25. MINOR ELEMENT GEOCHEMISTRY OF SEDIMENTS AT SITE 328, FALKLAND OUTER BASIN AND SITE 329, FALKLAND PLATEAU, LEG 36, DEEP SEA DRILLING PROJECT

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ABSTRACT

Site 328, a deep-water site in the Malvinas Outer Basin, is composed of siliceous and zeolitic clays and claystones. Site 329, an equivalent shallow-water site on the nearby Falkland Plateau, is composed of siliceous and calcareous oozes and chalks deposited mostly above the CCD. A total of 72 samples from Site 328 and 74 from Site 329 has been analyzed for Ti, Fe, Mn, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, and Th in order to establish in detail the downhole geochemical variations at each site and to compare the geochemical behavior of trace elements in a deep water and a shallow water environment.

There are significant short, medium-, and long-term geochemical variations at both sites, but particularly at Site 329, and well-marked sympathetic and antipathetic relationships between many of the minor and trace elements. Many of the downhole variations correlate with lithology and stratigraphy. Geochemically the two sites are very different, not only in terms of mean element compositions, but also in the way the trace elements interrelate. These differences are examined in detail by use of correlation coefficient matrices. The results emphasize the fact that the sediment sources and depositional environments were fundamentally different at the two sites.

INTRODUCTION

There were several reasons for undertaking geochemical studies of the sediments at Sites 328 and 329:

1) To compare the chemistry of sediments of approximately the same age range in two adjacent high latitude sites, one (328) deposited at great depth well below the carbonate compensation depth (CCD) and the other (329) deposited in a shelf environment on the Falkland Plateau mostly just above the CCD.

2) To assess whether there was any significant variation in the chemistry of the sediments with depth in the core. At both sites there was, for paleontological reasons, some continuous coring. As far as possible, to give close coverage, samples were taken every section. A related objective was to establish the degree of small-scale chemical variability in these continuously cored sections.

3) To establish whether there was any change in chemistry which might correlate with lithology and with change in depositional environments.

4) At Site 328 siliceous organisms showed increasing dissolution below Unit 2 (Miocene) and were replaced lower down the core by zeolitic clays and claystones. There was some shipboard interest as to whether this might be reflected in a major change in trace element chemistry.

LOCATION AND SAMPLING

Site 328 was located in the Malvinas Outer Basin (lat 49° 48.67'S; long 36° 39.53'W) in a water depth of 5103 meters. The sediments were drilled to a depth of 471 meters, only an estimated 90 meters above the acoustic basement. The top 50 meters consist of Plio-Pleistocene siliceous ooze, underlain by Oligocene and Miocene silty siliceous and zeolitic clay. There is a sharp change below 50 meters (mid-Oligocene) to a rather monotonous greenish-gray zeolitic clay which constitutes the remainder of the section and ranges in age down to Upper Cretaceous (Turonian).

Two of the three holes at this site were sampled. Hole 328 cored intermittently through the succession to a depth of 400 meters. Hole 328B cored continuously the uppermost 65 meters from Pleistocene through Pliocene, Miocene, Oligocene to reach uppermost Eocene, with further penetration (Core 7) at 450 meters in Late Cretaceous claystones.

Site 329, located on the elevated part of the Falkland Plateau (lat 50° 39.21'S; long 46° 05.73'W) in a water depth of 1530 meters, penetrated 464 meters of shallow water siliceous and calcareous oozes and chalks. The hole was cored continuously for almost 180 meters (Cores 1 to 19), and intermittently thereafter. The upper 4 meters consisted of Pleistocene silty clay-rich diatomaceous oozes, but the bulk of the section (375 m) was made up of Miocene nanno and diatom oozes overlying Oligocene to Paleocene nanno chalk. Variations in the proportion of diatom and nanno components throughout most of the core suggest that deposition took place near to, but mostly above the CCD.

Sampling at both sites was carried out onboard ship. As far as possible every core and most of the sections within each core were sampled, except where there had been severe drilling disturbance of the core. About 30-40 g of each sediment sample was taken, and stored in a sealed polythene vial prior to analysis.

A total of 146 samples was selected for analysis, 42 from Hole 328, 30 from Hole 328B, and 74 from Hole 329.

With the large number of samples selected for analysis, fairly rapid methods had to be employed in preparing the samples for analysis by X-ray fluorescence techniques. Nevertheless time spent in sample preparation far exceeded the time spent on the analysis itself.

The samples were oven-dried at 110°C for several hours in a disaggregated state; crushed in a tungsten carbide ball mill for 20 min, and pressed into a 4.6-cm diameter disc at 20 tons using a small amount of MOWIOL as a binder. The powder discs were then analyzed for Ti, Fe, Mn, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ce, La, Pb, and Th using an automatic Philips PW 1450 X-ray spectrometer. Calibration was based on international standard rocks and "spiked" samples. The trace element results were automatically corrected for interelement absorption effects using Mo Compton scatter and WLβ tube lines. Precision is better than ± 2 ppm for most trace elements.

Light elements (i.e., most major elements) were not analyzed for at this stage because seawater salt, coating the grains, had a serious absorption effect on the longer wavelengths. Ideally, each sample needs to be thoroughly washed with distilled water before drying in order to overcome this problem, but this would considerably extend the preparation time.

RESULTS

Analytical results for Hole 328, Hole 328B, and Hole 329 are given in Tables 1, 2, and 3, respectively, and are arranged in downhole order. Mean values for the siliceous clay sediments at Site 328 and the siliceous calcareous sediments at Site 329 are compared in Table 4. Also listed in Table 4 are the maximum and minimum values and the standard deviation for each element and element ratio. As may be expected, there are substantial differences in the mean values of most elements between the two sites. This is also shown in Table 4 as a ratio of Site 328/Site 329 for each element. All the elements studied have a higher concentration in the Site 328 clay section apart from Sr and to a smaller extent Ba.

Before comparing the geochemistry of the sediments at the two sites, it is necessary to discuss geochemical variations within each site individually.

Site 329

Downhole element variations at Site 329 are shown diagrammatically in Figure 1. To provide a compact picture of the geochemical variations on one diagram, the samples are plotted incrementally in downhole order without regard as to whether the cores were continuous or not, or even whether all individual sections within each core were represented. Hence the vertical scale is nonlinear. Nevertheless, variations in chemistry with depth in the core are clearly brought out.

Several interesting features are apparent from this diagram.

1) There are both sympathetic and antipathetic relationships between the different elements in the sediments. The variation pattern for Zn is almost the identical mirror image of that for Sr, indicating that Zn is associated with one major component of the sediment while Sr is associated with the other. That Sr is linked with the calcareous component can be seen from the pattern of the plotted shipboard $CaCO_3$ results which, although there are fewer determinations and they were not taken from the same sections of the cores, show variations comparable to that of Sr. Most of the other elements figured have variations sympathetic to a greater or lesser degree with Zn. Of these Cr, Ni Rb, Th, Pb, and Ba correlate strongly, while Zr, Nb, Y, Ce and La show comparable variations but of smaller magnitude. Ba follows Zn very closely in the oozes of the upper part of the core, but rather less closely in the chalks near the bottom of the hole.

