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Geochemistry of Surficial Sediments from Sebastián Vizcaíno Bay, Baja California

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ABSTRACT

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Thirty-seven surficial sediment samples from Vizcaíno Bay, Baja California, are analysed for their phosphate, organic matter, carbonate, as well as metal contents (Al, Fe, Mn, Zn, Cu, Ni, Cr, Cd and Sr). Highest organic carbon concentrations (up to 15.1%) are found in deeper waters of the outer bay and also in a narrow area extending NW–SE adjacent to the eastern coast. Total carbonates are also enriched proximal to the eastern coast, with the highest concentrations found on Ranger Bank (36.9%), where it is associated with foraminifer-rich sands. Phosphate (P_2O_5) content is highest (22.3%; mainly present as francolite pellets, nodules and bone fragments) in shallow waters (29–70 meters) adjacent to Punta Santa Rosaliita to the NE of the bay, showing a sharp offshore decrease.

Geochemical partition analyses indicate that, except for Sr and Cd, all the metals studied occur mainly in the detrital fraction of the sediment, with minor but varying proportions occurring in the more reactive fractions. The regional distribution of non-lithogenic Cu, Cr, Ni, Cd and, to a lesser extent Zn, is mainly controlled by their association with organic matter. These elements show high concentrations in an area under influence of upwelled waters, and in the organic-rich bathymetric deep in the outer bay. Cadmium is mainly associated with the most reactive fraction of the sediments (either loosely adsorbed, as carbonates and/or Fe-Mn oxihydroxides), being enriched (4.09 ppm) directly below the coastal upwelling region. Different precipitation processes for Cd compared to Cu, Cr and Ni occur in the area, possibly due to the preferential input of Cd via upwelling and/or the relatively shorter residence time of Cd in waters above continental margins. The distribution of Sr is related to that of calcium carbonate, except for an area proximal to the coastal lagoons on the SE coast, where relatively high Sr concentrations are found (< 1725 ppm). Various metal enriched samples throughout the study area, suggest different lithologies and sources of the detrital components deposited. Of these, detrital Mn is associated with sediments derived from the peninsular mainland NE of the bay and Fe, Cu, Cr, Ni and Zn with the lithogenic detritus on Ranger Bank.

ADDITIONAL INDEX WORDS: *Marine sediments, geochemistry, upwelling, organic carbon, metals, phosphorite.*

INTRODUCTION

The study of the geochemical partitioning of metals in the different marine sediment fractions is an important tool for distinguishing between the various metal bearing components and to assess the various processes that may have lead to their enrichment in the sediments. Of special interest is the study of those metals which in the marine environment have a biologic function, such as Cu, Zn, Co, Cr, Ni as well as Se and V, and/or like Cd, that has a nutrient-like distribution in the oceans. The enrichment of these metals in marine sediments has been related to high productivity zones, where organic matter in the water column plays an important role in their transport from sea water to the bottom sediments (BRULAND, 1983; CALVERT AND PRICE, 1983; COLLIER and EDMOND, 1984, MARTIN and THOMAS, 1994). Some metals may also be enriched in marine sediments due to their direct precipitation from sea water (hydrogenetic), as is the case for Fe-Mn oxihydroxides (LANDING and BRULAND, 1987) and the elements scavenged by them (*e.g.,* Zn, Cu, Ni and Co) by their incorporation and/or adsorption to authigenic carbonate fluor-apatite (*e.g.,* U, Y, Rare Earth Elements, Cd, Zn; ALTSCHULER, 1980), as well as their presence in lithogenic (detrital) material.

In the marine environment, the coastal shelf represents an important sink for suspended matter (YEATS and BREWERS, 1983). Marine inputs of metals such as Cd, Cu, Ni and Zn in this areas are significantly higher (by a factor from 2 to 10) than the dissolved input of these metals from land (MARTIN and THOMAS, 1994). Hence, the geochemistry of the sediments in these areas may provide important clues regarding the sources and processes through which metals have accumulated. In the Namibian shelf for example, where intense coastal upwelling occurs, it has been found that minor elements (*e.g.,* Cu, Ni, Mo and Zn) are significantly positively correlated with the organic fraction (high organic matter and opal contents) of the sediments (CALVERT AND PRICE, 1983). Humic substances in these sediments are thought to have complexed the metals which occur in excess compared with their concentrations in marine plankton (*cf.* CALVERT and MORRIS, 1977).

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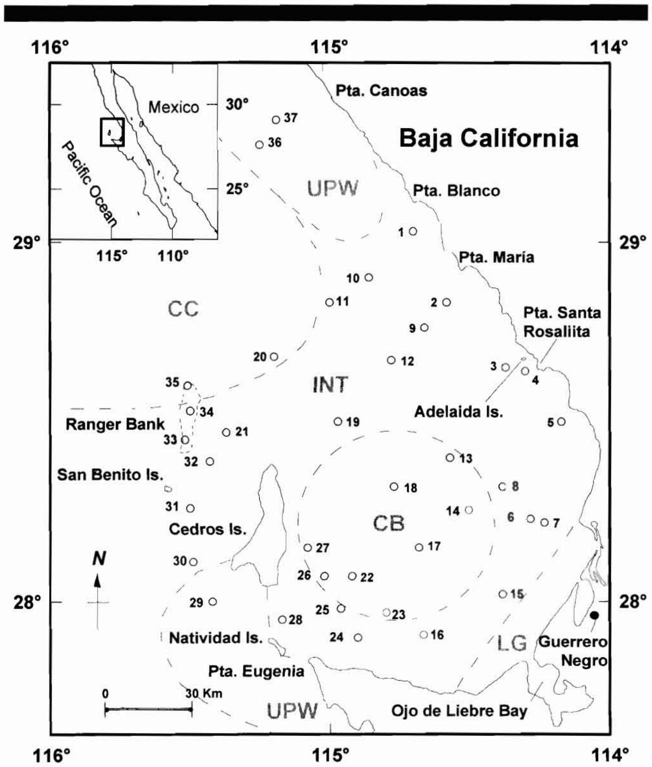

Figure 1. Location of surficial sediment samples and generalised distribution of water masses in Vizcaíno Bay according to Wyllie (1960): (UPW) upwelling. (CC) California current, (INT) intermediate, (CB) central bay and (LG) lagoon water.

Vizcaíno Bay is located on the central western coast of Baja California, Mexico and is influenced by various water masses including intense upwelling (Wyllie, 1960; Figure 1). Surficial sediments there have been studied mainly for their textural sedimentary characteristics and for their major component geochemistry (organic carbon, carbonate and phosphate; Emery *et al.,* 1957; Gorsline, 1957; Daesslé and Carriquiry, 1998). These authors observed the influence of local upwelling in the area on the abundance of biogenic material in the sediments and discussed several sedimentary processes. However, no studies have yet been carried out on the influence of oceanographic and/or sedimentary processes on the distribution of metals in the area. The only data published on metal geochemistry in, or adjacent to the bay, has focused on the phosphorites there (McComas and Neel, 1967 in Garrand, 1977; Daesslé and Carriquiry, 1998). Thus, the aim of the present work is to characterise the geochemical partitioning of Al, Fe, Mn, Zn, Cu, Cr, Ni, Sr and Cd, and the geographic distribution of these elements in the surficial sediments from Vizcaíno Bay. The distribution of these elements is then discussed in the context of the prevailing oceanographic and/or sedimentary processes in the area.

