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Iron-Rich Amorphous Sediment from Loihi Seamount

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ABSTRACT

Red x-ray amorphous sediment was collected from a dredge haul across the top of Loihi seamount, a recently active volcano southeast of the island of Hawaii. The sediment was examined using neutron activation analysis, x-ray diffraction and x-ray fluorescence.

The sample contained 36.7% Fe, 19% H_2O, 1.4% Ca, 1.0% P 0.07% Ti, and 0.1% Al. Minor element and rare earth element concentrations were low compared to typical marine sediments. The analyses were compared with those of sediments from the Galapagos Rise, East Pacific Rise, Red Sea brine pools, crystalline sediment from Loihi, sediments from the submerged parts of Banu Wuhu and Thera volcanoes and typical pelagic clays. This Loihi sediment showed closest affinity to those sediments from active deep-sea hydrothermal vents. The Fe/P ratio and low rare earth element content suggest recent (possibly less than 40 yrs) deposition and contact with sea water. This is a rare example of such material at the site of active volcanism not associated with hydrothermal vents on ridge systems.

INTRODUCTION

The Loihi seamount is an active submarine volcano rising from about 5000m to 950m below sea level, southeast of the island of Hawaii (Figure 1). It a separate volcanic center and not a rift zone extension of Mauna Loa or Kilauea volcanoes. Moore, Clague and Normark (1982) suggest that Loihi is the youngest volcano in the Hawaiian-Emperor volcanic chain.

During the 1981 survey of Loihi seamount conducted by the U.S. Geological Survey on the University of Hawaii R/V Kana Keoki, a mass of reddish brown sediment was recovered from a dredge haul across the top of the seamount. The material resembled sediments reported from active oceanic rift zones (Bostrom and Peterson, 1966; Bischoff, 1969; Corliss et al., 1978). Such sediments are characterized by high transition metal content, usually Fe and Mn, and low concentrations of Al and Ti when compared with other oceanic sediments, including those from volcanic regions and inactive ridges (Bostrom et al.,

1969). They are generally thought to be hydrothermal (Arrhenius and Bonatti, 1965; Bonatti and Joensuu, 1966; Bostrom and Peterson, 1966; Bostrom et al., 1969; Corliss, 1971; Dymond et al., 1973; Bonatti et al., 1976; Heath and Dymond, 1977; Humphris and Thompson, 1978a,b; Edmond, 1979). At two sites of submarine volcanism, Banu Wuhu (Zelenov, 1964) and Thera (Bonatti and Joensuu, 1966), metalliferous sediments were associated with hydrothermal activity. At Loihi, the material could be the result of hydrothermal action of sea water introduced into the volcano or as the result of the interaction of residual liquid lava with sea water.

No other sediment was found during 1981 dredging operations on Loihi. The sediment's unusual occurrence with volcanic rock from dredge hauls and its similarity in appearance to reported transition metal rich marine sediment indicated that more detailed analysis was required. This paper reports the results of those analyses done at the Lawrence Berkeley Laboratory (LBL) and the Berkeley campus of the University of California.

ANALYTICAL PROCEDURES

Sediment samples were collected from the dredge on Station 29 on the USGS cruise KK1-HW-81 to the Loihi Seamount (February, 1981). The sampling location is shown in Figure 2. Samples were taken from the surface of a basaltic glass fragment.

The sample was examined using x-ray diffraction and the elemental composition was determined using neutron activation analysis and x-ray fluorescence.

Neutron Activation Analysis

Neutron activation analysis was performed at LBL using procedures

described by Asaro, Michel and Burger (1981). The precision of each analysis depends upon the counting statistics for each element and depends upon the material analyzed. Precisions appear in Table 1.

X-Ray Fluorescence (XRF) Analysis

XRF was performed at the University of California, Berkeley, by Joachim Hampel using procedures described in Boaz and Hampel (1978). It was difficult to obtain appropriate standards. The closest available were DTS-1, a U.S.G.S standard, Br-N and BX-N, French standards, MRG-1 from Canada and two University of California rock standards. Errors in the XRF are greater than they would be with more comparable standards.