2) Short-, medium-, and long-term trends are evident in the element abundance levels in the sediments. Because the precision of XRF determinations for the elements studied is of the order of 1 to 2 ppm, these trends appear to be real. In the continuously cored section (Cores 1 to 19) smooth trends are evident (e.g., Sr, Rb) extending over several cores. Even in the discontinuously cored zones some smooth trends are present. Systematic long-term variations are seen within the medium-term scatter. For instance, Sr increases from 130 ppm to nearly 200 ppm between Core 4 and Core 17, while Zn decreases from 120 ppm to 20 ppm over the same interval. Again Ba increases from 200 ppm in Core 17 to 800 ppm in Core 33. Comparable long-term variations are seen for some other elements, while others show no long-term variation but do show sympathetic medium- to short-term variation. Significant short-term peaks for many elements are seen in the upper part of Core 2, in Core 8, and in Core 13. Some of the apparent short-term variation in the lower part of the core, however, may just be a result of discontinuous coring.

3) Some geochemical variations are directly related to lithology and stratigraphy. Hole 329 consists mainly of diatom-nanno oozes and chalks with variations in the proportion of diatom and calcareous nanno components, but with variations in the radiolarian and clay components too.

The sharp geochemical discontinuity between the upper and lower halves of Core 1, affecting every element, coincides with the hiatus between Pleistocene and Miocene. Higher trace-element concentrations in the Pleistocene are linked with the high proportion of clay (glauconite) and sand. The upper two sections of Core 2 have a similar geochemistry and lithology and may simply be a result of downhole contamination with Pleistocene sand.

In Core 4 there is a progressive change from diatom-bearing nanno ooze in the upper sections to a nanno- and clay-bearing diatom ooze in the lower part, and

TABLE 1
Geochemical Data for Siliceous Clays, Hole 328, Malvinas Outer Basin
(oxides in %, trace elements in ppm)

Sample (Interval in cm)	TiO_2	Fe_2O_3	MnO	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th
1-1, 140	0.604	5.31	0.136	48	66	283	112	74	131	30	151	8	506	28	40	11	9
1-2, 135	–	–	–	46	81	–	126	77	146	19	154	6	526	24	44	12	9
1-3, 124	–	–	–	59	63	223	137	90	146	20	155	11	674	24	41	20	10
1-4, 127	0.716	6.12	0.121	58	53	281	135	94	157	23	169	14	470	28	45	18	10
1-5, 127	0.622	4.99	0.112	50	110	355	126	64	132	15	141	11	620	17	43	13	8
2-2, 135	–	–	–	35	62	–	99	71	150	19	153	9	533	27	40	12	10
2-3, 125	0.410	5.46	1.789	30	300	488	125	81	157	19	157	10	443	22	33	15	5
2-4, 136	0.576	6.19	0.250	39	57	346	125	92	160	20	160	10	431	23	36	13	10
2-5, 136	0.475	5.19	0.117	37	40	322	117	89	157	20	202	11	384	23	36	10	9
2-6, 55	0.487	5.14	0.114	37	46	329	124	81	145	16	151	9	284	21	30	10	9
3-1, 126	0.488	4.65	0.164	43	61	431	143	99	161	20	174	11	544	31	49	10	9
3-3, 131	0.845	7.47	0.516	39	198	547	171	101	165	25	188	13	726	34	55	22	10
3-4, 131	0.770	7.36	0.296	41	154	603	175	105	176	27	198	12	1077	37	54	12	10
3-5, 115	0.734	7.08	0.287	34	116	533	196	96	171	30	199	11	1028	33	52	16	10
3-6, 74	0.814	7.59	0.278	–	–	451	181	85	165	29	–	–	1007	–	–	18	12
4-2, 130	–	–	–	57	137	276	172	111	114	23	145	10	308	40	63	15	13
4-3, 104	0.682	6.88	0.571	79	169	323	184	110	128	24	152	11	341	30	62	14	11
4-5, 131	0.981	9.08	0.435	54	125	227	200	111	131	29	174	13	427	43	101	25	19
5-2, 84	0.567	6.54	0.094	76	105	–	143	110	115	25	130	12	523	44	83	20	17
5-3, 133	–	–	–	907	399	–	153	110	120	24	132	8	478	25	45	27	17
6-1, 103	0.802	7.93	0.099	70	40	254	179	101	113	25	139	12	420	41	95	30	16
6-2, 123	0.707	8.66	0.107	63	66	259	118	94	109	22	132	11	354	42	79	27	14
6-3, 62	0.685	7.23	0.118	64	115	268	139	94	151	32	133	13	592	43	85	26	17
7-4, 138	0.784	8.41	0.103	80	60	239	117	102	115	26	135	13	366	44	91	26	15
8-2, 138	0.788	9.97	0.107	70	63	197	130	101	125	23	127	11	537	37	90	15	16
8-3, 38	0.824	9.80	0.104	74	68	213	139	98	120	23	138	10	341	44	96	16	15
9-1, 100	0.793	8.03	0.105	67	62	264	137	101	126	24	137	12	512	47	87	27	16
9-2, 33	0.807	9.48	0.120	74	69	238	143	99	117	24	136	11	397	36	90	17	15
9-4, 78	0.843	9.33	0.107	77	77	215	138	102	126	25	140	12	631	42	92	22	17
9-5, 100	0.840	7.31	0.106	80	79	300	149	101	134	25	156	14	478	42	95	31	19
9-6, 108	0.792	8.0	0.107	69	71	252	137	106	129	23	141	10	580	40	80	23	16
10-1, 42	0.743	10.21	0.104	60	40	197	109	105	125	31	134	10	733	43	79	12	16
10-5, 124	0.703	11.09	0.133	45	53	172	122	104	119	33	133	11	295	42	90	15	13
10-6, 125	0.764	6.25	0.106	61	82	260	179	99	146	36	406	32	504	53	126	23	19
11-1, 32	0.771	7.27	0.131	56	61	217	112	78	127	28	152	13	412	43	93	17	11
11-3, 102	0.467	6.46	0.103	63	72	268	145	87	136	27	146	11	415	42	88	32	15
11-4, 77	0.209	3.79	0.104	1089	266	169	120	88	129	23	117	10	460	24	49	15	10
11-5, 65	0.432	8.97	0.101	53	61	182	96	82	122	22	138	12	355	42	88	12	10
11-6, 16	0.644	6.43	0.098	48	65	335	114	81	127	24	151	11	343	37	75	30	12
12-1, 51	0.657	6.04	0.097	47	65	222	153	80	124	23	147	12	390	33	89	19	14
12-2, 33	0.644	5.41	0.109	82	82	–	183	102	136	34	177	15	455	56	120	25	16
12-6, 128	0.991	7.67	0.113	73	54	276	116	108	138	30	172	13	373	52	117	20	19

there is an equivalent sharp change in chemistry. The reverse situation is seen in Core 8 where there is a change within the core from micrite-diatom ooze to diatom-micrite ooze. But Core 9 sees a return to diatom-rich oozes.

Core 22 markes another abrupt change in chemistry which correlates with a change from diatom oozes to nanno chalks and coincides with the paleontological boundary between upper and middle Miocene. Below this the lithology is a more geochemically uniform nanno chalk, but there is a minor break at Core 27 which coincides with a hiatus between middle Miocene and Oligocene.