ENVIRONMENTAL SETTING

The water depth in Vizcaíno Bay averages 75 meters. It is situated in a ≤ 5 km thick sedimentary basin containing Lower Cretasic to Quaternary sediments. The Quaternary surficial sediments are mainly beach sands which disconformably overlie Eocene strata (Helenes, 1984). To the east, the bay is delimited by the peninsular batholith, the Vizcaíno Desert and volcanic rocks belonging to the Comondú Group. To the south are the Pleistocene marine terraces, which extent towards Punta Eugenia and to the west the Tertiary ophiolitic complexes of Cedros Island (Ranging *et al.,* 1983; Ortlieb, 1991). El Vizcaíno biosphere reserve is located south of 28°N and delimited to a great extent by Vizcaíno Bay. Submarine phosphorites have been reported to occur in relatively shallow waters (<100 m) proximal to Punta Santa Rosaliita to the NE of the bay (Daesslé and Carriquiry, 1998), on Ranger Bank (Emery, 1948) and some 18 km SW of Cedros Island (McComas and Neel, 1967 in Garrand, 1977). Faulting across the most recent strata and a major slide scar to the west of the bay have been described by Normark (1990). The sediments are mainly composed of calcareous particles (shell fragments and foraminifers), terrigenous particles (quartz, rock fragments, and some clay sized material), organic matter and, in some samples from the eastern sector of the bay, francolite pellets, nodules and bone fragments (*cf.* Daesslé and Carriquiry, 1998).

Seven water "sources" have been suggested to affect Vizcaíno Bay (Reid *et al.,* 1958; Wyllie, 1960): (1) the California subsurface current water, (2) upwelled water off the Punta Canoas region (in the north), (3) central bay water, (4) coastal lagoon water, (5) upwelled water at Punta Eugenia (to the south), (6) southern oceanic surface water, and (7) intermediate water (an extension of the Equatorial Pacific Water; Figure 1). An anticyclonic gyre develops in the centre of the bay (c. 28°15′ N; Wyllie, 1960). It is responsible for the transfer of cold water from the upwelling zone off Punta Baja (some 40 km NW of Punta Canoas), southwards along the coast (Dawson, 1952; Mancilla-Peraza *et al.,* 1993). During strong northwesterly winds, the cold upwelled waters may extend as far as southern Cedros Island (Amador-Buenrostro *et al.,* 1995). In addition, warm water from the lagoons to the SE flow northward, becoming part of the anticyclonic circulation pattern in the area (Emery *et al.,* 1957). Except for Guerrero Negro, no major populated areas are located along the Vizcaíno coastline, thus the bay remains relatively unaffected by anthropogenic metal pollution.

METHODS

Thirty-seven surficial sediment samples were collected using a Van Veen grab in Vizcaíno Bay on board the R/V Alejandro de Humboldt cruises in 1991/92 (Figure 1; Table 1). The samples were kept frozen prior to drying, grinding and analysis. Organic carbon and biogenic carbonate were determined after loss by ignition (Biggs, 1970; Dean, 1974), at temperatures of 450°C for organic carbon and subsequently 1000°C for calcite. Phosphate content was determined using the volumetric method (Vogel, 1962). Replicate analysis for the above methods indicate an overall precision ±10% or better. Analytical bias (< ±5%) for P_2O_5 analysis was checked by analysing phosphorite currently mined in San Juan de la Costa, Baja California Sur.

Table 1. *Location, depth, mean grain size and textural description of surficial sediments from Vizcaíno Bay, Baja California.*

Sample I.D.*	Latitude (°N)	Longitude (°W)	Depth (m)	Grain size mean (ϕ)	Textural description
1 (H91-1)	29°01.7′	114°42′	68	3.4	Moderately well sorted fine sand
2 (H91-8)	28°50.3′	114°35′	78	3.7	Poorly sorted fine sand
3 (H91-9)	28°39.1′	114°22.3′	70	0.2	Poorly sorted coarse sand
4	28°38.15′	114°18′	60	3.7	Poorly sorted fine sand
5	28°32′	114°10.2′	29	3.1	Poorly sorted medium sand
6	28°13.92′	114°16.69′	25	2.7	Moderately well sorted medium sand
7	28°12.9′	114°13.3′	45	1.5	Moderately well sorted coarse sand
8 (H91-21)	28°18.91′	114°23′	80	3.6	Very poorly sorted fine sand
9 (H91-22)	28°45.57′	114°39.7′	85	3.5	Poorly sorted fine sand
10 (H91-2)	28°56.1′	114°51.4	186	3.0	Moderately sorted medium sand
11	28°49.7′	115°0.1′	115	4.9	Very poorly sorted sandy silt
12 (H91-7)	28°39.9′	114°47′	105	3.8	Very poorly sorted fine sand
13 (H91-24)	28°26.6′	114°37.7′	100	4.1	Poorly sorted sandy silt
14	28°14′	114°29.9′	85	4.1	Poorly sorted sandy silt
15 (H91-18)	28°01.3′	114°22.2′	30	2.8	Moderately well sorted sand
16	27°56.7′	114°39.2′	28	5.2	Very poorly sorted silt
17 (H91-23)	28°09′	114°40.9′	81	3.1	Well sorted medium sand
18 (H91-25)	28°18′	114°51.5′	106	3.4	Poorly sorted fine sand
19 (H91-6)	28°29.9′	114°58′	127	4.4	Poorly sorted silt
20 (H91-3)	28°41′	115°11.9′	180	4.2	Poorly sorted silt
21 (H91-4)	28°27.8′	115°21.9′	244	5.1	Poorly sorted silt
22	28°03.4′	114°55′	79	4.2	Poorly sorted silt
23 (H91-16)	27°59.3′	114°47′	70	3.1	Very poorly sorted medium sand
24 (H91-15)	27°54′	114°54′	51	2.3	Very poorly sorted medium sand
25 (H91-14)	27°58.8′	114°57.5′	65	3.7	Very poorly sorted fine sand
26 (H91-13)	28°04.2′	115°01.0′	76	3.3	Very poorly sorted fine sand
27 (H91-12)	28°08.9′	115°05.2′	81	4.4	Very poorly sorted silt
28	27°59.2′	115°12′	27	0.5	Poorly sorted coarse sand
29	27°59.9′	115°25.2′	82	2.2	Poorly sorted medium sand
30	28°06.7′	115°29.4′	83	1.8	Poorly sorted medium sand
31	28°15.88′	115°29.9′	275	5.8	Poorly sorted silt
32	28°23.4′	115°25.9′	310	6.0	Poorly sorted silt
33	28°27.06′	115°30.9′	125	1.0	Moderately sorted coarse sand
34	28°31.53′	115°30.14′	130	2.1	Moderately sorted medium sand
35	28°36.04′	115°30.36′	180	1.9	Moderately sorted medium sand
36	29°16.3′	115°15.1′	90	4.6	Very poorly sorted silt
37	29°20.5′	115°11.4′	57	3.0	Poorly sorted medium sand

* I.D. numbers in brackets correspond to those used by Daesslé and Carriquiry (1998)

Bulk metals were extracted from the sediments, after strong acid attack (HNO_3+HCl+HF) and neutralised with 1M HBO_3, according to Loring and Rantala (1992). Partition analyses (including Cd) where carried out after Tessier *et al.* (1979). The method was modified and simplified to group the three first most reactive geochemical fractions of the sediments in a single leach. Fraction 1: metals exchangeable or loosely adsorbed, bound to carbonates, and bound to iron and manganese oxides, extracted at 96 °C for 6 h with 0.04M $NH_2OH.HCl$ in 25% (v/v) HOAc (referred to as A/C/O). Fraction 2: bound to organic matter and sulphides, extracted at 85 °C for 5 h with 30% H_2O_2 adjusted to pH 2 with HNO_3 and then at room temperature with 3.2M NH_4Oac in 20% HNO_3. Fraction 3: the residue remaining after dissolution of fractions 1 and 2, was leached following the procedure used for the bulk metal analysis, and referred to as detrital or lithogenic fraction. The metals were quantified with a Thermo Jarrell Ash (TJA) atomic absorption spectrophotometer, model Smith-Hiefftje 12. An air-acetylene flame was used for Fe, Zn, Mn, Cu and Ni, and nitrous oxide-acetylene flame for Al and Cr, in the bulk and detrital fraction. Except for Fe, Mn and Al, a TJA graphite furnace, model CTF 188, with a Smith-Hiefftje background correction and TJA FASTAC II deposition module was used to analyse the metals in fractions 1 and 2. With each set of 12 samples, a procedural blank and a reference material MESS-1 (marine sediment from the Canadian National Research Council) was used as analytical control. The analytical precision determined was better than ±5%. When comparing the sum of the separate fraction with the bulk results, these agree within ±8%. The discrepancies between the sum of the fractions and the bulk result concentrations are inherent to the precision of the analyses of each individual fraction, especially at low element concentration.

