31. TERRIGENOUS SEDIMENTATION AT CEARA RISE[1]

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ABSTRACT

A series of 47 samples was taken at Ceara Rise from Sites 925 and 929 during Ocean Drilling Program Leg 154. The samples spanned the entire cored section from the late Paleocene to the present. A series of chemical extractions was performed on these samples to isolate the terrigenous component. The magnitude of the terrigenous component was calculated both as weight percent and as a mass accumulation rate, which is not affected by fluctuations in nonterrigenous deposition. The mass accumulation rate of terrigenous materials at Ceara Rise has varied widely over the period studied, culminating in a ten-fold increase since 8 Ma. This was probably caused by Andean uplift and increased Amazon river flow. Thirty of the extracted samples were then analyzed for elemental compositions by instrumental neutron activation analysis. The results divide the terrigenous materials into three chemically distinct groups. These chemical distinctions also split the samples by age, implying that the source of terrigenous materials for Ceara Rise has changed through time. Interestingly, the three chemical groupings are not on the same mixing line and must then represent at least three independent terrigenous signals. The timing of the shifts between groups is consistent with South American tectonic history. Finally, the terrigenous fraction (by weight percent) of the extracted samples was regressed against high-resolution shipboard measurements. This allows estimation of weight percent terrigenous materials at any depth or age from pre-existing natural gamma, magnetic susceptibility, and color reflectance. Only samples from the last 12 Ma produced useful estimates.

INTRODUCTION

The delivery of terrigenous material (material weathered from continents) to the world's oceans is a poorly defined process but one that it is vitally important to a variety of geologic inquiries. Knowledge of the rate of terrigenous delivery is necessary to solve problems ranging from deciphering local sedimentary regimes and seismic stratigraphy to global flux balances and continental weathering rates. Information on the chemical composition of terrigenous material can help answer questions concerning sediment source regions, weathering and transport regimes, and global or regional chemical mass balances.

Ceara Rise, drilled during Ocean Drilling Program Leg 154, is an excellent area to address some of these questions. It lies just seaward of the distal edge of the modern Amazon Fan (Fig. 1) and has received a significant terrigenous sediment contribution from South America throughout its 80-m.y. history. Shipboard measurements of carbonate typically range from 40% to 80% of the bulk sediment, leaving an average 20%−60% non-carbonate fraction (Curry, Shackleton, Richter, et al., 1995). Ceara Rise sedimentation is dominated by biogenic carbonate and terrigenous materials, so most of the non-carbonate fraction is terrigenous and is composed mainly of clay-sized hemipelagic grains. Given the massive sediment load of the Amazon (Milliman and Meade, 1983; Meade, 1994) and the equatorial setting of Ceara Rise, other possible sources of terrigenous material, such as eolian dust, volcanic ash, and dropstones, are likely to be negligible if present at all.

This study focuses on a series of 47 samples taken throughout the entire sedimentary section sampled during Leg 154, spanning 55 Ma to the present. Thirty-six of the samples used in this study came from Holes 925A and 925B (4°12′N, 43°29′W, 3053 m water depth). Site 925, located near the crest of Ceara rise, was selected because it had the longest continuous temporal coverage of any Leg 154 site (middle Eocene to present). Eleven more samples from Hole 929E (5°59′N,
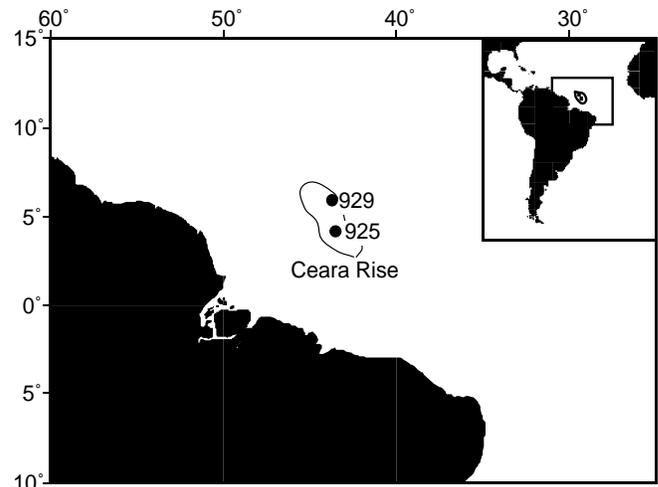

Figure 1. Locations of the Leg 154 Ceara Rise sites. From Curry, Shackleton, Richter, et al. (1995).

43°44′W, 4368 m water depth) were used to extend temporal coverage back into the late Paleocene. It should be noted, however, that Site 929 is much deeper than Site 925 and is located on the northwest flank of Ceara Rise, so terrigenous sedimentation at the two sites may well have been significantly different. The goal in sample selection was to choose one set of samples covering the period from shortly before the initiation of Andean tectonics to the present, and another set reflecting pre-Andean conditions. This has left a gap in coverage from 28 to 42 Ma, which will be filled by future work. Ceara Rise sediments also show significant high-resolution (less than 100 k.y. period) fluctuations, but the long period of coverage and low sample density of this study (~1/m.y.) preclude discussion of this variability here.

Our objectives in analyzing the samples were: (1) to isolate the terrigenous fraction of these sediments through chemical extraction and to calculate terrigenous mass accumulation rates; (2) to provide a preliminary chemical characterization of the extracted mineral

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component of Ceara Rise sediment and to use the elemental and isotopic chemistry of extracted (lithogenous) material to infer its provenance (e.g., Olivarez et al., 1991; Jones et al., 1994; Weber et al., 1996); and (3) to use data generated during completion of (1) and (2) to conduct regression analyses to determine whether it is possible to predict the terrigenous component from routine and readily available shipboard measurements of natural gamma emission, gamma-ray attenuation porosity evaluator (GRAPE), and color reflectance.

ANALYTICAL METHODS

Extraction

Ceara Rise bulk sediment consists primarily of only two components: hemipelagic terrigenous aluminosilicates and biogenic calcium carbonate. Traces of iron oxyhydroxides and sulfides occur frequently throughout the Neogene section. Significant amounts of biogenic silica occur infrequently and only at the deeper sites (Sites 926, 928, 929). Holes 925A and 925B contained only a few scattered traces of silica (Curry, Shackleton, Richter, et al., 1995), and the higher silica concentrations of 929E did not persist to the depths from which the 11 samples used here were collected.

The samples were subjected to a chemical extraction procedure to remove nonterrigenous materials. The technique is a derivative of one used to prepare minerals for X-ray diffraction. Acetic acid was used to dissolve calcium carbonate, and sodium dithionate, a strong reducing agent, was used to remove oxides and hydroxides, which were common in these sediments. The procedure is based on that of Rea and Janecek (1981) with modifications by Clemens and Prell (1990) and Hovan (1995). Ceara Rise sediments allow the added simplification of omitting the opal removal phase, which involves chemicals that may dissolve some of the terrigenous materials.