The reasons for these variations in geochemistry may be complex. Medium- to long-term variations may be related to fluctuations in the CCD, changes in the relative productivity and type of siliceous and calcareous organisms, or variations in the current activity or sediment source. Some of these changes appear to have taken place gradually; others very rapidly.

Site 328

Downhole variations at Site 328 are shown in Figure 2 and displayed in a similar manner to those for Site 329 in Figure 1. However, there are complications in that, apart from the first three cores, Hole 328 was cored discontinuously with only moderate recovery and with appreciable gaps between each core. Hole 328B yielded six continuous cores (Cores 1-6) which overlap Cores 2-4 of Hole 328, but Core 7 of Hole 328B lay stratigraphically below Core 12 of Hole 328. Hence in Figure 2, Core 7 of Hole 328B is included with the Hole 328 results.

Hole 328B is plotted separately and was sampled primarily to assess the geochemical differences between the biogenous siliceous clays of Pliocene-Miocene age (Cores 2-4) and the underlying zeolitic clays of the Oligocene (Cores 5 and 6).

The relevant geochemical features of Site 328 can be summarized as follows:

TABLE 2
Geochemical Data for Siliceous Clays, Zeolitic Clays, and Claystones, Hole 328B, Malvinas Outer Basin (oxides in %, trace elements in ppm)

Sample (Interval in cm)	TiO_2	Fe_2O_3	MnO	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th
2-5, 121	–	–	–	35	164	–	143	99	176	30	205	11	1388	39	65	17	13
2-6, 121	0.958	8.64	0.375	38	147	533	193	103	173	31	206	12	1216	40	72	19	11
3-1, 97	–	–	–	34	101	392	155	83	154	25	188	11	751	35	67	21	9
3-2, 95	–	–	–	37	156	–	–	–	–	–	179	9	–	34	59	–	–
3-3, 91	0.854	7.69	0.566	32	487	414	160	85	147	25	167	10	803	33	57	18	10
3-4, 95	0.651	6.40	0.280	28	114	305	135	80	142	25	155	8	613	27	49	13	7
3-5, 121	–	–	–	36	226	435	158	88	153	25	160	9	918	31	56	19	11
4-1, 118	0.814	7.67	0.216	57	87	–	157	128	147	29	168	11	922	36	73	16	15
4-2, 111	0.805	7.81	0.622	52	183	295	172	150	138	28	173	10	782	43	80	25	18
4-3, 104	0.602	7.74	0.545	55	163	308	171	146	136	28	170	10	772	39	76	23	16
4-4, 121	0.653	7.70	0.508	52	164	299	176	147	135	42	178	10	733	36	77	26	17
4-5, 135	–	–	–	36	170	216	135	99	104	18	129	7	432	21	50	20	11
5-1, 81	–	–	–	52	97	248	204	116	114	35	172	11	364	56	150	17	17
5-2, 91	0.954	8.78	0.806	51	186	283	205	113	153	30	187	11	733	51	116	21	15
5-3, 100	0.646	7.08	0.523	43	121	224	196	99	128	27	170	10	347	45	152	15	17
5-4, 121	0.976	8.98	0.362	48	113	–	192	103	141	27	177	11	435	41	94	19	14
5-5, 129	–	–	–	51	126	256	192	112	131	27	168	10	585	44	113	26	13
5-6, 81	0.924	9.09	0.910	52	215	263	216	111	132	25	166	11	603	40	99	30	14
6-1, 32	1.031	10.02	0.304	63	117	250	172	122	104	35	153	10	426	56	141	34	19
6-2, 82	0.885	9.41	0.256	62	108	244	174	119	97	31	156	11	343	46	123	28	20
6-3, 102	–	–	–	63	114	–	180	116	107	33	157	11	330	51	122	29	17
6-4, 102	1.025	9.75	0.298	69	119	260	195	117	106	33	159	12	423	50	117	22	18
6-5, 102	–	–	–	66	114	–	175	117	104	33	161	14	377	54	118	21	18
6-6, 86	–	–	–	71	131	–	117	122	108	32	152	13	457	51	122	30	18
7-1, 97	–	–	–	70	176	293	116	94	149	25	176	15	452	45	123	19	13
7-2, 98	0.489	11.10	0.154	57	68	203	103	99	131	21	163	14	307	46	92	20	15
7-3, 112	0.868	5.37	0.133	70	90	232	143	90	149	22	180	15	419	40	100	21	16
7-4, 25	0.841	14.19	0.178	49	81	183	103	96	133	24	148	12	253	48	112	25	12
7-5, 27	–	–	–	66	96	221	135	92	141	24	184	14	205	48	112	26	18
7-6, 56	0.094	10.50	0.253	60	78	222	118	103	142	50	178	17	679	76	227	27	15

1) Although there is some geochemical coherence in the downhole element variations, the strong sympathetic and antipathetic relationships noted for Site 329 are much less well developed. The most marked change relates to Sr, which had a strong antipathetic relationship with Zn, Rb, Cr, Ni, Th, Pb, and most other elements at Site 329, but here varies sympathetically with Zn, Rb, Ba, and Zn, at least with respect to short- and medium-term variations. Likewise, Ni and Cr, while varying sympathetically with each other and with Zn, Rb, Th, and Pb in Hole 329, now display very little geochemical coherence with these elements, nor indeed with each other, expecially in Hole 328B.

2) Long- and medium-term trends are displayed by many elements. La and Ce show an increasing concentration with depth in both Holes 328 and 328B, while Y shows little long-term variation. The significance of this is difficult to understand, but implies that rare-earth element patterns might be increasingly light-RE enriched with depth in the core. Cr shows a similar increase in Hole 328B. On the other hand, Zn increases between Cores 1-4 in Hole 328, and then decreases for the remainder of the core. Similar variations are apparent for other trace elements, but there is no consistent pattern of long-term behavior. This would suggest that there is no single variable responsible for these trends, but that each element is acting independently. The most likely explanation is that the variations reflect a constantly changing source of sediment. Short-term variations, where several elements show simultaneous fluctuations in abundance (although to variable degrees) may be linked to new sediment sources or changing bottom currents.

3) Referring to the continuously cored section in Hole 328B which records the lithological change between the Pliocene-Miocene siliceous clays (Cores 2, 3, and 4) and the zeolitic clays of Cores 5 and 6, there are certainly sharp fluctuations for many elements at the boundary between Core 4 and Core 5. This is most marked for Zn, Cr, La, and Ce which are of lower abundance in the siliceous clays, while Rb, Sr, and Ba are more concentrated in the siliceous clays. On the other hand, there is no obvious change in Ni, Y, Th, and Pb. However, with Ba, Cr, Ce, and La, the changes are merely an accentuation of longer term trends evident in this core, and a sharper discontinuity might have been expected if the Core 4/Core 5 boundary also represents a hiatus in sedimentation.

The equivalent horizon in Hole 328 lies between Cores 3 and 4. In general, the same geochemical differences are evident in that Zn, Cr, La, and Ce have lower concentrations in Cores 1 and 3 than in the deeper parts of the core, while Zr and Sr have higher values. Ni is distinctly higher in Cores 3 to 5 than in the sediments above and below. This interval obviously coincides with Cores 2 to 6 in Hole 328B. The high Ni content is clearly related to the high proportion of manganese micronodules at this point in the section.

