TRACE ELEMENT GEOCHEMISTRY OF A BOX-CORE FROM SAN PEDRO BASIN, NE PACIFIC

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RESUMEN

Se midieron 16 elementos "trazas" y 3 elementos "mayores" en los sedimentos de una caja proveniente de la cuenca de San Pedro, situada en la zona costera de California, utilizando el método de análisis instrumental de activación por neutrones (AIAN). La precisión bastante buena de estas mediciones (cerca de ± 10%) permite la observación de variaciones significativas en las concentraciones de estos elementos aun en los 26 cm superiores de la caja.

Los elementos 'tierras raras' presentan un patrón tipo "lutita" para estos sedimentos. La razón de K/Cs indica que el cesio sigue al potasio en sedimentación fina. El valor promedio de K/Cs $\sim 1.2 \times 10^3$ junto con el valor de 12.4 ppm de Cs corresponden a sedimentos finos argiláceos no-carbonáceos. Las concentraciones de Th ($\sim$7.5 ppm) son parecidas a las de arcillas pelágicas. Estos sedimentos se caracterizan más por valores normales de Cr, Zr y Ta, concentraciones relativamente altas de Na y Sb, y bajos contenidos de Fe y Sc, cuando se les compara con los reportados para sedimentos marinos de otras áreas.

ABSTRACT

16 trace elements and 3 major elements were measured in sediments of a box-core from San Pedro Basin, an inshore basin situated in the California Continental Borderland, by Instrumental Neutron Activation Analysis (INAA). Fairly good precision of these measurements (about ± 10%) permits the observation of significant variations in the concentrations of these elements even in the upper 26 cm of the core.

Rare earth elements show a "shale" like pattern for these sediments. K/Cs ratios indicate that cesium follows potassium in the fine sediments. A mean K/Cs value of $\sim 1.2 \times 10^3$ together with a value of 12.4 ppm for Cs corresponds to fine non-carbonaceous argillaceous sediments. Th concentrations ($\sim$7.5 ppm) are closer to those of pelagic clays. These sediments are further characterized by normal values for Cr, Zr and Ta, higher concentrations of Na and Sb, and lower Fe and Sc contents, when compared to those reported for marine sediments from other areas.

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INTRODUCTION

Many geochemical studies have been carried out on marine sediment cores from different tectonic environments (e. g., Bender *et al.*, 1971; Tieh and Pyle, 1972; Angino *et al.*, 1972; Dymond *et al.*, 1976). Most of these have been directed towards the study of long-term chemical variations registered in the cores.

We undertook the present study keeping the following objectives in mind. (1) to study short-term chemical variations in a box-core, (2) to test whether the experimental technique (instrumental neutron activation analysis) employed to estimate the concentrations of trace elements could give sufficiently reliable results in order to show that such short-term effects are really significant, (3) to look for inter-relations between all elements by utilizing correlation coefficients, (4) to see whether the geochemistry of the box-core agree in general with the known geology and geophysics of the area and (5) to provide first such data (especially the rare earths) on sediments of California continental borderland.

EXPERIMENTAL PROCEDURE

Instrumental neutron activation analysis (INAA) was used to analyze eleven sediment samples of a box-core taken by researchers of the scripps institution of Oceanography, from San Pedro Basin (lat. 33.6°N, long. 118.5°W, water depth ~sill depths approximately 700 meters). Samples taken at depths of 2, 4, 5, 7, . . . cm, were labelled as b, d, e, g, . . . for convenience. The method of analysis is similar to that of Gordon *et al.* (1968) and has been described in detail elsewhere (Pal, 1972, 1975; Terrell and Pal, 1977). Precisions of around 10% or better were obtained for most elements measured in this study, except for Th, Nd and Yb (~15%), for Sb (~20%) and for Gd (20-30%). Accuracies of these measurements were also satisfactory as judged by analysis of some international geochemical reference samples (Pal and Terrell, 1978).