X-Ray Diffraction Analysis.

X-ray diffraction was done on a Norelco diffractometer and an Rigaku Geigerflex diffractometer with Cu $K\alpha$ radiation and Ni filter at the University of California, Berkeley. The samples were mixed with Si powder (standard), ground to finer than 325 mesh, dispersed in a balsam solution and coated on a glass slide. Diffraction was measured from 3° 2θ to 70° 2θ.

RESULTS and DISCUSSION

The material appeared in reddish-brown discrete masses, rather than as a uniformly distributed deposit on the surface of the basalt or as a coating or impregnation of other minerals. X-ray diffraction showed that the material was essentially x-ray amorphous with minor amounts of clays and feldspar. Hereafter, this material will be referred to as Loihi amorphous sediment (LAS).

The LAS differed from other sediment from Loihi reported by Malahoff and

others (1982). Their samples were crystalline Fe nontronite, more yellow, finely distributed on the surface of the basalt and sparsely distributed.

The elemental composition of the Loihi amorphous sediment, determined using neutron activation analysis and x-ray fluorescence, appears in Table 1.

Major Elements

The Fe concentration, 36.7% (Table 1), is high. The LAS released approximately 19% water on ignition to 1000°C. Accordingly, the LAS is considered stoichiometrically $Fe(OH)_3$ as calculations show that 36.7% Fe in $Fe(OH)_3$ upon ignition would release 18% water.

Iron-rich sediments have been reported from active oceanic ridge-rise systems such as the Red Sea hydrothermal area, (Bischoff, 1969; Ross and Degens, 1969), and the East Pacific Rise (Bonatti and Joensuu, 1966; Bostrom, 1970; Bostrom and Peterson, 1969) and the Galapagos Rise (McMurtry and Yeh, 1981; Sayles and Bischoff, 1973). In addition, Zelenov (1964) and Bonatti and Joensuu (1966), respectively, reported similar material from fumarole fields on Banu Wuhu submarine volcano off Indonesia and from a hydrothermal spring in the submerged caldera of Thera in the Aegean. Major element concentrations found in sediments from each of these sites and of more typical oceanic sediments are compared in Table 2. The iron concentration the LAS is comparable to sediments with a high Fe/Mn ratio (Table 2), but the LAS differs significantly from pelagic clay.

Manganese concentrations in the LAS are lower than in sediments from the East Pacific Rise with low Fe/Mn ratio, Galapagos Rise, and Banu Wuhu, but in the same order of magnitude as the Red Sea and Thera. Manganese in hydrothermal fluids or in solution due to action of lava with seawater would be

oxidized more slowly upon interaction with seawater than would soluble iron complexes (Stumm and Morgan, 1970; Burns and Burns, 1979). Edmond et al. (1979) find the formation of Fe-Mn-rich sediments at the Galapagos Rift problematical because the kinetics of oxidation of soluble Mn complexes is so much slower than those of soluble Fe. If the iron-rich sediment from Loihi had been precipitated recently, lower Mn concentrations might be expected. In samples collected at the Galapagos Rift, Corliss et al. (1978) found greater Mn concentrations in crystalline samples than in amorphous ones. All of this evidence suggests that the Loihi amorphous sediment is a very recent deposit.

The Ca, Ti, and Al concentrations in the LAS are low (1.4%, 0.07%, and 0.1%, respectively) compared to those in typical oceanic sediments, in sediments from the East Pacific Rise and other Pacific sediments (Bostrom and Peterson, 1966, 1969). They are similar to those found in the Red Sea hydrothermal area (Bischoff, 1969) and the Galapagos Rise (Corliss et al., 1978). Low Ca, Al and Ti concentrations indicate that the LAS is of recent authogenic origin with little or no pelagic contribution.

The Fe/Al ratio in metalliferous sediments is frequently orders of magnitude higher than the same ratio for more typical oceanic sediments. The Fe/Al value of 367 in the LAS is typical of sediments from rise systems and volcanism.

