

## 19. RARE EARTH ELEMENTS IN NEOGENE SEDIMENTS, SITE 1014, TANNER BASIN, CALIFORNIA BORDERLANDS<sup>1</sup>

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### ABSTRACT

Neogene sediments recovered over a continuous interval to a depth of 447 meters below seafloor at Site 1014, Tanner Basin, are dominantly calcareous nannofossils and foraminifers and siliciclastic clays. Their rare earth element composition, normalized to North American Shale Composite standard shale, shows a distribution pattern that closely mirrors that of modern seawater. With a distinct negative Ce anomaly and enhanced heavy rare earth elements over light rare earth elements, the field enclosing 48 different analyses (from Hole 1014A) spans a range of 37–109 ppm in total rare earth elements. Weathering and transportation from a terrestrial source contributed little to the rare earth element composition because the latter was mainly acquired during the course of organic matter production and sedimentation. Pore-water reactions and biogenically driven processes subsequently also contributed a diagenetic overprint.

### INTRODUCTION

The lanthanide or rare earth elements ([REE]; <sup>57</sup>La to <sup>71</sup>Lu) form ions that are nearly all trivalent with gradually decreasing ionic radii. The notable exceptions are Ce<sup>4+</sup> and Eu<sup>2+</sup>, stable respectively, under suitable oxidizing and reducing conditions. Ranging continuously in behavior from the incompatible light rare earth elements (LREE; La–Sm) to the selectively compatible heavy rare earth elements (HREE; Gd–Lu), comparisons among REE are facilitated by normalizing the analyses to a reference standard such as chondrite. However, for sedimentary rocks, the North American Shale Composite (NASC; Taylor and McClennan, 1985; Condie, 1991) is preferred as representative of the average upper crust of the earth. Compared to this reference, some fractionation effects may enhance light over heavy REE, and the effects can be quantified by the ratio of normalized  $La_n/Lu_n > 1$  or  $La_n/Lu_n < 1$ , respectively (Holser, 1997). Enhancement of the middle rare earth elements (MREE) may occur relative to both LREE and HREE. More significant deviations from normal concern anomalous amounts of Ce and Eu. An anomalous Ce value may be quantified as a ratio to Ce\*, the anticipated value for Ce<sup>3+</sup>, by interpolating adjacent trivalent REE values such that  $Ce_{an} = Ce_n/Ce^*$ . Whereas modern oceans show marked depletion (negative anomaly) of Ce because of prevalent oxidation to Ce<sup>4+</sup> (Elderfield, 1988), much of the sedimentary record of REE geochemistry reportedly (Holser, 1997) supplies an equivocal signal with respect to redox conditions in contemporaneous seawater. Here, the REE composition and distribution is evaluated in a 447-m-thick continuous interval of sedimentary core from Site 1014 in the Tanner Basin, and the possible link with diagenesis is examined along a highly productive continental margin (Emery, 1960; Shipboard Scientific Party, 1997).

### ANALYTICAL METHOD

A total of 48 different samples typical of the main sedimentary rock types present in any given section of core in Hole 1014A were analyzed by instrumental neutron activation (INAA). Nine of these samples were chosen as “representative” of the REE distribution pat-

terns. Several centimeter-thick intervals of atypical lithologies (e.g., volcanic ash) near the base of the sequence were purposely omitted. Overall, two main lithologic intervals (subunits) are represented:

1. Subunit IA (0–140 meters below seafloor [mbsf]) = interbedded clays and foraminifers and nannofossil ooze of Quaternary age, and
2. Subunit IB (140–449 mbsf) = nannofossil ooze and nannofossil chalk alternating with clays and an increasing amount of calcareous nannofossils, age 5–7 Ma (late Miocene).

Sedimentation rate throughout is estimated at ~79 m/m.y. (Shipboard Scientific Party, 1997).

A combination INAA/total digestion–inductively coupled plasma spectroscopy (ICP) analytical method was chosen because of its high efficiency, sensitivity, and low cost. A 30-g aliquot is encapsulated in a polyethylene vial and irradiated with flux wires and an internal standard at a thermal flux rate of  $7 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ , where n equals neutrons. After a 7-day delay to allow Na-24 to decay, the samples are counted on a high-purity Ge detector with a resolution of better than 1.7 KeV for the 1332 KeV Co-60. Using the flux wires, the decay-corrected activities are compared to a calibration developed from multiple certified international reference materials. Corrections are made for interference. The standard is a check on accuracy of the analysis and is not used for calibration purposes.

Detection limits (ppm) and precision (%), respectively, for the REE are as follows: La (0.5; 0.06), Ce (3; 0.27), Nd (5; 0.13), Sm (0.1; 0.04), Eu (0.2; 0.11), Tb (0.5; 0.5), Yb (0.2; 0.1), and Lu (0.05; 0.02).

