

Concentrations of Gold and other Ore Metals in Volcanics Hosting the Pacmanus Seafloor Sulfide Deposit

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The metal content of volcanic rocks in the vicinity of the PACMANUS seafloor volcanogenic massive sulfide deposit is the subject of an ongoing investigation with two principal aims : to add to the limited data set of metals in seafloor volcanics, and to determine whether the volcanics could provide the metals found in the hydrothermal precipitates. Average metal contents of dacitic volcanics include Ba 318 ppm, Au 3 ppb, As 3 ppm, Sb 0.17 ppm, Zn 84 ppm, Co 7 ppm, Cu 18 ppm, and S 0.02%. Zinc, appears to behave incompatibly, becoming enriched in the dacite melt, whereas cobalt behaves compatibly, and shows a significant negative correlation with SiO₂ in the dacites. A single sample of basaltic andesite shows higher Au, Co and Cu and lower S, As, Zn, Sb and Ba contents than the dacites. PACMANUS sulfides and dacites show similar primitive mantle normalized metal contents, suggesting that leaching of a source with similar metal contents as the dacites could produce the relative metal contents seen in the hydrothermal precipitates.

Key words : PACMANUS, metal content, volcanics, dacite, volatiles

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1. Introduction

The PACMANUS deposit is situated in the eastern Manus Basin east of the Papua New Guinea mainland (Fig. 1). Discovered in 1991, during the PACMANUS I cruise (Binns & Scott, 1993; Scott & Binns, 1995; Binns et al., 1996), PACMANUS is a currently active seafloor volcanogenic massive sulfide deposit. Since the initial discovery, several cruises have visited the site, including the 1995 "Yokosuka" "Shinkai 6500" Manus-Flux cruise (Auzende et al., 1996a, b).

PACMANUS lies near the bathymetric minimum of a Y-shaped volcanic edifice known as Pual Ridge, and is now known to be comprised of at least four distinct sites of active venting, each with a different character of hydrothermal activity and with resultant differences in hydrothermal precipitates (Binns et al. 1996). Both high temperature (up to 262°C) venting associated with black smokers and lower temperature (45–63°C) venting (shimmering water), was observed during the ManusFlux cruise (Auzende et al., 1996a). The hydrothermal precipitates include both zinc-rich and copper-rich massive sulfides, iron-manganese oxide mounds and crusts, and bacterial mat (Binns et al., 1996). The volcanics comprising Pual Ridge are dominated by da-

cite with lesser rhyodacite occurring to the northeast. Pillowed and lobate andesite and basaltic andesite is present at deeper levels, generally between the two arms of the ridge, and to the north and south of the ridge (Binns & Scott, 1993; Waters et al., 1996).

Recently, there has been much discussion concerning the likelihood of magmatic fluids contributing some or all of the metals to VMS hydrothermal systems (Urabe, 1987; Urabe & Murumo, 1991; Stanton, 1991; de Ronde, 1995; Yang & Scott, 1996). Although there are convincing arguments for such a process in some cases, it remains necessary to evaluate whether the metal content of the host volcanic sequence is sufficient to produce a deposit before a leaching process can be entirely discarded. To date, there have been few studies of the metal content of modern seafloor volcanics (Keays & Scott, 1976; Cawood and Fryer, 1994; Doe, 1994; Terashima et al., 1994), and none of these studies have examined felsic volcanics. The attraction of studying modern seafloor volcanics lies in the fact that, if properly selected, they can represent the most pristine rocks associated with massive sulfide deposits, and give valuable information regarding the evolution of a magmatic-hydrothermal system. An investigation of the ore metal