RESULTS

Sediment Distribution

The sediments from Vizcaíno Bay are mainly poorly to very poorly sorted, green coloured, fine sands and sandy silts (Table 1). Overall, the mean grain size decreases offshore towards deeper waters in the west. Coarsest sediments are found adjacent to Punta Santa Rosaliita due to the presence of gravel sized lithogenic (andesite pebbles), authigenic phosphorite nodules and biogenic (bone fragments) material, and to the south of Cedros Island due to the presence of in situ (sediment attached) calcareous algae fragments. The high abundance of calcareous algae in the straits south of Cedros Island is also described by EMERY *et al.* (1957). Relatively coarse material comprising foraminifer-rich coarse sands is also found on Ranger Bank, indicating that reworking of the sediments on this bathymetric low recently took place during sea-level low stand periods (*cf.* EMERY, 1948). No phosphorite was found in the present study on Ranger Bank (as described by EMERY, 1948), suggesting a patchy distribution for it in that area.

The finest sediments (based on their mean size) were found in a topographic low (down to 310 m depth) to the NW of Cedros Island (samples 21, 31 and 32), where the input of coarse material may be restricted. These samples, in addition to other samples mainly located within the bay (11, 13, 14, 16, 19, 20, 22, 27 and 36), are formed of silts and sandy silts.

Sediment Geochemistry

The concentration of P_2O_5 in the bay shows a sharp decreasing gradient off Adelaida Island–Punta Santa Rosaliita towards the SW of the bay (Figure 2A). The high concentrations of P_2O_5 (≤ 22 % wt.; Table 2) are controlled by a few samples rich in phosphatic nodules, pellets and bone fragments (cf. DAESSLÉ and CARRIQUIRY, 1998). Unlike previous reports on phosphorites on Ranger Bank (EMERY, 1948; NORMARK et al., 1987), we found P_2O_5 concentrations to be low in that area. Biogenic carbonate however, which in the study area ranges 0.9–37 %, is enriched in the three sediment samples collected on Ranger Bank (samples 33, 34 and 35), where moderately medium to coarse sands are dominant. Calcium carbonate there is mainly present as foraminifer sand and shell fragments (Figure 2B). The concentrations of organic carbon in the bay range between 0.8 and 15.1 % and are highest in a silt sample located in a bathymetric low (310 m deep) NW of Cedros Island (Figure 2C). In addition, relatively high organic carbon and carbonate concentrations are found in a NW–SE trending area along the eastern sector of the bay (*cf.* EMERY *et al.* 1957). No correlation is seen between the regional distribution of P_2O_5 and carbonate or organic carbon.

Of the metals studied (Table 2; Figures 2D–F, 3A–F) Al and Fe are the main sediment constituents, ranging 1.99–5.32% and 0.6–4.13% respectively. Highest Al concentrations (are found in a deep silt sample (sample 21; c. 244 m depth) located east of Ranger Bank, as well as in two coarser sediment samples: sample 13 located in the central bay, formed of sandy silt, and sample 28 formed of coarse sand at only 27 m depth south of Cedros Island. While in samples 13 and 21 the enrichment in Al could probably be explained by a higher abundance of clay minerals present in this sample, the enrichment in Al in coarse sample 28 is more difficult to explain. This sample is also anomalously enriched in Fe (4.13%) and Mn (572 ppm). The coarseness of sample 28 (at only 27 m depth) is attributed to the presence of calcareous algae, which in turn are responsible for the high carbonate content of the sample (21.4%).

In the central bay, sample 13 is not only enriched in Al (4.39%) but also has high Fe (3.68%), Zn (84 ppm) and, to a lesser extent, Cu (21 ppm) concentrations. The high concentrations of these metals in sample 13 led to a distinctive enrichment pattern of these elements in the central bay. However, and unlike Fe and Zn, the relatively high Cu concentrations in the central bay may not only be associated with the presence of the "anomalous" sample 13, but also to the organic-rich samples adjacent to the eastern coast. It is possible that Al, Fe and Zn in this sample are associated to the composition and abundance of clay minerals. However, detailed mineralogical analyses will be required to assess this possibility.

Overall, Mn shows a decreasing gradient from the NE coast (up to 571 ppm, between Punta Blanco and Santa Rosaliita) towards the centre of the bay. The concentrations of Mn are lowest where Sr is most abundant: 80 ppm off the lagoons north of Guerrero Negro (sample 7) and in two samples from Ranger Bank (58 and 71 ppm in samples 34 and 35 respectively), where like Sr, calcium carbonate is most abundant. The highest Zn, Cu, Cr and Ni concentrations in the study area are also found on, or adjacent to Ranger Bank (Figures 3 A–D). In this zone the concentration of Zn ($\sim$130 ppm), as well as Fe ($\sim$ 3.6%) and Sr ($\sim$ 2000 ppm) are highest in the samples to the north of the bank (34 and 35). Nickel, Cu and Cr however, are more enriched on southern Ranger Bank (sample 33) as well as in the deeper "silty" sample 32 south it. In these samples Ni, Cu and Cr concentrations are 83–85 ppm, 43–44 ppm and 328–346 ppm respectively.

Cadmium concentration in Vizcaíno Bay are high (0.23–4.28 ppm; based on the sum of fractions), compared with average shale values (Cd = 0.3 ppm; TUREKIAN AND WEDEPOHL, 1961), or with sediments from the California continental margin at about 100 m depth (0.17–0.28 ppm; HCl leach data by VAN GEEN *et al.,* 1995). Although published data on Cd in sediments underneath coastal upwelling zones is scarce, the upper range values for Cd in Vizcaíno Bay are below the range of 10–15 μg/g Cd found off the southern borderlands of Baja California (ALEXANDER VAN GEEN, *pers. comm.,* 1999). The regional distribution of Cd in the bay is unlike that of any other element described in the present work, with highest Cd concentrations found off Punta Canoas (4.09 ppm in sample 37) and toward the SE of this area (4.28 ppm in sample 8).

From the bivariate correlation matrix in Table 3, it can be seen that at $\alpha = 0.001$ a significant positive correlation exists for organic carbon/Zn, Ni, Cu and Cr, as well as for Fe/ Cu and Zn. Neither the grain size, carbonate, P_2O_5, Al, Sr or Cd contents correlate significantly with any other sediment component studied. Bivariate plots of all the elements studied confirm these significant correlations, which are shown in Figure 4 A–F. For statistical correlation purposes, the "anomalous" samples from Ranger Bank (33, 34 and 35) are discussed separately due to their distinctive composition compared to the remainder of the samples.

