Bull. Environ. Contam. Toxicol. (2005) 75:308–315

DOI: 10.1007/s00128-005-0754-4

Bulletin of Environmental Contamination and Toxicology

Lanthanide Contamination and Strong Positive Europium Anomalies in the Surface Sediments of the Santa Rosalía Copper Mining Region, Baja California Peninsula, Mexico

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Received: 15 February 2005/Accepted: 7 June 2005

Anthropogenic inputs of rare earth elements (REEs) into the coastal marine environment are provided by disposal of wastes from ore mining, oil refineries, the electronics and the semiconductor industry (Elbaz-Poulichet and Dupuy 1999; Hedrick 1995; Protano and Riccobono 2002; Ravichandran 1996). For example, the zeolites (catalyzers used in oil reprocessing, strongly enriched in light REEs-LREEs) have caused the pollution of the sediments of the San Pedro shelf, off Loss Angeles, southern California (Olmez et al. 1991).
Distinct shale-normalized REE patterns were found in the sedimentary materials of the tectonically active east coast of the central Baja California peninsula near Santa Rosalía (Alekseev et al. 1998; Rodríguez-Figueroa et al. 1998). This part of the Sierra de La Giganta geological sub province is made up of volcanic and volcanoclastic rocks of the Miocene age Comondú Formation, as well as marine sedimentary rocks of the Infierno and Santa Rosalía formations of Pliocene and Pleistocene age, respectively (Anonymous 1999; Hausback 1984; Wilson and Rocha 1955). Several ephemeral streams ("arroyos") traverse the mineralized zones of the "El Boleo"mining district, where copper mining and ore processing was carried for almost a century between 1896 and 1984 (Anonymous 1999). These past mining and smelting activities in Santa Rosalía have resulted in strong anthropogenic pollution of both adjacent land and sea floor by heavy metals (Rodríguez-Figueroa et al. 1998; Shumilin et al. 2000a).

The objective of our work was to study the range of concentrations of REEs and to characterize their shale-normalized signatures in different types of sedimentary materials from the mining region and in the surface sediments of the adjacent Gulf of California.

MATERIALS AND METHODS

The sediments of the arroyos, solid wastes and "black sands" of the Santa Rosalía beach zone were sampled in October 1997 using a clean plastic shovel and sealable clean plastic bags. Marine sediment samples were collected from a boat using a Van Veen grab sampler and were kept frozen until analysis. The location of sampling stations, determined by means of GPS "Magellan-2", are presented in Figure 1.