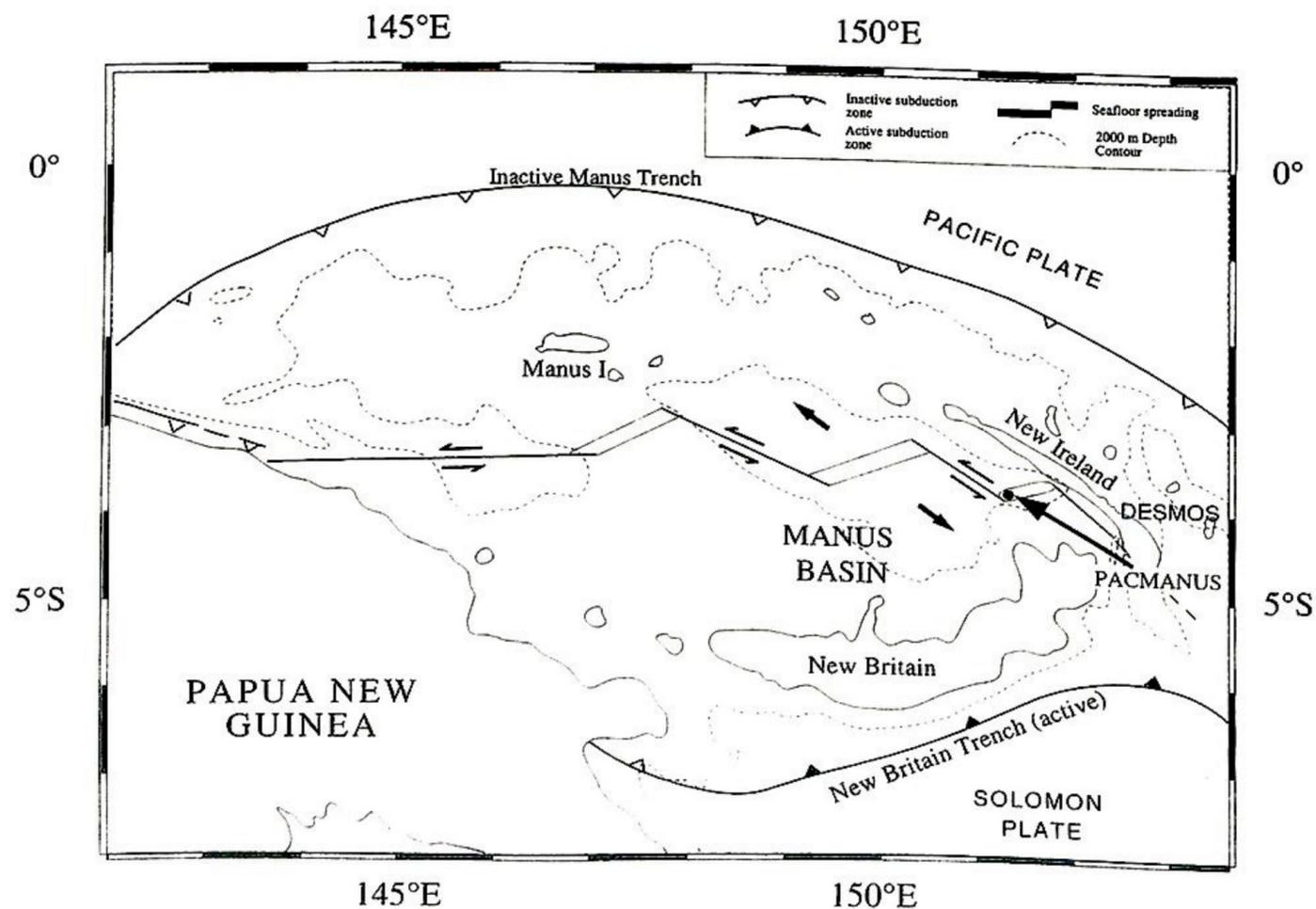


Fig. 1 Simplified tectonic and bathymetric map of the Manus Basin region, showing the location of the PACMANUS deposit. (modified from Benes et al., 1994).

content of volcanic samples from the vicinity of the PACMANUS deposit was therefore undertaken to add to the limited data set of metals in seafloor volcanics, but in particular, to investigate the concentration of metals in volcanics associated with a seafloor massive sulfide deposit. This ongoing investigation has included the analysis of an extensive collection of dredged samples from PACMANUS and other areas of eastern Manus Basin (Moss et al., 1996a, b, 1997). Here we report results for samples collected during the Manusflux cruise.

2. Sample Collection and Analysis

All samples used in this study were collected by the "Shinkai 6500" submersible during the 1995 "Yokosuka" "Shinkai 6500" cruise to the Manus Basin, as part of the Japan/France New Starmer Program (Auzende et al., 1996b). A series of five dives (297, 299, 301, 304 & 305) were performed in the vicinity of the PACMANUS vent sites, of which three resulted in the collection of volcanic samples.

In order to minimize the effect of post-eruption changes in the gold content of the volcanics, unaltered glassy volcanic rocks, selected by visual examination, were used for analysis (cf. Connors et al., 1993). Gold and other trace elements were analyzed by instrumental neutron activation analysis (INAA) using 200 milligram samples following the technique of Stix & Gorton (1992). Major elements were analyzed by X-ray fluorescence spectroscopy, sulfur by the LECO infrared spectrometric technique, and Cu, Ag and Pb by ICP-MS fol-

lowing a total acid digestion at Activation Laboratories Ltd, Ancaster, Ontario.

3. Sample Description

All but one of the samples used in this study were collected in the vicinity of the four vent sites comprising the PACMANUS deposit on the crest and eastern flank of Pual Ridge. The remaining sample, 299-R-01, is a mafic basaltic andesite from lobate flows with glassy rinds, outcropping on the floor of a valley immediately east of Pual ridge, at 2134 m depth. A description of the samples is given in Table 1.

Dacite observed in outcrop consists of blocky flows that are lightly to moderately sedimented (Photo 1). Large blocks of dacite observed in some areas, appear to be rafts that were carried along on the top of the flow. In hand specimen, the dacite is typically very fresh, has a glassy appearance and shows variable vesicularity. Vesicles tend to be elongated, a result of flow, and are homogeneously distributed in the samples (Waters et al., 1996). Examination of thin sections of dacite ensured that the glass to be analyzed was unaltered, and phenocrysts were rare (Photo 2). Such unaltered glass, free of phenocrysts, is essential if results of the analyses are to be used to draw conclusions regarding metal availability, either in magmas or in volcanic products.

4. Results

A total of twelve samples of Pual Ridge volcanics from the vicinity of the PACMANUS vent sites have

Table 1 Description and location of volcanic samples.

SAMPLE #	LOCATION	DESCRIPTION
297-1	PACMANUS area	wk. vesicular dacite, thin Mn coating & plag microphenocrysts
297-4	PACMANUS area	wk. vesicular glassy dacite, elongated vesicles
297-C	PACMANUS area	
299-1	S flank of Pual Ridge	piece of pillow basalt, mod vesicular, glassy rind
299-2	PACMANUS area	wk. vesicular glassy dacite, elongated vesicles, plag microphenocrysts
299-3	PACMANUS area	wk. vesicular glassy dacite, plag & opx microphenocrysts
299-4	PACMANUS area	mod. vesicular glassy dacite, plag microphenocrysts
299-5	PACMANUS area	wk. vesicular glassy dacite, plag & opx microphenocrysts
299-6	PACMANUS area	mod. vesicular glassy dacite
305-2	SW of PACMANUS	mod. vesicular glassy dacite, plag microphenocrysts
305-3	SW of PACMANUS	mod. vesicular glassy dacite, elongated vesicles
305-4	SW of PACMANUS	mod. vesicular glassy dacite, plag & opx microphenocrysts

Abbreviations: plag plagioclase, opx orthopyroxene, wk. weakly, mod. moderately, str. strongly.