In summary, the geochemical variations in the sediments at Site 328 are more complex than at Site 329. While some of these variations might be connected

TABLE 3
Geochemical Data for Siliceous-Calcareous Sediments at Site 329, Falkland Plateau
(oxices in %, trace elements in ppm)

Sample (Interval in cm)	TiO_2	Fe_2O_3	MnO	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ca	Pb	Th
1-1, 131	0.263	7.36	0.099	103	25	168	124	98	140	15	200	15	484	15	21	10	5
1-2, 81	0.351	6.91	0.103	87	34	166	135	87	124	17	192	16	575	20	27	16	10
1-1, 41	0.218	6.47	0.100	59	33	183	137	79	111	23	130	6	548	14	15	13	1
1-4, 41	0.129	2.11	0.094	12	19	168	59	28	625	15	80	5	583	9	12	6	5
1-5, 131	0.113	2.83	0.096	8	21	193	58	22	648	10	76	4	531	8	8	7	6
1-6, 49	0.250	2.68	0.104	9	18	193	68	27	567	12	99	4	490	11	20	9	3
2-1, 121	0.318	4.54	0.104	1190	282	180	139	55	463	28	97	5	936	9	1	9	3
2-2, 102	0.340	5.08	0.106	39	38	195	132	56	418	29	128	2	944	20	23	6	3
2-3, 131	0.128	2.21	0.098	8	17	172	58	29	866	13	100	4	306	7	11	5	6
2-4, 132	0.109	2.75	0.093	8	14	167	45	22	1087	13	87	3	268	8	12	10	1
2-5, 83	0.120	2.07	0.100	8	20	174	55	38	922	15	94	4	358	8	9	3	2
2-6, 71	0.098	1.87	0.099	8	15	185	51	23	919	11	83	5	326	7	11	9	2
3-1, 67	0.158	2.50	0.097	18	22	174	74	35	597	14	95	4	480	9	14	8	5
3-2, 82	0.179	2.36	0.094	10	16	168	59	29	865	11	98	4	339	8	11	7	2
3-3, 72	0.204	3.39	0.099	13	24	169	51	26	749	7	97	3	316	10	11	7	3
3-4, 89	0.186	2.37	0.100	14	22	191	71	30	786	12	100	4	364	10	13	8	1
3-6, 116	0.072	2.40	0.095	4	6	163	30	12	1242	6	73	2	275	5	7	3	1
4-1, 108	0.168	2.34	0.096	11	21	193	70	28	572	11	91	4	557	8	12	4	1
4-3, 105	0.260	2.83	0.098	22	45	253	120	37	181	15	94	4	794	13	18	8	7
4-5, 26	0.180	1.57	0.097	11	25	211	89	35	257	15	95	4	455	6	9	9	6
5-1, 62	0.160	1.84	0.101	14	30	222	95	35	342	14	95	6	676	8	14	6	3
5-4, 76	0.252	2.46	0.103	20	30	225	112	36	306	16	98	4	814	14	14	5	3
5-6, 123	0.100	1.72	0.093	14	23	207	97	35	237	15	92	5	423	5	10	7	3
6-2, 126	0.151	1.44	0.098	12	22	205	79	26	427	12	79	3	528	10	11	5	1
6-5, 84	0.076	1.50	0.094	9	27	218	88	34	314	13	90	3	261	8	7	11	5
7-6, 86	0.115	1.06	0.095	8	25	218	68	22	503	9	71	4	510	7	11	8	3
8-2, 125	0.074	1.58	0.093	5	15	170	45	15	879	9	70	2	258	5	6	6	2
8-5, 56	0.043	2.23	0.093	3	6	154	26	8	1234	5	62	1	134	4	10	2	1
9-4, 137	0.178	2.74	0.101	13	29	187	87	41	562	18	112	3	459	9	13	8	4
9-5, 86	0.242	2.99	0.100	18	29	193	93	44	592	18	114	5	631	11	16	10	8
10-1, 114	0.138	2.18	0.097	10	20	185	76	30	593	12	88	5	541	6	13	9	5
10-4, 58	0.065	1.69	0.091	6	18	187	54	20	595	8	67	1	332	4	4	4	1
10-6, 60	0.067	1.59	0.093	10	15	185	46	16	901	7	67	1	275	4	9	4	1
11-2, 66	0.090	1.67	0.090	6	15	185	50	15	924	6	72	4	362	4	7	3	1
11-5, 19	0.115	1.87	0.093	11	17	183	57	21	810	9	77	2	428	6	10	5	2
12-2, 26	0.118	1.99	0.097	9	18	174	66	21	757	9	77	3	467	8	10	8	1
12-5, 112	0.147	2.05	0.097	18	21	189	63	27	838	10	85	2	627	8	8	4	3
13-2, 23	0.184	2.10	0.101	15	32	225	112	43	359	13	109	5	483	9	12	12	4
13-4, 41	0.126	2.10	0.096	9	24	185	62	26	732	12	83	2	475	6	12	7	2
14-2, 69	0.084	1.66	0.097	7	11	187	46	20	899	14	79	2	370	7	8	6	1
14-6, 62	0.086	1.71	0.096	8	16	176	49	21	1089	10	82	3	420	6	9	5	2
15-2, 62	–	–	–	6	16	152	29	14	1224	8	79	2	171	7	9	4	2
15-3, 139	0.087	2.59	0.097	7	15	156	34	16	1202	7	76	2	237	6	7	7	1
15-5, 123	0.100	1.75	0.098	9	15	176	39	21	1142	8	84	2	324	7	16	5	1
16-1, 80	0.127	1.99	0.099	9	20	185	53	23	932	10	85	4	419	9	11	5	1
16-4, 63	0.037	2.21	0.094	1	6	163	21	9	1348	6	66	2	130	5	6	6	1
17-2, 88	0.062	1.43	0.094	4	11	180	36	11	1068	6	67	2	281	6	11	5	1
17-4, 54	0.050	2.29	0.093	6	6	158	28	10	1149	7	63	1	193	4	6	4	3
18-4, 129	0.086	2.59	0.098	5	11	159	38	20	1147	9	82	2	255	5	9	6	2
18-6, 26	0.130	1.93	0.094	11	19	187	58	22	853	10	83	2	399	5	10	6	3
19-2, 123	0.080	1.63	0.095	7	16	174	43	15	886	7	70	3	206	6	7	7	1
19-3, 105	0.139	2.15	0.098	10	19	180	62	27	602	10	80	5	312	6	10	11	4
20-2, 39	0.106	1.14	0.091	6	22	192	57	21	444	8	69	4	368	5	9	7	1
20-5, 113	0.082	1.59	0.097	7	13	180	42	16	729	9	66	3	357	5	9	6	3
21-3, 31	0.124	1.81	0.097	12	28	214	92	32	254	12	100	4	465	9	9	7	3
21-4, 59	0.107	1.91	0.099	10	18	180	54	24	854	14	86	2	522	8	11	4	3
22-2, 47	0.086	1.17	0.094	8	24	201	71	23	179	6	67	3	366	6	5	5	3
22-4, 109	0.103	1.74	0.096	9	12	191	46	17	818	11	74	1	628	7	10	4	1
23-1, 98	0.171	2.24	0.091	12	23	197	62	29	805	9	90	2	501	8	11	8	3
23-2, 44	0.087	1.58	0.091	6	13	183	42	17	1259	10	81	1	298	8	13	3	5
23-3,132	0.076	2.45	0.092	6	11	160	32	15	1406	9	77	1	333	4	9	5	2
14-2, 132	0.133	1.96	0.095	9	16	183	54	24	926	10	84	2	471	8	7	4	4
24-3, 123	0.084	1.65	0.094	10	13	170	46	24	970	15	82	2	359	8	6	8	5
26-1, 65	0.084	1.63	0.093	10	15	178	43	18	943	9	75	1	393	7	6	5	4
26-3, 106	0.192	1.82	0.098	14	25	218	74	21	143	5	64	3	400	9	8	6	4
27-1, 31	0.103	2.57	0.098	5	10	152	33	16	1205	14	77	1	997	8	12	8	2
28-1, 132	0.113	2.88	0.112	11	26	154	43	29	1120	11	82	3	458	8	13	5	2

