

aggregates. They are subhedral, lath-shaped and are altered to clayey aggregates. At places, they contain inclusions of clinopyroxene, opaques and glassy droplets in their cores.

In groundmass, plagioclase and clinopyroxene (average  $C\bar{Z}=36\%$ : augite) together show subophitic texture. The anhedral to subhedral, prismatic opaque grains occupy polygonal interspaces left by plagioclase and/or clinopyroxene and thus exhibit intergranular texture. Invariably altered, dirty moss green to yellowish brown glass forms irregular intersertal patches in the groundmass and the inner linings of the vesicles. The central portions of these cavities are filled by a variety of cavity minerals including quartz and zeolites (Figure 2a and b).

The textural and mineralogical characters indicate the rock to be 'basaltic' in character.

Keeping in view the controversial stratigraphic position of the Krol Formation<sup>2-12</sup>, it is felt that further efforts must be made to i) identify and map the lava flows in Krol sequence, and ii) study their geochemical and isotopic characters. Such studies will

not only help in understanding the basin evolution but may also offer 'much wanted' geochronological data for assigning either the late-Proterozoic or Permo-Carboniferous age to the controversial Krol sequence.

The thin sections studied as a part of this study have been registered in the Petrology Division, Geological Survey of India (NR), Lucknow, under the registration number TS/3/302 and TS/3/303. The support of the Training Institute, Geological Survey of India, is gratefully acknowledged.

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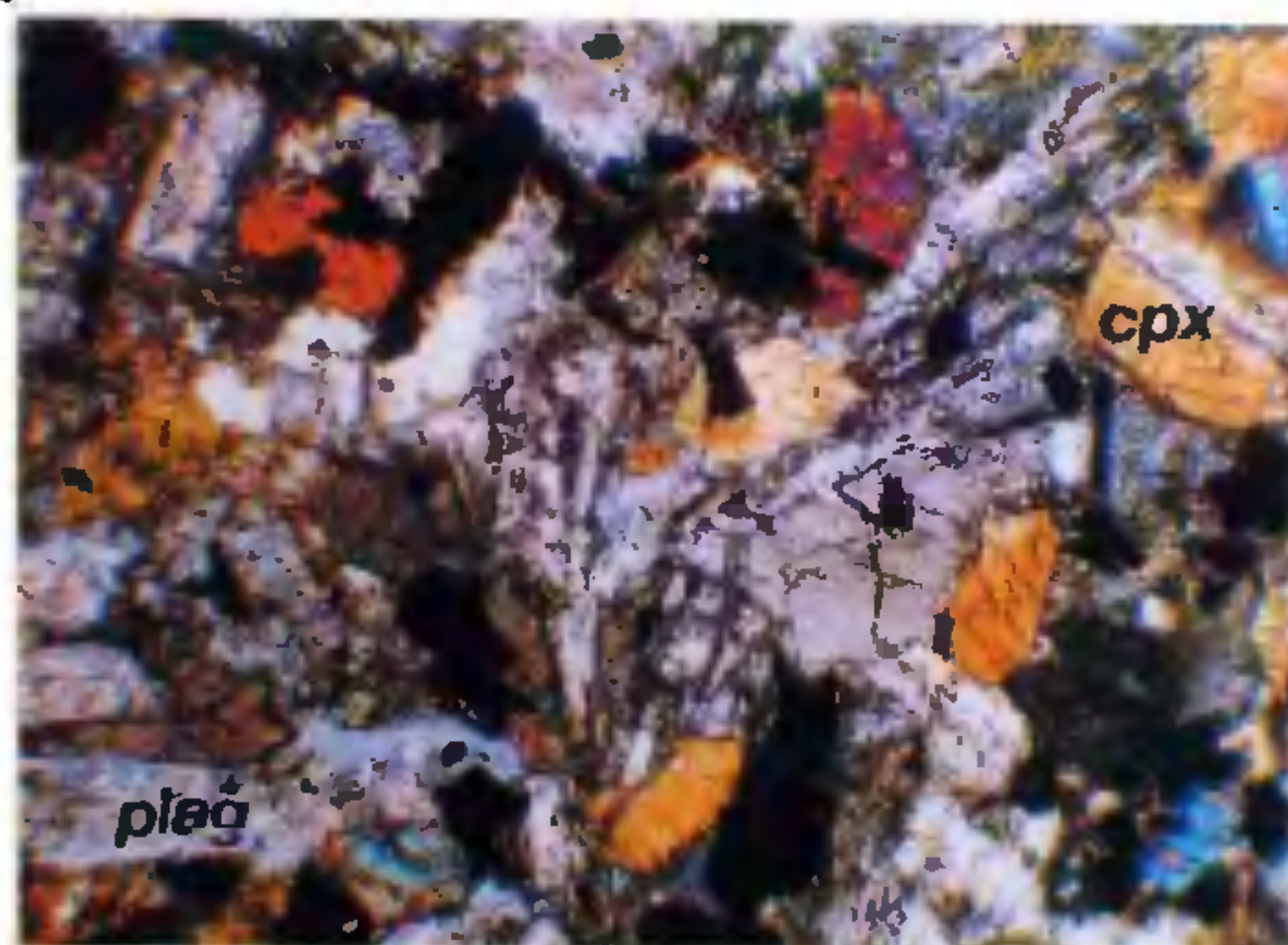