The samples were weighed after being freeze dried and before extraction to allow the calculation of the weight percent terrigenous materials. The mass accumulation rate of terrigenous materials was then calculated from these weight percent values and shipboard discrete density measurements using the Leg 154 biostratigraphic time scale (Curry, Shackleton, Richter, et al., 1995).

Instrumental Neutron Activation Analysis

Thirty of the 47 extracted samples were analyzed for concentrations of As, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sb, Sc, Sm, Tb, Th, and Yb by instrumental neutron activation analysis (INAA) using the nuclear reactor and counting facilities at the Phoenix Memorial Laboratory, University of Michigan. Sample preparation and procedure for these INAA analyses were the same as those detailed in Dickens and Owen (1995), with the exception of a new data processing system that allows higher resolution measurements. Half-lives and gamma lines used for these elemental analyses also were the same as those listed in Dickens and Owen (1995), with the exception of Na. Sodium was analyzed using a half-life of 14.659 hr and a gamma line of 1368.60 KeV (Browne and Firestone, 1986).

Analytical precision (1σ) was within 5% for analyses of As, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Sb, Sc, Sm, Th, and Yb, and between 5% and 10% for Lu, Na, and Tb. Including other random errors (see Dickens and Owen, 1995), we estimate total errors (1σ) in reported concentrations to be between 2% and 8% for the first suite of elements, and less than 13% for the second suite of elements, which indicates good precision for this technique. We also analyzed 3 NBS-SRM-679 (brick clay) and 3 USGS-SCo-1 (Cody Shale) standards in the same batches as extracted samples from the Ceara Rise to evaluate INAA precision and accuracy. Results from these standard analyses are presented in Table 1. The standard deviations for these repeated analyses are within the ranges determined for individual analyses of extracted samples. Published elemental concentrations for the two standards generally are within the standard deviation of measured

Table 1. Comparison of INAA results for NBS-SRM-679 (brick clay) and USGS-SCo-1 (Cody Shale) to values published in literature.

| Element | NBS-SRM-679 (brick clay) | | | | USGS-SCo-1 (Cody Shale) | | |
	Meas. (N = 3)	SD	Pub.[a]	Pub.[b]	Meas. (N = 3)	SD	Pub.[c]
As (ppm)	9.2	0.14	Not rep.	9.7	12.4	0.38	12.4
Ce (ppm)	103	1.1	105	106	60	1.4	62
Co (ppm)	26.5	0.87	26	26	11.5	0.17	10.5
Cr (ppm)	106	2.6	109.7	109	71	1.1	68
Cs (ppm)	9.4	0.24	9.6	9.9	7.9	0.12	7.8
Eu (ppm)	1.84	0.035	1.9	1.84	1.18	0.022	1.19
Fe (%)	8.87	0.087	9.05	9.1	3.56	0.026	3.63
Hf (ppm)	4.64	0.069	4.6	4.7	4.98	0.16	4.6
La (ppm)	51	1.1	Not rep.	53	30.8	0.66	29.5
Lu (ppm)	0.51	0.017	Not rep.	0.52	0.34	0.020	0.34
Na (ppm)	1400	120	1304	Not rep.	6700	170.000	6700
Sb (ppm)	0.97	0.085	Not rep.	0.87	2.50	0.062	2.5
Sc (ppm)	22.7	0.21	22.5	23.1	11.91	0.060	10.8
Sm (ppm)	8.9	0.12	Not rep.	9.17	5.21	0.036	5.3
Tb (ppm)	1.1	0.14	Not rep.	1.2	0.68	0.063	0.7
Th (ppm)	14.0	0.26	14	13.9	9.5	0.13	9.7
Yb (ppm)	3.5	0.16	Not rep.	3.6	2.2	0.16	2.27

Notes: N = number of analyses, SD = standard deviation, not rep. = value not reported.
[a] Mean consensus values reported in Gladney et al. (1987).
[b] Average values from seven replicates reported in Dickens and Owen (1995).
[c] Recommended values reported in Govindaraju (1994).

values. The exceptions are the high Co and Sc values for the USGS-SCo-1 standard. At present we are unclear why this discrepancy exists (an opposite effect was observed by Dickens and Owen (1995), for repeated analyses of NBS-SRM-688, basalt rock). Note, however, that the analytical precision is high (within 3.5%) for these two elements.

Regression Analysis

The terrigenous fraction of Ceara Rise sediments can be measured directly by chemical extraction as described above or inferred from measurements of biogenic calcium carbonate. However, both of these methods are fairly labor intensive, and it would be useful to be able to estimate the terrigenous weight percent from other high-resolution measurements that are more easily made. To that end, the measured weight percent terrigenous materials was compared with four high-resolution data sets collected during Leg 154: magnetic susceptibility, natural gamma emissions, GRAPE, and percent visible light reflectance.

All four of these parameters would be expected to covary with the terrigenous content of the sediments. Natural gamma-ray emissions from sediments are more likely to come from aluminosilicates than from biogenic materials because of the higher radionuclide content of continental materials relative to dissolved ions in seawater. Similarly, terrigenous clays are more likely to contain magnetic or paramagnetic minerals than are biogenic carbonates, so the magnetic susceptibility of sediment should increase with higher terrigenous content. Terrigenous clays are generally darker than carbonates, so the amount of visible light they reflect is likely to be lower. GRAPE measurements could also reflect terrigenous influence if the terrigenous materials have different porosity or density than biogenic sediments. For example, most sites drilled on Leg 138 showed a strong positive correlation between GRAPE and percent carbonate (Mayer, Pisias, Janecek, et al., 1992). All four parameters used were measured at 5- to 15-cm intervals throughout almost all the recovered cores. Values for each of these measurement types were calculated for each extracted sample by linear interpolation between the nearest two measurements. Nearly all samples were less than 10 cm from the nearest measurements used in interpolation.

The fraction of terrigenous material (by weight percent) of 47 samples was measured by comparing sample weights before and after chemical extraction as described above. Once the shipboard measure-

ments were interpolated to the location of each sample, a series of regression analyses was performed using Microsoft Excel's multiple linear regression package with the goal of developing an easy method of terrigenous fraction estimation. Regressions were constructed for all the samples combined and then for the three chemically distinct age groupings defined using INAA (see below).

RESULTS AND DISCUSSION

Terrigenous Weight Percent and Mass Accumulation Rates

The weight percent of terrigenous materials varies between 4% and 42% (Fig. 2). Since 8 Ma, the terrigenous fraction has increased from about 10% to about 35%. Prior to 8 Ma, the terrigenous component varied widely, but it was generally higher (20%–40%) in the Paleocene–Eocene samples (55–40 Ma) than in the Oligocene and early to middle Miocene samples, where almost all values are in the 5%–20% range.