TABLE 4
Average Element Compositions for Site 328 Siliceous and Zeolitic Clays and Site 329 Siliceous and Calcareous Oozes, with Standard Deviations and Maximum and Minimum Values for Each Element

	Site 328				Site 329				
	Mean	S. D.	Max.	Min	Mean	S. D.	Max	Min	328/329
TiO_2 (%)	0.734	0.176	1.031	0.209	0.134	0.067	0.351	0.037	5.5
Fe_2O_3 (%)	7.76	1.99	14,19	3.79	2.40	1.16	7.36	1,06	3.2
MnO (%)	0.272	0.297	1.790	0.094	0.098	0.005	0.112	0.090	2.8
Cr[a]	82	146	1089	28	29	139	1190	<1	2.8
Ni	117	80	487	40	23	32	282	6	5.1
Cu	293	–	593	164	182	21	253	150	1.6
Zn	150	32	216	96	62	29	139	21	2.4
Rb	100	17	150	64	27	16	98	8	3.7
Sr	135	18	176	97	757	335	1406	111	0.2
Y	26	6	50	15	12	5	29	5	2.2
Zr	163	41	406	117	86	24	200	49	1.9
Nb	12	3	32	6	3	2.5	16	<1	4.0
Ba	558	–	1367	291	463	194	997	130	1.2
La	39	10	76	17	8	4	20	4	4.9
Ce	84	35	227	30	12	5	28	<1	7.0
Pb	20	7	34	10	7	3	16	2	2.9
Th	14	4	20	5	3	2	10	<1	4.7
Cr/Ni	0.70		4.09	0.07	1.23		4.2	0.10	0.6
Fe/Mn	16.5		98.2	3.1	24.5		74	11.1	0.7
Rb/Sr	0.74		1.23	0.47	0.036		0.71	0.006	20.6
Ba/Rb	5.4		14.02	2.64	17.1		62	4.9	0.3
Ba/Sr	4.0		7.89	1.48	0.61		4.9	0.10	6.6

with the increase in biogenous components in the upper part of the core, or with the varying adsorption of cations by the clay and zeolite components, or with the presence of manganese nodules, the general lack of geochemical coherence between the trace elements suggests that the main variable might be the source of the sediments.

GEOCHEMICAL COMPARISONS BETWEEN SITES 328 AND 329

Table 4 shows a comparison of mean values of Site 328 and Site 329 sediments and illustrates the distinctly higher trace-element values (Sr excepted) in a deep water site compared with a shallow water site, a feature which has been noted previously (Cook, 1974). Mere comparison of averages can, however, obscure other geochemical relationships such as those noted above with regard to downhole variations in sediment chemistry.

In order to extend this study, correlation matrices, containing correlation coefficients between each different pair of elements, and some important element ratios, have been calculated using a computer program (CORRCLUST) written by A.C. Skinner. Combined correlation matrices for Site 328 and Site 329 sediments are tabulated in Figure 5. In order to clarify presentation, the coefficients have been increased by a factor of 100 (i.e., $R \times 100$) and quoted to only two significant figures. Correlation matrices have been used previously in the study of Indian Ocean sediments by Cook (1974), although his sample populations were rather small.

The correlation coefficient between two variables, x and y, in a set of data is defined as the ratio of the covariance of the variables to the product of their standard deviations. Thus the correlation coefficient (R) is given by

$$R = \frac{\Sigma_1^n (x - \bar{x})\ (y - \bar{y})}{\left[\Sigma_1^n (x - \bar{x})^2\ ^{1/2}\right] \left[\Sigma_1^n (y - \bar{y})^2\ ^{1/2}\right]}$$

where x and y denote the values of the two variables, $\bar{x}$ and $\bar{y}$ are the means of the two variables in the set, and n is the number of samples in the set.

However, it is also necessary to determine whether the correlation coefficients are significant or not since the significant values of the coefficients are dependent on the number of samples in the set, although this is of progressively less importance as the number of samples increases. Accordingly, Student's "t" test has been used to calculate the significance of the correlation coefficients. In Table 5 those correlations which are significant at the 99.5% confidence level are shown in bold type. The limiting correlation coefficient value at this level of significance is ±0.27 for the sample size used. Both positive and negative correlations are shown.

The correlation matrices in Table 5 emphasize the geochemical differences between the two sites studied. It is not possible to examine or even explain all the interelement relationships, but certain features are worthy of particular note.

1) Some element pairs are strongly correlated at both sites, as may be expected from their normal geochemical coherence in many crustal rocks. Examples are: Ce-La, Ce-Y, La-Y, Zr-Nb, Th-Pb, Ti-Fe, Cu-Zn, Fe-La, Fe-Ce, Ti-La, Ti-Ce, Th-La, and Th-Ce.

2) At Site 329 there is a much higher level of correlation between most element pairs than at Site 328. Furthermore, most of the significant correlation coefficients are positive. The main exception is Sr, where all significant correlations are negative. An obvious reason