Figure 2. Photomicrographs showing the textural characters of the Krol lava flows. a, cpx: Clinopyroxene, plag: Plagioclase. Between X nicols b, zeo: Zeolite, gl: Altered, glassy, inner lining of the amygdale. Between X nicols.

## Heavy metal concentrations in air, water and rock samples at Antarctica during 1989-1990

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Concentrations of lead, cadmium, zinc and copper have been measured in air particulates and seawater samples collected enroute to Antarctica and at the Indian station Maitree (11 44' E, 70 45' S) at Antarctica for the period December 1989 to February 1990 during the IX Indian Expedition. The analysis was carried out using highly sensitive technique of differential pulse anodic stripping voltammetry (DPASV). The atmospheric concentrations as well as seawater concentrations showed a decreasing trend towards Antarctica except near Mauritius island. The atmospheric concentrations of lead at different locations at Maitree varied between 0.23 and 0.41  $\text{ng m}^{-3}$  and that of copper varied between 0.4 and 1.7  $\text{ng m}^{-3}$ . Levels of lead, cadmium, copper and zinc were also measured in different types of rock samples collected around the Maitree station. Some of these findings are briefly discussed here.

ANTARCTICA is very well known to be the reference point for all environmental and pollution studies because of



its remoteness and the climatic conditions, restricting human activities to minimal in this region. An examination of potential pollutants, therefore, should give a base value for comparing with time their increase in the marine environment.

Man's impact on the oceanic environment has always been the cause for great concern. Several investigations on trace metals in different waters have been carried out but the information from the world oceans is never complete either due to small number of sampling over a vast area or due to lack of reliable data because of varying techniques of sampling and analysis. Comparison of the coastal data with the open sea data (Antarctic data) is necessary to understand the magnitude of human influence on the oceanic environment. Water and air particulate samples were collected for trace metal analysis during the IX Indian Expedition to Antarctica (December 1989 to February 1990). Rock samples were also collected near the Maitree station in order to know the distribution of these metals in rocks.

Air and seawater samples were collected at regular intervals en route to Antarctica. Air particulate samples were collected by sucking air through a filter paper (Whatman EPM-2000) with the help of a suction head. As the concentrations of the metals of interest (Pb, Cd, Cu, Zn, etc.) were expected to be very low at Antarctica each sampling was done for 36 h duration. The locations of the sampling points en route to Antarctica as well as at Antarctica (near the Indian station Maitree) are shown in Figure 1. Water samples were also collected and kept in pretreated clean polyethylene containers. Rock as well as lake water samples were collected at different locations near Maitree.

Air particulate samples were decomposed by the acid digestion method using nitric, hydrochloric and perchloric acids. A minimum amount of acid was used for digestion in order to reduce the blank values. Rock samples were digested with nitric acid (electronic grade) under pressure in a teflon vessel. The pressure digestion unit was first heated slowly up to 80°C for 30 min. The temperature was then raised to 150°C and the sample heated at this temperature for 30 min. Finally the sample was taken in 10 ml of 0.25% nitric acid. The details of the procedure are described elsewhere<sup>1</sup>.