GEOLOGIC AND OCEANOGRAPHIC SETTINGS

An excellent description of the California Continental Borderland (in which the San Pedro basin is situated) has been given by Moore (1967). The California Continental Borderland is located near the center of a large geographical area of great topographic and geologic diversity. This diversity is, in large measure, attributable to an extraordinary system of major faults which throughout much of the region, has been intermittently active during long periods of Cenozoic time. Emery (1960) has discussed the sources of sediment being contributed to the Borderland off southern California and has considered all sources of significance, including streams, winds, sea-cliff erosion, organic remains and chemical precipitates. Organic materia in the basin sediments of the northern Borderland were found to average 7% by dry wt. of the total sediment, but varied widely, depending upon local depositional rates, being a greater percentage of total sediment in areas of slow deposition. Authigenic constituents were found in areas of slowest depositional rate and were negligible or undetected in basin deposits. The relative magnitudes of these sources compared to detritus from mainland drainage systems clearly demonstrated that streams are by far the most important of the sources. Streams also were estimated to contribute at least ten times the combined contributions of wind and sea-cliff erosion. Emery's estimate of total contribution of detritus to the area was 10 million tons/yr, which is at least one order of magnitude greater than estimates for other sources of clastic sediments. Thus, one might expect that the proximity to major streams should be a fundamental factor in controlling volume of deposits within a given area. Predominating coastal tidal and semipermanent currents can, of course, significantly modify distribution patterns from streams and river mouths.

San Pedro basin is one of the several inshore basins in the Continental Borderland. The inshore basins are areas of greatest accumulation of sediments. Many streams and rivers drain near the San Pedro basin in San Pedro Bay.

Based upon the study of sedimentary structure, Moore (1967) has

concluded that many inner basins are filled predominantly with turbidites. Similar sand layers interbedded with normal deep-water "green muds" have been found in San Pedro basin.

No specific data on rate of deposition in the San Pedro basin are available. Mean deposition rates in the Borderland area vary between 4 and 212 cm /1000 yr (Moore, 1967, p.70). A geochronological study of the sediments (used in the present study) did not give satisfactory results as the ^{210}Pb concentration was quite low even at the surface, implying that the sediments are older than 100 years (Bruland, 1974, written communication). Brooks *et al.* (1968) have given annual sedimentation rates of about 28 mg/cm^2 for adjacent Santa Catalina basin and an oxidising environment for the top two or three meters of sediments. Koide *et al.* (1976) have applied ^{226}Ra chronology to the sediments of San Clemente basin and found values of 5.2 or 5.3 cm/1000 years as sedimentation rates for this basin.

There is some controversy regarding the relative importance of processes of transportation to and deposition in Borderland basins (Moore, 1967, p. 77). The examination of many cores by sedimentalogists shows that turbidity current deposition is not important and the cores seem to represent particle-by-particle deposition. The seismic evidence presented by Moore (1967) on the other hand shows that the turbidity-current might indeed be important in controlling the deposition of these basins.

The transportation-deposition system proposed to explain regional structural and distributional characteristics as well as known small-scale lithologic characteristics of the superficial deposits contain three kinds of turbidity currents: (1) flows having a high concentration of sand-sized particles initiated in the upper reaches of canyon or gully, (2) flows deriving their density from suspended lutum as a result of turbid-layer transport, and (3) flows carrying a mixture of sand and lutum and ussually initiated at intermediate depths within the canyon systems. The relative activity of these kinds of turbidity currents is believed to vary both regionally and in time as controlling factors change which are related primarily to coastal and continental shelf processes.

According to Moore (1967, p.18) the San Pedro basin close to sediment sources has only very thin postorogenic sediment cover and is strong evidence of predominance of turbidity-current deposition which seeks topographic low of adjoining basin.