Table 2 Whole rock and selected trace element analyses of glassy volcanic rocks.

Sample		297-1	297-4	297-C	299-1	299-2	299-3	299-4	299-5	299-6	305-2	305-3	305-4
SiO ₂	%	69.21	66.39	66.89	55.23	67.8	67.55	67.79	67.8	65.49	66.82	66.93	66.49
Al ₂ O ₃	%	14.35	14.17	14.41	15.66	14.38	14.27	14.48	14.33	14.16	14.28	14.59	14.25
Fe ₂ O ₃	%	4.87	5.66	5.65	11.48	5.29	5.23	5.26	5.3	5.59	5.32	5.37	5.46
MnO	%	0.13	0.15	0.15	0.19	0.14	0.14	0.14	0.14	0.14	0.13	0.15	0.14
MgO	%	0.83	1.61	1.61	4.15	0.91	0.87	0.88	0.88	1.54	1.16	0.94	1.19
CaO	%	3	3.74	3.72	8.05	3.25	3.2	3.16	3.21	3.65	3.45	3.3	3.42
Na ₂ O	%	4.82	4.56	4.62	3.31	4.78	4.71	4.78	4.71	4.54	4.59	4.74	4.63
K ₂ O	%	1.77	1.49	1.51	0.76	1.73	1.69	1.69	1.7	1.52	1.68	1.61	1.55
TiO ₂	%	0.64	0.68	0.68	0.95	0.72	0.71	0.72	0.72	0.67	0.65	0.74	0.71
P ₂ O ₅	%	0.14	0.16	0.17	0.25	0.17	0.17	0.17	0.17	0.17	0.17	0.18	0.19
LOI	%	1.2	1.45	1.41	0.87	1.2	1.18	1.02	1.22	1.51	1.18	1.52	2.71
TOTAL	%	100.94	100.05	100.8	100.91	100.37	99.7	100.09	100.17	99.99	99.43	100.04	100.77
Ba	ppm	329	305	324	164	331	310	328	299	299	330	333	305
Au	ppb	3	3	7	15	2	3	4	4	3	3	2	3
As	ppm	2	3	3	2	3	2	3	3	2	3	3	3
Sb	ppm	0.20	0.16	0.18	0.12	0.14	0.24	0.15	0.15	0.15	0.19	0.15	0.13
Zn	ppm	86	79	83	76	83	87	88	88	79	85	83	81
Co	ppm	5	9	8	32	6	7	6	7	8	7	8	7
Cu	ppm	19	21	23	406	16	na	na	8	20	8	23	20
Pb	ppm	5	<5	<5	<5	<5	na	na	<5	<5	5	9	<5
S	%	0.01	0.01	0.02	0.01	0.02	na	na	0.01	0.02	0.04	0.01	0.01

Table 3 Correlation coefficient matrix for selected metals in PACMANUS dacites.

	SiO ₂	Ba	Au	As	Sb	Zn	Co	Cu	S
SiO ₂	1.00								
Ba	0.46	1.00							
Au	-0.04	-0.04	1.00						
As	-0.15	0.50	0.09	1.00					
Sb	0.31	0.13	0.16	-0.28	1.00				
Zn	0.75	0.29	0.21	-0.22	0.42	1.00			
Co	-0.87	-0.41	0.28	0.25	-0.12	-0.73	1.00		
Cu	-0.24	0.07	-0.00	0.03	-0.12	-0.65	0.45	1.00	
S	-0.22	0.34	0.17	0.27	0.45	0.09	0.04	-0.48	1.00

been analyzed for gold and other ore metals (Table 2). With only one exception, a sample of basaltic andesite from the southern flank of Pual Ridge, the samples are dacitic in composition. The barium content of the PACMANUS dacites ranges from 299 (basaltic andesite) to 333 parts per million (ppm) and averages 318 ppm. This average is at the low end of the wide range of 260 to 798 ppm (average=421) for dacitic lavas from modern island arcs (Stanton, 1994). Gold in the dacites varies from 2 to 7 ppb (Fig. 2). No significant correlations are observed between gold and other trace metals considered here, nor are there any significant correlations between gold and the major elements Si, Fe and Mg (Table 3). The dacites contain 2 to 3 ppm As,

values that are similar to andesites (mean 2.0 ppm) and rhyolites (mean 2.7 ppm) given by Stanton (1994). Similarly, antimony varies from 0.12 to 0.24 ppm and averages 0.17 ppm close to the average abundance in andesite of 0.2 ppm (Stanton, 1994). Copper ranges from 8 to 23 ppm and averages 18 ppm (Fig. 2), significantly less than the average of 30 ppm for arc dacites given by Stanton (1994). Copper in the PACMANUS dacites shows a strong, significant negative correlation with zinc (Table 3).