Voltammetric measurements were carried out with Princeton Applied Research (PAR) 174-A polarographic analyser and voltammograms were recorded with PAR X-Y recorder (model RE0074). A static mercury drop electrode assembly (PARC-303) was used with PARC-305 stirrer.

All chemicals used were Merck, Suprapur, AnalaR or electronic grade. Standard stock solutions (0.01 M) of Pb, Cd, Cu and Zn were prepared and necessary dilutions were made as and when required. Ammonium

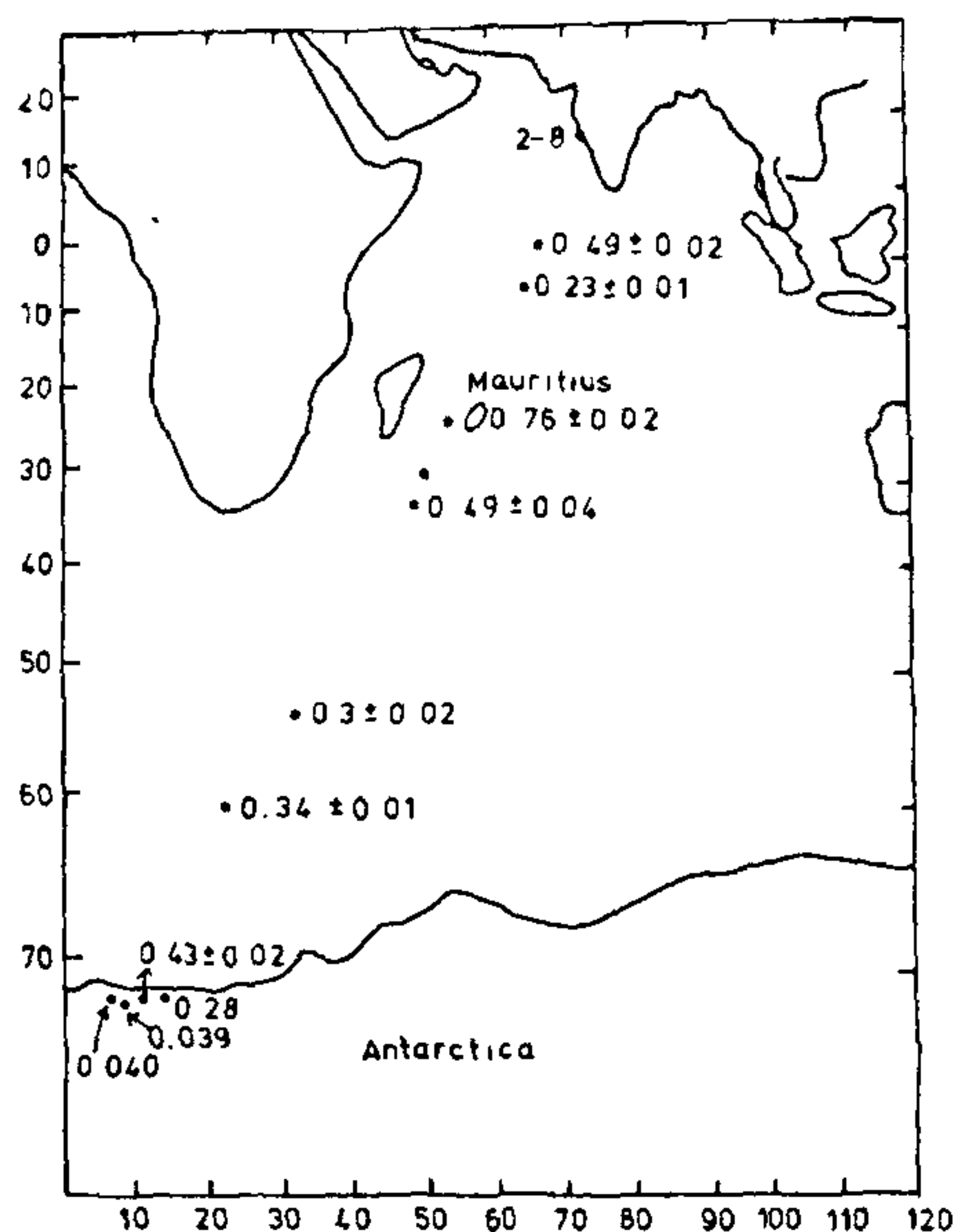


Figure 1. Lead content in (µg/l) seawater (en route to Antarctica) and lakewater at Maitree station in Antarctica (IX Indian Expedition).

acetate (1.5 M) solution was purified using a controlled potential electrolysis assembly for 48 h with -1.5 V as initial potential.

An aliquot of digested solution (0.1–0.5 ml) was added to 10 ml of supporting electrolyte (5 ml of 0.25% HNO<sub>3</sub> + 5 ml of 0.15 M ammonium acetate) which was then taken into the electrolytic cell. The solution was deaerated for 8 min with highly purified nitrogen gas (IOLAR-1). The initial potential was kept at -1.2 V. The solution was then stirred and the electrolysis was carried for 1 min. After a rest period of 30 sec the stripping voltammogram was recorded. The details of the method used are reported elsewhere<sup>2</sup>. The concentrations of metals were calculated with the help of calibration curves as well as by standard additions method.

The reliability of the procedure of estimation of heavy metals in surface soil by differential pulse anodic stripping voltammetry (DPASV) has been checked by analysing the standard reference materials. Soil and sediment samples from IAEA (SL-1, S-5) as well as orchard leaves, animal blood and bovine liver from NBS were analysed. The results obtained for the standards matched within ± 1–2% of the certified

values. The validity of the method as well as of the data were ascertained by keeping low blanks, duplicate analysis and cross method checks.