Direct evaluation of variations in the terrigenous component requires elimination of uncertainty caused by variations in other components. This can be achieved by conversion from weight percents to mass fluxes. The mass accumulation rate (MAR) of terrigenous materials (Fig. 3) shows several interesting features. The MAR of terrigenous materials has increased by an order of magnitude over the last 8 Ma, which is likely due to increased sediment delivery through the Amazon River from the continually uplifting Andes mountains (Hoorn et al., 1995). The terrigenous MAR was relatively low from 8 to 20 Ma. Prior to this time, the more sparsely spaced data indicate a slightly higher MAR, but not as large a flux as the younger (<8 Ma) Andean-influenced values.

Elemental Chemistry of Terrigenous Materials

Elemental concentrations for 30 extracted samples spanning from 42 Ma to the present are presented in Table 2. Note, however, that only one sample is older than 30 Ma, so extending interpretations back to the lone 42 Ma sample may be suspect. All concentrations are well within an order of magnitude of those determined for the clay and shale standards. The significance of this observation is twofold. First, on the basis of our accuracy for repeated analyses of NBS-SRM-679 and USGS-SCo-1, reported concentrations in Table 2 are highly accurate (except, perhaps, for Co and Sc). Second, all extracted samples have a chemical composition roughly similar to that of shale. As shown in Figure 4, the overall average chemical composition of extracted samples indeed approximates that of a well-characterized shale, the North American Shale Composite (NASC; Gromet et al., 1984).

In spite of the overall similarity between extracted samples and shale, there is significant chemical variability among the extracted samples (Fig. 4). Most of this variability (i.e., for 29 of the 30 extracted samples) can be explained if three distinct chemical compositions exist in the extracted component of Ceara Rise sediment. This observation is exemplified by plots of various elemental ratios (e.g., La/Sm vs. Sc/Th, As/Sb vs. Cs/Na) that show three distinct chemical fields (Fig. 5). The ratios shown were not selected for any special geological meaning; they merely serve to emphasize the differences in composition between the sample groups.

Sample 154-925A-18R-4, 63 cm, 21 Ma, is problematic. The chemistry of extracted material from this particular sample is different from all other samples analyzed (both in terms of absolute concentrations and elemental ratios) and its weight percent terrigenous material is very high relative to its chronological neighbors. Because this sample is from an unusual banded "minor lithology" at Site 925 (see Curry, Shackleton, Richter, et al., 1995, p. 461), we omit this sample from further discussion. However, because apparently similar bands also were described for early Miocene sequences at Sites 926,
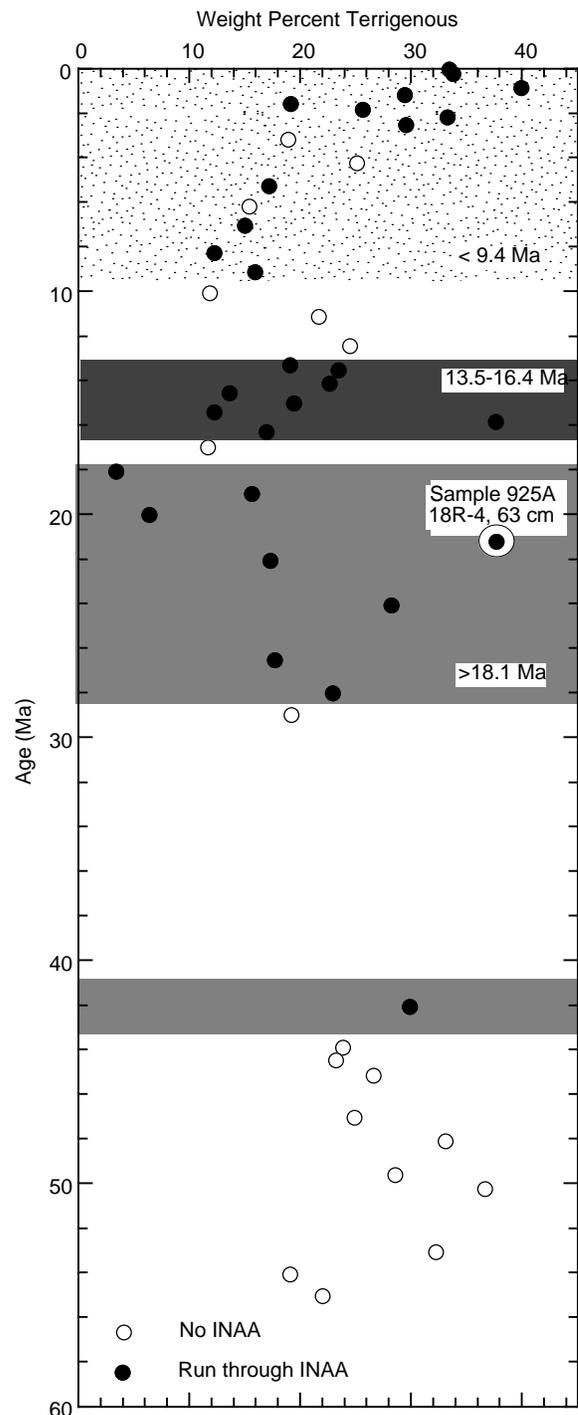

Figure 2. Terrigenous weight percent of all analyzed sediments. The 30 solid circles represent the subset of samples to which INAA was applied. The shaded fields represent the three temporally and chemically distinct groups revealed by INAA. These patterns are consistent for the groups for all figures.

928, and 929 (Curry, Shackleton, Richter, et al., 1995), a good explanation for the chemistry and origin of this lithogenous material might be of interest to future investigations.