The phosphate concentration in the LAS is anomalous relative to the iron concentration. Berner (1973) reports finding and Fe_2O_3:P_2O_5 ratio of 4:1 in the red clay sediments of the East Pacific Rise, whereas the Loihi sample had an Fe_2O_3:P_2O_5 of 30:1. This high Fe/P ratio and the fact that $Fe(OH)_3$ readily takes up phosphate when exposed to sea water (Berner, 1973) suggested that the LAS has been exposed to seawater recently.

Minor Elements

Table 3 compares the minor element concentrations found in the LAS with those found on the Galapagos Rise, the East Pacific Rise (both high and low Fe/Mn) and the Red Sea hydrothermal area. The concentrations of nickel, copper, zinc and arsenic in the LAS are comparable to those from the Galapagos Rise and the high Fe/Mn sediments from the East Pacific Rise, but significantly lower than those found with low Fe/Mn at the East Pacific Rise and those from the Red Sea.

Rare Earth Elements

The REE concentrations of the LAS were compared with those from the East Pacific Rise, the Galapagos Rise, sea water and Loihi glass (Table 4). The concentrations measured are low when compared to basalts from the Loihi area and even when compared to the sediments from the East Pacific Rise, but more comparable to those from the Galapagos Rise. In the Loihi sediment, the concentration of Ce is a factor of 30 less than that of the local basalt, and a factor of 5 less than the East Pacific Rise sediment. The concentrations of Sm, Eu and Yb are at least than an order of magnitude less than the local basalts and about an order of magnitude less than that observed at the East Pacific Rise. Sm and Eu are about a factor of 3 less than reported for the Galapagos Rise, and Yb is comparable.

The pattern of the REE's (normalized to chondrite) also differs from those of the basalts of the region (Figure 4) indicating that the REE's in the LAS are not derived from basaltic impurities in the sediment. The REE pattern of the Loihi sediment shows no resemblance to the pattern exhibited in the sediment from the Galapagos Rise (Figure 3) even though their concentration levels

are more comparable. The pattern also differs from that of sea water and of the sediments of the East Pacific Rise which echo that of sea water (Figure 3). Bender et al. (1971) propose that the REE pattern found in sediments from the East Pacific Rise means that those elements are adsorbed from sea water. Thus, the extremely low levels of REE's found in the LAS, coupled with the pattern which shows no particular resemblance to that of sea water also suggests a recent age for the LAS.

Estimated Age of Sediment

The youngest basalt associated with the LAS in dredge haul 29 was dated as 300 years, based on palagonite thickness. Several basalts in the haul had no palagonite layer (D. Clague, personnel communication). The LAS was probably formed more recently because the high heat associated with active volcanism would have caused the LAS to crystallize to hematite (Bischoff, 1969). The high Fe, low P content, the concentration and pattern of the REE with respect to sea water and other marine sediments and low detrital or pelagic component all indicate that the LAS has been exposed to sea water recently. In the absence of some absolute age determination, the age is estimated from the Fe/P ratio. The LAS may be expected to adsorb P until the equilibrium ratio of $Fe_2O_3:P_2O_5$ is reached (Berner, 1973). Accordingly, the equilibrium values for the LAS would be 52.4:13. The uptake may be approximated as a one dimensional diffusion plus equilibrium adsorption process using Fick's Second Law (Berner, 1980 p. 76):

$$\left[\frac{\delta \bar{C}}{\delta t}\right] = \left[\frac{D_s}{1 + K}\right] \frac{\delta^2 \bar{C}}{\delta z^2} \qquad (1)$$

Where $\bar{C}$ = concentration of adsorbed phosphate on solids

D_s = diffusion coefficient

K = adsorption constant

t = time

z = depth

assuming diagenesis and pelagic burial are negligible. Equation 1 is solved for a layer of infinite depth, uniform diffusion and equilibrium at the surface with the concentration of sea water at this location as:

$$\overline{C} = \overline{C}_D\left(1 - \mathrm{erf}\left[\frac{z}{2}\left(\frac{D_s}{1 + K}\right)^{1/2} t^{1/2}\right]\right) \qquad (2)$$