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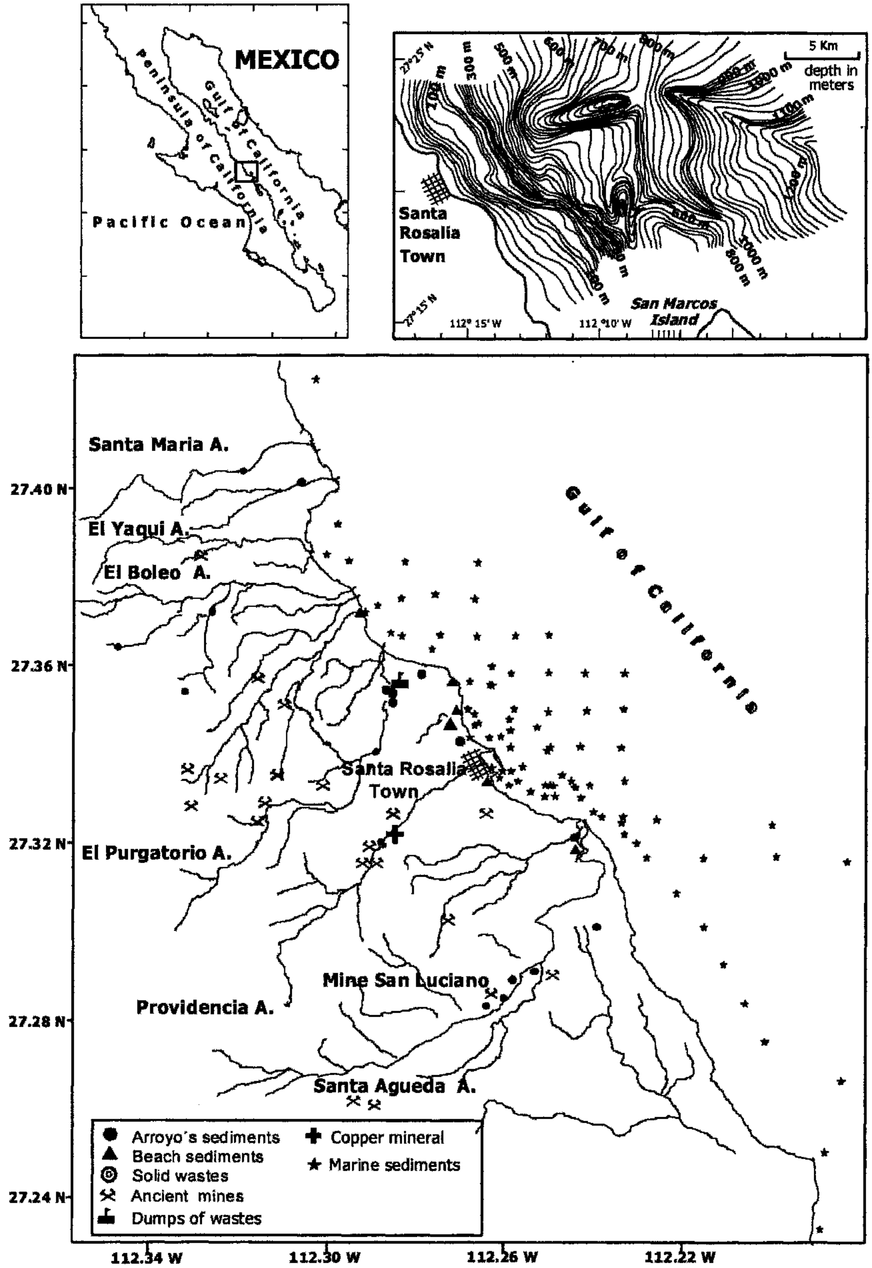

Figure 1. Study area and location of the sampling sites from the Santa Rosalía mining region.

Samples were dried (60^{o}C, 12 hours), then homogenized by grinding using an agate mortar and the powder was then fractioned for subsamples.

Instrumental neutron activation analysis (INAA) was used to determine the REE concentrations. The precision was better than 7 % for Yb and Lu, and better than 17 % for La, Ce, Nd, Sm and Tb. The accuracy of the analysis was checked with the certified reference materials (marine sediments SDN-1/2, IAEA-356 and estuarine sediments SRM 1646a) showing the recoveries in the range 88-104 % for most of elements with the best results for Eu and Lu (near 100 %). Limits of detection were 0.03 mg kg^{-1} for Eu, 0.04 mg kg^{-1} for Lu, 0.05 mg kg^{-1} for Sm and Tb, 0.1 mg kg^{-1} for Ce, 0.2 mg kg^{-1} for La and Yb and 5.0 mg kg^{-1} for Nd. Surfer-7 was used to present the spatial distributions of the elements in the coastal sediments. The lanthanide contents in the samples were normalized versus the North America Shale Composite (NASC). The europium anomaly was calculated as: $Eu_{anom} = 2\ Eu_{norm} / (Sm_{norm} + Gd_{norm})$.

RESULTS AND DISCUSSION

Average values, ranges and the standard deviations of the REE concentrations in arroyo bed samples, a copper mineral, solid wastes, beach sands and marine sediments of the Santa Rosalía mining region are presented in Table 1.

Average REEs concentrations in the different sedimentary materials of the study area (Table 1) decrease in the following order: solid wastes> copper mineral> beach sands> arroyo sediments> marine sediments. This indicates that the copper-bearing mineral deposits and solid wastes of ore smelting are the principal sources of these elements for the marine sediments of the coastal zone of Santa Rosalía, as has been previously reported Cu, Zn and Co (Rodríguez-Figueroa et al. 1998; Shumilin et al. 2000).