The samples have an average zinc content of 84 ppm, greater than the mean zinc content of arc dacites (59 ppm), and closer to the mean values of MORB and arc basalts of 84 ppm and 77 ppm respectively (Stanton,

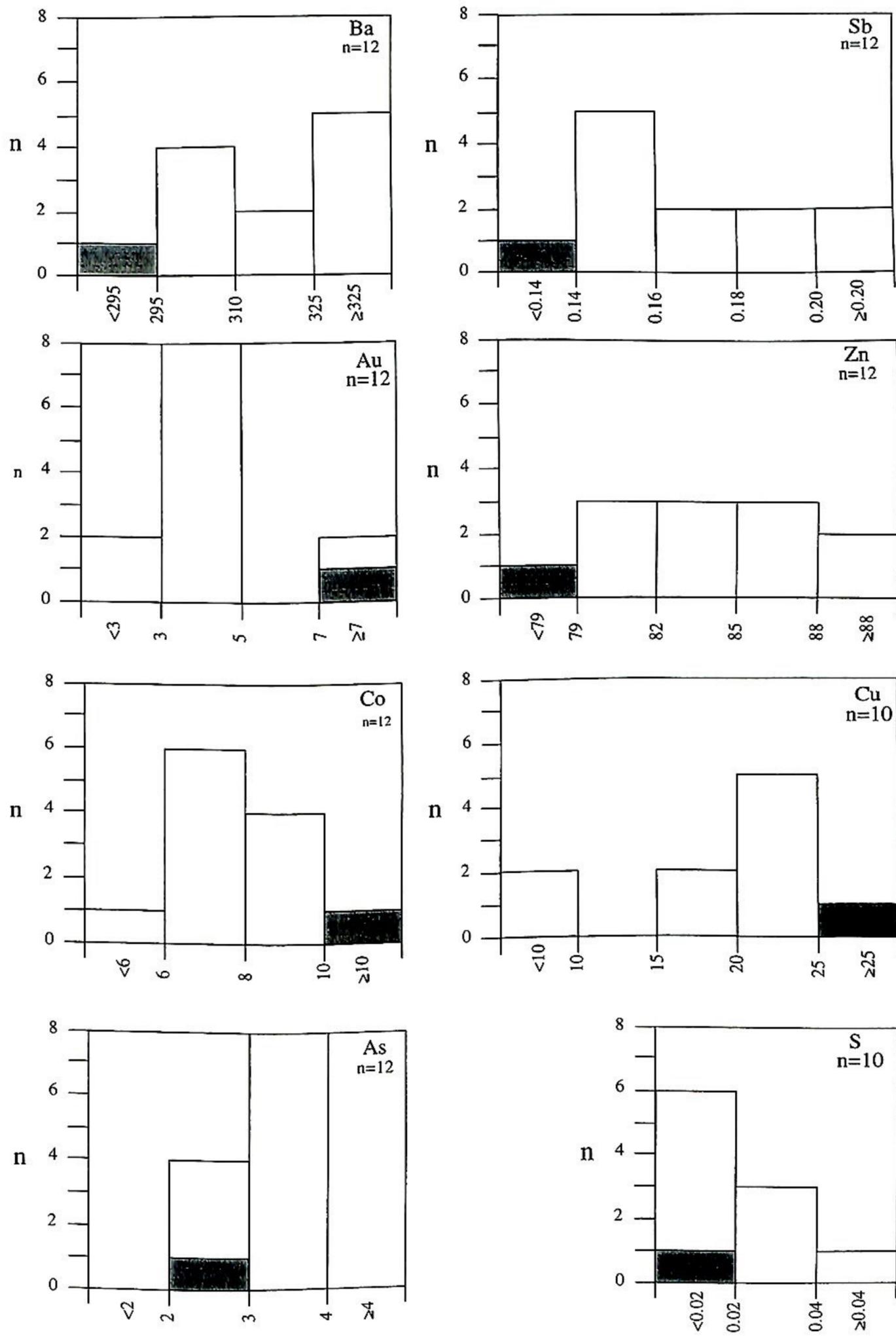


Fig. 2 Frequency distributions of selected metals in PACMANUS volcanics. Shaded sample is basaltic andesite, the remainder are dacite.

1994). The zinc content of the dacites is positively correlated with SiO_2 (Fig. 3), but shows significant negative correlations with Fe_2O_3 , MgO , Co and Cu . Besides showing a negative correlation with zinc, cobalt shows a significant negative correlation with SiO_2 (Fig. 3), and

positive correlations with Fe_2O_3 and MgO . In this respect, the behaviour of cobalt in the dacites is opposite to that of zinc. The mean cobalt content of the PACMANUS dacites is 7 ppm, approximately half the mean for arc dacites of 12 ppm given by Stanton (1994). Sulfur in