The concentrations of lead and copper in air particulate matter at different locations en route to Antarctica are summarised in Table 1. A wide range of variations have been observed: atmospheric Pb levels were found to vary from  $26.2 \text{ ng m}^{-3}$  to  $0.74 \text{ ng m}^{-3}$  from Goa (Indian coast) to Maitree; Cu concentration of  $49.7 \text{ ng m}^{-3}$  was observed at Goa while near Antarctica it was  $4.05 \text{ ng m}^{-3}$ . The data in literature on the levels of these metals in ice and snow are plenty while only a few studies have been carried out for the levels of these metals in air. Some data on the concentrations and the sizes of aerosol particles over parts of Antarctic continent and the surrounding oceans are reported by Hogan<sup>3-5</sup> and Dick and Peel<sup>6</sup>. They have concluded that it was very difficult to measure small concentrations of aerosols over Antarctica (sometimes as low as  $0.2 \text{ ng m}^{-3}$ ). In another study Dick<sup>7</sup> has reported the Pb content in the Antarctic air to be as low as  $5 \text{ ng m}^{-3}$ .

The atmospheric levels of Pb and Cu at Maitree are summarised in Table 2. The variation in Pb concentration was found to vary much and the mean value observed was  $0.31 \text{ ng m}^{-3}$ . The Cu levels at different locations were found to vary from  $0.44 \text{ ng m}^{-3}$  to  $1.17 \text{ ng m}^{-3}$  with a mean value of  $0.70 \text{ ng m}^{-3}$ .

The concentrations of Pb, Cd and Zn in seawater from Goa, en route to Antarctica, are summarized in Table 3. In general the levels of the metals were found to decrease from Goa to Antarctica except near Mauritius where the contribution of local sources cannot be ruled out. The Pb levels near the Goa coast

were found to vary from  $2.0$  to  $8.0 \mu\text{g l}^{-1}$ , while at  $60^\circ$  south it was found to be  $0.34 \mu\text{g l}^{-1}$ . The cadmium concentration varied from  $0.04 \mu\text{g l}^{-1}$  to  $0.22 \mu\text{g l}^{-1}$ . The variation in the Zn concentration from  $28.1 \mu\text{g l}^{-1}$  to  $75.4 \mu\text{g l}^{-1}$  was observed from Goa to Antarctica. The maximum concentration of  $75.4 \mu\text{g l}^{-1}$  of Zn was measured near Mauritius and decreasing in either direction, towards Goa and Antarctica. A number of measurements of heavy metals have been carried out in Antarctica ice and water<sup>8,9</sup>. The average concentration of Zn in surface water at Antarctic regions reported by Sengupta *et al.*<sup>8</sup> is  $23.3 \mu\text{g l}^{-1}$  which is close to the present findings.

