). Analysis by ETV-ICP-MS using an ELAN 250 from SCIEX was attempted using the ETV setup described in Park and Hall (1987). However, the solutions were so acidic that the graphite platform could not hold the 2-mL aliquots long enough quantitatively to vaporize the solutions. This technique was thus rejected. The Pd and Pt were then iodized and extracted into MIBK, but the KI coprecipitated some of the Te (and precious metals), so this procedure was also rejected. Finally, the solutions were taken up to 2.5 mL with distilled water and nebulized into the ICP-MS by standard procedures. Unfortunately, this increased the detection limits to 0.1 ppb.

One mL of solution B was taken and spiked with Pd and Pt isotopes as above. As the Pd and Pt were in solution as chlorides, they were extracted into MIBK. The lower acidity of these solutions permitted analysis by isotope dilution ETV-ICP-MS. Running conditions were the same as in Park and Hall (1987) and are shown in Table 2.

Comments About Accuracy of Analyses

When analyzing such low concentrations of these elements, contamination is a considerable problem. All the samples were collected on the ship by the same method. The sediment samples were squeezed at the same temperature at which they were cored, in a stainless steel squeezer with the interstitial pore water collected into a cleaned plastic

Table 1. Instrumentation and operating conditions used for determining Au by graphite furnace atomic absorption.

Instrumentation:

AA spectrophotometer:	Perkin-Elmer Model 5000 with the model HGA 500 graphite furnace and AS-1 autosampler
Graphite Tubes:	Pyrolytic-coated

Conditions:

Wavelength:	242.8 nm
Slit width:	0.2 nm
Mode:	Absorbance
Injection volume:	65 μL , average of three readings taken

Gas interrupt used during atomization

Heating cycle:

Stage	Temperature ($^{\circ}\text{C}$)	Ramp period (s)	Hold period (s)
Dry	120	10	20
Ash	450	10	10
Atomize	2400	0	5

Table 2. Operating conditions used in the determination of Pd and Pt by electrothermal vaporization inductively coupled plasma mass spectrometry.

ETV:			
Carrier argon gas flow-rate	1.5 L/min		
Freon gas injection rate	3 mL/min		
Heating Cycle:			
Stage	Temperature	Ramp period	Hold period
	(°C)	(s)	(s)
Dry	100	15	45
Ash	1700	300	10
Vaporize	3000	0	5
ICP-MS:			
R.f. forward power	0.9 kW		
Reflected power	15 W		
Distance from sampling orifice to load cone	1.5 cm		
Plasma argon gas flow-rate	12 L/min		
Auxiliary argon gas flow-rate	2.1 L/min		
Ion lens settings	B = 10; EI = 70; P = 20; S2 = 45		
Data acquisition parameters:			
Measurement mode	Multichannel		
Measurement time	0.05 s (signal integration) 0.01 s (peak plotting)		
Dwell time	5 ms		
Signal integration time	3 s		

syringe. Plastic gloves were worn whenever the samples were handled, and the outermost sediment was scraped away before squeezing to minimize any contamination from the core barrel. All of the Teflon beakers were washed in ultrapure reagents, and any rinsing was by deionized, distilled water. Blanks and standards were run through all of the analytical procedures, and detection limits were calculated on three standard deviations of the blank. Synthetic standards were used during calibration. The detection limit for Pd and Pt for the whole procedure (fluid + leachate) is 0.10 ppb. Detection limits for Au vary between 20 and 40 ppt, depending on the initial volume of fluid. Where the leachate from the vial walls lay below the detection limit, but the element was measured in the fluid, the total concentration represents a minimum value. Concentrations in the leachates were calculated by assuming that all adsorbed elements came from the measured volumes in the vials. All three elements can be difficult to extract from the vial walls quantitatively. Falkner and Edmund (1990) found Au difficult to extract from some plastic bottles, even with hot aqua regia, and Pt is also difficult to recover, so the concentration of these elements may be a minimum estimate. No correlation exists between the original volume and the concentrations of the elements, suggesting that the values are real. All the other fluid analyses were undertaken on board the *JOIDES Resolution* by the methods described in Fryer, Pearce, Stokking, et al. (1990).

RESULTS

Data for the precious metals are presented in Table 3, together with other important fluid chemistry data and information on the type of sediment from which the pore fluid was squeezed. Several interesting observations can be made. First, Pd and Pt were detected only in fluids from Hole 783A, which were squeezed from a dominantly vitric-rich

Table 3. Concentration of Au, Pd, and Pt in the interstitial waters. Abbreviations: (t) = total concentration; (f) = concentration in the fluid; (l) = concentration in the acid leach.