RESULTS AND DISCUSSION

Results of these measurements on sediments are given in Table 1 and plotted in Fig. 1. From this, it is seen that errors are small enough to enable the observation of marked variations in concentrations even over a rather small depth range. Arrays giving correlation coefficients of all the elements are given in Table 2 , where the first row gives the correlation of Na with all other elements; the second row that of K with all the elements except Na (the correlation of K with Na is found in the first row), and so forth. From this table inter-relationships can be seen of all the elements measured in the present study. For example, Na shows poor correlations with most elements, while K, on the other hand, shows surprisingly good correlations with most elements. Excellent correlations are observed between several other elements such as between Yb and Hf, Ta or Co, between Hf and Ta, Sm, Fe or Th, and between Sc and Co or Cs. Such an approach utilizing correlation coefficients should thus prove helpful in looking for inter-relationships among a large number of elements.

At certain depths, sudden increase (or decrease) in concentration of various elements is observed which might be the result of sudden change in sedimentation rate or a physical or biological redistribution similar to that found in other places by Robins and Edginton (1975). The sediments analyzed in this work are fine-grained and non-carbonaceous (carbonate contents were found to be <15%). Evidence from Fig. 1 suggests that diagenetic remobilization of elements is not particularly important in the environment of San Pedro basin from which the box-core has been obtained and analyzed.

Data on abundances of cesium in common sediments have been summarized by Heier and Billings (1970a). Thus Welby (1958) found that 40% of Gulf of Mexico silicate sediments contained between 6 and 9

ppm Cs. The quartz-rich near-shore sediments generally contained less than 6 ppm. Sreekumaran *et al.* (1968) found an average of 1.1. ppm Cs in seven samples of suspended matter in western U. S. streams and an average of 2.6 ppm Cs in their bottom sediments. The data of Sreekumaran *et al.* (1968) and Smales and Salmon (1955) gives an average value of ~1 ppm for deep-sea sediments. Hirst (1962b) obtained Cs contents between 1 and 3.2 ppm for modern marine sands and between 7.9 and 13 ppm for modern marine clays. Thus Cs increases as a function of finer grain size, increased clay mineral content and increased number of ion exchange sites. Our data (average 12.4 ppm Cs) on fine-grained non-carbonaceous argillaceous sediments are consistent with this observation. Further, K/Cs ratio (average 1.2×10^3) is quite close to that for argillaceous sediments (Rankama and Sahama 1950) and is practically constant with depth (Correlation coefficient ~0.7). Hirst 1962b) has observed that varying rates of sedimentation seem to have little effect on K/Cs ratios.

Na contents of these sediments are rather high (mean of 11 samples being 4.3±0.9% Na). A mean of ~2.2±0.7 was obtained for 124 argillaceous marine sediments from Gulf of Mexico and Gulf of Paria by Heier and Billings (1970b).

Welby (1958) observed a range of 1.2-3.7% Na found for Gulf of Mexico sediments. Further, Na/K values average ~2.8) are also high as compared to other sediments (~0.4-1.1 found by Hirst, 1972a; ~ 0.2-1.6 by Welby, 1958). Higher amounts of certain detrital and/or clay minerals in our samples might be responsible for these differences.

Th contents of these sediments are similar to those found in other areas of marine environments (e.g., compilations by Rogers and Adams, 1970). On the other hand, their Fe contents are extremely low (~2%) as compared to those (~9%) of pelagic clays (Turekian and Wedepohl, 1961). This may partly be due to lower contents of Fe in parent material from which these sediments are derived. However, as significant chemical fractionation may take place during weathering, erosion and sedimentation, iron content of sediments is highly variable. Similarly low Fe contents were also observed in a box-core from the Gulf of California (Pal, 1974). Unlike Fe, Sc contents are only a little lower than

those of Atlantic and Pacific clays (Frondel, 1970; Young, 1968). Cr contents are similar to those of sediments from the Gulf of California (Pal, 1974). On the other hand, Sb contents of these sediments are higher than those found for pelagic clays and common sedimentary rocks (Onishi, 1969). Co contents are very low as compared to those for pelagic clays compiled by Turekian and Wedepohl (1961).