A wide range of variations in the levels of trace metals in seawater have been reported. Chester and Stoner<sup>9</sup> have carried out study of Cd in ocean waters and reported that the concentration of Cd ranges from  $0.02$  to  $0.18 \mu\text{g l}^{-1}$  with an average of  $0.07 \mu\text{g l}^{-1}$  for the world ocean waters<sup>1</sup>. Abdullah *et al.*<sup>10</sup> have reported as high as  $4.2 \mu\text{g l}^{-1}$  of Cd for English Channel. Hutchinson<sup>11</sup> has reported the average value of metals in surface water of lakes in colder countries of the northern hemisphere to be  $9\text{--}210 \mu\text{g l}^{-1}$  of Cu,  $5.6\text{--}18.0 \mu\text{g l}^{-1}$  of Zn,  $90\text{--}160 \mu\text{g l}^{-1}$  of Fe and  $2.6 \mu\text{g l}^{-1}$  of Pb.

The concentrations of Pb, Cd and Zn in lakewater samples at Maitree are summarised in Table 4. The Pb levels were found to vary from  $0.05$  to  $0.43 \mu\text{g l}^{-1}$ . The levels of Cd in lakewaters were found to be very low and the maximum observed was  $0.17 \mu\text{g l}^{-1}$  at the main lake. The Zn concentrations were found to vary from  $0.31 \mu\text{g l}^{-1}$  to  $1.87 \mu\text{g l}^{-1}$ . The maximum concentration of  $1.87 \mu\text{g l}^{-1}$  was found in the main lake water. It is evident from Table 4 that the levels of Pb, Cd and Zn are maximum in the main lake water, which is obvious

**Table 1.** Concentrations of Pb and Cu in air particulate matter enroute to Antarctica during IX Indian Expedition (1989–1990)

Location	Date of collection		Concentration ( $\text{ng m}^{-3}$ )	
	From	To	Pb	Cu
$12^\circ 01' \text{ N}, 72^\circ 02' \text{ E}$ (Goa)	1.12.89	—	15.91	49.70
$05^\circ 09' \text{ N}, 70^\circ 04' \text{ E}$	3.12.89	5.12.89	26.20	14.50
$13^\circ 08' \text{ S}, 58^\circ 32' \text{ E}$	6.12.89	8.12.89	23.30	5.98
$26^\circ 04' \text{ S}, 52^\circ 06' \text{ E}$ (Mauritius)	10.12.89	12.12.89	16.00	6.40
$35^\circ 06' \text{ S}, 46^\circ 51' \text{ E}$	12.12.89	14.12.89	8.00	4.30
$70^\circ 45' \text{ S}, 11^\circ 44' \text{ E}$ (Maitree)	05.01.90	08.01.90	0.74	4.05

**Table 2.** Concentrations of Pb and Cu in air particulate matter at Maitree (Antarctica) during 1990

Location	Date of collection		Concentration ( $\text{ng m}^{-3}$ )	
	From	To	Pb	Cu
$11^\circ 44' 5' \text{ E}, 70^\circ 45' 8' \text{ S}$	9.1.90	12.1.90	0.27	1.17
$11^\circ 44' 5' \text{ E}, 70^\circ 45' 8' \text{ S}$	19.1.90	22.1.90	0.23	0.96
$11^\circ 44' 5' \text{ E}, 70^\circ 45' 8' \text{ S}$	22.1.90	25.1.90	0.29	0.44
$11^\circ 44' 5' \text{ E}, 70^\circ 45' 8' \text{ S}$	28.1.90	31.1.90	0.41	0.51
$11^\circ 44' 5' \text{ E}, 70^\circ 45' 8' \text{ S}$	01.2.90	04.2.90	0.33	0.44