Where

$\overline{C}$ = concentration of adsorbed P as P_2O_5 in %, as a function of t,z

$\overline{C}_D$ = concentration of adsorbed P in equilibrium with seawater

D_s = diffusion coefficient of $(PO_4)^{3-}$ is 70 cm^2/yr

(Berner,1980, p. 173)

K = adsorption constant is 3000 (Hingston, Posner and Quirk, 1974)

t = time, in years

z = depth, in centimeters

The initial concentration of P_2O_5 is ~0%, based on the concentration observed in the Loihi basalt (D. Clague, personal communication). Using this equation a plot of concentration vs depth can be derived. The age of the sediment was estimated by comparing the derived with the measured P as P_2O_5. If the dredge is assumed to have sampled homogeneously over the top 10 cm, the age of the sediments will be on the order of 40 years. Even if the dredge sampled the top 20 cm homogeneously, the age of the sediment would be about 150 years.

These calculations indicate that the LAS was exposed to sea water recently, probably as recently as 40 years prior to sampling.

SUMMARY

The Loihi sediment is particularly interesting because it shows greatest similarity to the sediments found in active rift zones. This type of material has been found only rarely at sites of active volcanism and not associated with an oceanic ridge-rise system.

The amorphous structure, the high Fe:P ratio, the low and uniform rare earth element values, the negligible pelagic component (low Al, Si, Ti) indicate a recent age for the LAS. It is probably younger than the last dated eruption (300 years) probably on the order of 40 years.

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Figure 1. The Location of the Loihi seamount.

Figure 2. Bathymetry of the Loihi Seamount. The location of dredge haul 29 is circled.

Figure 3. Rare earth element distribution found for the Loihi mud compared to that of the Loihi glass, sea water and the sediment from the East Pacific Rise. All concentrations have been normalized to chondrite (chondrite values from Haskin *et al.*, 1966).

Table 1

Elemental analysis* of the amorphous sediment (<62μm) collected on the Loihi sea mount (Dredge haul 29, U.S.G.S. Cruise KK1-HW-81)

Major Elements		Minor Elements (ppm)				REE's (ppm)	
Na	0.8 ± 0.02	Sc	1.739 ± 0.030	Cs	<0.65	La	<3.0
Mg	1.29 ± 0.49	V	107 ± 12	Ba	80. ± 8	Ce	<2.6
Al	0.12 ± 0.02	Cr	27.43 ± 1.38	Hf	0.198 ± 0.067	Pr	
Si*	10.8	Mn	2944 ± 88	Ta	0.063 ± 0.004	Nd	<1.7
P*	1.0	Co	98.4 ± 1.1	W	<2.1	Sm	0.302 ± 0.00
S*	n.d.	Ni	70 ± 13	Pb*	n.d.	Eu	0.100 ± 0.01
K*	0.3	Cu	27	U	0.947 ± 0.024	Gd	
Ca	1.38 ± 0.39	Zn	98.8 ± 8.2	Th	<0.20	Tb	<0.6
Ti	0.073 ± 0.018	Ga*	n.d.			Dy	<0.94
Fe	36.7 ± .4	As	55.9 ± 4.3			Ho	
		Rb*	35 (<19)[naa]			Er	
		Sr*	497			Tm	
		Y*	n.d.			Yb	0.263 ± 0.35
		Zr*	10			Lu	
		Nb*	<7				
		Mo	12.2 ± 1.0				
		Sb	0.69 ± 0.12				

*Analysis by x-ray fluorescence. All other analyses by neutron activation analysis.

Table 2

Comparison of major element concentrations (in %) of the amorphous sediment, with sedimental major element compositions of amorphous oxic iron sediments from the Red Sea Hydrothermal Area, the East Pacific Rise and the Galapagos Rise. These are further compared with the major elemental composition of more typical oceanic sediments.