The spatial distribution of La and Yb concentrations, representative respectively of light REEs (LREEs) and heavy REEs (HREEs), provide more detail in support of this conclusion (Figure 2).

Lanthanum in the arroyo bed samples displays concentrations comparable or below those reported for NASC (32 mg kg^{-1}), varying in the range of 14-69 mg kg^{-1} (Figure 2a). The most elevated contents (53-69 mg kg^{-1}) are occurred in sedimentary material from the upper part of the El Boleo arroyo, which is very rich in copper minerals, transported from the mountain area during very rare, but intense rains. Lanthanum is enriched in the samples of almost all of the beds of the Santa Rosalía and El Purgatorio arroyos, those collected near abandoned mines (38-79 mg kg^{-1}), from deposits of solid wastes produced by copper ore smelting (208-289 mg kg^{-1}) and in beach sands (132-175 mg kg^{-1}). These beach "black sands" are strongly contaminated in Cu, Zn, Co and Pb and are composed mainly of heavy or coarse residual particles from the solid wastes of Cu smelting, which accumulate in the beach zone near the entrance to the Santa Rosalía harbor due to sorting by wave action (Shumilin et al. 2000).

Table 1. REE contents (mg kg^{-1}) in various samples from the drainage basin and in surface marine sediments associated with the Santa Rosalía mining region, as well as the NASC average: range underlined; average ± S.D (below).

Element	Arroyo's sediments	Beach sands	Solid wastes	Marine sediments	Copper mineral	NASC
La	14 – 69	19 – 175	64 – 289	5 – 178	80	32
	32±18	104±73	183±106	30±38		
Ce	25 – 120	38 – 279	110 – 460	10 – 298	134	73
	60±29	169±111	300±152	53±58		
Pr	3 – 12	5 – 27	12 – 45	0.9 – 28	12	7.9
	7± 3	17±10	29±15	5± 5		
Nd	10 – 43	19 – 90	40 – 146	4 – 91	40	33
	25± 9	57±32	96± 46	20±17		
Sm	3 – 10	5 – 21	9 – 32	0.9 – 21	9	5.7
	6± 2	13± 7	21± 10	5± 4		
Eu	0.6 – 3	1 – 5	2 – 9	0.1 – 7	4	1.2
	2 ± 0.6	3 ± 2	5 ± 2	2 ± 1		
Gd	3 – 11	7 – 22	9 – 32	1 – 20	8	5.2
	7 ± 2	14 ± 7	22 ± 10	6 ± 4		
Tb	0.4 – 2	1 – 3	1 – 4	0.2 – 3	1	0.9
	1 ± 0.3	2 ± 0.8	3 ± 1	0.8 ± 0.5		
Dy	2 – 10	6 – 15	8 – 20	0.9 – 14	6	5.8
	6 ± 2	10 ± 4	15 ± 6	3 ± 5		
Ho	0.4 – 2	1 – 3	2 – 4	0.2 – 3	1	1.0
	1 ± 0.4	2 ± 0.6	3 ± 1	1 ± 0.5		
Er	1 – 6	4 – 7	4 – 10	0.6 – 7	3	3.4
	3 ± 1	6 ± 1	8 ± 3	3 ± 1		
Tm	0.2– 0.8	0.6 – 1	0.6 – 1	0.1 – 1	0.4	0.5
	0.5 ± 0.2	0.7 ± 0.2	1 ± 0.3	0.4 ± 0.2		
Yb	0.8 – 4.2	3 – 5	3 – 7	0.5 – 5	2	3.1
	3 ± 1	4 ± 0.7	5 ± 2	2 ± 1		
Lu	0.1– 0.6	0.5 – 0.7	0.5 – 1	0.1 – 0.8	0.2	0.5
	0.4 ± 0.2	0.6 ± 0.1	0.7 ± 0.2	0.3 ± 0.1		

The lowest contents of La were found in the samples from the San Lucian arroyo (14-21 mg kg^{-1}), El Montado arroyo (19 mg kg^{-1}) and from the lower sections of the Santa Maria and El Yaqui arroyos (23-24 mg kg^{-1}). These values correspond to regional background La levels of arroyo sediments, which were not affected by copper ore mining operations.