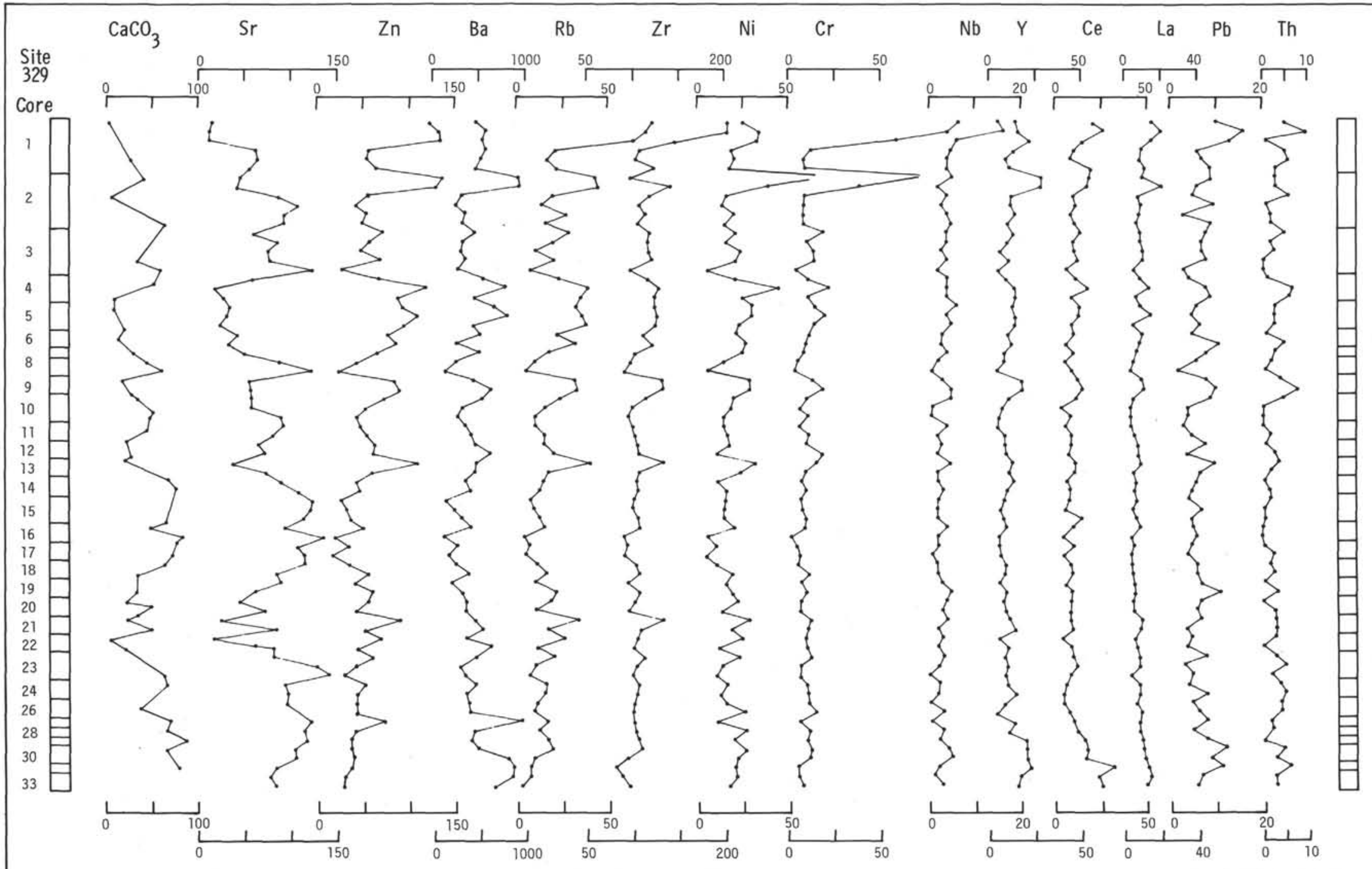

Figure 1. *Downhole trace element variations in the diatom and nanno oozes and chalks at Site 329, Falkland Plateau. Cores 1-19 are continuous to a depth of 180 meters, with intermittent coring to 464 meters in Cores 20-33. Vertical scale is not linear: samples are in incremental downhole order.*

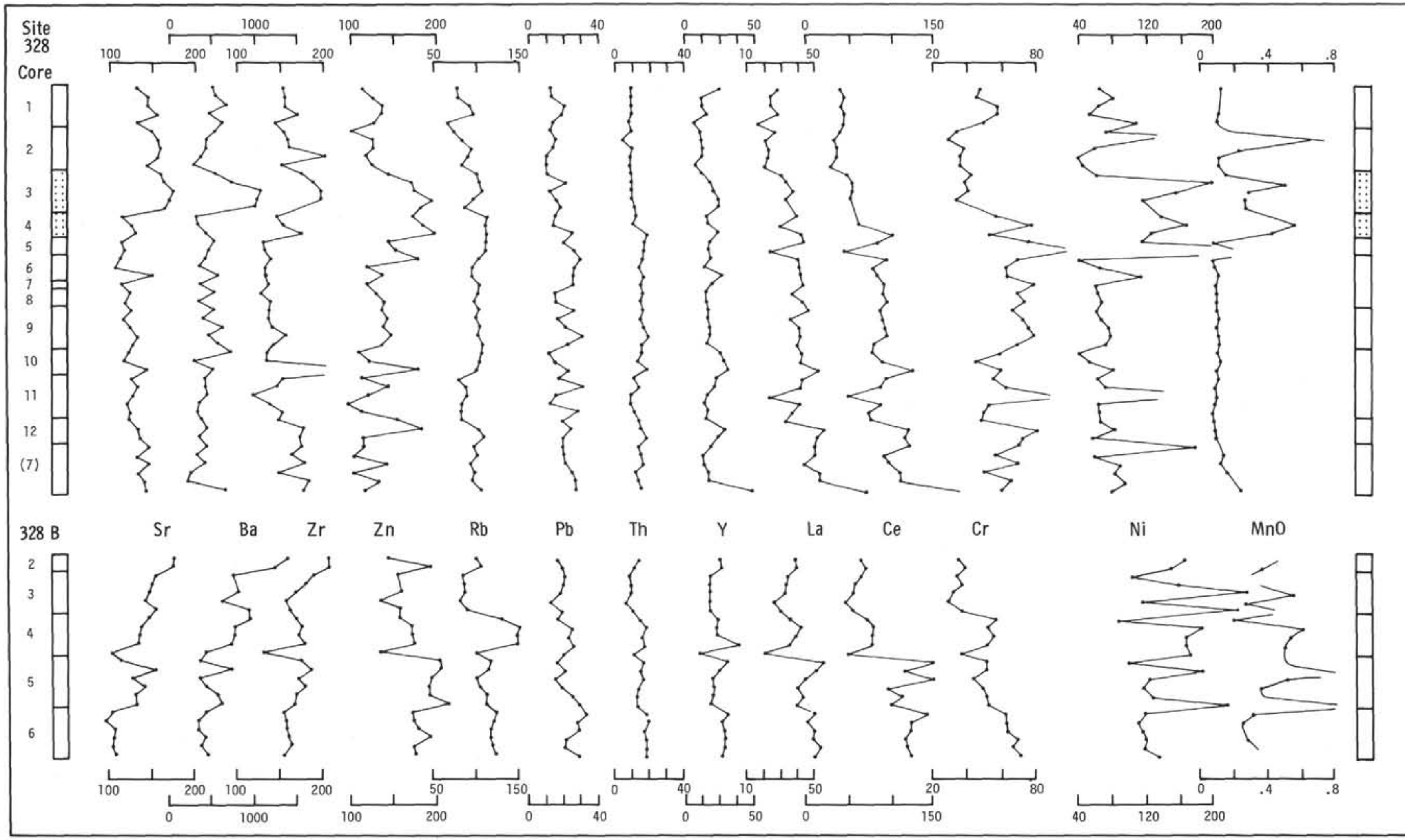

Figure 2. *Downhole trace element variations in the siliceous and zeolitic clays and claystones at Site 328, Falkland Outer Basin. The upper part of the diagram covers the discontinuous coring in Hole 328 (and Hole 328B, Core 7) to a depth of 450 meters. The lower section represents the continuous coring, for 65 meters, in Hole 328B, through the transition between siliceous and zeolitic clays. This section is equivalent to the interval between (and including) Cores 3 and 4 in the upper diagram. Vertical scales are nonlinear: samples are in incremental downhole order.*