Zr contents (average ~200) are similar to those (~160) of Gulf of Mexico sediments (Young, 1968) and of pelagic clays (~180 found by Goldberg and Arrhenius, 1958; and ~150 by Turekian and Wedepohl, 1961). Tieh and Pyle (1972) however obtained rather low (~80) Zr for Gulf of Mexico sediments. Zr/Hf ratio of our samples is about 70; somewhat higher than that for deep-sea clays (~37 by Turekian and Wedepohl, 1961) and for igneous rocks (11-37 obtained by Butler and Thompson, 1965). Ta values for these sediments are similar to those found for some common sedimentary rocks from Mexico (Pal, 1972).

Some typical data of rare-earth elements (REE) on these sediments are plotted in Fig. 3. The data for normalization are those for the Leedey chondrite given by Masuda et al. (1973) and Masuda (1975). The data on the composite of 40 North American shales (NASC) are also included for comparison (Haskin et al, 1968). These two patterns are quite similar except that the small negative Eu anomaly found in NASC is not found in some of the layers. This lack of Eu anomaly in recent sediments is rather inconsistent as only old (Archean) sediments are found to have such patterns (Wildeman and Haskin, 1973; Wildeman and Condie, 1973; Jakes and Taylor, 1974; Balashov and Tugarinov, 1976). The presence or absence of Eu anomaly might be related to the absence or presence of feldspar of a possible detrital origin. The lack or almost so of a significant negative Ce anomaly in these sediments might indicate a lack of equilibrium with sea water.

CONCLUSIONS

The present work clearly shows that the precision obtained for the determination of trace elements by INAA permits us to study short-term chemical variations in marine sediments. This would permit us to undertake similar studies on a regional basis. Some chemical similarities

have been pointed out between the San Pedro sediments and sediments from the Gulf of California. To our knowledge, no such studies have so far been carried out on California continental borderland basins rendering difficult at this stage to evaluate the present data in the context of more data on this area. Such studies seem to be promising and should be undertaken on a regional scale in order to evaluate their implications in the light of other geological and geophysical data on this area.

ACKNOWLEDGMENTS

Table 1 (contd.)

	Th	Zr	Hf	Ta	Co	Fe (%)	Sc	Cr	Sb
b	11 ± 1	230 ± 13	5.41 ± 0.13	0.91 ± 0.05	7.9 ± 0.2	2.5 ± 0.2	8.94 ± 0.05	52 ± 2	3.6 ± 0.5
d	11 ± 1	193 ± 12	3.84 ± 0.11	0.65 ± 0.04	7.6 ± 0.2	2.1 ± 0.3	8.44 ± 0.06	44 ± 2	5.7 ± 0.7
e	7.8 ± 0.8	193 ± 12	2.66 ± 0.09	0.69 ± 0.04	7.0 ± 0.2	1.9 ± 0.2	7.53 ± 0.05	42 ± 2	3.6 ± 0.5
g	6.3 ± 0.9	244 ± 14	2.51 ± 0.09	0.52 ± 0.04	6.0 ± 0.2	1.9 ± 0.2	6.52 ± 0.05	45 ± 2	2.1 ± 0.3
j	8.1 ± 0.9	242 ± 14	2.97 ± 0.10	0.56 ± 0.04	6.8 ± 0.2	1.9 ± 0.1	7.79 ± 0.05	39 ± 2	3.3 ± 0.6
o	6.8 ± 0.9	176 ± 11	2.55 ± 0.09	0.61 ± 0.04	6.5 ± 0.2	1.8 ± 0.2	7.05 ± 0.05	46 ± 2	1.5 ± 0.3
u	7.1 ± 0.9	277 ± 13	2.81 ± 0.10	0.69 ± 0.03	7.4 ± 0.2	1.9 ± 0.2	8.79 ± 0.06	57 ± 2	2.3 ± 0.3
w	6.1 ± 0.8	240 ± 13	2.69 ± 0.09	0.64 ± 0.04	6.9 ± 0.2	2.1 ± 0.2	7.98 ± 0.05	40 ± 2	1.8 ± 0.3
x	5.4 ± 0.7	192 ± 12	1.90 ± 0.07	0.53 ± 0.03	6.3 ± 0.2	1.8 ± 0.2	7.43 ± 0.05	51 ± 2	1.7 ± 0.3
y	5.6 ± 0.7	163 ± 11	2.12 ± 0.08	0.53 ± 0.03	6.9 ± 0.2	1.7 ± 0.2	7.22 ± 0.05	53 ± 2	2.0 ± 0.3
z	7.4 ± 0.6	144 ± 10	2.66 ± 0.09	0.58 ± 0.03	6.5 ± 0.2	2.0 ± 0.3	7.58 ± 0.05	33 ± 1	1.8 ± 0.3
M ± s	7.5 ± 1.9	204 ± 35	2.92 ± 0.96	0.63 ± 0.11	6.8 ± 0.7	2.0 ± 0.2	7.75 ± 0.74	46 ± 7	2.7 ± 1.3