The spatial distribution of ytterbium contents (NASC average abundance 3.1 mg kg^{-1}) displays almost the same pattern (Figure 2b), with somewhat higher enrichment in the beds of the El Boleo and El Purgatorio arroyos, while samples of solid wastes display only slight Yb enrichment (5-7 mg kg^{-1}), as do the beach sand samples (3-5 mg kg^{-1} of Yb) (Figure 2b).

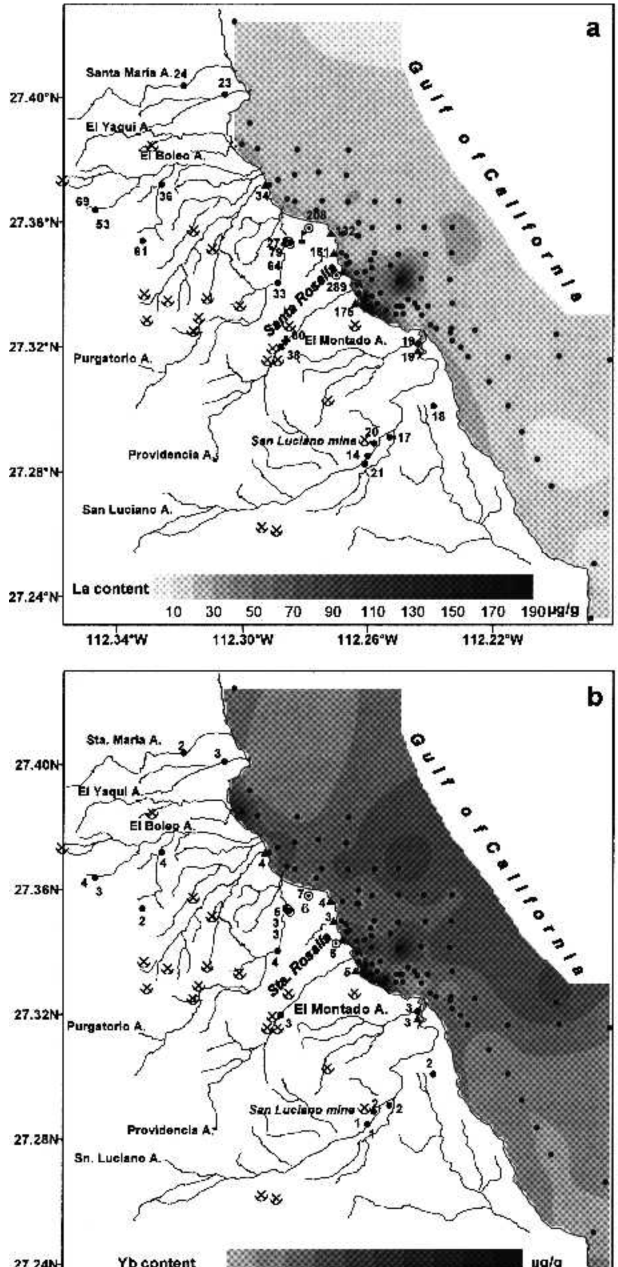

Figure 2. Spatial distribution of La (a) and Yb (b) concentrations in sediments of the Santa Rosalía mining region and adjacent Gulf of California.