TABLE 5
Correlation Coefficients (R x 100) for Element Pairs in Deep-Sea Sediments at Site 328, Malvinas Outer Basin (Bottom Left) and Site 329, Falkland Plateau (top right)

	Ti	Fe	Mn	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th	Cr/Ni	Fe/Mn	Rb/Sr	Ba/Rb	Ba/Sr
Ti		70	45	40	49	31	81	78	-60	59	75	61	57	77	52	48	44	59	68	59	21	70
Fe	54		44	32	31	-23	55	82	-29	56	80	67	36	72	55	53	32	75	99	80	-16	64
Mn	1	-5		17	24	-17	19	30	-13	64	25	24	60	68	66	37	24	16	35	16	32	27
Cr	-39	-26	-12		98	0	39	31	-16	42	15	17	32	10	-19	15	4	71	31	15	-6	21
Ni	1	-13	67	25		13	49	36	-28	49	18	19	40	18	-14	21	12	65	29	16	-8	29
Cu	-13	-47	8	-19	8		60	19	-70	-4	10	8	10	6	-9	5	21	-6	-19	14	-24	45
Zn	47	0	41	-13	38	17		85	-85	54	73	63	43	56	26	48	43	58	55	71	-39	83
Rb	40	38	24	-7	12	-18	51		-65	58	93	82	35	66	43	59	45	74	82	88	-42	77
Sr	-17	-41	28	-11	26	66	13	-14		-31	-49	-56	-35	-44	-20	-43	-43	-34	-29	-62	25	-79
Y	45	36	2	-7	2	-20	29	49	-8		47	29	71	70	54	50	35	41	51	35	10	45
Zr	15	-17	10	-18	7	27	37	13	42	31		84	23	63	49	55	46	67	81	82	-45	63
Nb	19	2	-17	-6	-15	0	9	-1	12	32	80		17	51	43	59	49	64	67	80	-37	64
Ba	22	-8	25	-8	40	44	46	26	60	30	27	-4		66	51	26	32	26	30	19	56	47
La	60	65	-12	-17	-18	-39	14	42	-32	70	18	42	-1		79	51	44	39	67	57	12	65
Ce	54	57	-9	-10	-17	-49	18	32	-41	66	14	39	-13	92		47	41	12	50	40	26	42
Pb	47	34	1	-7	1	-23	28	41	-37	39	1	22	-9	58	53		49	34	51	54	-15	47
Th	56	44	-21	-8	-22	-46	32	61	-51	48	11	32	-13	70	69	65		22	30	36	-7	44
Cr/Ni	-34	-14	-46	82	-20	-29	-41	-17	-31	-13	-28	2	-33	-5	-2	-5	7		76	68	-25	52
Fe/Mn	-1	38	-68	-1	-64	-35	-60	-25	-48	-13	-28	15	-44	24	17	9	26	47		82	-20	63
Rb/Sr	42	51	3	-1	-4	-46	33	81	-67	42	-14	-8	-14	49	46	51	73	2	5		-33	86
Ba/Rb	6	-26	14	-6	37	52	24	-20	62	7	20	-6	89	-23	-28	-27	-40	-28	-36	-49		-13
Ba/Sr	32	4	20	-5	37	22	48	39	29	39	15	-10	93	10	2	5	7	-26	-34	13	78	

Site 328: Siliceous and Zeolitic Clays

Site 329: Siliceous and Calcareous Oozes

Note: Correlation coefficients significant at 99.5% confidence level are shown in boldface type.

for this is that Sr is strongly associated with one of the major components, $CaCO_3$, in the calcareous oozes which is in effect "diluting" the remaining trace element-bearing component producing a close array effect. It might be suggested of course that a clay component similar in composition to the mean Site 328 clay is the main carrier of trace elements. The mean Site 328 clay is indeed richer in all trace element components apart from Sr (cf. Table 4). However, there are certain factors which rule against this. The first is that most element plots (Figures 3-8) of Site 328 clay sediments display a wide scatter, whereas equivalent plots for Site 329 sediments give much smoother linear trends which do not necessarily translate directly towards the origin as would be expected from a single dilution process with a relatively inert component such as $CaCO_3$. The second factor is that some elements (Fe, Mn, Ni, Cr, La, Ce, Pb, and Th) do not have a significantly increased negative correlation with Sr as might be expected for a simple dilution effect.

The alternative explanations are that either such a clay component differs in composition from Site 328 clay and is much more uniform, or that most of the transition and trace elements (except Sr) are associated directly with the siliceous component at Site 329.

3) There are some major differences in the correlation coefficients of many element pairs between the two sites. To illustrate this the actual differences in correlation coefficient are shown as a matrix in Table 6. Positive values indicate an increase in degree of correlation (whether positive or negative correlation) at Site 329 relative to Site 328, while negative values indicate a decrease. Only changes which are statistically significant at the 99.5% confidence level are shown. Some of the most notable changes occur with Cu-Sr, Zr-Sr, Zn-Sr, Ba-Sr, Fe-Zr, Fe-Nb, Zn-Nb, Rb-Zr, Fe/Mn-Nb, Fe/Mn-Zr, Rb/Sr-Fe/Mn, and Ba/Sr-Ba/Rb. Some of these differences are illustrated in Figures 3-8.

4) Iron and manganese have different relationships at the two sites. There is no correlation between Fe and Mn in the Site 328 clays, but a significant correlation between Fe and Mn at Site 329. Furthermore, the Fe/Mn ratio has only a moderate correlation with Fe in the clays, but a strong negative correlation with Mn, indicating that the latter is the main variable. But at Site 329, Fe/Mn is very strongly correlated with Fe and moderately with Mn, indicating that Fe is the main variable. This suggests differing redox conditions during sedimentation at the two sites.

5) A similar behavior is apparent with Cr and Ni. The correlation between the two is poor at Site 328, but very strong at Site 329, while the Cr/Ni ratio is strongly correlated with Cr, but not Ni, in the clays, yet strongly correlated with both Cr and Ni in the calcareous siliceous oozes.

6) Mn correlates significantly only with Ni and Zn in the deep water site, yet there is a very poor correlation between these three elements in the shallow water site. This suggests manganese micronodules as a major component governing the distribution of these elements at Site 328. At Site 329, on the other hand, there is a strong covariance between Mn and Ba, Ce, La, and Y.