### RESULTS

REE distribution patterns plotted for the nine representative samples plot in a restricted field (Fig. 1) (sample numbers are the same as the core number). Results for all of the REE analyses are available for these samples, except for samples 16 and 17, where Tb is <0.5 ppm (which is apparently below the detection limit). For some of the samples, one or more REE are reported as below the detection limit (not plotted in Fig. 1), including Eu (detection limit = 0.2 ppm). This means, in effect, that a negative Eu anomaly exists, although this is not readily apparent in Figure 1. Disregarding this aspect of the REE distribution, the pattern for the representative samples is contained within a field only slightly more compressed than that enclosing all 48

<sup>1</sup>Lyle, M., Koizumi, I., Richter, C., and Moore, T.C., Jr. (Eds.), 2000. *Proc. ODP, Sci. Results*, 167: College Station TX (Ocean Drilling Program).

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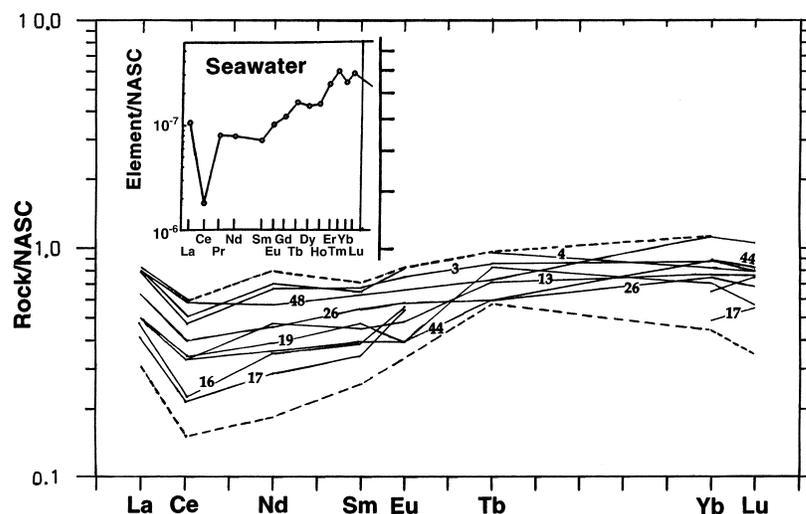


Figure 1. Rare earth element distribution patterns in sediments from Hole 1014A, Tanner Basin. The inset shows the total concentrations of REE in Atlantic and Pacific seawater, normalized to NASC (after Liu et al., 1988). NASC = North American Shale Composite. Numbers on lines represent core/sample number (Table 1); REE distribution of all 48 samples is enclosed by the dashed line.

samples (dashed lines). Except for their close similarity, these patterns exhibit no systematic relative order in quantitative terms. Thus, the pattern for one of the deepest samples, sample 48 (at 424.89 mbsf), plots at the top of Figure 1 directly adjacent to sample 3 (at 17.40 mbsf). The inset at top left of this diagram shows the total concentrations of REE in Atlantic and Pacific seawater, normalized to NASC (after Liu et al., 1988).

The average ratio of normalized La/Lu is 0.86 in these samples, thus quantifying a slight enhancement in HREE over LREE, a feature also evident in Figure 1. A distinct negative Ce anomaly is present in all samples and is here quantified using one of several algorithms,  $Ce_{an} = Ce_i / Ce^*$ , where  $Ce^*$  is the value expected for  $Ce^{3+}$ , interpolating neighboring trivalent REE (La–Nd). For Site 1014 samples,  $Ce_{an}$  ranges from 0.49 to 0.81.

Shale-normalized Eu/Sm ratios range from 0.19 to 0.46, averaging 0.26. The concentration of uranium ranges from 4.3 to 25 ppm, and U/Th ratios range from 1.45 to 5.68, averaging 2.64.

The extent of covariance among 16 selected samples (see Table 1) of the sum of the eight analyzed REE and  $CaCO_3$  through Subunits IA and IB, is shown in Figure 2. Plots of La/Lu and  $Ce^*$  vs. depth in Hole 1014A are shown in Figure 3.

## DISCUSSION AND CONCLUSIONS

Fluvial transport of weathering products of continental rocks and soils is generally agreed to be the main source of REE into the ocean (Holser, 1997). Relative to the REE composition of shale, REE content of seawater is enriched in heavy rare earth elements (Elderfield and Greaves, 1982; Piegras and Jacobsen, 1992). The phenomenon is attributed by Elderfield and Greaves (1982) to the greater stability of HREE complexes because of their smaller ionic radii and their enhanced interactivity with anions. Whether this hypothesis helps account for the pattern evident in Site 1014 sediments is a moot point. The surprising fact that the REE composition of these samples roughly mirrors that of seawater (despite orders of magnitude differences in concentration of REE in the two media) may simply result from the bias in the sediments toward the biogenic origin of the major initial particulate constituents.