Metal Partitioning

In order to further assess the element associations and their partitioning between the different sediment components, three separate sediment fractions were analysed geo-

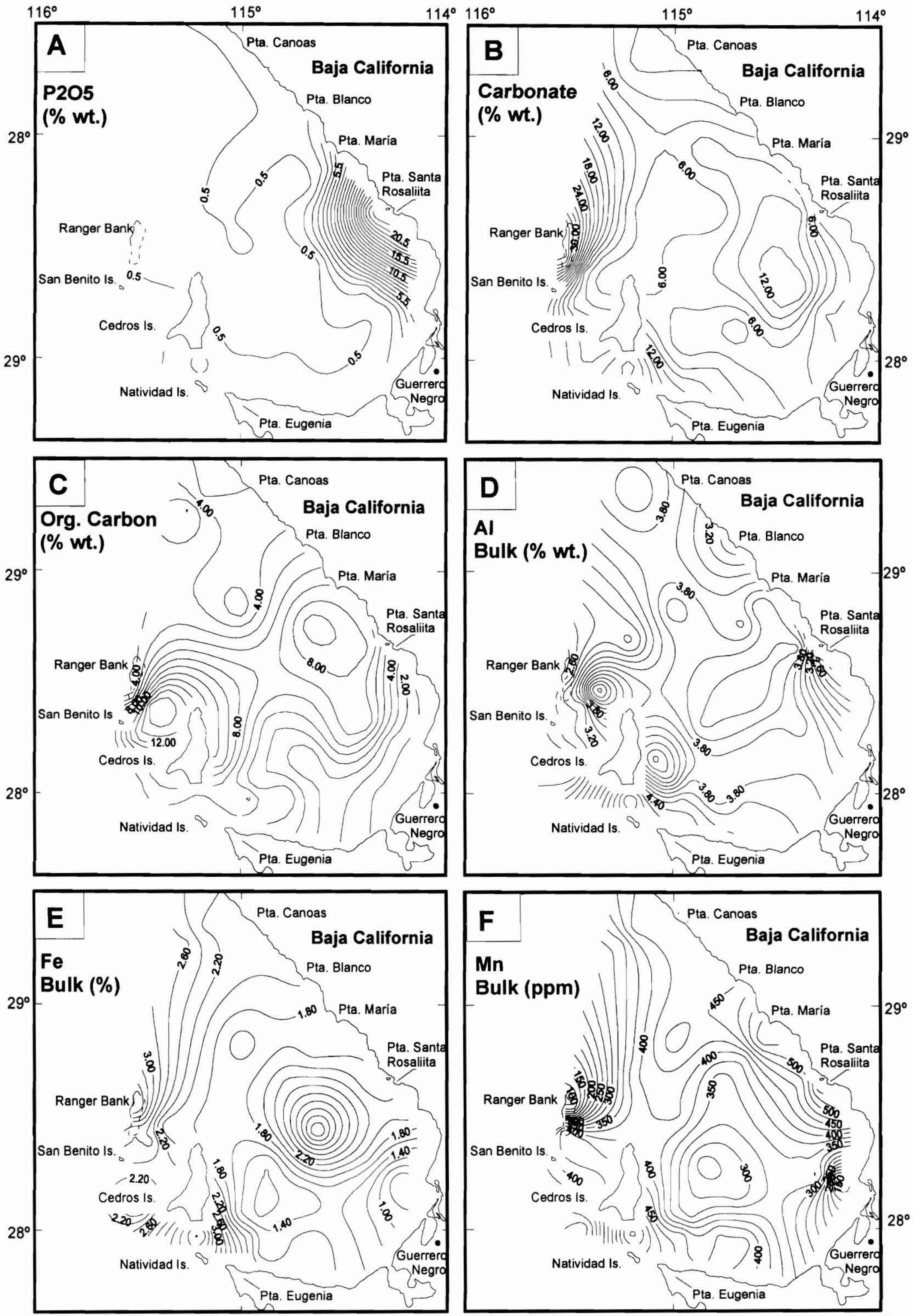

Figure 2. Regional distribution in % wt. of (A) P_2O_5, (B) carbonate (LOI 1000°C), (C) organic matter (LOI 450°C), (D) Al, (E) Fe and (F) Mn (ppm) in surficial sediments from Vizcaíno Bay.

Table 2. *Organic carbon, carbonate, phosphate, and bulk metal concentrations in surficial sediments from Vizcaíno Bay.*

Sample	C-org (%)	CO_3 (%)	P_2O_5 (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Ni (ppm)	Cu (ppm)	Cr (ppm)	Sr (ppm)	Cd* (ppm)
1	4.5	3.2	1.0	2.09	2.76	437	40	16	10	67	450	1.21
2	8.3	9.2	2.2	1.61	4.24	542	42	22	14	84	639	2.49
3	8.1	10.9	21.7	1.84	4.19	463	46	22	13	81	665	2.48
4	5.1	0.9	22.3	1.85	1.99	571	44	18	10	80	776	1.20
5	0.8	0.9	21.9	2.17	2.11	532	43	17	11	72	845	1.43
6	1.8	1.8	1.4	0.83	3.65	343	21	5	2	43	1725	0.50
7	1.2	2.1	3.1	0.60	3.42	80	10	5	1	27	1601	0.56
8	8	14.1	2.1	1.83	3.92	347	58	25	20	94	766	4.28
9	9.8	9.1	0.5	1.80	3.51	383	58	30	22	101	883	3.32
10	4.6	9.9	0.9	1.80	3.58	450	39	20	11	61	936	2.80
11	2.2	4.1	0.8	1.46	4.18	465	28	14	6	59	1196	2.03
12	7.3	4.2	0.5	2.20	3.9	338	59	30	17	84	693	2.56
13	6.4	11.5	0.2	3.68	4.39	340	84	17	21	89	617	1.11
14	6.7	11.9	1.2	1.62	3.55	338	41	20	15	65	1204	1.96
15	1.2	4.3	0.7	1.25	3.89	279	24	4	3	35	764	0.29
16	3.3	6.2	0.5	1.75	4.05	433	32	12	5	61	871	0.23
17	1.6	2.1	0.4	1.25	3.68	287	30	21	9	60	924	0.55
18	4.2	7.5	0.2	1.22	4.24	262	28	20	9	53	794	0.37
19	7.6	7.1	0.6	1.76	3.91	403	50	26	16	83	799	0.74
20	5.9	6.1	0.5	1.92	2.69	387	52	24	17	95	837	0.58
21	13.4	8.7	0.2	1.81	5.32	352	36	30	13	78	840	0.54
22	3.8	5.1	0.3	1.19	3.8	317	24	15	7	49	857	0.44
23	6.2	7.7	0.6	1.55	3.6	423	36	19	10	69	868	0.44
24	5.2	10.8	0.6	1.48	4.4	412	34	21	10	49	777	0.43
25	7.3	7.3	0.7	1.89	4.19	433	40	24	15	95	711	1.07
26	5.8	6.3	0.1	1.50	2.86	351	34	25	13	78	701	0.94
27	9.9	7.8	0.3	2.07	2.48	420	51	47	21	100	786	1.14
28	5.7	21.4	1.8	4.13	5.23	572	93	18	29	46	723	0.23
29	6.5	15.3	0.2	2.89	3.4	281	49	28	14	80	1427	0.47
30	6	17.4	0.1	1.63	2.27	343	57	42	15	92	1518	0.49
31	12.9	9.7	1.5	2.29	2.95	406	75	85	33	122	882	1.04
32	15.1	8.5	0.1	2.65	3.06	434	98	85	44	346	847	1.62
33	3.2	36.9	0.1	2.64	3.09	442	97	83	43	328	902	1.41
34	4.1	33.8	0.2	3.61	2.52	58	130	41	31	201	1982	0.29
35	3.7	35.1	0.4	3.60	2.27	71	134	32	28	203	2151	0.32
36	6.2	3.8	0.1	2.62	3.9	337	51	23	11	132	673	4.09
37	2.7	1.4	0.1	2.18	4.24	435	40	18	7	86	549	1.20

* Calculated on the sum of Cd in the geochemical fractions analysed.

chemically: (1) loosely adsorbed phases, calcium carbonates, Fe-Mn oxihydroxides (A/C/O), (2) organic matter and sulphides, and (3) lithogenic detritus. Except for Sr and Cd, in average, all the elements studied are mainly partitioned in the lithogenic fraction (c. 62–97 %), with only relatively minor proportions in the organic/sulphide (c. 2–24 %) and A/C/O (c. 1–11 %) fractions (Table 4; Figure 5). The geochemical partitioning of metals indicates their primary association with the detrital lithogenic component of the sediments. However, significant proportions of Cr, Cu, Ni and Cd are also associated with the organic matter/sulphide fraction (c. 15–27%), and about 67–72 % of Cd and Sr is associated with the A/C/O fraction.