	Na*(%)	K*(%)	Cs	La	Ce	Nd	Sm	Eu	Gd	Yb
b	5.1 ± 0.2	2.04 ± 0.09	13.9 ± 0.6	29 ± 2	55 ± 5	46 ± 5	3.7 ± 0.1	1.19 ± 0.06	7 ± 1	2.7 ± 0.3
d	4.6 ± 0.1	1.71 ± 0.09	12.5 ± 0.5	22 ± 2	40 ± 5	21 ± 4	3.1 ± 0.1	1.00 ± 0.05	4 ± 1	2.0 ± 0.3
e	5.4 ± 0.1	1.51 ± 0.09	12.2 ± 0.5	25 ± 2	44 ± 4	15 ± 3	2.7 ± 0.1	0.88 ± 0.05	4 ± 1	1.8 ± 0.2
g	5.8 ± 0.2	1.37 ± 0.07	10.4 ± 0.5	13 ± 1	38 ± 4	27 ± 4	2.6 ± 0.1	1.11 ± 0.06	3.0 ± 0.8	1.3 ± 0.2
j	4.9 ± 0.2	1.58 ± 0.08	12.1 ± 0.5	14 ± 1	35 ± 4	10 ± 4	2.7 ± 0.1	1.11 ± 0.06	< 2	1.5 ± 0.2
o	4.2 ± 0.1	1.49 ± 0.09	12.2 ± 0.5	21 ± 2	49 ± 5	16 ± 3	3.0 ± 0.1	0.94 ± 0.05	2.6 ± 0.9	1.5 ± 0.2
u	3.2 ± 0.1	1.55 ± 0.09	14.1 ± 0.6	29 ± 2	44 ± 4	11 ± 3	3.0 ± 0.1	1.03 ± 0.05	6 ± 1	1.9 ± 0.2
w	3.6 ± 0.1	1.51 ± 0.09	12.6 ± 0.5	18 ± 1	43 ± 4	13 ± 3	2.4 ± 0.1	1.14 ± 0.06	< 2	1.8 ± 0.2
x	3.7 ± 0.1	1.32 ± 0.07	12.2 ± 0.5	22 ± 2	30 ± 3	16 ± 3	2.3 ± 0.1	0.86 ± 0.05	2.2 ± 0.9	1.4 ± 0.2
y	3.5 ± 0.1	1.36 ± 0.07	11.8 ± 0.5	19 ± 1	33 ± 3	14 ± 3	2.3 ± 0.1	0.88 ± 0.05	3.1 ± 0.9	1.5 ± 0.2
z	3.8 ± 0.1	1.43 ± 0.08	11.9 ± 0.5	18 ± 1	37 ± 3	14 ± 2	2.3 ± 0.1	0.88 ± 0.05	4 ± 1	1.4 ± 0.2
M± s	4.3 ± 0.9	1.53 ± 0.20	12.4 ± 1.0	21 ± 5	41 ± 7	18 ± 10	2.7 ± 0.4	1.00 ± 0.12	3.6 ± 1.8	1.7 ± 0.4

* K was determined by flame Photometry, while Na values are the mean of those of Flame Photometry and INAA.