The presence of a distinct negative Ce anomaly in the Site 1014 sediments reflects an important characteristic feature of seawater. In modern seawater, the anomaly is attributed to the dominant oxidation to  $Ce^{4+}$  and its incorporation into Mn and/or Fe oxyhydroxides (Shaw and Wasserburg, 1985) or to its enrichment in authigenic minerals. Rare earth elements are also incorporated into phosphate grains from

seawater during the transportation and deposition stages (Ilyin, 1998). A prominent feature of various ancient and modern sedimentary environments, strongly negative Ce anomalies, and—less commonly—zero and positive Ce anomalies associated with local anoxia (the Japan Trench presumably serves as an example of the latter [Lerche and Nozaki, 1998]) used to be regarded as a reliable indicator of redox conditions in water masses and associated sediments (e.g., Wright-Clark and Holser, 1981; Wright et al., 1987). However, the REE composition in sedimentary rocks is now considered to be complicated not only by a large range of primary effects but also by diagenetic effects (Holser, 1997). At Site 1014, diagenetic effects include bioturbation, pyritization, incipient organic carbon maturation, biogenic opal dissolution, and possibly various authigenic mineral reactions. But to what extent has the REE signature been diagenetically overprinted?

One well-known constraint (Wright et al., 1987) on REE distribution is their tendency to accrete in phosphatic remains during early diagenesis. Thus, pelagic sediments of the equatorial Pacific are reported by Toyoda et al. (1990) to have high P content and correspondingly high REE. In Site 1014 sediments, phosphatic debris is sparse, and a low P content (0.002%–0.139%) is accompanied by low total REE. However, P content reportedly (Shipboard Scientific Party, 1997) decreases significantly at the base of Subunit IB (below 340 mbsf), whereas over this interval, REE content registers an increase and therefore cannot be strictly resident in phosphatic components.

The REE content is better accounted for by uptake in the seawater column by calcareous fossils and siliciclastic clays, organic matter, and/or by detritals (Sholkovitz et al., 1994). Under strictly diagenetic conditions, even the precipitation of calcite within microburrows (e.g., chondrites, etc.), and bioturbation generally, can be expected to have contributed to the trace element signature. Thus, acquisition of REE as well as other elements such as uranium from pore waters was probably an important factor. Plots of La/Lu and  $Ce^*$  vs. depth for eight samples (Fig. 3) in Hole 1014A appear to vary sympathetically and reflect the general enrichment in LREE; however, these patterns reveal very little about possible changes in pore-water conditions (Palmer, 1985; German and Elderfield, 1990). At Site 1014, the uranium content ranges from 4.3 to 25 ppm, far in excess of the low abundances (~0.08 ppm) reported by Liu et al. (1988) for many marine carbonates.

A distinctly negative Eu anomaly present in the chondrite-normalized plot (not shown) of all samples is, as indicated earlier, far less evident in the NASC-normalized plot (Fig. 1). The reason for this is not clear. However, the Eu/Sm ratio provides a measure of the Eu anomaly and ranges from 0.19 to 0.46 in Site 1014 sediments. If dia-

Table 1. Geochemical data on selected sediment samples, Hole 1014A, Tanner Basin.

Core, section	Depth (mbsf)	CaCO <sub>3</sub> (wt%)	Sum of 8 REE (ppm)	La/Lu	Ce*	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
1H-1	0.30	43.6	62.35			17	27	13	2.5	0.8	<0.5	1.8	0.25
3H-4	17.40	32.7	89.04	1.10	53.3	25	35	21	3.7	0.9	0.7	2.4	0.34
4H-4	26.89	34.7	92.08	0.95	56.9	24	37	23	3.4	1.0	0.8	2.5	0.38
5H-4	36.41	33.0	61.15			17	27	13	2.4	<0.2	<0.5	1.5	0.25
12X-4	97.34	24.8	84.61			24	32	21	3.8	0.9	<0.5	2.5	0.41
13X-3	106.07	35.9	61.35	0.68	34.3	16	24	15	2.5	0.6	0.6	2.3	0.35
16X-4	135.46	42.1	49.26	0.67	29.2	16	16	12	2.2	0.7	<0.5	2.0	0.36
19X-4	165.20	61.2	60.27	0.89	32.1	16	25	13	2.7	0.5	0.7	2.1	0.27
24X-3	210.48	59.8	36.54			11	14	8	1.8	<0.2	<0.5	1.5	0.24
26X-4	228.29	61.0	70.81	0.97	40.9	20	29	15	3.1	0.7	0.5	2.2	0.31
32X-3	268.77	61.6	74.09			20	30	17	3.3	0.7	<0.5	2.7	0.39
35X-4	299.19	47.1	59.95			16	24	15	2.3	<0.2	<0.5	2.3	0.35
44X-4	385.29	47.6	58.36	0.67	31.4	16	24	12	2.2	0.5	0.5	2.6	0.36
48X-3	422.36	45.1	95.25	0.76	51.1	25	43	18	3.7	0.8	0.6	3.7	0.49
50X-4	446.58	15.4	108.79										