The geochemical study of metals in the "labile" fractions of the sediment is important when assessing the more reactive, non-lithogenic, metal associations in them. This information in turn, is useful when searching for underlying relationships between sediment composition and any recently active geochemical and/or oceanographic processes taking place in the area. The association between Cr, Cu, Ni and Cd with organic rich sediments, becomes evident from the regional distribution of these metals in the organic fraction, especially in the eastern sector of the bay (Figures 6A–D). Since these surficial sediments are not anoxic, any sulphide metal contribution to this fraction is expected to be relatively minor.

The regional distribution of Cd and Sr in the A/C/O fraction is shown in Figures 6E and 6F. Similar Sr concentrations to those found in Vizcaíno Bay (mean Sr = 951) have been reported for the Namibian Shelf (Sr = 255–2410 ppm; CALVERT and PRICE, 1983). The enrichment of Sr in the A/C/O fraction of sediments from Ranger Bank is in good agreement with the high carbonate concentrations there, and is explained by Sr^{2+} in the marine environment substituting for Ca^{2+} in the $CaCO_3$ mineral lattice. The high concentration of Sr in the samples adjacent to the lagoons in the SE coast however, cannot solely be explained by the mechanism described above, especially since relatively low calcium carbonate concentrations are found in this area, and no correlation exists between these two components. A distinguishing feature of Cd in the A/C/O fraction, is its decreasing pattern from a point of maximum concentration (sample 37) off Punta Canoas, southeastwards proximal to the coast. High Cd concentrations are found in sediments lying under the upwelling region described by AMADOR-BUENROSTRO *et al.* (1995).

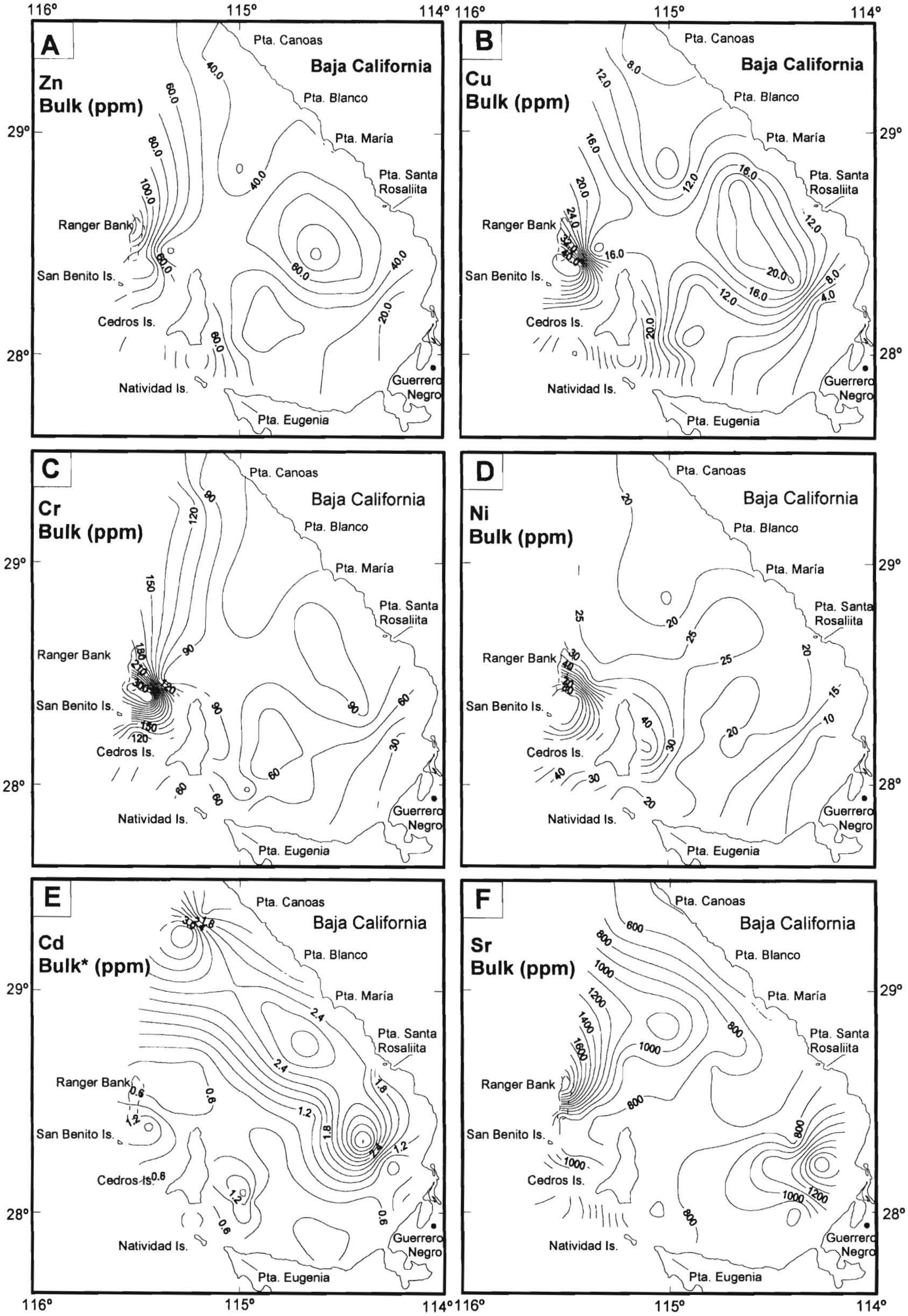

Figure 3. Regional distribution in ppm of bulk (A) Zn, (B) Cu, (C) Cr, (D) Ni, (E) Cd and (F) Sr in surficial sediments from Vizcaíno Bay. (*For Cd the sum of the three separate fractions is considered).

Table 3. *Bivariate statistical correlation for bulk geochemical data and mean grain size of sediments from Vizcano Bay, Baja California (n = 34, excluding samples from Ranger Bank). Values ≥0.55 (bold) are statistically significant at α = 0.001.*

	Mean (ϕ)	C org.	CO_3	P_2O_5	Fe	Al	Mn	Zn	Ni	Cu	Cr	Sr
C org.	**0.57**											
CO_3	−0.15	0.43										
P_2O_5	−0.03	−0.14	−0.21									
Fe	−0.02	0.35	0.50	0.01								
Al	−0.05	0.06	0.28	−0.34	0.16							
Mn	0.25	0.18	0.12	0.43	0.41	−0.06						
Zn	0.17	**0.63**	**0.56**	−0.03	**0.84**	−0.01	0.38					
Ni	0.44	**0.80**	0.28	−0.13	0.30	−0.28	0.13	**0.65**				
Cu	0.33	**0.80**	0.51	−0.10	**0.63**	−0.08	0.30	**0.91**	**0.84**			
Cr	0.47	**0.67**	0.09	−0.06	0.35	−0.22	0.18	**0.64**	**0.78**	**0.76**		
Sr	−0.42	−0.24	0.07	−0.10	−0.38	−0.20	−0.46	−0.30	−0.08	−0.25	−0.17	
Cd	0.47	0.26	0.03	0.13	0.12	0.01	0.50	0.22	0.10	0.20	0.27	−0.24