The three distinct chemical compositions of extracted material are age dependent (Figs. 4, 5). Each of the time intervals between 0 and 9.4 Ma, 13.5 and 16.4 Ma, and 18.1 and 28 Ma has a distinct chemical composition (with the aforementioned exception of Sample 154-
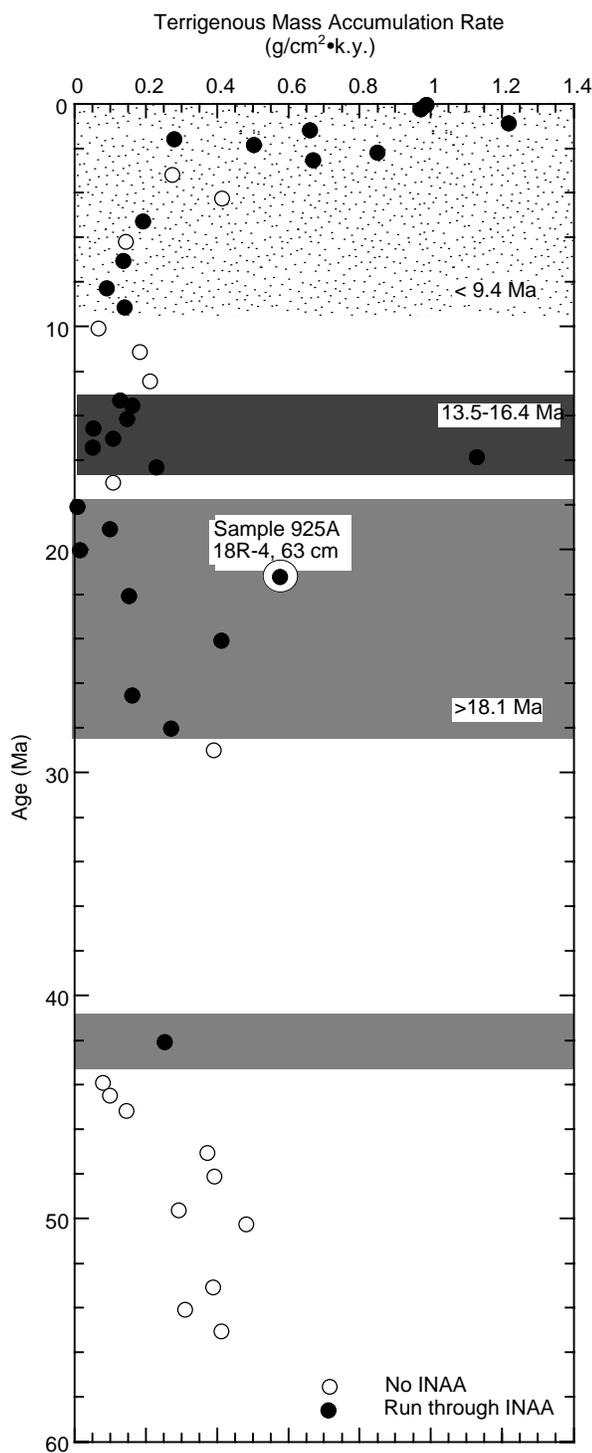
Figure 3. Terrigenous mass accumulation rate, calculated using the weight percent terrigenous material, dry bulk density from shipboard physical properties samples, and linear sedimentation rates from the Leg 154 biostratigraphy.

925A-18R-4, 63 cm). The relationship between depositional age and chemical composition of extracted material is not a procedural artifact because samples were not extracted and/or analyzed by INAA in stratigraphic order.

The 42-Ma sample (154-925E-15R-1, 80 cm) is extremely similar in composition to the other samples from 18.1 to 28 Ma. In the absence of other chemical or tectonic information, we are cautiously assuming that the compositional group persisted between 42 and 28

Ma. Future study of more samples will allow a more thorough evaluation of this period.

The existence of these three distinct groups strongly suggests that the overall chemical composition of detritus delivered to the Ceara Rise changed at least twice in the last 42 m.y. (between 9.4 and 13.5 Ma and between 16.4 and 18.1 Ma). This inference is made on the basis of recent studies concerning extracted material from surface sediment of the North Pacific and analysis of specific elements. A series of investigations (Olivarez et al., 1991; Nakai et al., 1993; Jones et al., 1994; Weber et al., 1996) has clearly demonstrated that the extraction procedure used here renders material from bulk surface sediment that is very similar to the known lithogenous source material's composition for many of the elements we analyzed. We can thus be confident that our results have (1) maintained the chemical integrity of the lithogenous component (except as mentioned below) and (2) removed all phases of bulk sediment not associated with the lithogenous component. Observed down-core changes in the chemistry of extracted material, therefore, argue for temporal changes in the source or weathering regime of the source material unless post-depositional diagenesis has altered the composition of the lithogenous material. In our case, post-depositional diagenesis is not a concern; numerous studies (see references in Taylor and McLennan, 1985) have shown that ratios of certain elements (e.g., Sc, Th, and the rare earth elements) in lithogenous material are not significantly affected by post-depositional diagenesis. Because the three distinct chemical compositions of extracted Ceara Rise material have pronounced differences in their ratios of Sc, Th, and the REEs (e.g., Fig. 4), we can safely dismiss post-depositional diagenesis as an explanation for the variation in the chemical composition of our extracted samples.

The observed variations in chemical composition of lithogenous material over the last 42 m.y. are important to the understanding of the geological evolution of northern South America. The vast majority of lithogenous material supplied to the Ceara Rise at present is derived from erosion and weathering of rocks in the Andes and transport through the Amazon Basin via the Amazon River (Milliman and Meade, 1983; Meade, 1994). The two marked variations in chemical composition, therefore, suggest that two deviations from this general process occurred during the Tertiary. Moreover, these deviations are roughly synchronous with the previously discussed variations in the flux of lithogenous material, such as the rapid increase in terrigenous MAR after 9 Ma and the period of very low MARs between 16 and 13 Ma. The similar timing for changes in these two very different proxies may reflect some fundamental change in either provenance, erosion, weathering, and/or transport of the lithogenous material.

Lithogenous material deposited between 13.5 and 16.4 Ma (Table 2, Samples 154-925A-3R-1, 91–95 cm, through 7R-4, 42–45 cm) is significantly depleted in Na with respect to other such sediments from this site. The tan color of extracted material from this time (depth) interval also is markedly different from that of extracted material deposited prior to 9.4 Ma and after 18.1 Ma (gray to olive green). Together, these observations strongly indicate that the mineralogy of lithogenous material from sediment deposited between 13.5 and 16.4 Ma is fundamentally different from that of other sediment deposited at the Ceara Rise. Note, however, that the direct cause of these very low Na concentrations is unclear at present. The extraction procedure involves multiple Na dithionate–Na citrate rinses, and we have not evaluated the amount of Na that can be incorporated into samples (via cation exchange) during the extraction procedure. Hence, enrichment of Na in extracted Ceara Rise samples could reflect either (1) a high content of Na-rich minerals and/or (2) a high abundance of a particular mineral that can readily incorporate Na during the extraction procedure (e.g., smectite).

The overall chemical composition of lithogenous material deposited prior to 18.1 Ma is similar to that of lithogenous material deposited after 9.4 Ma with one notable exception: it is characterized by a general depletion of those elements that are enriched in the crust relative to the primitive mantle (Fig. 6). This observation suggests that the source of material deposited prior to 18.1 Ma was an Archean

Table 2. Chemistry of extracted samples from Ceara Rise sediment.