Core, section, interval (cm)	Volume (mL)	pH	Chlorinity (mmol/kg)	Sulfate (mmol/kg)	Ammonia (mmol/kg)	Au (t) (pmol/L)	Pt (t) (nmol/L)	Pd (t) (nmol/L)	Au (f) (pmol/L)	Pt (f) (nmol/L)	Pd (f) (nmol/L)	Au (l) (pmol/L)
Hole 778A												
1-R-4, 145-150	9.5	8.48	547.5	27.17	11	<101.5	<0.5	<0.9	<101.5	<0.5	<0.9	<101.5
Hole 779A												
5-R3, 085-095	5.1	9.08	542.6	22.46	27	<203.1	<0.5	<0.9	<203.1	<0.5	<0.9	<101.5
36-R-2, 135-150	5.5	10.32	529.4	24.06	66	548.3	<0.5	<0.9	<203.1	<0.5	<0.9	548.3
37-R-1, 135-150	4.6	9.93	515.5	21.33	66	<203.1	<0.5	<0.9	<203.1	<0.5	<0.9	101.5
Hole 779B												
1-R-1, 145-150	5.5	8.16	522.3	27.45	5	<203.1	<0.5	<0.9	<203.1	<0.5	<0.9	<101.5
5-R-1, 145-150	4.4	7.99	537.9	29.25	5	<203.1	<0.5	<0.9	<203.1	<0.5	<0.9	<101.5
Hole 783A												
1-R-1, 145-150	5.5	7.72	538.8	27.31	7	<203.1	2.7	11.7	<203.1	1.6	3.9	<101.5
1-R-2, 145-150	5.0	7.85	543.6	27.41	10	411.2	5.0	3.9	411.2	1.0	1.7	<101.5
1-R-5, 145-150	5.5	7.95	544.5	28.20	103	456.9	2.3	4.1	456.9	1.5	2.3	<101.5
4-R-3, 140-150	12.0	7.95	547.5	27.77	70	233.5	3.3	8.4	121.8	2.8	4.5	111.7
7-R-1, 140-150	9.5	8.18	553.3	27.11	94	340.2	2.6	3.8	157.4	1.5	2.6	182.8
Hole 784A												
1-R-2, 140-150	10.5	7.95	552.3	26.14	134	198.0	<0.5	<0.9	<101.5	<0.5	<0.9	198.0
4-R-2, 140-150	9.6	7.84	546.5	25.42	150	126.9	<0.5	<0.9	<101.5	<0.5	<0.9	126.9
6-R-4, 140-150	7.1	8.19	548.4	22.05	221	446.8	<0.5	<0.9	172.6	<0.5	<0.9	274.2
8-R-4, 140-150	7.0	8.21	552.3	25.07	246	<101.5	<0.5	<0.9	101.5	<0.5	<0.9	<101.5
16-R-5, 140-150	9.6	8.00	549.4	21.82	288	<101.5	<0.5	<0.9	101.5	<0.5	<0.9	<101.5
19-R-1, 000-010	5.0	8.17	543.6	20.58	282	1116.9	<0.5	<0.9	731.1	<0.5	<0.9	385.9
22-R-3, 140-150	6.3	8.00	550.4	19.61	250	182.8	<0.5	<0.9	126.9	<0.5	<0.9	182.8
26-R-1, 140-150	4.9	7.65	550.4	19.23	241	<203.1	<0.5	<0.9	<203.1	<0.5	<0.9	<101.5
29-R-4, 140-150	3.6	8.07	549.4	17.84	216	<203.1	<0.5	<0.9	<203.1	<0.5	<0.9	<101.5

clay which had only a minor serpentine content. This correlation with sediment type suggests that no sample contamination occurred during the analysis. No correlation exists among the two elements. The Pd values range from 3.8 to 11.8 nmol/L and Pt values, from 2.3 to 5.0 nmol/L. No Pt or Pd was detected in interstitial waters squeezed from serpentinite muds from Conical Seamount. Au was detected in 9 of the samples, eight of which were from squeezed vitric-clays from Holes 783A and 784A. One sample (125-779A-36R-2, 135–150 cm) had detectable Au and was squeezed from serpentinite mud. However, this pore water had the highest pH, 10.32. Values for Au lie between 126.9 and 1116.9 pmol/L.

Sources For Pd, Pt, and Au

The complex history of the Leg 125 fluids and the contrasting types of sediment from which the fluids were squeezed means that there are several possible sources for the precious metals. The first is seawater itself. Pt and Pd concentrations in Pacific seawater lie between 0.1–0.2 and 0.02–0.06 ppt, respectively (Hodge et al., 1985; Jacinto and van den Berg, 1989), and Au values lie between 0.10 and 0.30 ppt (Falkner and Edmund, 1990). These values are several orders of magnitude below the concentrations measured and, to account for the high values observed, the Pt and Pd would have to be pre-concentrated and then remobilized into solution. During the formation of manganese nodules, Pt and Pd are both scavenged from seawater and precipitated with Mn to give high Pt and Pd values in the nodules (Halbach et al., 1989). However, only one ferromanganous sediment was discovered during Leg 125, in a serpentinite mud. Also, Pt/Pd ratios in ferromanganese crusts are on the order of 20–300, whereas our fluids have Pt/Pd ratios between 0.42 and 2.33.

Second, the ultramafic clasts could be a good source for the precious metals, which could be released to the fluids during serpentinization. However, no Pt or Pd was detected in fluids that were squeezed from the serpentinite muds, and Au was detected in only

one sample with an extremely high pH. In addition, beta autoradiography and reflected light microscopy failed to identify or resolve any PGE or Au phases in the peridotites, although it is possible that any precious metal phases present may have been leached during serpentinization. Again, the fact that Pt values are usually higher than Pd in harzburgites from ophiolites fails to explain the low Pt/Pd ratios in the fluids.

The fact that the high precious metal values are almost all restricted to the vitric-rich clays suggests that the latter are the most likely source of the Pt, Pd, and Au. The high Au may be explained by the clays having been derived from volcanic-arc rocks, which often have high Au values. Few PGE analyses have been carried out on volcanic-arc rocks. Hamlyn et al. (1985) reported high (6.9–35 ppb, mean 15 ppb) Pd values for boninites from the Bonin forearc and this may explain the low Pt/Pd ratios in the fluids. Alternatively, the clay minerals could act as surfaces for adsorption of the precious metals, which could then be desorbed during squeezing. The low Pt/Pd ratios may then better be explained by the higher solubility of Pd compared with Pt under similar conditions (Wood and Vlassopoulos, 1990). On the same theme, the low Pt/Pd ratios may be related to the difficulty in extracting Pt from the vial walls during sample preparation.

Speciation of Pd, Pt, and Au in the Pore Fluids

To understand the transport and deposition of precious metals in natural waters, a knowledge of the solubility of stable metal complexes is needed. Recent experimental and theoretical studies by Mountain and Wood (1988a, b), Wood and Mountain (1989), Wood et al. (1990), Vlassopoulos and Wood (1990), and Vlassopoulos et al. (1990) have allowed a more thorough understanding of speciation of precious metals in natural waters.

Wood et al. (1989) consider that chloride, hydroxide, reduced sulfur, and ammonia are the most important species in the complexing of precious metals. However, plots of pH, annotated according to detection or nondetection of Pd, Pt, and Au vs. chlorinity, sulfate, and ammonia (Figs. 3–5) for the fluids fail to reveal any systematic relationship between precious metal content and any of these species.

Figure 6 shows the $\log a_{Cl^-}$ vs. pH diagram for Pt and Pd, from Wood et al. (1989), with the composition of the Leg 125 fluids marked. The low activity of chloride ($\log a_{Cl^-} = -0.5$) and the high pHs indicate that the uncharged hydroxide complexes $Pd(OH)_2^0$, $Pt(OH)_2^0$, and $AuOH(H_2O)^0$, rather than chloride complexes, may have been the most stable inorganic complexes of these elements for the types of fluids sampled on Leg 125.