	Loihi	Galapagos Rise[a]	East Pacific Rise[b]		Red Sea Brine[c]	Thera 6	Red Clay[d]
			high Fe/Mn	low Fe/Mn			
Na	0.8	-	-	-	0.7	-	-
Mg	1.3	-	0.5	0.5	1.7	0.3	-
Al	0.1	0.32	0.5	<0.5	2.7	0.1	8.4
Si	10.8	13.2	5.8	6.5	6.5	11	25.0
P	1.0	-	-	-	<0.3	-	-
S	n.d.	-	-	-	0.25	-	-
K	0.3	-	0.3	0.4	0.07	0.2	-
Ca	1.4	1.4	1.9	1.6	1.6	1.8	-
Ti	0.07	-	-	-	0.22	-	0.46
Fe	36.7	27.4	31.1	28.8	39.9	40.5	6.50
Mn	0.3	7.8	0.6	2.4	0.5	0.4	-

a. Corliss *et al.*, 1978. Samples A1-A2 averaged; "reddish amorphous deposit."
b. Bonatti and Joenssu, 1966. High Fe/Mn; sample a_3 from dredge haul Amph D_2; low Fe/mn, sample a_2, same haul.
c. Bischoff, 1969. Amorphous geothite facies, sample 85-320.
d. Average chemical composition of pelagic clay, Turekian and Wedepohl, 1961.

Table 3

Comparison of minor element concentrations (ppm) of the Loihi amorphous sediment, Red Sed brine deposit, East Pacific Rise sediment and sediment from the Galapagos Rise.

Element	Loihi	Galapagos Rise[a]	East Pacific Rise[b]		Red Sea[c]
			high Fe/Mn	low Fe/Mn	
Sc	1.7	1.1	-	-	-
V	107	-	-	-	-
Cr	27.4	8	20	20	-
Mn	2,944	78,500	5,800	24,300	5,000
Co	98.4	3.2	32	120	-
Ni	70	62	90	460	-
Cu	27	48	60	120	400
Zn	99	150	-	-	5,000
As	56	42	-	-	-
Sr	497	-	480	800	680
Mo	12	-	-	-	-
Sb	0.7	6	-	-	-
Ba	80	705	100	100	<270
Hf	0.2	0.4	-	-	-
U	0.95	-	-	-	-
Th	<0.2	0.03	-	-	-

a. Corliss *et al.*, *1978*; an average of the two amorphous sediments, A1 and A2.
b. Bonatti and Joenssu, 1966. High Fe/Mn material, sample a_3 in dredge haul Amph D2 and low Fe/Mn, sample a_2, same haul.
c. Bischoff, 1969; sample 85-320.

Table 4

REE concentrations detected in the amorphous sediment compared to REE concentrations in sediments from the East Pacific Rise, Galapagos Rise, Seawater and Loihi Glass.

	Loihi, Sediment		EPR		Galapagos		Seawater		Loihi, Glass	
REE	Conc. (ppm)	R/C[a]	Conc. (ppm)[b]	R/C[a]	Conc. (ppm)[d]	R/C[a]	Conc. (ppt)	R/C×10[3a]	Conc. (ppm)	R/C[a]
La	<3.0	<10	19.1	63	6.7	22.3	13.3	10.0	15.7	52
Ce	<2.6	<3.1	5.5	6.5	4.2	5	1	1.4	34.4	41
Nd	<1.7	<2.9	15	26	-	-	3.2	4.8	19.6	34
Sm	0.302	1.4	3.2	15.2	0.96	4.6	0.4	2.1	5.2	25
Eu	0.100	1.5	0.99	13.4	0.32	9.3	0.1	1.8	2.8	28
Tb	<0.6	<12.2	-	-	0.16	3.3	0.1	2.9	0.8	17
Dy	<0.94	<3.0	4.73	15.2	-	-	0.9	2.9	5.2	17
Yb	0.263	1.5	3.73	-	0.38	2.2	0.8	4.8	2.0	12

a. normalized to chondrite based on Haskin *et al.*, 1966.
b. Bender *et al.*, 1971., 1968
c. Hogdahl, Melsom, and Bowen in parts per trillion.
d. Corliss *et al.*, 1978 - amorphous species dredged from Galapagos. Classified as hydrothermal.