Core, section, interval (cm)	Depth (mbsf)	Depth (mcd)	As (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Eu (ppm)	Fe (%)	Hf (ppm)	La (ppm)	Lu (ppm)	Na (%)	Sb (ppm)	Sc (ppm)	Sm (ppm)	Tb (ppm)	Th (ppm)	Yb (ppm)
154-925B-																			
1H-1, 93−98	0.93	0.93	6.1	81	12.1	86	12.1	1.07	3.39	5.00	46.1	0.35	1.76	0.93	16.43	6.05	0.74	11.1	2.46
2H-3, 49−54	7.99	8.69	10.4	82	12.9	89	11.4	1.04	3.85	4.58	47.1	0.30	1.97	0.74	16.27	5.80	0.67	11.0	2.18
4H-3, 70−73	27.20	30.70	9.8	84	13.6	88	10.8	1.08	3.96	4.28	47.1	0.25	2.74	0.72	16.14	5.93	0.54	10.6	2.04
5H-3, 70−74	36.70	40.64	10.2	87	12.0	84	11.5	1.18	3.59	4.96	49.9	0.30	1.71	0.97	15.91	6.27	0.79	10.9	2.29
6H-4, 78−83	47.78	51.44	9.3	81	12.2	92	11.0	1.10	3.53	4.76	48.3	0.41	1.86	1.16	15.92	5.88	0.64	10.4	2.15
7H-3, 15−18	55.15	59.49	5.7	89	12.5	91	11.4	1.25	3.49	4.73	50.1	0.36	1.26	0.97	16.43	6.67	0.85	11.2	2.26
8H-3, 69−74	65.19	69.30	11.6	84	11.9	81	10.7	1.34	3.61	4.50	49.2	0.40	2.27	0.76	15.08	6.95	0.64	11.7	2.26
9H-3, 80−85	74.80	80.13	7.0	95	13.1	86	10.8	1.44	3.87	4.90	50.0	0.44	1.31	0.83	16.69	7.17	0.69	12.7	3.05
17H-1, 111−115	148.11	163.33	7.4	108	15.4	91	12.2	2.03	3.95	4.66	62.6	0.49	1.16	0.86	16.10	10.12	1.04	14.5	3.95
21H-3, 129−134	189.29	210.58	5.5	108	13.8	96	12.5	1.91	3.67	5.05	62.0	0.47	1.05	0.82	15.99	9.58	1.16	13.2	2.83
24H-3, 99−104	217.49	242.66	6.8	95	16.0	121	8.2	1.88	4.99	4.46	61.5	0.32	0.86	0.67	15.26	9.22	0.92	16.6	2.18
26H-3, 117−123	236.67	264.45	5.4	88	19.3	130	8.4	1.65	4.99	4.51	54.6	0.29	0.79	0.70	15.37	7.89	0.79	14.2	1.80
154-925A-																			
3R-1, 91−95	304.61	347.30	2.1	80	14.5	116	7.5	0.93	4.73	5.31	49.3	0.25	0.11	1.17	16.08	4.75	0.49	14.4	2.25
3R-3, 90−94	307.60	350.29	2.1	75	19.7	113	6.7	0.83	5.23	4.78	44.9	0.22	0.10	0.69	15.15	4.24	0.40	14.5	1.48
4R-1, 54−58	314.24	352.58	1.8	61	14.8	115	6.6	0.67	5.05	4.60	39.4	0.16	0.08	0.55	14.95	3.57	0.36	13.2	1.31
4R-4, 54−58	318.62	357.08	1.3	62	13.9	108	6.7	0.80	4.46	4.25	41.1	0.28	0.13	0.64	15.15	3.87	0.35	13.2	1.49
5R-1, 48−52	323.88	362.22	1.8	64	18.4	103	6.3	0.74	4.86	4.08	39.1	0.22	0.09	0.65	15.11	3.82	0.43	13.0	1.29
5R-4, 48−52	328.38	366.72	1.0	62	15.1	102	6.7	0.70	4.52	4.40	40.4	0.18	0.12	0.71	14.24	3.49	0.28	10.6	1.15
6R-1, 50−55	333.60	371.94	2.1	98	18.5	125	4.6	1.09	3.89	7.47	59.4	0.34	0.10	1.10	15.96	5.63	0.84	14.1	2.79
7R-4, 42−45	347.62	385.96	1.1	55	13.8	102	6.3	0.58	4.65	4.01	36.3	0.18	0.10	0.55	13.89	3.11	0.30	9.7	1.05
13R-1, 41−44	400.81	439.15	***	34	12.2	95	5.4	0.38	3.40	2.77	22.2	0.10	2.88	0.41	10.86	1.95	***	4.1	0.85
15R-1, 104−107	420.74	459.08	2.8	35	17.2	113	5.8	0.38	4.50	3.22	25.4	0.12	2.85	0.60	14.17	2.10	***	4.1	0.81
16R-4, 134−137	435.14	473.48	***	32	9.7	83	5.0	0.37	2.93	2.50	22.4	0.16	3.08	0.42	10.34	2.05	0.20	4.1	0.68
18R-4, 63−66	453.73	492.07	7.4	180	20.1	210	9.2	2.04	5.53	14.66	107.6	0.63	2.04	2.10	26.30	10.52	0.99	22.91	4.32
20R-1, 59−63	468.39	506.73	0.9	47	11.8	112	7.0	0.55	3.91	3.66	29.9	0.13	1.89	0.49	13.92	2.83	0.15	5.7	0.86
24R-1, 79−82	507.09	545.43	5.0	49	13.5	112	7.6	0.58	4.74	3.86	31.8	0.16	2.11	0.69	14.56	2.89	0.36	5.2	0.98
29R-1, 39−42	554.99	593.33	1.2	39	11.6	112	7.3	0.45	4.02	3.69	26.3	0.18	2.35	0.48	12.92	2.28	0.27	4.4	0.84
32R-1, 54−57	584.04	622.38	3.3	56	14.5	107	7.2	0.64	5.00	4.16	35.9	0.17	1.93	0.59	13.44	3.32	0.14	5.4	1.02
154-929E-																			
13R-3, 67−71	590.87†	611.45†	2.2	18	7.4	39	2.6	0.28	1.59	1.50	13.1	0.06	1.57	0.35	5.99	1.48	0.12	2.3	0.47
15R-1, 80−83	607.30†	627.88†	1.0	19	6.9	47	2.7	0.23	1.73	1.91	13.2	0.05	1.81	0.47	6.72	1.09	***	1.9	0.41

Notes: A triple asterisk (***) denotes that concentration was below detection limit. A dagger (†) is to stress that these depths are for Site 929 (other depths are for Site 925).

shield, while the younger sediments were derived from post-Archean source rocks. Furthermore, McLennan et al. (1980) have shown, on the basis of over 80 samples, that the La and Th in sedimentary rocks can be used to discriminate between Archean and post-Archean rocks. In the case of our samples, the La and Th concentrations also suggest that the source of material prior to 18.4 Ma was an Archean shield (Fig. 7). The course of the present-day Amazon is bracketed by two shields as it passes through eastern South America, the Guyana Shield to the north and the Brazilian Shield to the south. Without the elevation gradient currently supplied by Andean uplift, the sediments reaching Ceara Rise from South America might have come from these more proximal sources prior to 18.4 Ma. Strontium and neodymium isotopic analyses of the extracted material from that time could confirm this inference (e.g., Basu et al., 1990, Nakai et al., 1993; Jones et al., 1994).