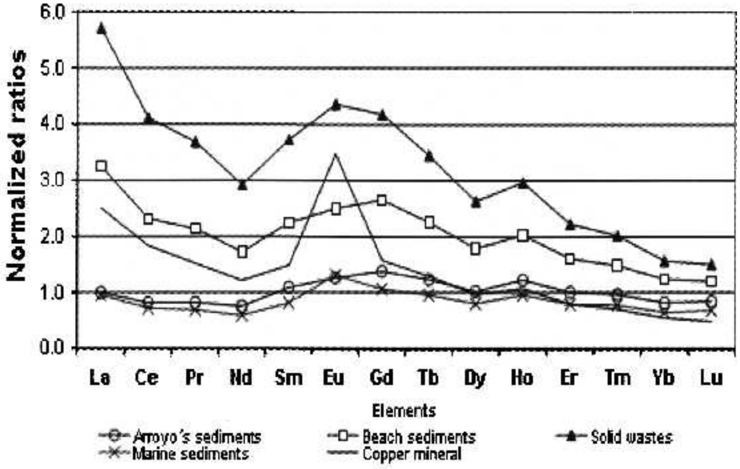

Figure 3. Shale-normalized patterns of various types of deposits from Santa Rosalía mining region.

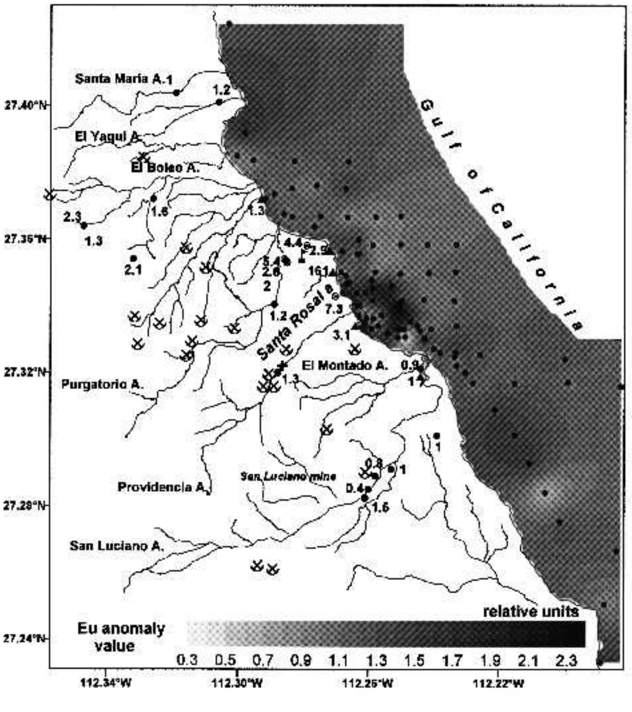

Figure 4. Spatial distribution of the Eu anomaly in sediments of the Santa Rosalía region and adjacent sea.

The spatial distributions of the La and Yb contents in marine sediment samples reveal the existence of two "hot spots" where concentrations of these REEs are much higher than values typically registered for the sediments at the margin of the Santa Rosalía mining region. The first one includes the Santa Rosalía harbor and the second occupies an adjacent, deeper part of the Gulf of California. A somewhat smaller accumulation of Yb can be seen in sediments off the mouth of the El Boleo arroyo (Figure 2b).

A general feature of shale-normalized REE pattern (Figure 3) of both the copper mineral (mainly atacamite $Cu_2(OH)_3Cl$) and the ore smelting wastes are LREE enrichment and a positive Eu anomaly. The strongly positive Eu anomaly is an additional argument supporting the previously proposed hypothesis on a marine hydrothermal origin for the copper ore deposits in this area (Escandón 1995).

Such types of the REE signature correspond to the pattern found for hydrothermal sources on the mid-ocean ridges (Michard et al.1983).

The spatial distribution of the europium anomaly values in the terrigenous deposits and marine sediments of the study area is shown in Figure 4.

The information presented demonstrates the tendency of samples with high positive Eu anomaly to be related to the solid wastes of ore smelting and beach sands. Three areas with strong positive Eu anomalies in surface sediments can be easily distinguished along the coastal line. The northern area is presumably influenced by the supply of sediments from the Santa Maria and El Yaqui arroyos. The area in front of the Santa Rosalía is clearly a product of smelting waste disposal. The southern area of positive Eu anomaly is probably caused by littoral transport and redistribution of polluted materials, initially discharged in front of Santa Rosalía harbor.