Wood et al. (1989) propose that reduced sulfur species may be important in complexing the precious metals. The role of reduced sulfur species in the Leg 125 fluids is difficult to assess. Although no reduced sulfur species were detected in these fluids and only sulfate was measured, the fluids that reacted to produce serpentine are thought to be reducing, because the reaction between olivine and water extracts oxygen from the aqueous phase (Eckstrand, 1975). However, oxidation of the fluids, may have taken place during squeezing so that the true species in solution were not measured.

Wood et al. (1989) proposed that precious metal ammonia complexes are most soluble in basic, reducing fluids at low temperatures. The high pH and ammonia content of the fluids suggest that ammonia is a possible complexing species, although Wood et al. (1989) suggested that the predicted Pt and Pd solubilities as ammonia complexes are several orders of magnitude below that of bisulfide and hydroxide complexes under similar conditions.

Organic acids may also be important in speciation of precious metals (Vlassopoulos et al., 1990), and organic acid studies of the fluids have been undertaken by Haggerty and Fisher (this volume). However, the very low concentrations of these acids, coupled with the higher concentration of other competing ions (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) compared with the precious metals mean that organic acid speciation was unlikely to be very important in these fluids.

Table 3 (continued).

Pt (l) (nmol/L)	Pd (l) (nmol/L)	Sedimentary rock type
<0.5	<0.9	Serpentinite mud
<0.5	<0.9	Amphibole-rich serpentinite
<0.5	<0.9	Silty serpentinite
<0.5	<0.9	Chlorite-rich serpentinite mud
<0.5	<0.9	Aragonite-rich serpentinite
<0.5	<0.9	Serpentine mud
1.1	7.8	Glass-rich clay
0.9	2.3	Glass-rich clay
0.8	1.9	Glass-rich clay
0.5	3.9	Glass-rich clay
1.0	1.1	Pumice/glass-rich clay
<0.5	<0.9	Glass-rich clay
<0.5	<0.9	Vitric clay
<0.5	<0.9	Vitric clay
<0.5	<0.9	Glass-rich clay
<0.5	<0.9	Vitric clay
<0.5	<0.9	Glass-rich clay
<0.5	<0.9	Glass-rich clay
<0.5	<0.9	Glass-rich clay
<0.5	<0.9	Glass-rich clay

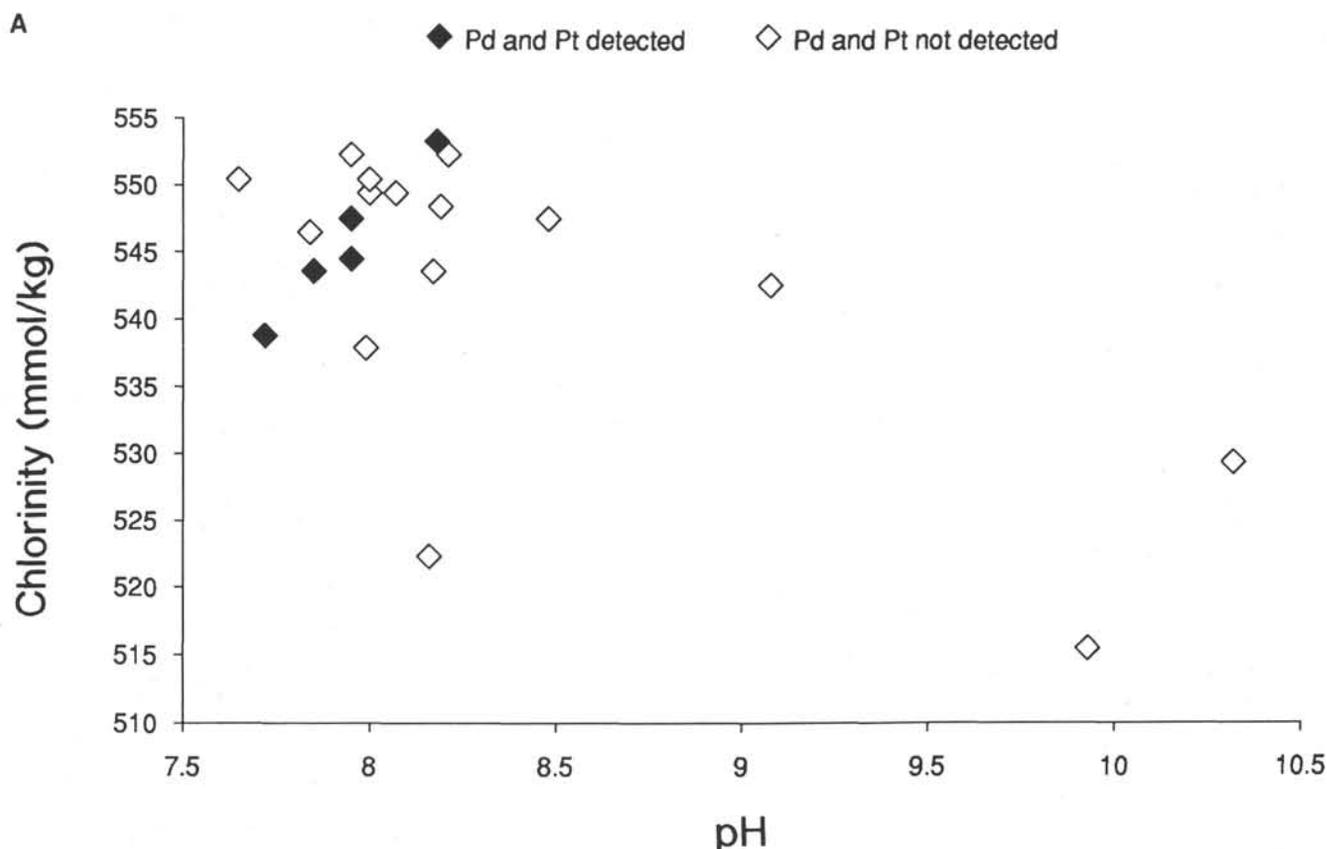


Figure 3. Plot of pH against chlorinity showing the fluid compositions for which (A) Pd and Pt were detected and (B) Au was detected.

From the above discussion it can be shown that precious metal solubility in the cold, high-pH fluids from Torishima Seamount is probably as hydroxide and reduced sulfur species, although the significance of the latter is difficult to assess. Ammonia and organic acid complexing possibly play a minor role in their solubility.