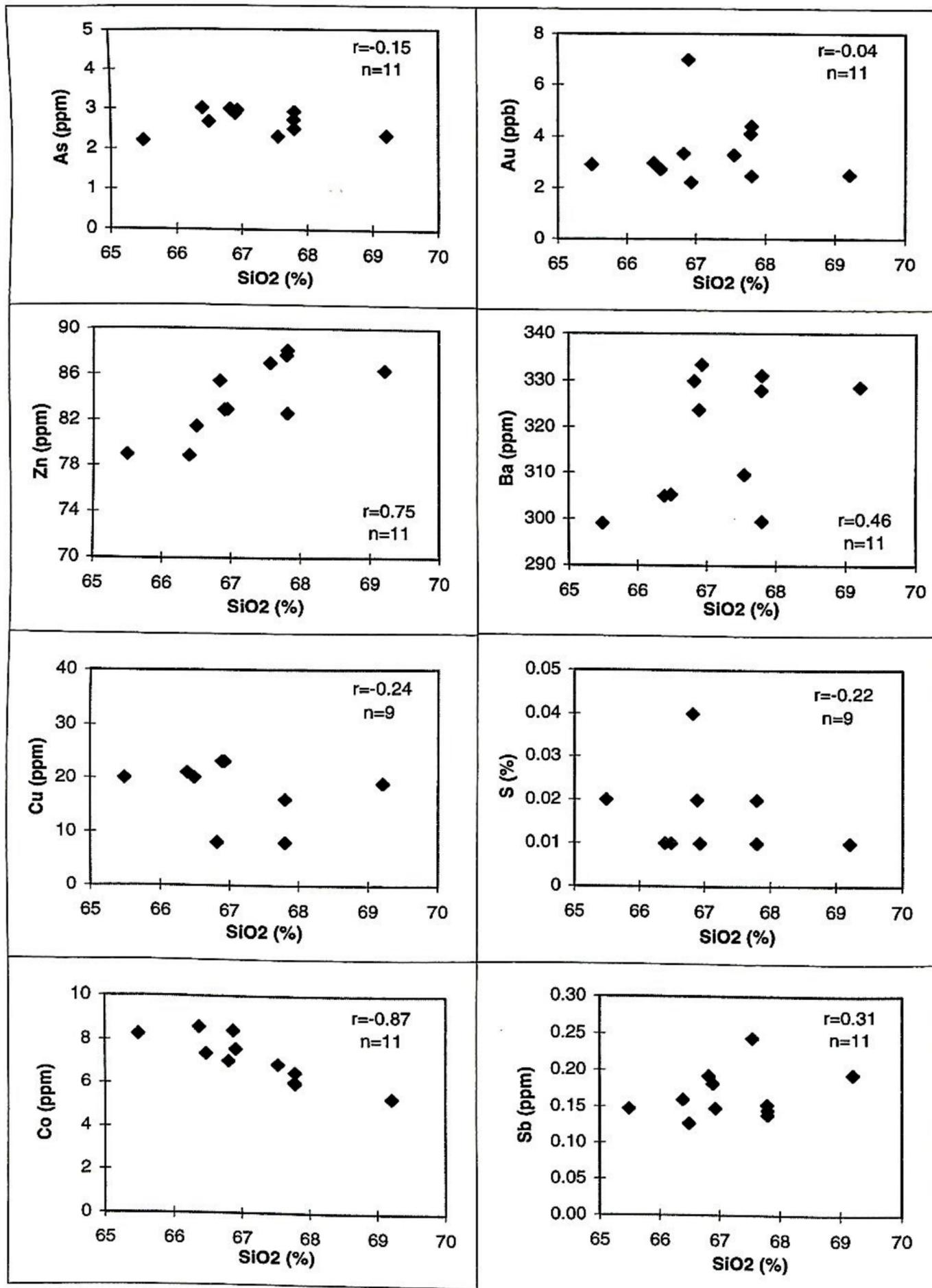


Fig. 3 Scatter plots of selected metals against SiO₂.

the dacites varies from 0.01 to 0.04%, and gives an average of 0.02%. No significant correlations are observed between sulfur and any of the metals considered here (Table 3).

As expected, the basaltic andesite shows quite different trace metal concentrations than the dacite (see Fig. 2) having higher Au, Co and Cu and lower S, As, Zn, Sb and Ba contents. For this reason, and because it is only one sample, the basaltic andesite was not included in cor-

relation calculations, nor in plots of metal content. Both Au (15 ppb) and Cu (406) are significantly enriched in the basaltic andesite compared to the PACMANUS dacites.

5. Discussion

Magmatic and hydrothermal processes known to affect the metal content of volcanic rocks include the following (Connors et al., 1993; Doe, 1994; Togashi &

Terashima, 1997) :

- concentration of metal in the source ;
- the degree of partial melting ;
- magma differentiation, mixing and crustal assimilation ;
- degassing of magma, both pre- and syn-eruption ;
- hydrothermal and seawater alteration

The use of fresh unaltered glassy volcanic rocks in this study limits the effect of the post eruption processes on the metal content of the volcanics, and allows an estimate to be made of the metal content of the magma. With the exception of zinc and cobalt, the metals considered here do not show significant correlations with SiO_2 , Fe_2O_3 or MgO (Table 3), suggesting that, at least for these metals, there is little effect from differentiation processes. Zinc, appears to behave incompatibly, showing a significant positive correlation with SiO_2 , and negative correlations with Fe_2O_3 and MgO . This is in contrast to the findings of Stanton (1994) for felsic lavas of the Solomon Islands, but agrees with the findings of Doe (1994) for the behaviour of zinc in MORB. The strong positive correlations of cobalt with Fe_2O_3 and MgO , and strong negative correlations with SiO_2 and Zn indicate that cobalt is behaving compatibly in the dacite melt. None of the metals show significant correlations with sulfur, suggesting that metal distribution is not controlled by possible submicroscopic sulfides.

It has been suggested that the metal content of VMS deposits should reflect the metal content observed in the associated volcanic rocks (Franklin et al., 1981 ; Doe, 1994 ; Barrie & Hannington, in press). However, this is true only if metals are leached from those volcanics, and possible contributions of a metal-rich volcanic fluid to the hydrothermal system are ignored. Recent investigations of melt inclusions in pyroxene phenocrysts from Pual Ridge andesite, and of vesicles in the andesitic glass, have shown that a volatile phase was present in the magma, and that the volatiles degassed on eruption of the magma (Yang & Scott, 1996). Analysis of dacites has produced similar results (Yang, pers. comm.). Zn, Cu and Fe were among the metals reported in the observed volatile phase. Gold is also known to partition strongly into the volatile phase, and so concentrations of these metals, presented here for the PACMANUS vol-