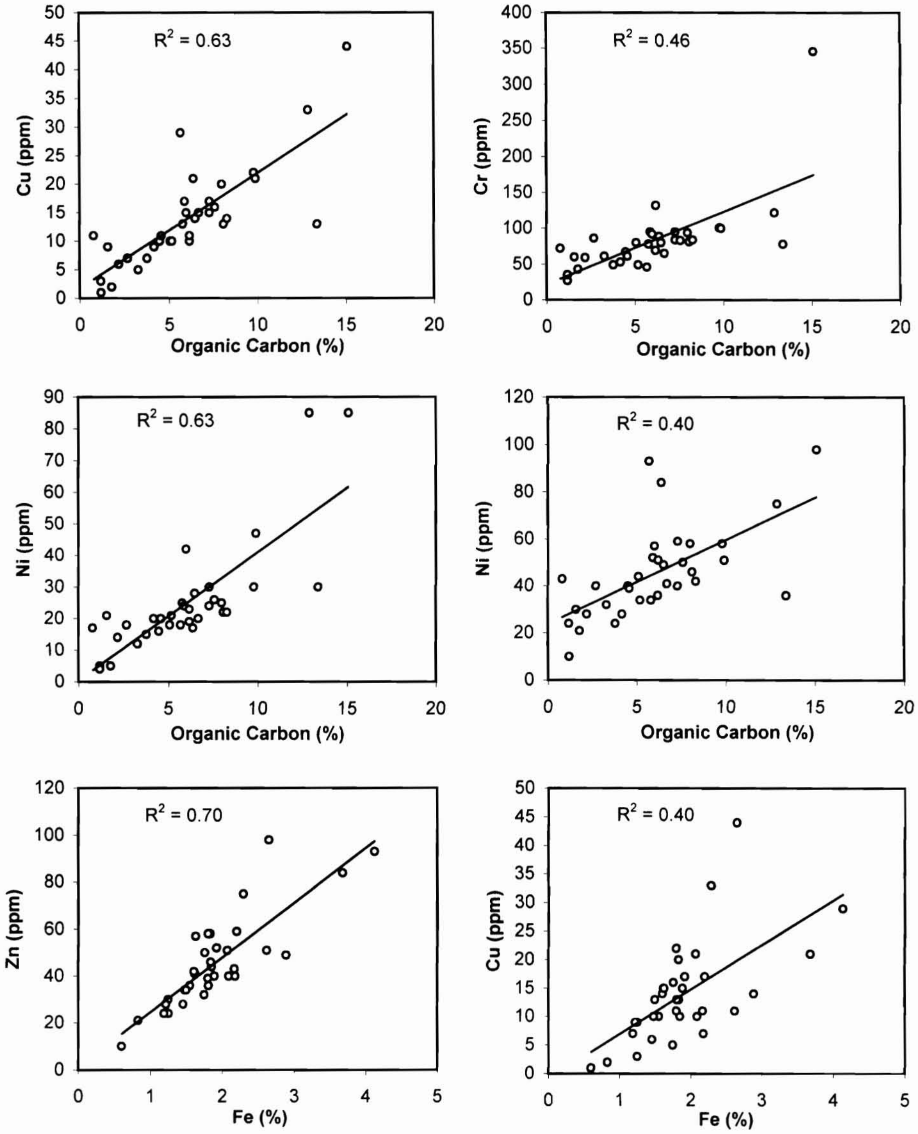

Figure 4. Bivariate plots for organic carbon vs. bulk (A) Cu, (B) Cr, (C) Ni and (D) Zn, and for bulk Fe vs. (E) Zn and (F) Cu, in surficial sediments from Vizcaíno Bay, excluding three outlying samples from Ranger Bank.

Table 4. *Average concentrations and ranges of major components and metals in surficial sediments from Vizcaíno Bay (n = 37), and relative percentages of these concentrations in three operational geochemical sediment fractions: (1) loosely adsorbed phases, carbonates, and Fe-Mn oxihydroxides (A/C/O), (2) organic matter and sulphides, and (3) detrital material.*

			Geochemical partitioning					
Bulk element concentrations			% Detrital		% Organic/sulphide associated		%A/C/O	
Element	Mean	Range	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
C-org. (%)	5.8	0.8–15.1						
CO_3 (%)	9.8	0.9–36.9						
P_2O_5 (%)	2.4	0.1–22.3						
Al (%)	93.55	1.99–5.32	97.3	1.2	1.5	0.8	1.2	0.5
Fe (%)	92.0	0.6–4.13	91.4	4.2	2.9	1.1	5.8	3.8
Mn (ppm)	372	58–572	91.3	8.2	2.1	1.2	6.7	7.5
Zn (ppm)	52	10–134	83.8	5.3	5.9	3.1	10.3	3.6
Cr (ppm)	96	27–346	73.2	7.3	15.4	5.7	11.5	3.2
Cu (ppm)	16	1–44	74.7	7.7	18.2	8.0	7.1	6.8
Ni (ppm)	27	4–85	62.0	14.1	24.1	10.8	13.9	7.7
Sr (ppm)	951	450–2151	23.7	8.1	9.3	6.1	67.0	9.5
Cd (ppm)	91.27*	0.23–4.28*	1.6	4.3	26.7	15.9	71.8	17.7

* Calculated as the sum of Cd in the geochemical fractions analysed.

DISCUSSION

Regional Sediment Geochemistry

From the regional distribution and element partitioning of the sediments from Vizcaíno Bay, a relationship between the various sedimentary and oceanographic influences on the sediment geochemistry can be observed. The distribution of P_2O_5 is unlike that for any other element studied in the area and is not correlated with any other geochemical variable studied. The sediment samples controlling this distribution are confined to a relatively shallow area adjacent to Isla Adelaida–Santa Rosaliita. The phosphatic particles in these sediments (authigenic pellets, nodules and bone fragments) may have either been redeposited via the nearby riverbeds, or belong to an unconformable Miocene (?) unit (*cf.* DAESSLÉ and CARRIQUIRY, 1998). The latter possibility is preferred, since no phosphorite particles have yet been identified by the authors along the coastline adjacent to Santa Rosaliita nor were reported by FIFE (1974) during a geological reconnaissance study in the onshore area.

The overall distribution of organic carbon appears to be controlled by depth, fine grain size and possibly also a lower dilution by the terrigenous sediment component. This is especially evident from its high concentrations in deep samples NW of Cedros Island. Carbonate concentrations however, are highest on relatively shallower sediments on Ranger Bank, where foraminifer rich sands are found. Both organic carbon and carbonates are also enriched in an area adjacent to the eastern coast, where enrichments of Cu, Ni, Cr, Cd and, to a lesser extent Zn, are found. As described below, the enrich-

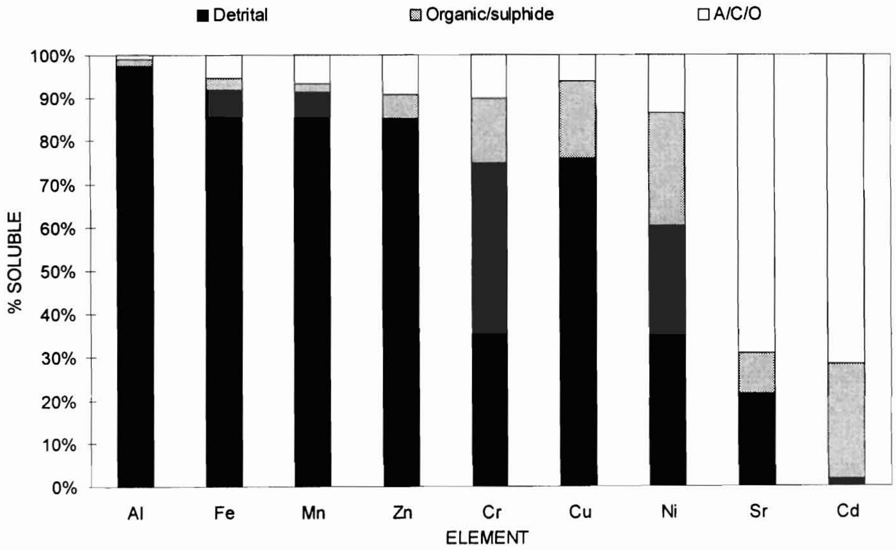

Figure 5. Average geochemical partitioning of metals in the sediments from Vizcaíno Bay associated to: (1) loosely adsorbed phases, carbonates and/or amorphous Fe-Mn oxihydroxides (A/C/O), (2) organic matter and sulphide minerals (organic/sulphide) and (3) detrital or lithogenic material.