SUMMARY

Our preliminary investigations into the distribution of Pd, Pt, and Au in the serpentinite seamounts indicate the following conclusions:

1. Pore waters squeezed from serpentinite muds suggest that present-day, low-temperature, seawater-peridotite interaction does not mobilize Pd, Pt, and Au into the serpentinizing fluids above the detection limit of our analyses, although Au may be mobilized at high (>10) pH.

2. Harzburgites and dunites from both Conical Seamount and Torishima forearc Seamount have no discrete PGE and Au phases and are an unlikely source for the precious metals detected in solution.

3. High Pd, Pt, and Au concentrations are found in pore waters from Holes 783A and 784A. All these pore waters were squeezed from vitric-rich clays. Precious metals are thought to have been mobilized and possibly adsorbed onto the clay mineral surfaces during diagenesis of these arc-derived sediments. Desorption during squeezing of the mud samples may have produced the elevated precious metal concentrations in the fluids.

4. Pd, Pt, and Au are most likely to be in solution as neutral hydroxide, bisulfide and ammonia complexes. Organic acid complexing may also be important. Pd is more soluble than Pt, producing the low Pt/Pd ratios, although many of the sources for the precious metals have high Pt/Pd ratios.

ACKNOWLEDGMENTS

We thank J. C. Pelchat and J. E. Vaive for analyzing the solutions at the Geological Survey of Canada in Ottawa and for their considerable effort and patience while the analyses were conducted. We thank P. J. Potts (Open University, U.K.) for producing the beta autoradiographs and M. J. Mottl for discussions on fluid geochemistry and for his help in preparing shipboard samples. We thank M. Palmer and D. Vlassopoulos for thoughtful reviews of the paper. This research was supported by a NERC (U.K.) studentship (GT4/89/GS/27) to I.J.P. and a NERC ODP Special Topic research grant (GR3/416) to J.A.P.

REFERENCES

- Barnes, I., and O'Neil, J. R., 1969. The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, *Western U. S. Bull. Geol. Soc. Am.*, 80:1947-1960.
- Barnes, I., Rapp, J. B., and O'Neil, J. R., 1972. Metamorphic assemblages and the direction of fluids in four instances of serpentinization. *Contrib. Mineral. Petrol.*, 35:263-276.
- Boudreau, A. E., Matez, E. A., and McCallum, I. S., 1986. Halogen geochemistry of the Stillwater and Bushveld Complexes: evidence for transport of the platinum-group elements by Cl-rich fluids. *J. Petrol.*, 27:967-986.
- Bowles, J.F.W., 1988. Further studies of the development of platinum-group minerals in the laterites of the Freetown layered complex, Sierra Leone. In Prichard, H. M., Potts, P. J., Bowles, J.F.W., and Cribb, S. J. (Eds.), *Geo-Platinum 87*: London (Elsevier), 273-280.
- Eckstrand, O. R., 1975. The Dumont Serpentinite: a model for control of nickeliferous opaque mineral assemblages by alteration reactions in ultramafic rocks. *Econ. Geol.*, 70:183-201.
- Falkner, K. K., and Edmund, J. M., 1990. Gold in seawater. *Earth Planet. Sci. Lett.*, 98:208-221.

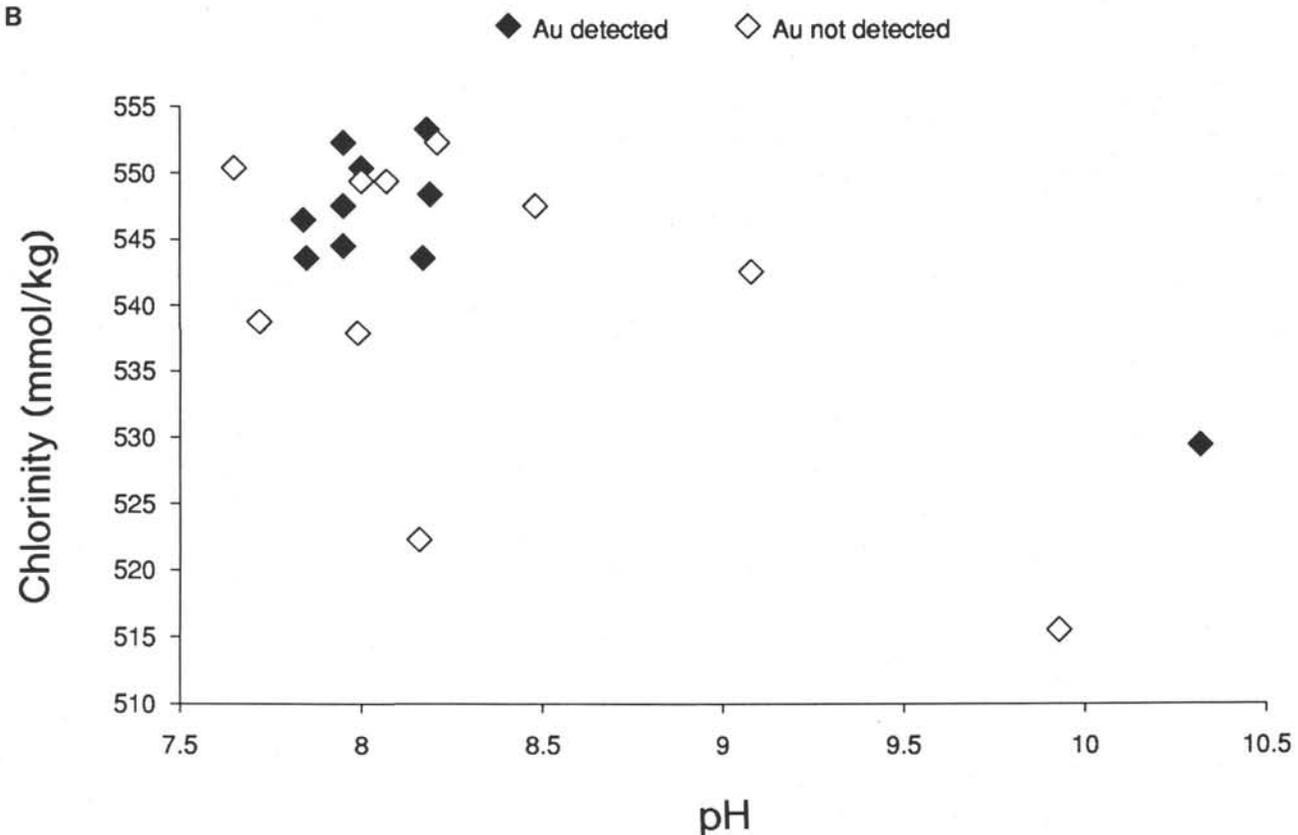


Figure 3 (continued).