Table 2

Correlation coefficients of different elements based on the concentration data of Table 1.

|	Na	K	Cs	La	Ce	Nd	Sm	Eu	Gd	Yb	Th	Zr	Hf	Ta	Co	Fe	Sc	Cr	Sb
Na	1	0.34	-0.36	-0.18	0.27	0.55	0.38	0.36	0.10	0.17	0.44	0.16	0.40	0.22	-0.03	0.32	-0.20	-0.24	0.45
K		1	0.66	0.54	0.74	0.70	0.90	0.61	0.69	0.93	0.89	0.29	0.98	0.90	0.84	0.88	0.77	0.14	0.62
Cs			1	0.85	0.56	0.19	0.61	0.25	0.68	0.77	0.44	0.36	0.56	0.77	0.81	0.51	0.91	0.46	0.23
La				1	0.58	0.32	0.61	-0.05	0.78	0.73	0.40	0.14	0.47	0.77	0.71	0.39	0.71	0.59	0.25
Ce					1	0.57	0.82	0.47	0.62	0.75	0.59	0.26	0.70	0.85	0.56	0.66	0.47	0.15	0.20
Nd						1	0.69	0.50	0.59	0.67	0.58	0.13	0.79	0.66	0.39	0.76	0.28	0.26	0.30
Sm							1	0.53	0.72	0.83	0.80	0.36	0.87	0.83	0.73	0.69	0.63	0.35	0.54
Eu								1	0.24	0.51	0.40	0.76	0.62	0.46	0.35	0.66	0.40	0.03	0.21
Gd									1	0.77	0.61	0.23	0.71	0.81	0.72	0.62	0.69	0.43	0.34
Yb										1	0.76	0.31	0.90	0.96	0.91	0.85	0.84	0.33	0.55
Th											1	0.09	0.90	0.71	0.76	0.76	0.66	-0.06	0.85
Zr												1	0.25	0.29	0.24	0.27	0.39	0.33	0.09