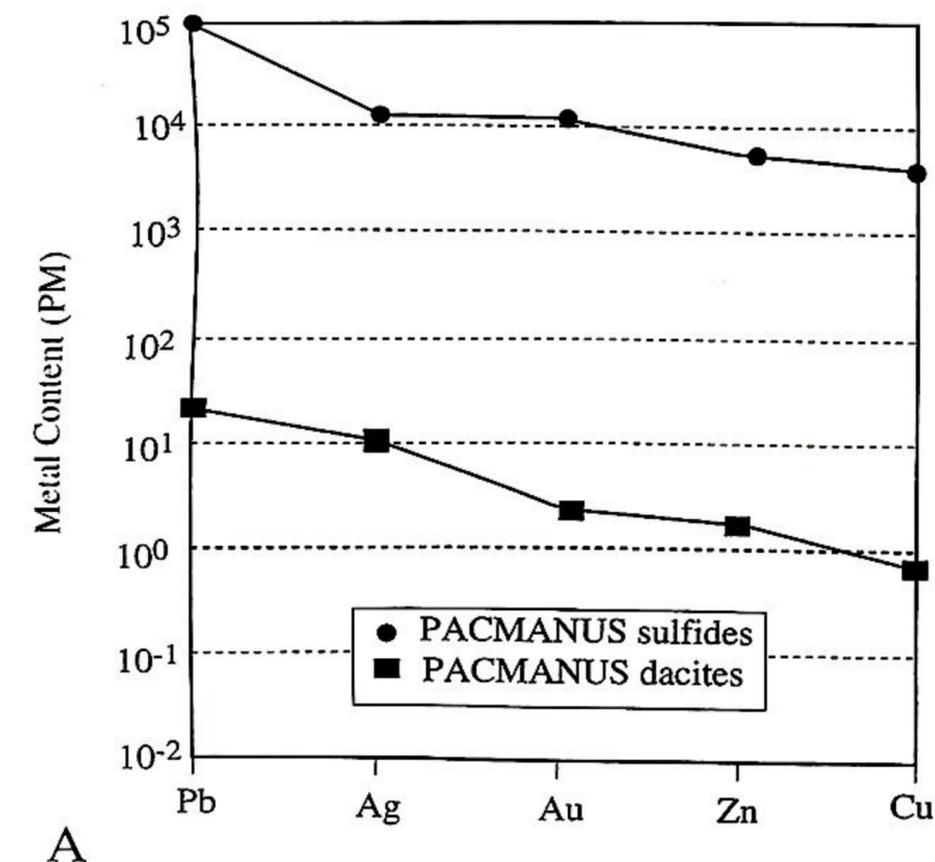
canics, should be considered a minimum for the dacite melt, as much of the original metal content could be lost by pre-eruptive degassing.

Primitive mantle normalized plots of metal content are useful for comparing potential source rocks and deposits from different districts (Barrie & Hannington, in press). Such plots for PACMANUS sulfides and dacites show similar "negative" slopes, but the dacites show a relative enrichment of silver compared to Pb and Au, whereas the sulfides show a relative depletion (Fig. 4A). This difference in the normalized Ag content should however be treated with caution, as the Ag value for PACMANUS dacites is based on only one analysis. The broadly parallel patterns of the dacites and the sulfides are consistent with leaching of metals from a source with a similar metal content as the PACMANUS dacites. This conclusion is consistent with previous mass balance calculations indicating the viability of a leaching mechanism to provide the metal concentrations observed in the hydrothermal precipitates (Moss et al., 1996b, 1997).

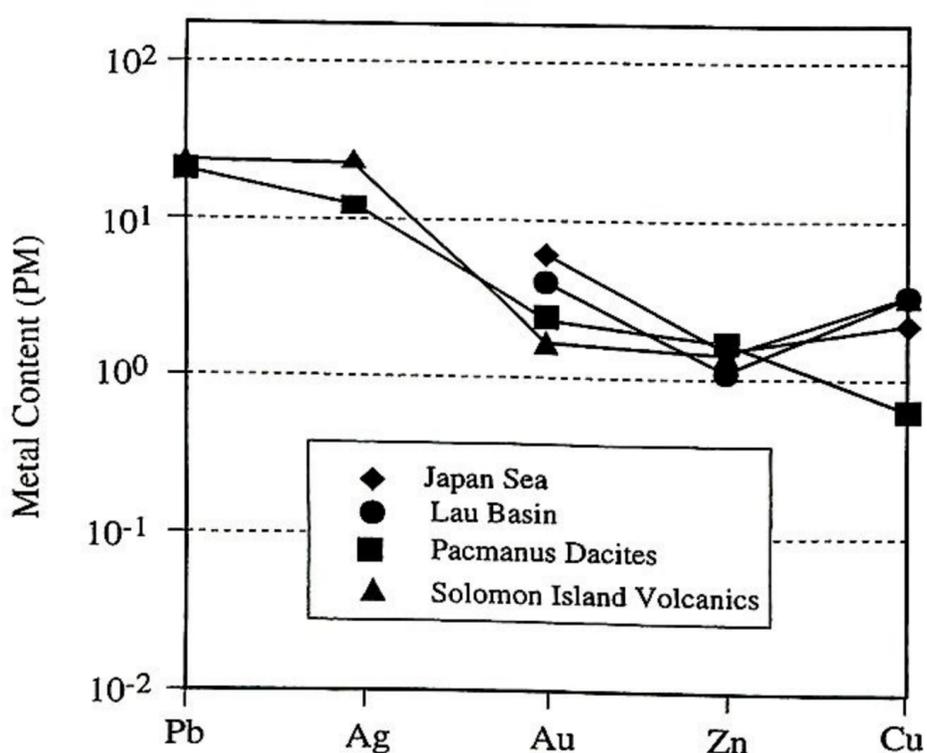
In terms of ore metal content, dacites from the PACMANUS area are similar to arc volcanics from the Solomon Islands (Fig. 4B), which is in agreement with the previously noted arc-like signature of Pual Ridge volcanics (Binns & Scott, 1993 ; Scott & Binns, 1995 ; Binns et al., 1996b). Back arc basalts from the Lau Basin and from the Japan Sea both show depletions in Zn relative to Au and Cu, in contrast to relatively flat Au-Zn-Cu pattern showed by the PACMANUS and Solomon Island volcanics. A distinctive feature of PACMANUS dacites is a depletion in Cu relative to Zn, whereas the other volcanic suites considered show a general enrichment in Cu relative to zinc (Fig. 4B).