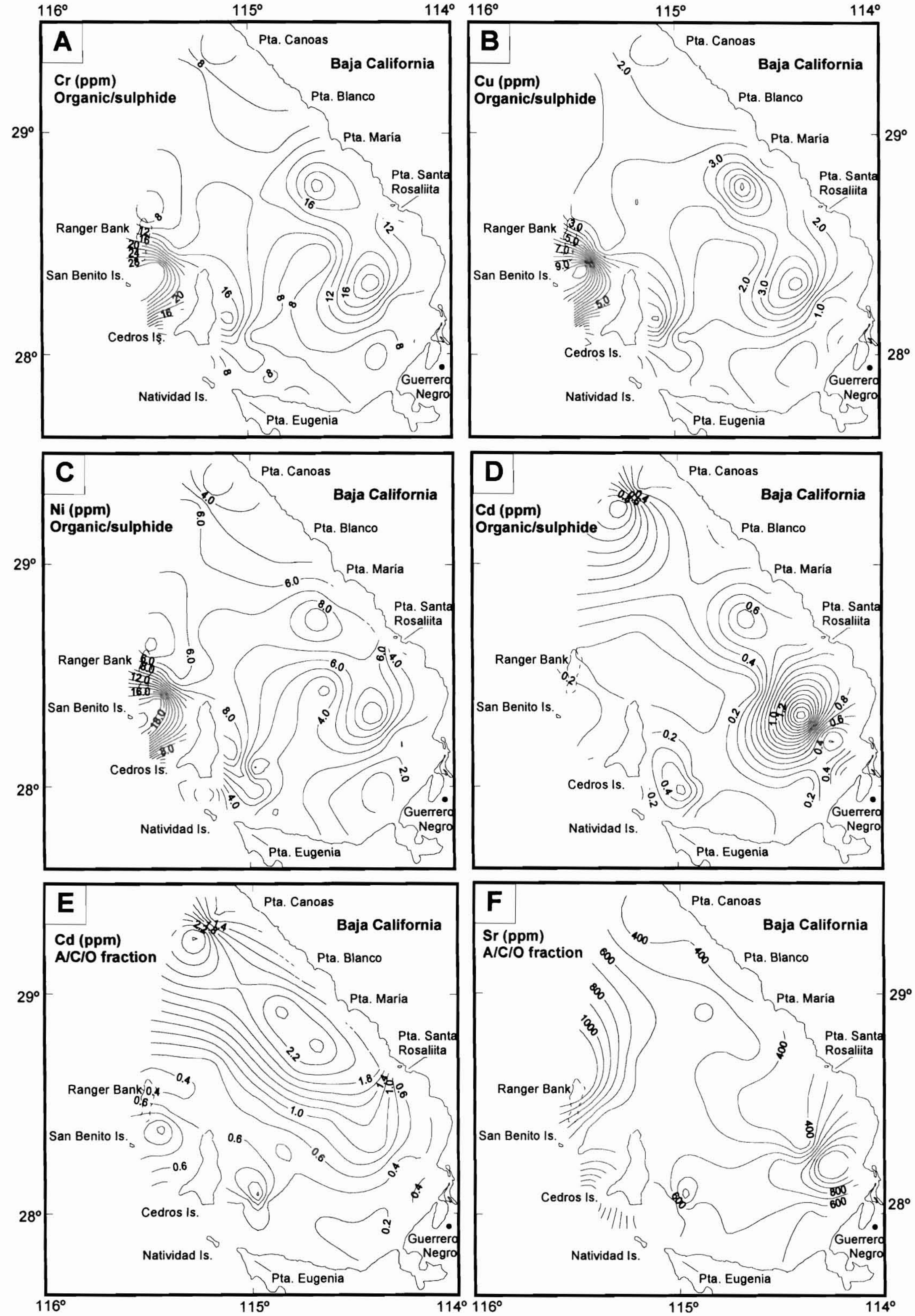

Figure 6. Regional distribution in ppm of (A) Cr, (B) Cu, (C) Ni and (D) Cd in the organic/sulphide fraction, and (E) Cd and (F) Sr in the loosely adsorbed phases, carbonates and/or amorphous Fe-Mn oxihydroxides (A/C/O) fraction of surficial sediments from Vizcaíno Bay.

ment of these elements in shallow sediments is associated with the influence of upwelled waters some 100 km to the north (AMADOR-BUENROSTRO *et al.,* 1995).

The regional distribution pattern of bulk Al and Fe in the area can, at least in part, be explained by the dissolution (by the strong acid attack used) of clay minerals and other Al–Fe rich lithogenic material in the sediments. However, the enrichment of these and other metals in the lithogenic fraction of coarser samples, probably indicates the presence of distinct lithologies in the bay, associated with Ranger Bank, the straits south of Cedros Island and one sample in the central bay. The sediments on and/or adjacent to Ranger Bank have the highest carbonate, Zn, Ni, Cu, Cr and Sr, and amongst the highest Fe concentrations recorded for the study area. Manganese concentrations however, are lowest in two samples from the bank (34 and 35). Except for Sr (associated with the A/C/O fraction), all these metals in sediments from the northern and central bank are mainly partitioned in the detrital fraction (82–97%), and have only a low proportion in the organic/sulphide fraction (0.4–12%). A different element association is seen for the southern bank and in the bathymetric deep south of it (samples 32 and 33). While still relatively enriched in the detrital fraction of these samples (61–82% of Cu, Zn, Ni and Cr is detrital), a transition towards a more significant organo-metallic association is seen in deeper areas. In these sediments about 25–27% Cu, 24–28% Ni, 22% Cr and 10% Zn are partitioned in the organic/sulphide fraction. Thus it is suggested that, although a significant detrital influence derived from Ranger Bank is found in sediments south of it, an organic source of Cu, Cr, Ni and Zn becomes increasingly significant. Although glauconite in some sediment samples on Ranger Bank forms about 13.5% (*cf.* EMERY *et al.,* 1957), the lack of any anomalous Al enrichment parallel to Fe in these sediments makes it unlikely that galuconite is the mineral phase responsible for these metal enrichments. Thus it is more likely that heavy detrital minerals (forming about 1.4% of the sediments) associated to the rhyolitic to basaltic rocks found in the area (*cf.* EMERY *et al.,* 1957), contribute to a metal enrichment.

Lithogenic Mn is enriched directly adjacent to the NE coast off Punta Santa María and Santa Rosaliita and decreases towards deeper waters. This enrichment is unlike any other described and signals the influence of the terrigenous material derived from the mainland, possibly from the erosion of the nearby batholith. No association with the phosphorites in that area is likely, since any Mn associated to the carbonate fluor-apatite mineral, either as a coating or as part of the mineral lattice, would form part of the more reactive, non-lithogenic fractions. Anomalously high Mn concentrations are also seen for sample 28, at 27 m depth south of Cedros Island. This carbonate-rich sample has the highest Fe, Al and Mn concentrations in the entire area. However, while Al and Fe are mainly detrital, about 45% of Mn is associated with the A/C/O fraction. The coarse grain size of this sample make any adsorption of Mn due to a higher surface/mass ratio in the finer sediments unlikely. It is possible that a Mn carbonate such as rhodocrosite ($MnCO_3$, the end-member of a transformation series towards manganese micronodules; BORELLA and ADELSECK, 1979), or an hydrogenic Mn oxide phase is responsible for the enrichment of Mn in this sample. No Mn micronodules however, could be seen under the microscope in sample 28.