Meade (1988) has found that 90%−95% of sediment delivered to the Atlantic by the Amazon comes from the Andes, whereas most of the water comes from lowland sources. Pinet and Souriau (1988) found through modeling that, for young river systems in active tectonic environments (such as the Amazon), relief is by far the most important factor controlling denotation and sediment removal. These two observations suggest that from pre-Andean times until significant Andean relief was developed, the source area of sediments delivered to Ceara Rise was much farther east. Hoorn et al. (1995) indicate that tectonic activity in several Andean orogenic belts increased in the Miocene, with most activity (and the initialization of modern-style Amazon flow) occurring in the late Miocene.

This early-eastern-source interpretation meshes well with the chemical distinctions. The oldest and apparently longest-lasting chemical grouping is the 18 Ma to 28−42 Ma group. The composition of these sediments indicates it is derived from an Archean source (Figs. 6, 7), with the most likely candidates being the shield rocks that make up the northeast part of South America. The middle group, covering roughly 17−13 Ma, corresponds in age to the suggestion of Hoorn et al. (1995) of the onset of eastward flow after a series of middle to late Miocene uplifts reshaped the South American continent.

The last group, beginning at 10−12 Ma and continuing on to the present, is likely representative of weathering in all regions in the Amazon watershed. Today, Amazonian sediments are derived from two sources with roughly equal contributions: the Peruvian Andes to the west, and the Bolivian Andes to the south (Meade, 1994). The chemical compositions for the youngest (<12 Ma) group cluster well (Fig. 5) regardless of age, so its sources have also likely remained relatively constant in composition, if not in magnitude.

Interestingly, the change in chemical makeup precedes the increase of terrigenous flux by 2−4 Ma. This is possibly related to sediment storage on the continent and the gradually increasing relief. It also suggests that new drainage patterns were established well before the onset of a major influx of sediments to the ocean.

Regression Analyses

Single linear regressions of each of the four parameters measured on board the drill ship were made on measured weight percent terrigenous and on each other. Correlation coefficients for these regressions (Table 3) show the expected signs: magnetic susceptibility and natural gamma emissions show positive correlations to the amount of terrigenous material, whereas percent light reflectance shows a negative correlation. GRAPE shows no correlation to terrigenous materials at all, which could either be because the Ceara Rise terrigenous fraction is indistinguishable by GRAPE from the carbonates or because the accuracy of the GRAPE measurements was compromised by shipboard instrumental problems. No further use of GRAPE measurements was made for the purposes of the regressions.

Although the expected correlations exist, no single parameter seems useful for predicting the size of the terrigenous fraction. A series of multiple linear regressions using different combinations of the available data were performed utilizing the information gained from the simple linear regressions above. Resulting regression models were of low quality and thus were not useful estimates of terrigenous weight percent. Given the very distinct chemical differences between sedimentary regimes revealed through INAA, however, it seemed
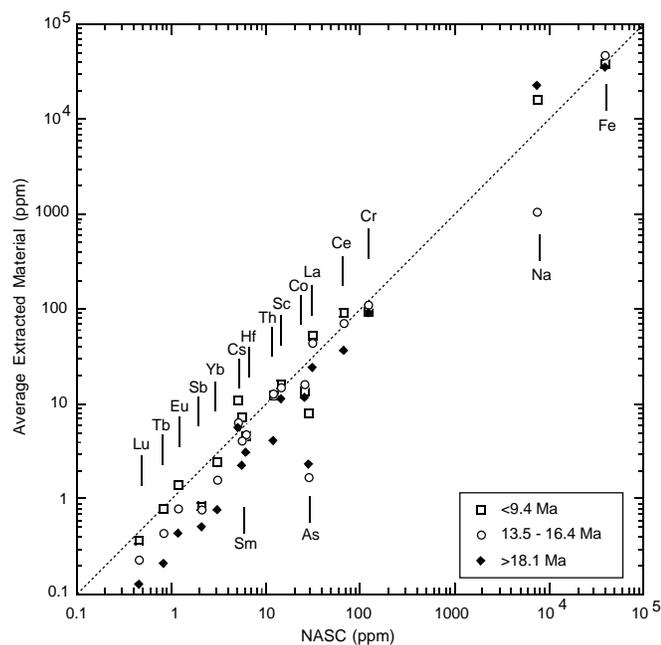
Figure 4. Elemental chemical composition of extracted sediments as compared to the North American Shale Composite (NASC; Gromet et al., 1984). The NASC represents standard terrigenous sediments. The three chemistry/age groupings (see Fig. 5) are represented by different symbols.

reasonable to run multiple regressions on subsets of the data corresponding to the three age/chemistry zones described previously.

The results of this work are presented in Table 4. The regressions for the oldest (18–55 Ma) and middle (13–17 Ma) groups are still not particularly useful, with R^2 values of 0.22 and 0.69, respectively. It is interesting, however, that the middle interval shows a stronger dependence on natural gamma and has an inverse correlation with reflectance. The youngest group (0–12 Ma) does provide a useful, reasonably statistically sound ($R^2 = 0.89$) predictive model (Fig. 8).

This regression model appears to be a useful tool for estimating terrigenous input to Ceara Rise over the last 12 Ma. Estimates can be made at any arbitrarily chosen depth or age spacing, although a lower limit of 10–20 cm would ensure that the estimates are not more dense than the data upon which they are based. Useful regression models for the older intervals (>12 Ma) will likely result from adding more terrigenous measurements for these time periods and making further chemical investigations to detect any potential terrigenous source shifts. Geochemical logs might also be potentially useful, although they were not produced for all holes or at all depths.

CONCLUSIONS

This work has addressed three main issues: measurement of long-term terrigenous MAR trends, analysis of chemical composition of extracted terrigenous materials through time, and the possibility of estimating terrigenous weight percent from readily available shipboard measurements. A summary of our findings from the three parts of the project is presented in Figure 9.