6. Conclusions

The ore metal concentrations determined in unaltered glassy volcanic rocks from the vicinity of the PACMANUS deposit are considered to reflect minimum metal contents of the dacitic melt, due to the partitioning of many of these metals into a volatile phase. Only zinc and cobalt show any significant correlations with indices of differentiation. Zinc behaves incompatibly, showing enrichment in the glass with increasing silica content in the



A



B

Fig. 4 Plots of primitive mantle normalized metal content for (A) PACMANUS sulfides and dacites, and (B) PACMANUS dacites and other arc and back arc volcanics. Sources of data : PACMANUS sulfides Scott & Binns, 1995, Ag in PACMANUS dacites Binns & Scott, 1993, PACMANUS dacites this study, Japan Sea Allan & Gorton, 1992, Lau Basin Cawood & Fryer, 1994, Solomon Islands Stanton, 1994.

dacite suite, whereas cobalt behaves compatibly, decreasing as the silica content increases. The lack of any correlation between sulfur and the ore metals suggests no sulfide or sulfate control on metal distribution

in the dacite glass.

Primitive mantle normalized metal contents of the PACMANUS dacites and hydrothermal precipitates show broadly similar patterns, although the sulfides are three to four orders of magnitude enriched over the volcanics. The similarity of the patterns indicates that leaching of a substrate with a metal content similar to the dacites, would provide the right metal ratios for the sulfides. The ore metal content of the dacite is most similar to that in arc volcanics from the Solomon Islands, although the PACMANUS volcanics show a distinct Cu depletion.

Acknowledgments

Co-Chief Scientists Jean-Marie Auzende and Tetsuro Urabe are thanked for providing RAB and RM with the opportunity to participate in the ManusFlux 1995 cruise. We thank the captain and crew of the R/V "Yokosuka" and the "Shinkai 6500" chief pilot and his team for their contribution to the success of the cruise. This research was funded by grants from the Natural Sciences and Engineering Research Council of Canada and the Bank of Nova Scotia to SDS, and by University of Toronto Doctoral Fellowship to RM.

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(Manuscript received 4, July 1997)

(Notice) Photos are given on the following page.