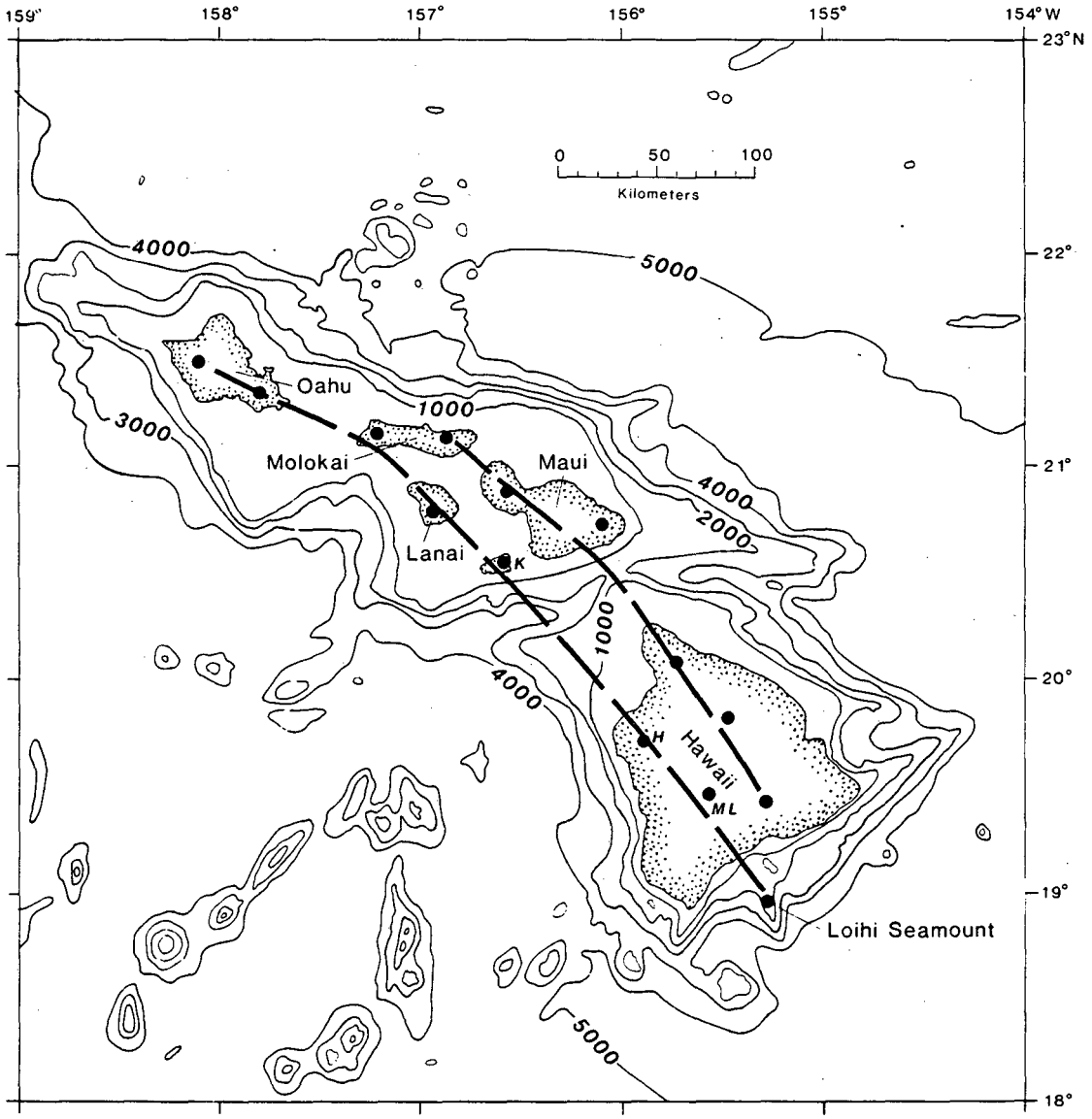

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Figure 1