A negative anomaly in Eu, found in some tailing wastes and in some arroyo sediments, is probably attributable to the sedimentary rocks of this area. There is a similarity with a REE pattern of dust and soils of southern California, from a similar geologic and climatic zone (Reheis et al. 2002).

To summarize, copper-bearing minerals and most of the samples from local arroyos, mining wastes and their derivatives – heavily contaminated black beach sands and polluted sediments from the impact zone (mainly Santa Rosalía harbor and vicinity) very frequently display the LREE enrichment and a positive Eu anomaly.

Acknowledgments. This study was supported by a grant (SEMARNAT-2002-C01-1425) from the Secretaría de Recursos de Medio Ambiente y Recursos Naturales and Consejo Nacional de Ciencia y Tecnología of Mexico, as well as Project #20040093 from the Coordinación General del Posgrado e Investigación (CGPI) of the Instituto Politécnico Nacional of Mexico.

REFERENCES

Alekseev AV, Shumilin E N, Nava-Sanchez E, Sapozhnikov DYu (1998). Anomalous europium behaviour in the coastal bottom sediments of the

southwestern Gulf of California. Doklady Earth Sciences (translated from Doklady Rossiyskoy Akademii Nauk) 361a: 876-878
Anonimous (1999) Monografía geológico-minera del estado de Baja California Sur. Secretaría de Comercio y Fomento Industrial, Consejo de Recursos Minerales, Pachuca, Hidalgo, México (in Spanish)
Elbaz-Poulichet F, Dupuy C (1999) Behaviour of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). Appl Geochem 14:1063-1072
Escandón V F (1995) Génesis de los yacimientos polimetálicos del Boleo, Santa Rosalía, Baja California Sur. Academia Mexicana de Ingenería, México. (in Spanish)
Hausback B P (1984) Cenozoic volcanism and tectonic evolution of Baja California Sur, Mexico. In: Frizzel VA (ed) Geology of the Baja California Peninsula. P.S.S.E.P.M., Los Angeles, p 219
Hedrick JB (1995) The global rare-earth cycle. J Alloys Compds 225: 609-618.
Michard G , Albarede F, Michard G, Minstr JF, Charlou JL (1983) Rare earth elements and uranium in high-temperature solutions from East Pacific Rise hydrothermal vent field (13 °N). Nature 303: 795-797
Olmez I, Sholkovitz E R , Hermann D, Eganhouse R P(1991). Rare earth elements in sediments off Southern California: a new anthropogenic indicator. Environ Sci Technol 25: 310-316
Protano G, Riccobono F (2002) High contents of rare earth elements (REEs) in stream waters of a Cu-Pb-Zn mining area. Environ Pollut 117: 499-514
Ravichandran M (1996) Distribution of rare earth elements in sediment cores of Sabine-Neches estuary. Mar Pollut Bull 32: 719-726
Reheis M C, Budahn JR, Lamothe PJ (2002) Geochemical evidence for diversity of dust sources in the southwestern United States. Geochim Cosmochim Acta 66:1569-1587
Rodríguez Figueroa G , Shumilin E, Páez- Osuna F, Nava-Sánchez E, Sapozhnikov D (1998) Ocurrencia de metales y metaloides en sedimentos superficiales de cuatro abanico-deltas de la costa oriental de Baja California Sur. Actas INAGEQ 4:43-50 (in Spanish)
Shumilin E , Rodríguez-Figueroa G, Morton Bermea O, Lounejeva Baturina E, Hernández E, Rodríguez Meza G D (2000) Anomalous trace element composition of coastal sediments near the copper mining district of Santa Rosalía, Peninsula of Baja California, Mexico. Bull Environ Contam Toxicol 65: 261-268
Wilson IF, Rocha VS, 1955. Geology and mineral deposits of the El Boleo copper district Baja California, Mexico.Geological Survey Professional Paper 273.US Government Printing Office, Washington