Terrigenous Fluxes to Ceara Rise

There has been a ten-fold increase in the delivery of hemipelagic terrigenous materials to Ceara Rise since 8 Ma (Fig. 2). The timing of this change corresponds roughly to the onset of major Andean uplifts in the early and middle Miocene and to the initialization and increasing strength of cross-continent, eastward Amazon River flow in
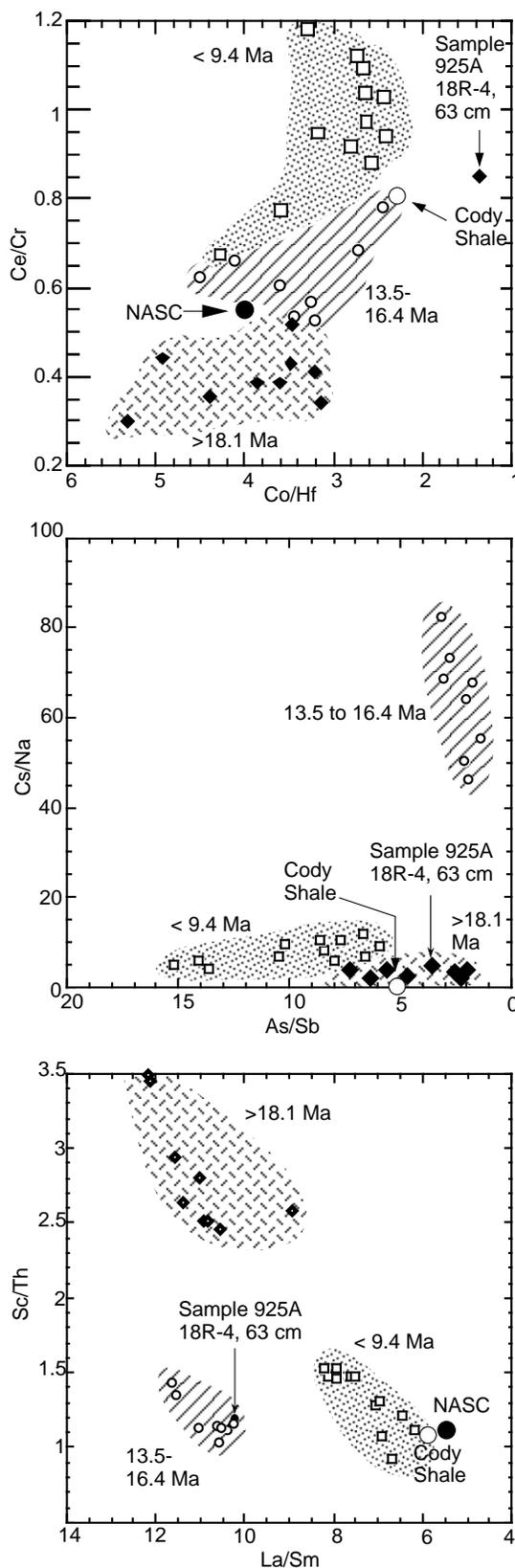

Figure 5. Selected ratios of elemental chemical concentrations. For many of the elements analyzed in INAA, the concentrations cluster at very different values for three different periods. Compositions of Cody Shale (from Table 1) and NASC (where available) are plotted on each figure for comparison. The symbols correspond to those used in Figure 4.
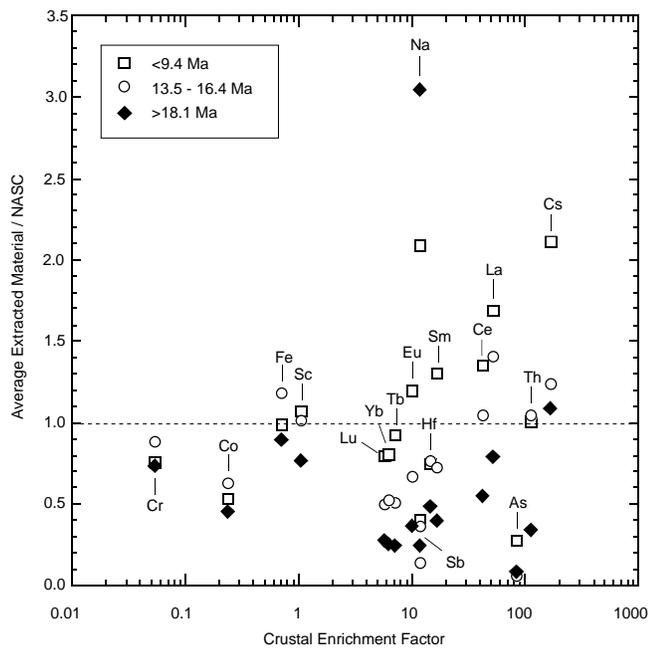
Figure 6. The degree to which the various analyzed elements are concentrated relative to NASC plotted against their relative enrichment in the crust. The crustal enrichment factor for an element is the ratio between the concentration of that element in the crust and the concentration in the whole Earth. The oldest group of samples is enriched in rare earth elements relative to NASC, whereas the younger groups are progressively more enriched, indicating that the older (>18.1 Ma) samples were derived from a source composition much closer to Archean shield rocks.

the middle to late Miocene (Hoorn et al., 1995). Depending on when these events occurred in the Miocene (roughly 14−10 Ma), there could be up to several million years of lag between uplift and changes in terrigenous flux at 9−8 Ma. This might be explained by the temporary storage of newly eroded sediments in the Andean foreland basin followed by their eventual washing out onto the lower regions of eastern South America. Data from Meade (1988) suggests that recent global riverine sediment output is roughly ten times the amount of sediments forming from current weathering processes, so such storage and later re-erosion in a newly formed basinal area, through which no large river flowed prior to uplift, is conceivable.

Chemical Composition of Terrigenous Ceara Rise Sediments

INAA of extracted material from Ceara Rise shows marked clustering of elemental compositions by age. The groupings were not caused by diagenesis, were not an artifact, and the transitions between groups represent a real change in the composition of terrigenous input. It is impossible to tell from INAA whether this represents a change in the source region for terrigenous sediments or a change in weathering or transportation processes, but the fact that the three groups we have named do not lie upon a mixing line indicates that there have been at least three different Amazonian terrigenous weathering or source regimes in the past. Transitions between these source regions are also loosely correlated in age with changes in terrigenous mass accumulation rates and to South American tectonic events.

Estimation of Terrigenous Fluxes from Pre-existing High-Resolution Data Sets

Regressions using Leg 154's extensive shipboard measurements produce a useful predictive model for terrigenous components for the
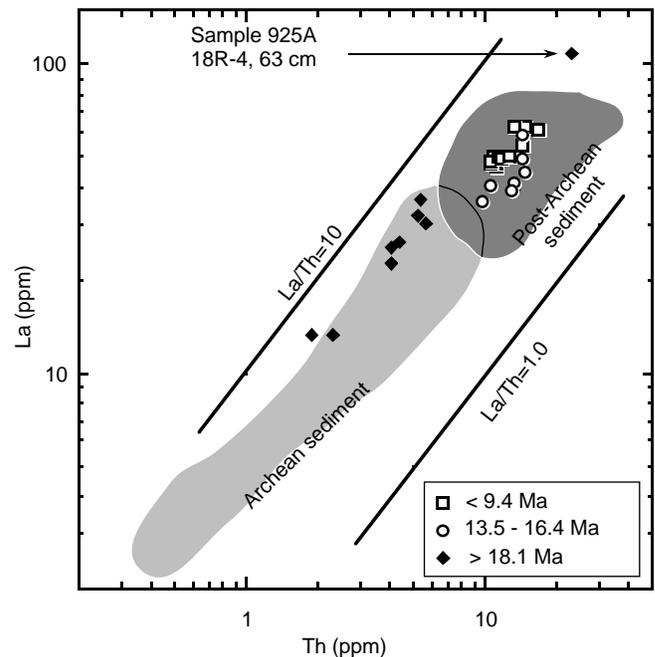

Figure 7. Lanthanum and thorium concentrations have been shown to be an indicator of the age of source rock for sediments (McLellan et al., 1980). The oldest group of sediments appears to have an Archean source signature, while the two younger groups show typically post-Archean ratios.