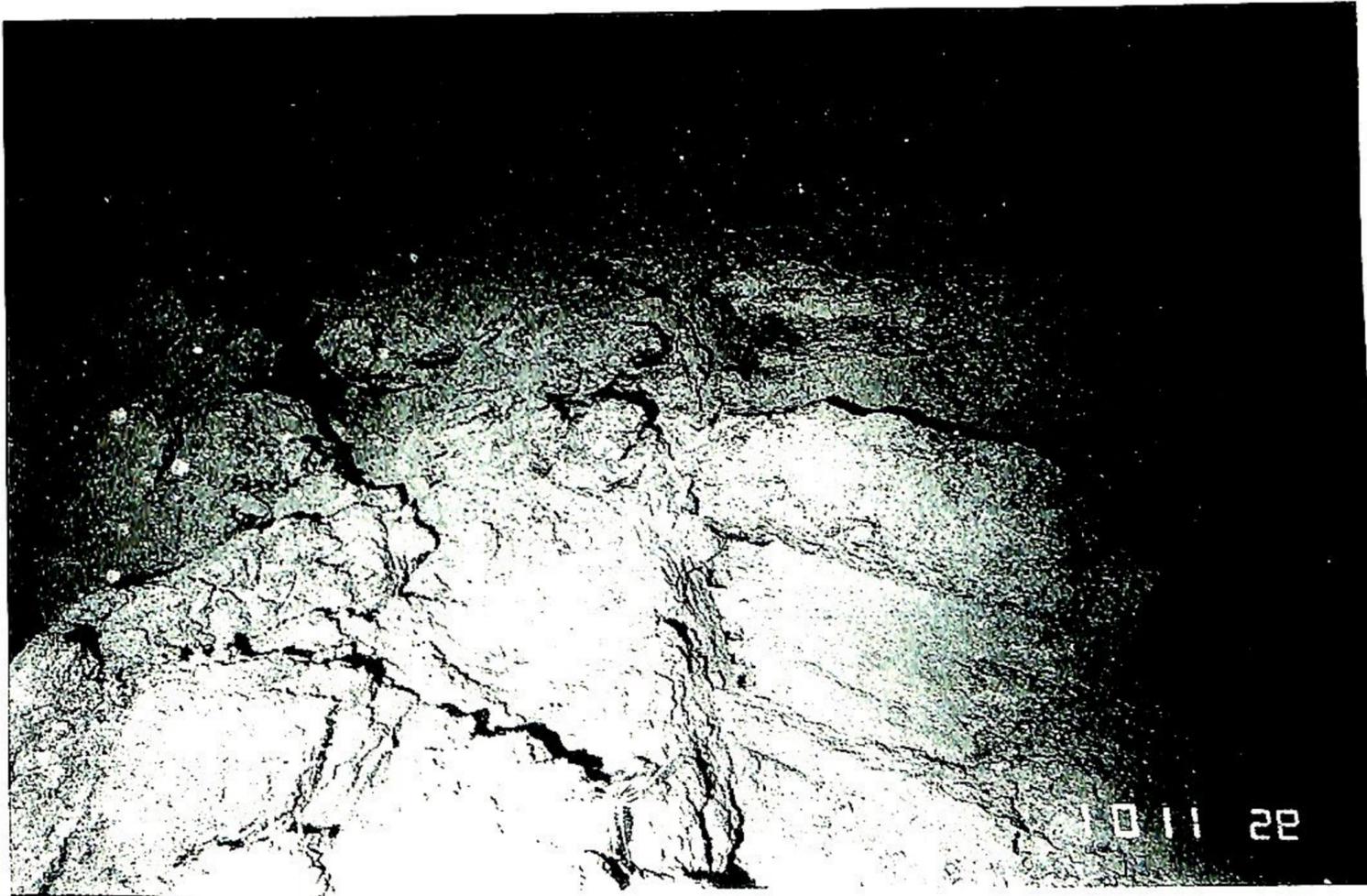


Photo 1 PACMANUS dacite in outcrop to the northwest of Roman Ruins, Dive 304.

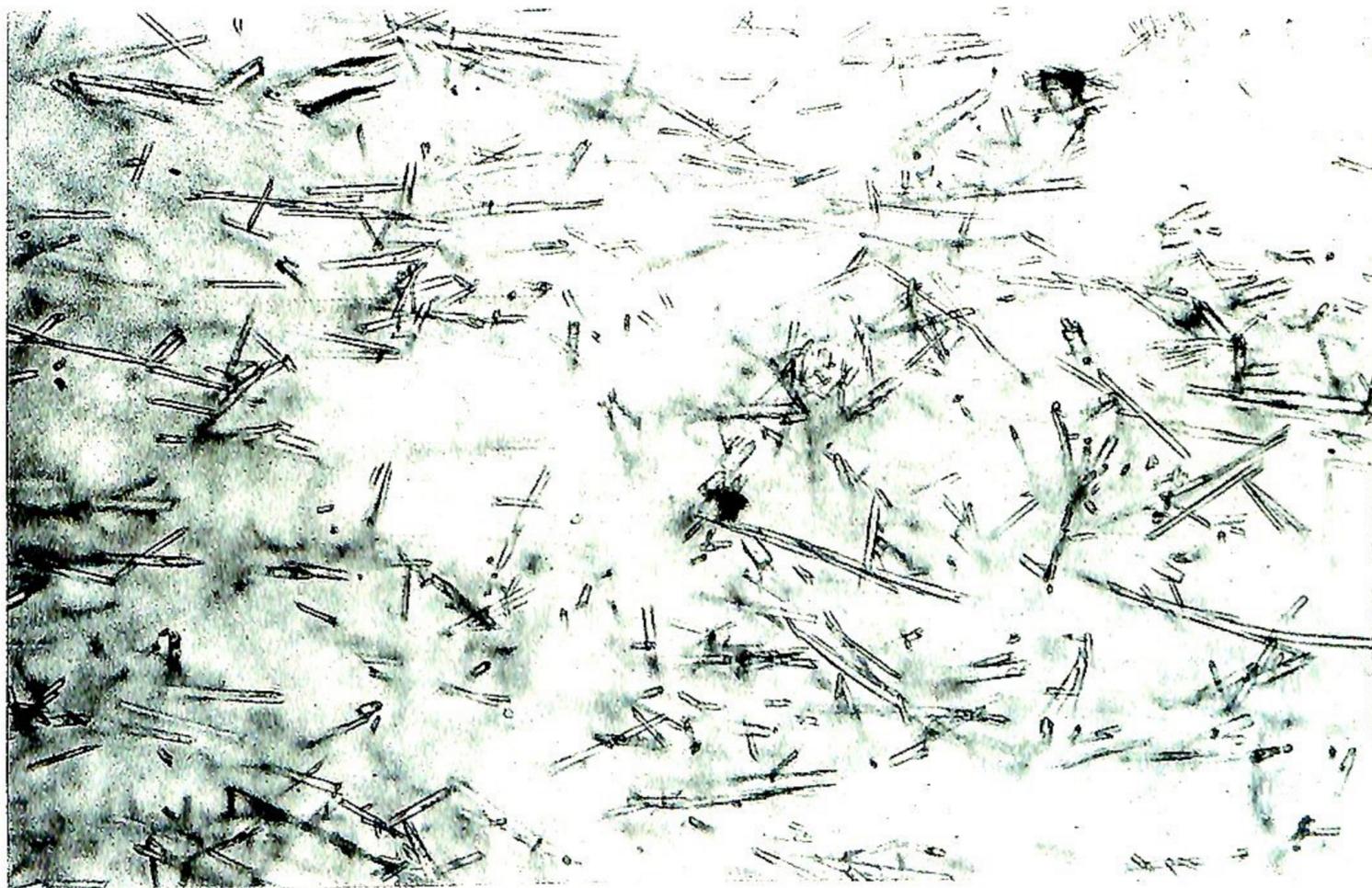


Photo 2 Thin section of PACMANUS dacite showing unaltered nature of glass, and the presence of microlites, and rare phenocrysts. Field of View 200 μ M.