- Fryer, P., Ambos, E. L., and Hussong, D. M., 1985. Origin and emplacement of Mariana forearc seamounts. *Geology*, 13:774-777.
- Fryer, P., and Fryer, G. J., 1987. Origins of non-volcanic seamounts in a forearc environment. In Keating, B. H., Fryer, P., Batiza, R., and Boehlert, G. W. (Eds.), *Seamounts, Islands and Atolls*. Am. Geophys. Union, Geophys. Monogr. Ser., 43:61-69.
- Fryer, P., Pearce, J. A., Stokking, L. B., et al., 1990. Explanatory notes. Proc. ODP, Init. Repts., 125: College Station, TX (Ocean Drilling Project), 15-40.
- Halbach, P., Kriete, C., Prause, B., and Puteanus, D., 1989. Mechanisms to explain the platinum concentrations in ferromanganese seamount crusts. *Chem. Geol.*, 76:95-106.
- Hall, G.E.M., and Vaive, J. E., 1989. The effect of palladium as a matrix modifier in the determination of gold by graphite furnace atomic absorption spectrometry. In *Current Research* (Pt. F), Geol. Surv. Can. Pap., 89-1F:27-30.
- Hall, G.E.M., Vaive, J. E., Coope, J. A., and Weiland, E. F., 1989. Bias in the analysis of geological materials for gold using current methods. *J. Geochem. Expl.*, 34:157-171.
- Hamlyn, P. R., Keays, R. R., Cameron, W. E., Crawford, A. J., and Waldron, H. M., 1985. Precious metals in magnesian low-Ti lavas: implications for metallogenesis and sulfur saturation in primary magmas. *Geochim. Cosmochim. Acta*, 49:1797-1811.
- Hodges, V. F., Stallard, M., Koide, M., and Goldberg, E. D., 1985. Platinum and the platinum anomaly in the marine environment. *Earth. Planet. Sci. Lett.*, 72:158-162.
- Ishii, T., 1985. Dredged samples from the Ogasawara forearc seamount or "Ogasawara Paleoland"—or "forearc ophiolite." In Nasu, N., Kobayashi, K., Uyeda, S., Kushiro, I., and Kagami, H. (Eds.), *Formation of Active Ocean Margins*: Tokyo (Terra Sci. Publ.), 307-342.
- Jacinto, G. S., and van den Berg, C.M.G., 1989. Different behavior of platinum in the Indian and Pacific Oceans. *Nature*, 338:332-334.
- Janecky, D. R., and Seyfried, W. E., Jr., 1986. Hydrothermal serpentinization of peridotite within the oceanic crust: experimental investigations of mineralogy and major element chemistry. *Geochim. Cosmochim. Acta*, 50:1357-1378.
- Kucha, H., 1982. Platinum-group metals in the Zechstein copper deposits, Poland. *Econ. Geol.*, 77:1578-1591.
- Leg 125 Shipboard Scientific Party, 1989. Plumbing the Pacific sinks. *Nature*, 339:427-428.
- Mountain, B. W., and Wood, S. A., 1988a. Chemical controls on the solubility, transport, and deposition of platinum and palladium in hydrothermal solutions: a thermodynamic approach. *Econ. Geol.*, 83:492-510.
- , 1988b. Solubility and transport of platinum-group elements in hydrothermal solution: thermodynamic and physical chemical constraints. In Prichard, H. M., Potts, P. J., Bowles, J.F.W., and Cribb, S. J. (Eds.), *Geo-Platinum 87*: London (Elsevier), 57-82.
- Park, C. J., and Hall, G.E.M., 1987. Analysis of geological materials by inductively coupled plasma mass spectrometry with sample introduction by electrothermal vapourisation. *J. Anal. At. Spectrom.*, 2:473-480.
- Potts, P. J., 1984. Neutron activation-induced beta autoradiography as a technique for locating minor phases in thin sections: applications to rare earth element and platinum group element mineral analysis. *Econ. Geol.*, 79:738-747.
- , 1988. New detection techniques for locating precious metal minerals by beta autoradiography: preliminary results for rhodium and silver grains. In Prichard, H. M., Potts, P. J., Bowles, J.F.W., and Cribb, S. J. (Eds.), *Geo-Platinum 87*: London (Elsevier), 47-56.
- Prichard, H. M., and Lord, R. A., 1988. The Shetland ophiolite: evidence for a supra-subduction zone origin and implications for platinum-group element mineralization. In Prichard, H. M., Potts, P. J., Bowles, J.F.W., and Cribb, S. J. (Eds.), *Geo-Platinum 87*: London (Elsevier), 161.
- Seward T. M., 1984. The transport and deposition of gold in hydrothermal systems. In Foster, R. P. (Ed.), *Gold '82*: Rotterdam (A. A. Balkema), 165-181.
- Seyfried, W. E., Jr., and Dibble, W. E., Jr., 1980. Seawater-peridotite interaction at 300°C and 500 bars: implications for the origin of oceanic serpentinites. *Geochim. Cosmochim. Acta*, 44:309-321.
- Stumpfl, E. F., 1974. The genesis of platinum deposits: further thoughts. *Minerals. Sci. Eng.*, 6:120-141.