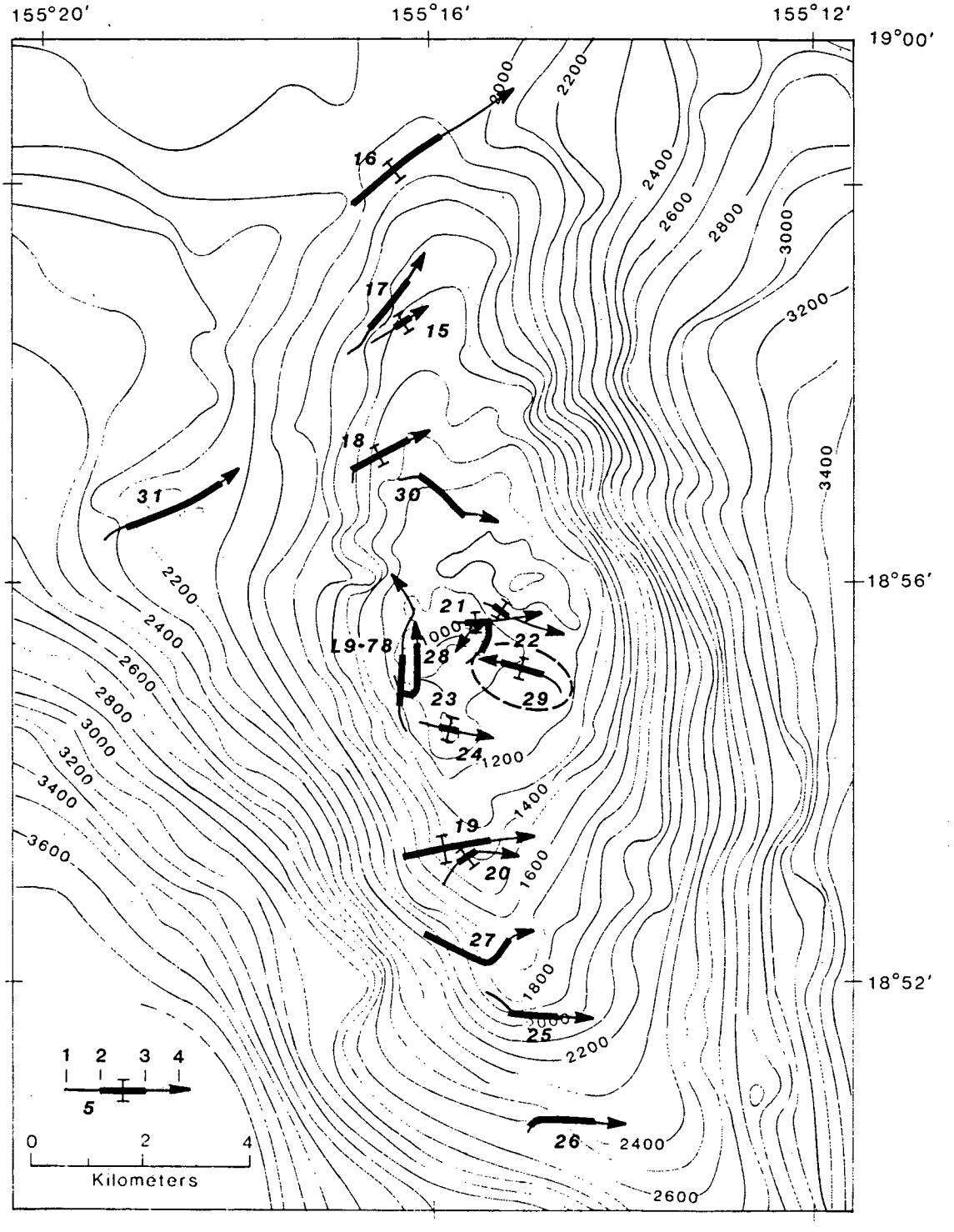

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Figure 2

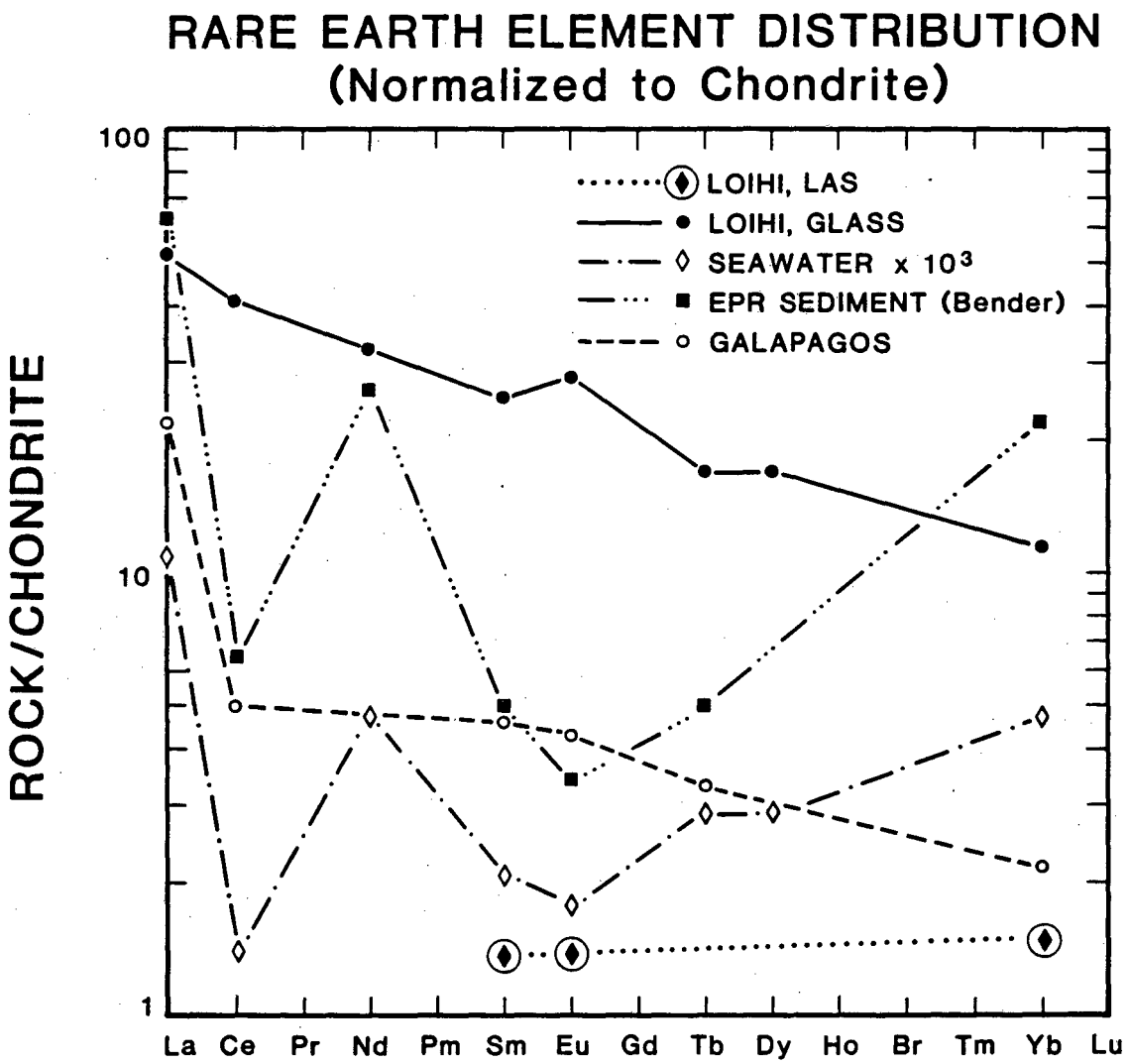

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Figure 3

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