Notes: REE = rare earth elements. Ce\* represents the anticipated value for Ce<sup>3+</sup> (see "Results" for details). Sample numbers in text correspond to core numbers except that 17X (145 mbsf) is not included in table.

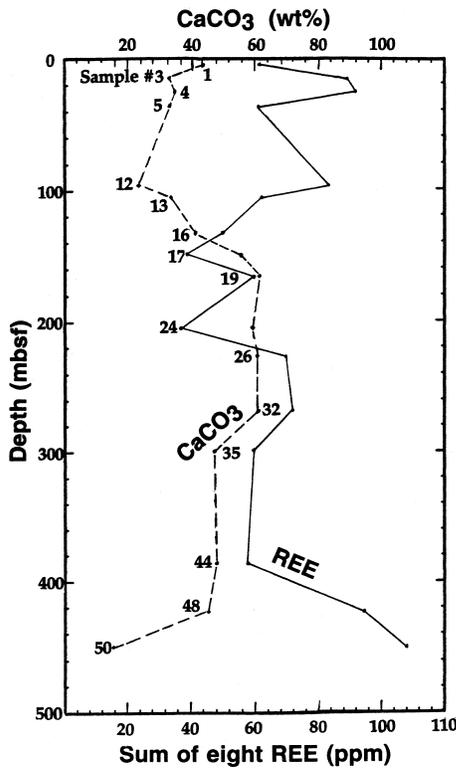


Figure 2. Plot of CaCO<sub>3</sub> and total rare earth elements (REE) vs. depth for selected samples across Subunits IA and IB in Hole 1014A, Tanner Basin.

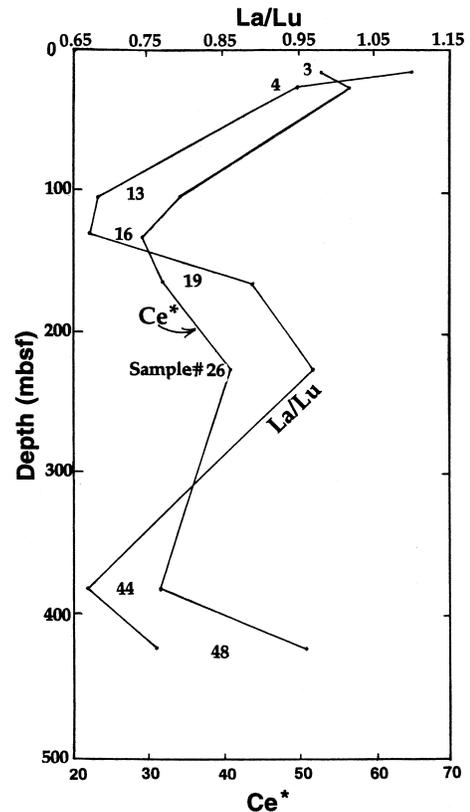


Figure 3. Plots of La/Lu and Ce\* for eight selected samples vs. depth in Hole 1014A, Tanner Basin.

genesis was a factor, this ratio perhaps ought to be of a more uniform value—closer, say, to the NASC value of 0.22 (Chaudhuri and Cullers, 1979).

Results of experimental work by Aja (1998) and studies conducted by Zhao et al. (1992) leave little doubt that REE mobilization may occur during diagenesis and that adsorption by clay minerals plays an important role in such fractionation processes. In this respect, the clays at Site 1014, although of primarily authigenic origin (and so, at best, only faintly representative of provenance), will have contributed to REE mobilization. Note, however, that the Quaternary clay-rich Subunit IA does not show the maximum enrichment in REE (see Fig. 2); there is also a distinct tendency for CaCO<sub>3</sub> and total REE to vary

antithetically. Thus, by process of elimination, the REE are linked to the siliciclastic clay component and probably also to biogenic opal dissolution. The latter is a classic diagenetic process common toward the base of the sequence at Site 1014 and likely elsewhere in the California Borderland at these depths.

ACKNOWLEDGMENT

Helpful discussions with Dr. Rick Behl of California State University at Long Beach are gratefully acknowledged.

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**Date of initial receipt: 19 October 1998**

**Date of acceptance: 10 May 1999**

**Ms 167SR-220**