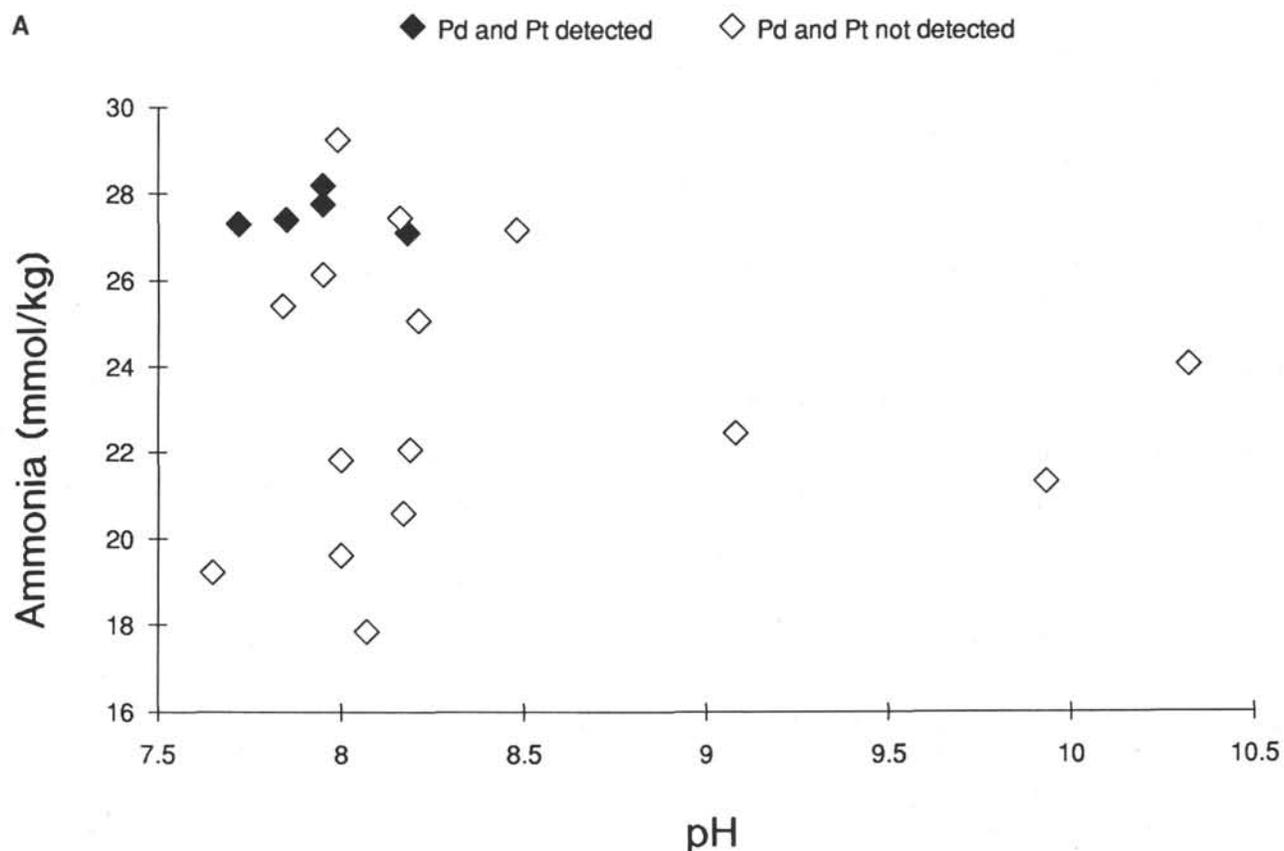


Figure 4. Plot of pH against sulfate showing the fluid compositions for which (A) Pd and Pt were detected and (B) Au was detected.

Vlassopoulos, D., and Wood, S. A., 1990. Gold speciation in natural waters. I. Solubility and hydrolysis reactions of gold in aqueous solution. *Geochim. Cosmochim. Acta*, 54:3-12.

Vlassopoulos, D., Wood, S. A., and Mucci, A., 1990. Gold speciation in natural waters. II. The importance of organic complexing. *Geochim. Cosmochim. Acta*, 54:1575-1586.

Wood, S. A., Mountain, B. W., and Fenlon, B. J., 1989. Thermodynamic constraints on the solubility of platinum and palladium in hydrothermal solutions: reassessment of hydroxide, bisulfide and ammonia complexing. *Econ. Geol.*, 84:2020-2028.

Wood, S. A., and Vlassopoulos, D., 1990. The dispersion of Pt, Pd and Au in surficial media about two PGE-Cu-Ni prospects in Quebec. *Can. Mineral.*, 28:649-663.