Table 3. Correlation coefficients for weight percent terrigenous vs. all shipboard measurements (using all 47 samples).

	Wt% terrigenous	Magnetic susceptibility	Natural gamma	Percent reflectance	GRAPE
Wt% terrigenous	1				
Magnetic susceptibility	0.533	1			
Natural gamma	0.600	0.810	1		
Percent reflectance	−0.626	−0.586	−0.712	1	
GRAPE	−0.100	0.049	0.039	0.093	1

past 12 m.y., but fail for periods prior to that time. Figure 9 shows terrigenous MARs from the regression estimates of terrigenous weight percent at a 5-k.y. spacing. Although the regression model reproduces the initial data well (Fig. 8), the estimates, with a much higher temporal resolution, tend to average somewhat higher than the measured values suggest. More measured weight percents will allow the regression to be refined. More data and a better understanding of the sediment provenance for the older chemical groups (>12 Ma) may also allow regression-based terrigenous estimates for these older sediments.

ACKNOWLEDGMENTS

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Table 4. Regression model parameters for prediction of weight percent terrigenous from shipboard measurements.

| Regression statistics	All samples	<13 Ma	13–17 Ma	18–55 Ma
Model coefficients				
Intercept	0.2697	0.2708	−0.2369	0.1722
Magnetic susceptibility	0.0017	0.0090	0.0174	0.0053
Natural gamma	0.0051	−0.0021	0.0215	0.0065
Percent Reflectance	−0.0045	−0.0039	0.0016	−0.0024
Statistical parameters				
R squared	0.4457	0.8934	0.6867	0.2181
Standard error	0.0654	0.0301	0.0564	0.0860
Number of samples	47	18	9	20
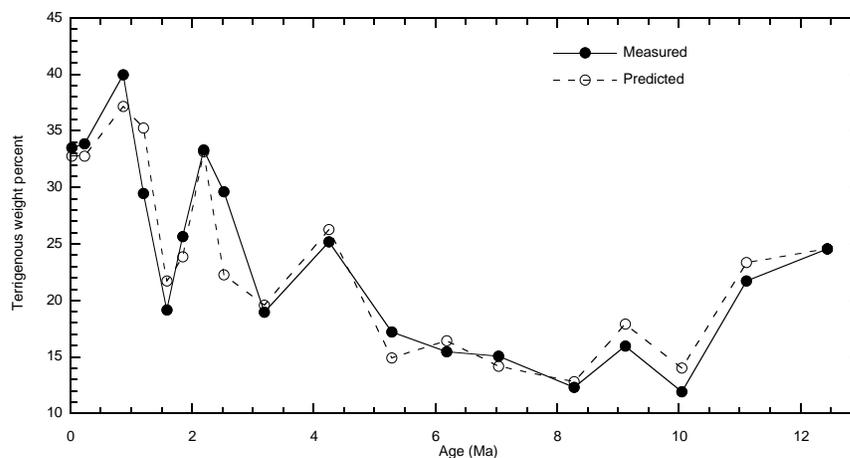
Figure 8. Estimates of terrigenous weight percent over the last 12 Ma from regression against high-resolution shipboard data sets as compared to the original measured values.
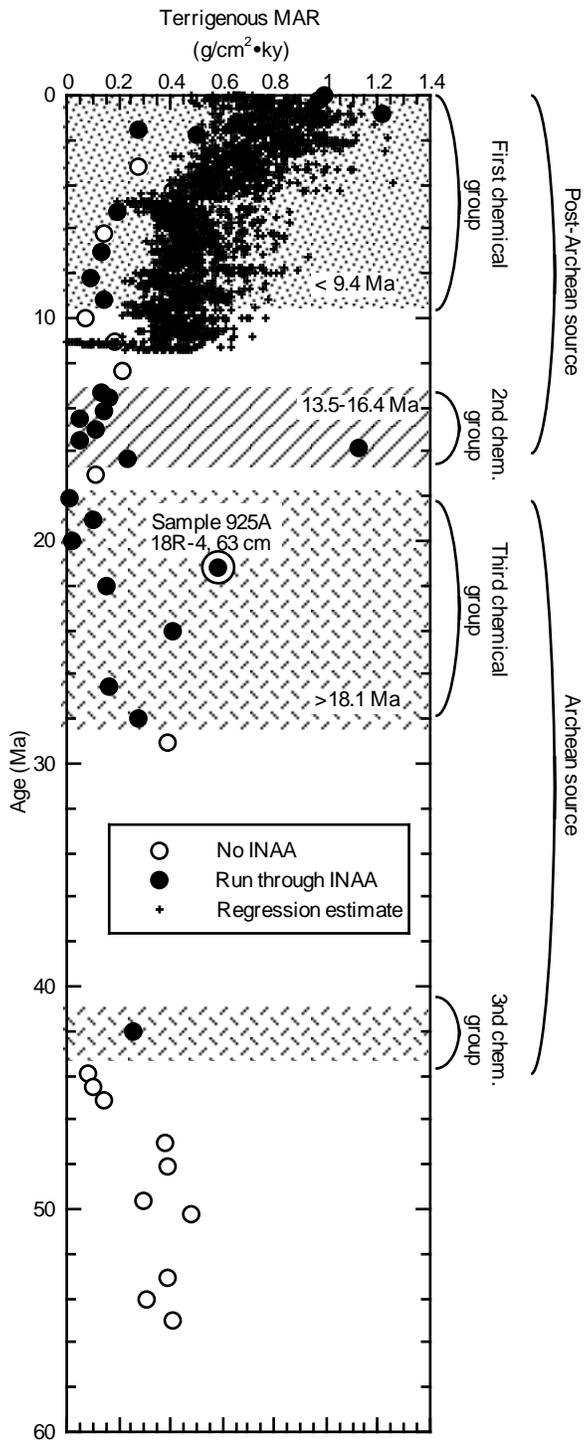
Figure 9. Summary of all work done in this project. Terrigenous MARs from measurements and from estimates for the last 12 Ma and the inferred sources are shown.

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