Hf													1	0.87	0.78	0.92	0.71	0.10	0.62
Ta														1	0.82	0.84	0.77	0.26	0.42
Co															1	0.66	0.90	0.33	0.67
Fe																1	0.68	-0.06	0.46
Sc																	1	0.28	0.51
Cr																		1	-0.06
Sb																			1
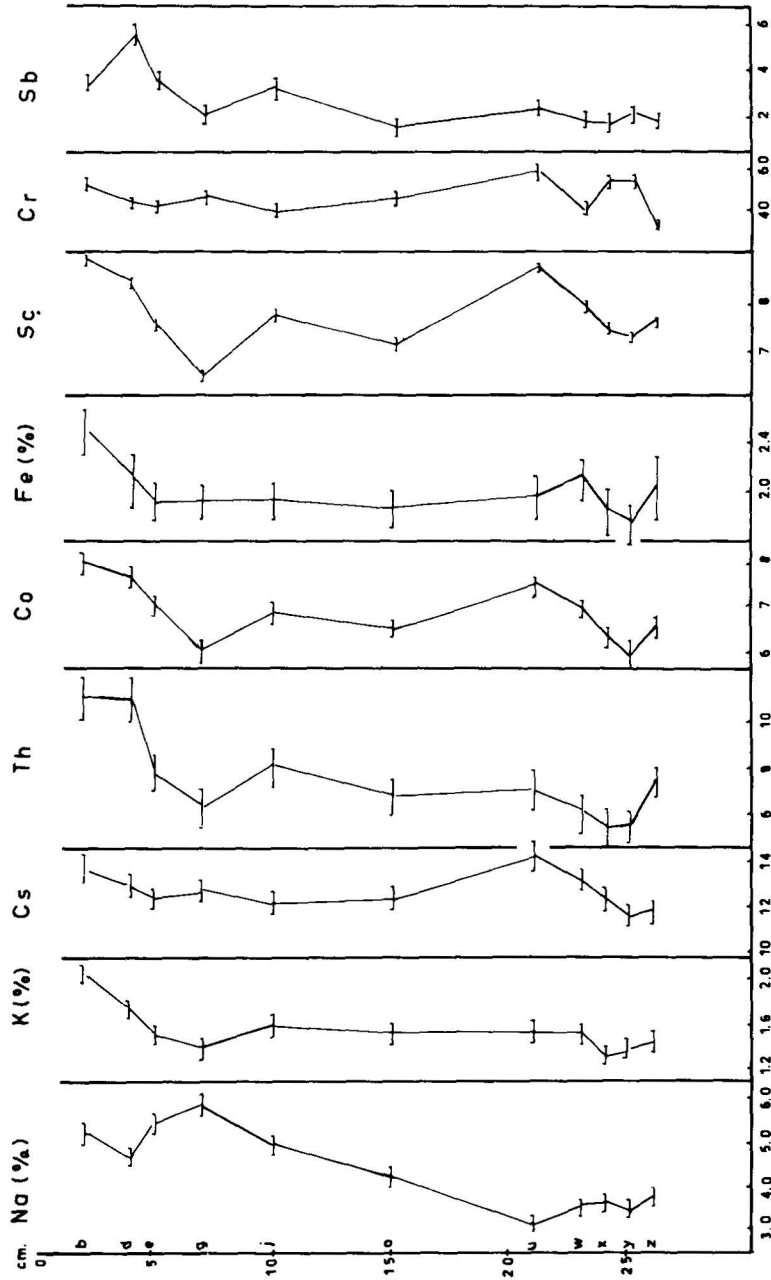
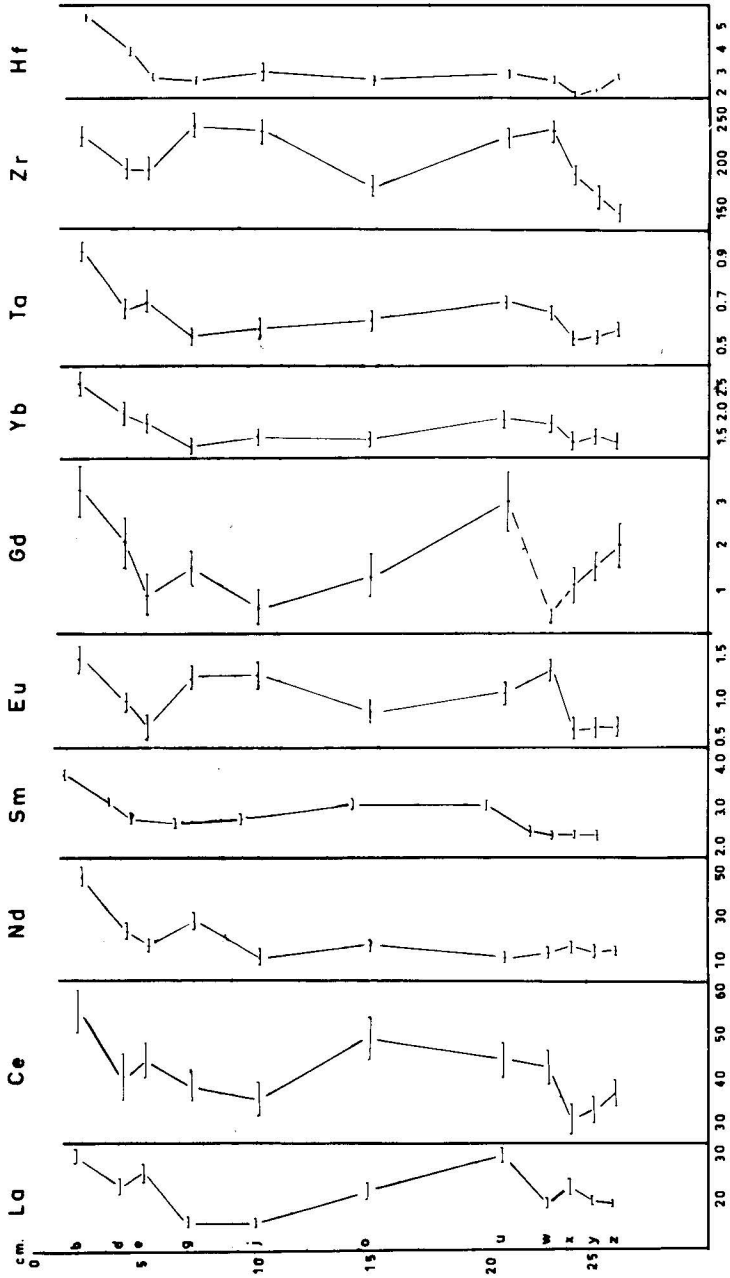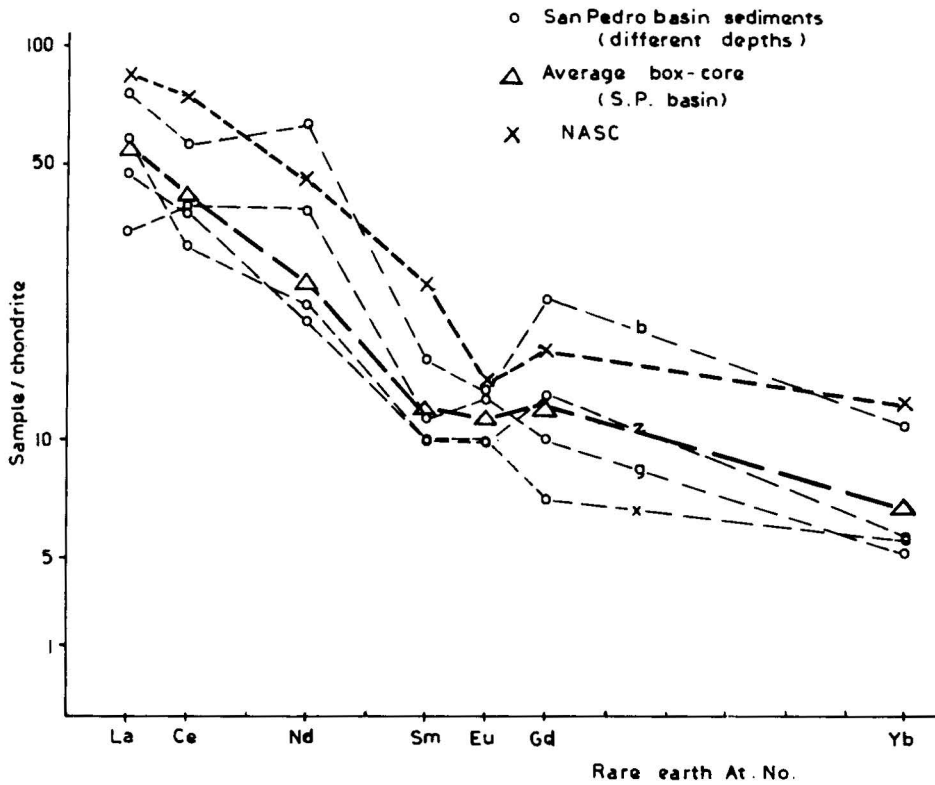Fig. 1   Variation of element concentrations as a function of depth.

Fig. 1 (Cont d.).

FIG. 2   Normalized   REE   plots

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