Date of initial receipt: 1 October 1990

Date of acceptance: 19 July 1991

Ms 125B-132

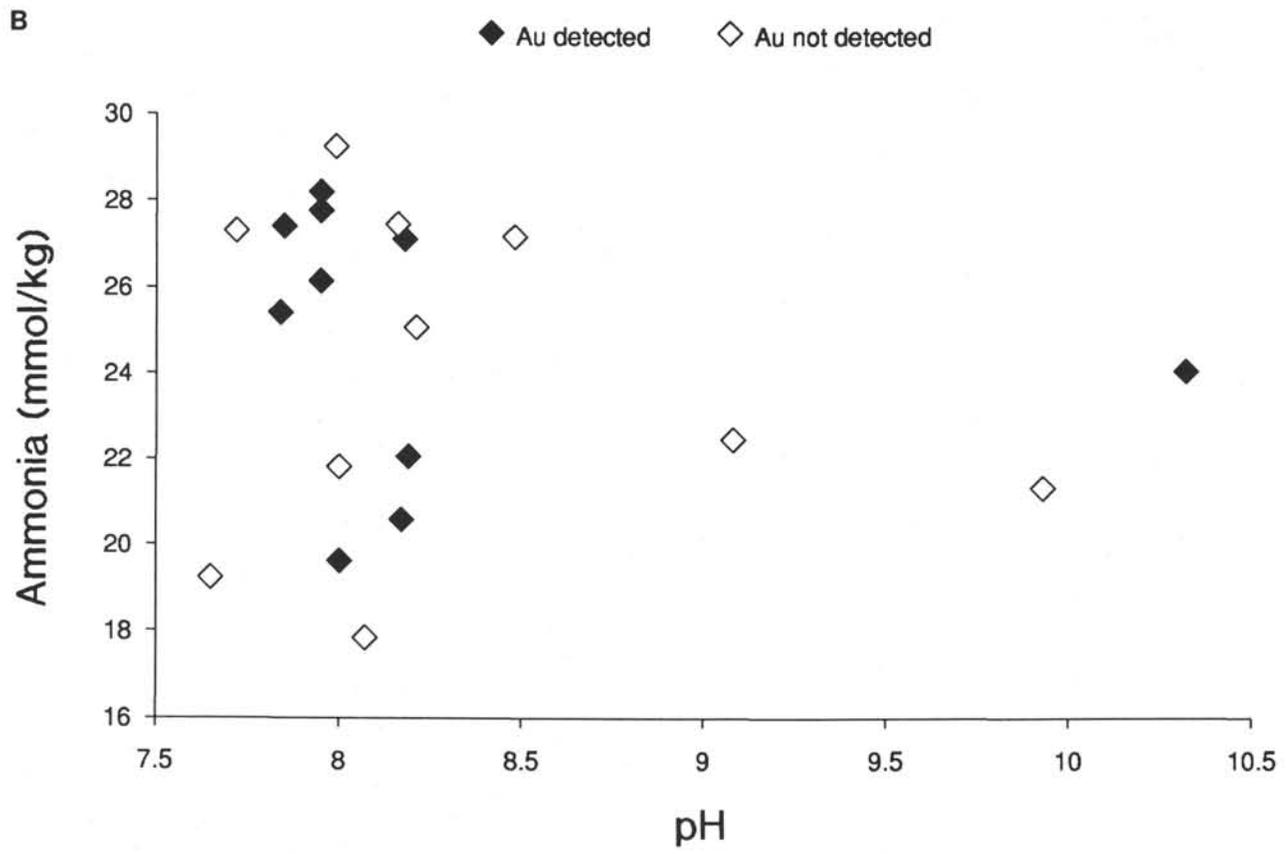


Figure 4 (continued).

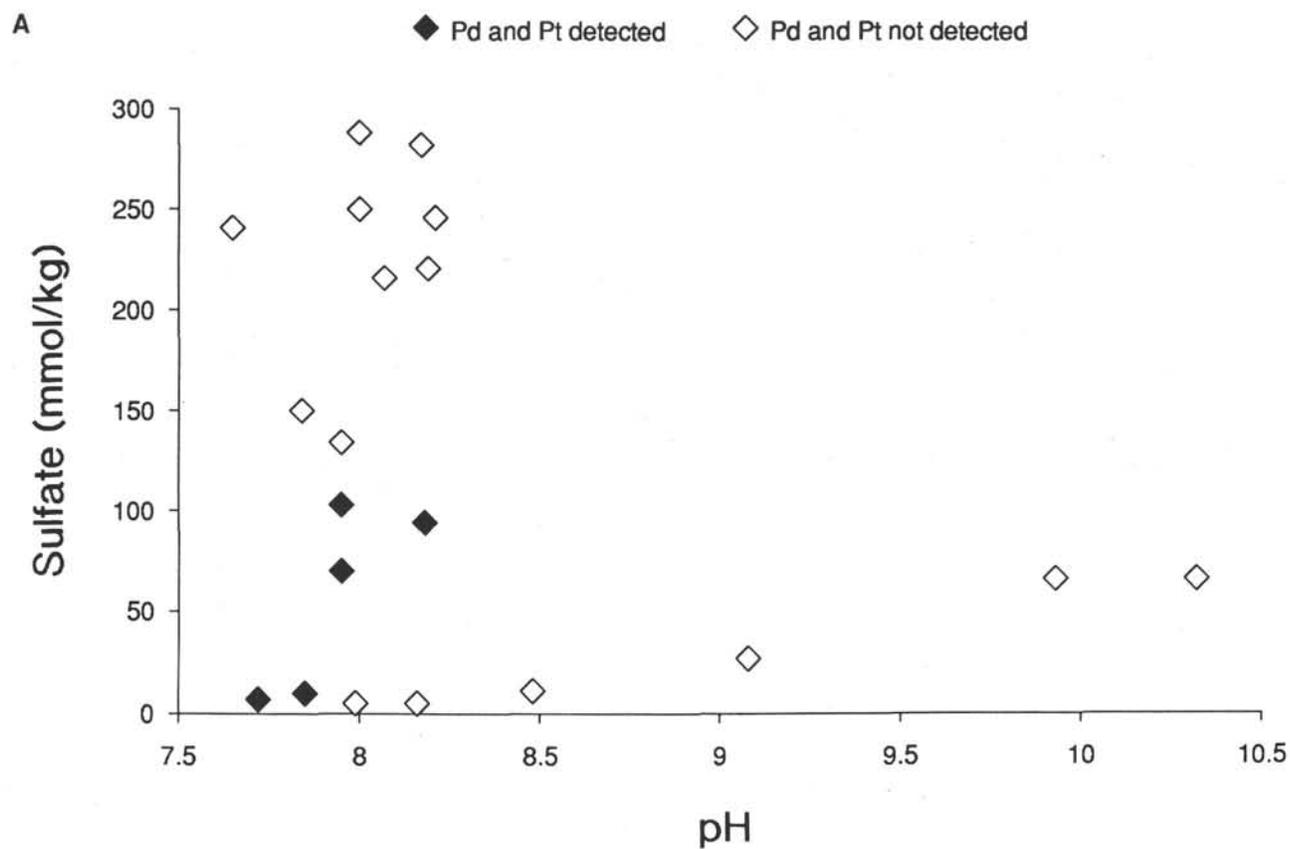


Figure 5. Plot of pH against ammonia showing the fluid compositions for which (A) Pd and Pt were detected and (B) Au was detected.