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**Table 3.** Concentrations of Pb, Cd and Zn in seawater enroute to Antarctica during 1989-1990

Location	Concentration ( $\mu\text{g l}^{-1}$ )		
	Pb	Cd	Zn
Near Goa coast	20-80	0.20	9.8-38.7
0° S	0.49	0.15	37.5
10° S	0.23	0.04	29.0
25° S (near Mauritius)	0.76	0.22	75.4
32° S	0.49	0.13	44.0
55° S	0.30	0.09	28.6
60° S	0.34	0.05	28.1

**Table 4.** Concentrations of Pb, Cd and Zn in lakewater samples collected at Maitree (Antarctica) during 1989-1990

Location	Concentration ( $\mu\text{g l}^{-1}$ )		
	Pb	Cd	Zn
Russian Camp, 4 km E	0.046	ND	0.41
2 km east	0.039	ND	0.31
2 km west	0.28	0.015	0.98
Main lake	0.43	0.17	1.87

ND, Not determined

because of human activities near this lake.

Different types of rock samples, e.g. basalt, pegmatite, granite, gneiss, etc. were collected and analysed for heavy metal contents. The concentrations of Pb, Cu, Cd and Zn in different types of rock samples are summarised in Table 5. The Pb content in basalt was found to vary from 2.68 to 8.03  $\mu\text{g g}^{-1}$  while Zn varied from 8.52 to 17.78  $\mu\text{g g}^{-1}$ . The Pb levels in granite samples were found to vary from 1.16 to 4.24  $\mu\text{g g}^{-1}$ . The Cd level in most of the rock samples observed was very low and varied from 0.04 to 0.28  $\mu\text{g g}^{-1}$ . The Cu content in different types of rock samples was found to vary from 0.27 to 10.5  $\mu\text{g g}^{-1}$ . The maximum Cu concentration of 10.5  $\mu\text{g g}^{-1}$  was found to be in gneiss samples. A large variation in the levels of Zn was observed. The Zn concentrations were found to vary from 1.1 to 17.78  $\mu\text{g g}^{-1}$ . The maximum concentration of 17.78  $\mu\text{g g}^{-1}$  was found in basalt samples. Only a few studies have been carried out for finding the trace metal contents in

**Table 5.** Concentrations of Pb, Cd, Cu and Zn in rock samples collected near Maitree station (Antarctica) during 1989-1990

Rock	Concentration ( $\mu\text{g g}^{-1}$ )			
	Pb	Cd	Cu	Zn
Basalt	8.03	ND	2.50	17.78
Basalt	2.68	0.28	—	8.52
Pegmatite	0.29	ND	2.70	7.06
Granite	4.24	ND	1.13	4.49
Granite	1.16	0.04	0.27	1.48
Gneiss	0.69	ND	8.00	—
Gneiss	2.0	ND	10.50	1.1
Leucogreits	0.2	ND	0.76	2.81

ND, Not determined.

rock samples at Antarctica. Kaul et al.<sup>12</sup> have reported the Pb content in basaltic rock at Antarctica to be  $< 5 \mu\text{g g}^{-1}$ .

The use of improved analytical methods has allowed the determination of background concentration levels of the natural aerosol, at remote areas. Such sampling sites are supposed to be free from any pollutant influence, but it appears that atmospheric long-range transport is responsible for the contamination of many remote locations in the world<sup>13</sup>. Bourton and Patterson<sup>14</sup> have shown that four fifths of the total Pb in the Antarctic troposphere is due to human activities. Patterson and Settle<sup>15</sup> have resolved the anthropogenic and natural Pb at Antarctica and suggested that atmospheric concentrations of industrial Pb are five-fold greater than natural levels in this area. Taking into account that Antarctica must be the cleanest area of the globe, the higher trace metal concentrations obtained in the present study may be interpreted in terms of contamination. Additional analytical data from a closely spaced station is likely to provide proper insight in terms of degree of contamination and nature of contaminants.

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