Upwellings, Organic Matter and Metal Distribution

The regional distribution of Cr, Cu, Ni, Cd and, to a lesser extent Zn, in the sediments adjacent to the eastern coast of Vizcaíno Bay is associated with the distribution of organic matter in that area. The contours drawn for Cr, Cu, Ni and Cd in the organic/sulphide sediment faction in the bay closely resemble those for organic carbon, in that high concentrations are found off the eastern coast of the bay. The contours for Cd in the A/C/O fraction (were it is mainly partitioned) however, show highest concentrations further north (off Punta Canoas), although relatively high concentrations of this element in the A/C/O fraction are found along the organic/sulphide Cu-Cr-Ni-Cd rich area (Figure 6A–E). The contours for these metals are strikingly similar to the southward pattern of a cold surface water plume derived from a zone of intense seasonal upwelling, some 40 km to the NW of Punta Canoas, as identified by infrared satellite imagery (AMADOR-BUENROSTRO *et al.,* 1995). This similarity suggests an association between metal enrichment in the area and the nutrients and/or enhanced primary productivity in the water column. From the geochemical data available, it can be seen however, that Cd in the A/C/O fraction has high concentrations relatively close to the upwelling area, with a decreasing trend southward as the cold water plume progresses. Except for a slight enrichment in Cd in the organic/sulphide fraction, Cu, Cr and Ni are not enriched in this fraction proximal to the upwelling area but some 100 km or more SE of it, below the plume described by AMADOR-BUENROSTRO *et al.* (1995). Both, the upwellings and the south-eastward flow of the upwelled waters are controlled by the varying intensity of northwesterly winds (MANCILLA-PERAZA *et al.,* 1993; AMADOR-BUENROSTRO *et al.,* 1995).

Primary productivity in eastern Vizcaíno Bay is triggered by the nutrient rich waters flowing SE of the area of intense upwelling. According to BRULAND (1983), it is possible that the bulk of the marine component of particulate Cu and Cd, and probably also Cr, within the modern open ocean is incorporated in organic matter. The role of organic matter in the flux of these metals to the sea floor appears to be even more important in areas of high bioproductivity in shelf-slope environments (COLLIER and EDMOND, 1984). Furthermore, Cd is known to be enriched in surface waters of upwelling regions compared to areas of lower productivity (*cf.* VAN GEEN AND HUSBY, 1996). The contours for non-detrital Cd suggest a precipitation process for this metal that takes place adjacent to the upwelling area as well as south of it, associated with water mass transport by winds. As seen from the contours for Cd, Cu, Cr and Ni, a major flux of Cd towards the sediments appears to occur earlier after deep waters are upwelled, than for Cu, Cr and Ni, which are not enriched directly under the upwelling zone. Relatively lower organic carbon content in the zone of highest Cd concentrations and the preferential association of this element to the A/C/O in the northern bay, suggest a "sink" for Cd being authigenic rather than organic in nature. According to MARTIN and THOMAS (1994) the ocean residence times of Cd in continental margins (0.3–0.9 yr; mostly supplied via upwelling), are much lower than those of Cu, Ni and Zn (0.7–2.7 yr). Thus the relatively short residence time of Cd in the area could, in part, be reflected by an earlier removal of this element from the water column closer to the upwelling zone. However, high Cd concentrations bound to the organic/sulphide fraction of the sediment are also seen in the eastern–organic rich sector of the bay. Studies on the temporal variation of the metals described in the present work, especially those associated to the reactive fractions of the sediments influenced by coastal upwelling in the area, may lead to important information on the paleoceanographic evolution of this upwelling system.

Metals in the Phosphorites from Vizcaíno Bay

Three phosphorite samples (sediments with $P_2O_5 > 18\%$; BENTOR, 1980) were located at around 10 km to the west of the main coastline proximal to Adelaida Island–Punta Santa Rosaliita (Figure 2C). Phosphate (P_2O_5) concentrations in these samples (3, 4 and 5) are c. 22 % (Table 2), and are within the range for the on-land Upper Oligocene phosphorites in Baja California Sur (PIPER, 1991). When compared to the on-land phosphorites from Baja California Sur, it can be seen that bulk Al, Fe, Cr and Cd in the Vizcaíno phosphorites are close to, or below the lower range values for the on-land deposits. The concentration of Mn and Cu however, fit well with the ranges reported by PIPER, 1991. Phosphorites are generally enriched in Cd, Zn, Ag, La and other elements, compared to average shale (ALTSCHULER, 1980). However, the enrichment of these metals in phosphorites is not necessarily associated with their presence in the francolite mineral lattice, but probably to other sediment phases, such as organic matter, Fe-Mn oxihydroxides or be adsorbed (*cf.* JARVIS *et al.*, 1994). In the present research, no correlation was found between P_2O_5 and any of the metals analysed. This suggests that other sediment components (*e.g.*, organic matter and lithogenic detritus) in the phosphate rich samples play a more important role than the apatite minerals in the precipitation of metals into the sediments of the area. The phosphorites from Vizcaíno Bay however, appear to be reworked from older sedimentary units (*cf.* DAESSLÉ and CARRIQUIRY, 1998), and their geochemistry may not be associated to recent processes within the bay.

CONCLUSIONS

(1) The P_2O_5 distribution in Vizcaíno Bay shows a sharp decreasing gradient offshore from the Punta Santa Rosaliita–Isla Adelaida area, the highest concentrations being 22.3 %. No association between P_2O_5 and the biogenic components or the metals analysed was found, supporting previous suggestions that the phosphorites in the bay are reworked from older strata.

(2) The biogenic component of the sediments (sum of organic carbon and carbonates) averages 16 % of the sediments studied. Organic carbon is more abundant in deep sediments NW of Cedros Island, and carbonate on Ranger Bank, outside the bay. Both biogenic components are also enriched proximal to the northeastern coast of the Bay, extending south of Punta Blanco. The enrichment in biogenic material in this latter area is associated with cold nutrient rich surface waters driven south from an area of intense upwelling some 40 km NW of Punta Canoas.

(3) The regional variations of Al, Fe, Mn and to a lesser extent Zn, are mainly attributed to the enrichment of these elements in the lithogenic fraction. Lithogenic Mn appears to be preferentially derived from the peninsular mainland to the NE of the bay, while Al is enriched in deep silts adjacent to Ranger Bank. Various metal enriched samples and element associations throughout the bay suggest different lithologies and possibly sources for the detrital component in the area.

(4) High Fe, Cu, Zn, Ni and Cr and low Mn concentrations partitioned mainly in the detrital fraction of the sediments on and adjacent to Ranger Bank, reflect a distinctive lithology in that area, which is unlike that found for the detrital fraction in the NE coast of the bay where Mn becomes more abundant. The geochemical influence of Ranger Bank-derived detritus toward deeper sediments in the south decreases and the organic Cu, Zn, Ni and Cr component becomes more significant.

(5) Copper, Cr, Ni, Cd and partially Zn, vary regionally in a fashion similar to organic matter, suggesting their association with the biogenic component, especially in the area under the influence of upwelled waters along the eastern coast. The regional distribution of Cd in the A/C/O fraction closely resembles the southward flow of the water plume derived from a zone of intense upwelling, this element precipitating early after upwelling, possibly as an authigenic phase.

(6) Strontium is mainly associated with the calcareous sediments on Ranger Bank. However, the relatively high concentration of this element proximal to the coastal lagoons SE of the bay, and its lack of correlation with carbonate in that area, has to be considered in further detail.

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