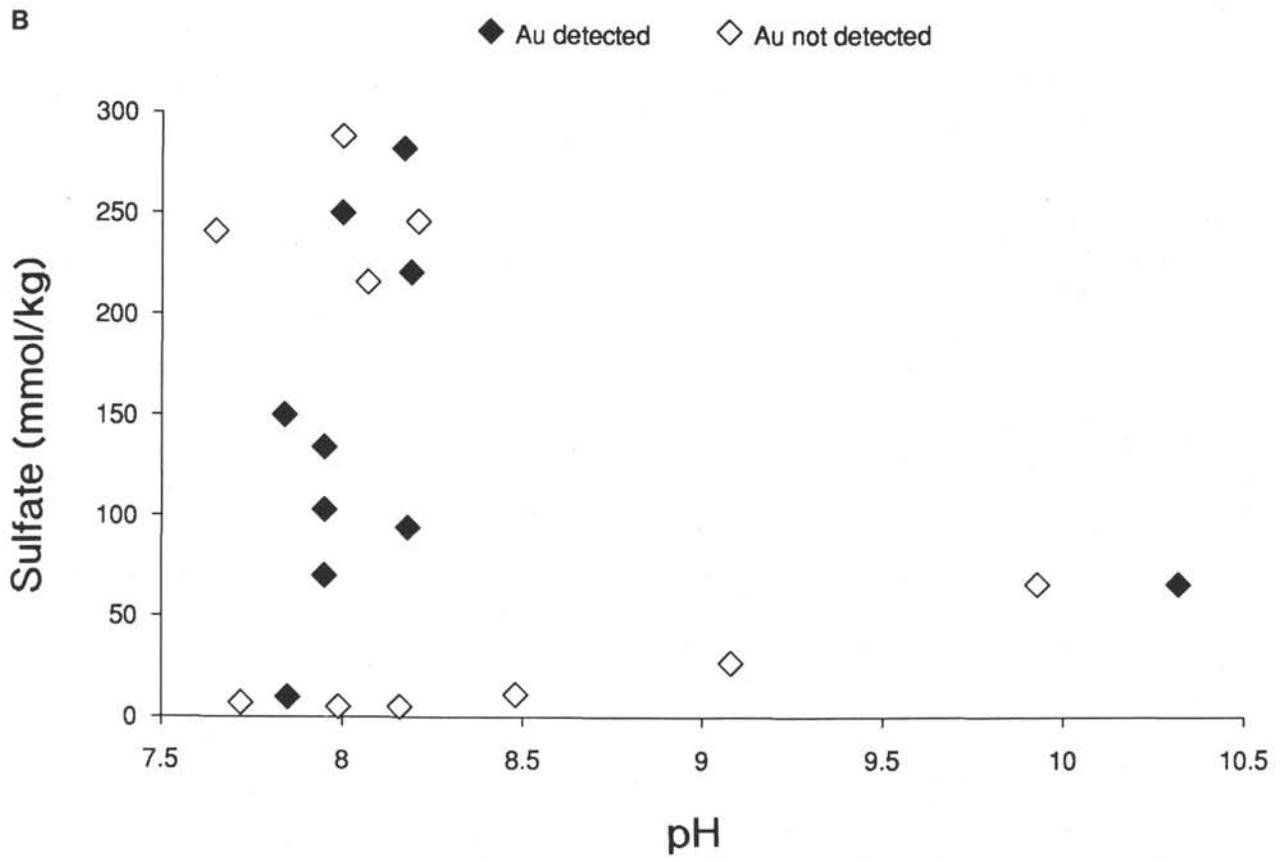


Figure 5 (continued).

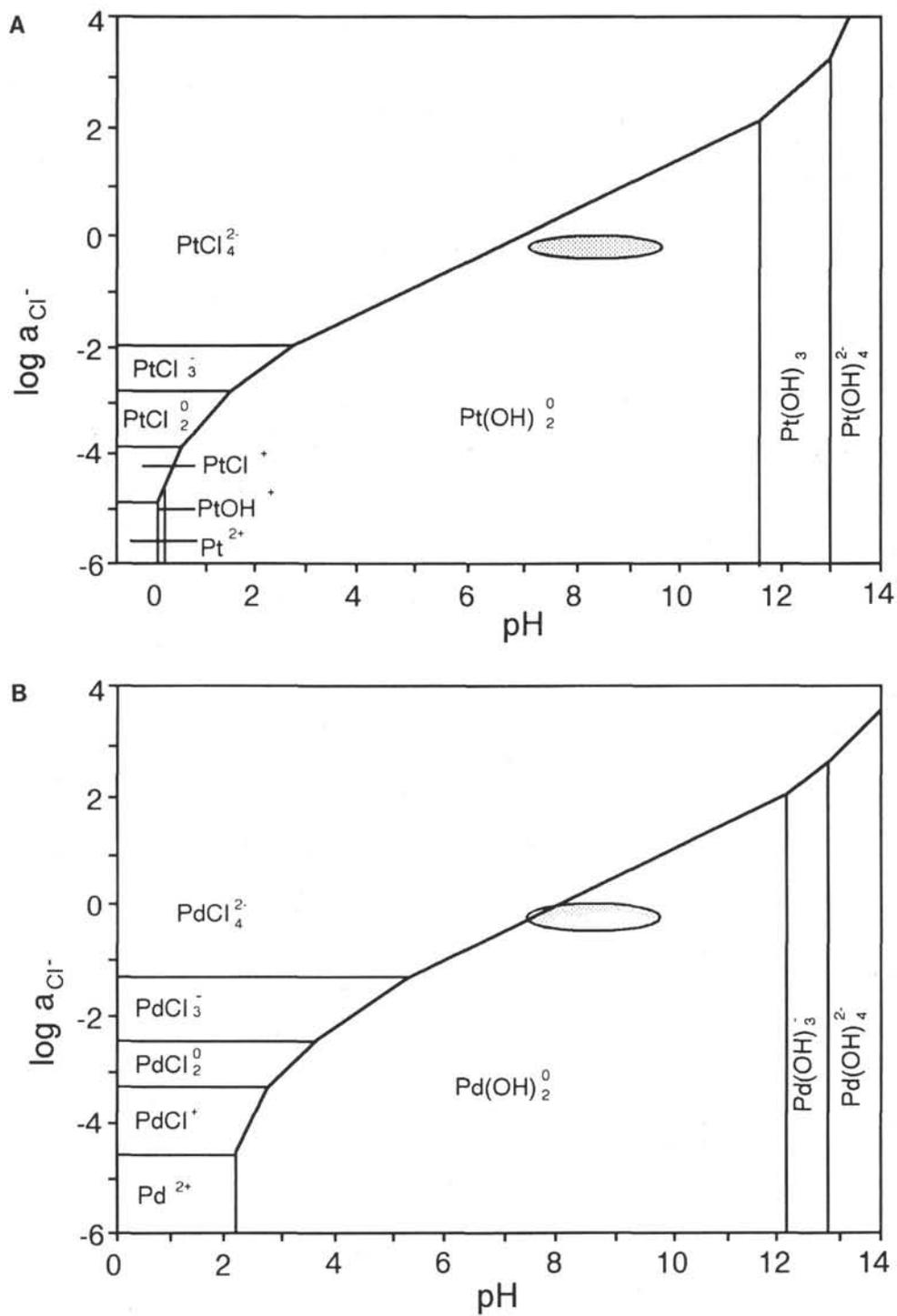


Figure 6. Log a_{Cl^-} vs. pH diagram constructed at 25°C for (A) Pt and (B) Pd from Wood et al. (1989). The stippled field shows the composition of the Leg 125 fluids.