CONCLUSIONS

Studies by a number of workers on the major and minor element geochemistry of deep-sea sediments have established the overall range of composition of different types of ocean sediment, some areal-, time-, and depth-dependent variations and some interelement relationships (see, for instance, Goldberg and Arrhenius, 1958; El Wakeel and Riley, 1961; Donnelly and Nalli, 1972; Pimm, 1974; Marchig and Vallier, 1974; Fleet and Kempe, 1974; Cook, 1974). There is also considerable data on oceanic iron-rich basal sediments (see review by Bonatti, 1975). Rather than duplicate these studies, the present investigation has

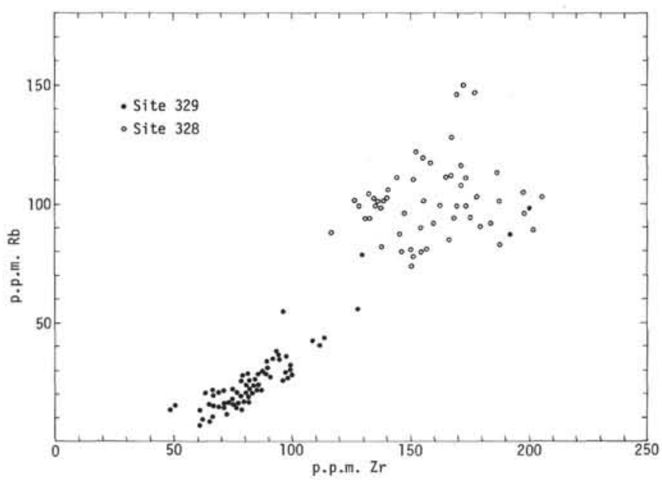

Figure 3. *Rb versus Zr for Site 328 and Site 329 sediments.*

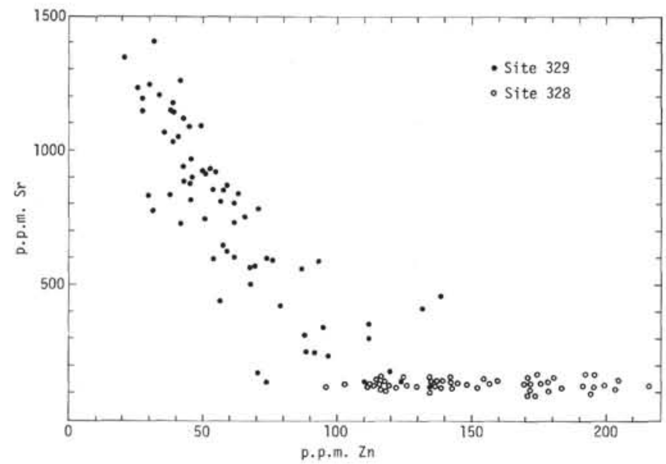

Figure 4. *Sr versus Zn for Site 328 and Site 329 sediments.*

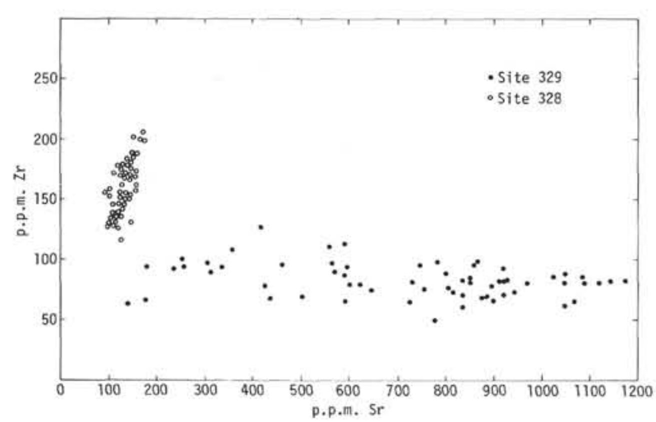

Figure 5. *Zr versus Sr for Site 328 and Site 329 sediments.*

concentrated on providing precise minor and trace element data on a large number of samples from two adjacent sites of differing bathymetry, but equivalent agerange, with the object of establishing trace element behavior patterns under differing conditions of abyssal sedimentation.

It is clear that there are very substantial differences in trace element abundance levels and interelement relationships at the two sites. At Site 329, on the Falkland Plateau, the sequence is dominated by variations in proportion of the two major biogenous components, calcareous coccoliths, and siliceous diatoms. Most of the trace elements, with the exception of Sr, are associated with the siliceous component and there is strong covariance between many of the trace elements. In the deep water clay successions of Site 328 in the Falkland Outer Basin, there is much less coherence in trace element behavior, which may reflect differences in the mineralogy and source of the sediments, and (in the case of Fe-Mn) with differing Eh conditions during deposition or diagenesis. The differing trace element relationships indicate that clay, equivalent in composition to that at Site 328, is not primarily acting as a carrier for trace elements in the siliceous component at Site 329, but suggests either that trace elements are directly associated with the siliceous component, or that any clay component is different in composition to that at Site 328.

Although the two sites are not very far apart, it appears that the sediment source was very different. In a paleogeographic context, by the time the sediments under consideration were being deposited, Africa had effectively cleared the eastern end of the Falkland Plateau and the proto-Atlantic was established. The

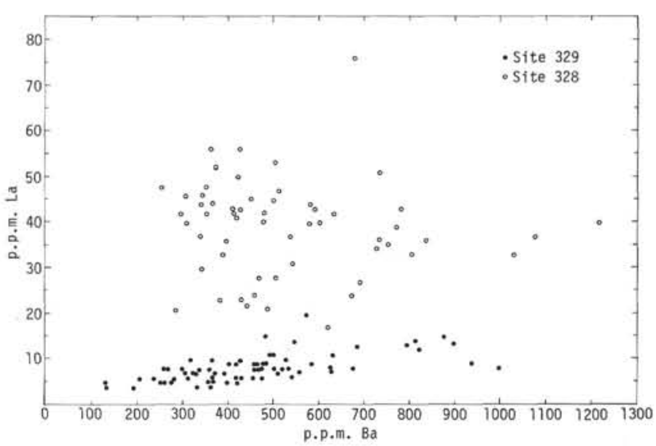

Figure 6. *La versus Ba for Site 328 and Site 329 sediments.*

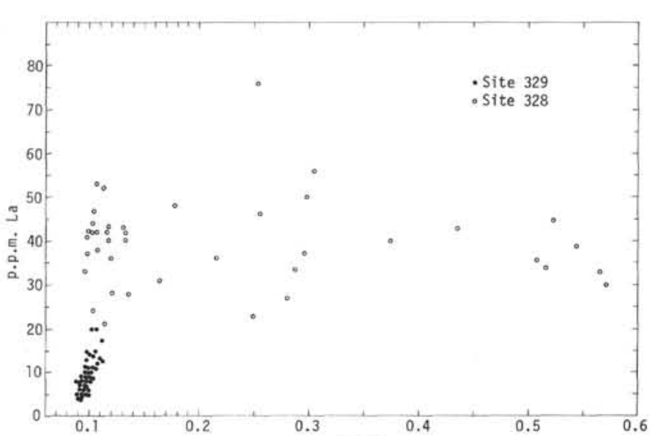

Figure 7. *La versus Mn for Site 328 and Site 329 sediments.*

TABLE 6
Matrix Showing the Difference in the Correlation Coefficients for Element Pairs Between Sites 328 and 329

	Ti	Fe	Mn	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th	Cr/Ni	Fe/Mn	Rb/Sr	Ba/Rb
Fe	-																				
Mn	0.44	0.49																			
Cr	0.79	0.58	-																		
Ni	0.48	0.44	-0.43	0.73																	
Cu	-	-	-	-																	
Zn	-	0.55	-	0.52	-	53															
Rb	0.38	0.44	-	0.38	-	-	-														
Sr	0.43	-	-	-	-	1.36	0.98	0.51													
Y	-	-	0.62	0.49	0.47	-	-	-	-												
Zr	0.60	0.97	-	-	-	-	0.36	0.80	0.91	-											
Nb	0.42	0.65	-	-	-	-	0.54	0.83	0.68	-	-										
Ba	0.35	-	0.35	0.40	-	-	-	-	-0.95	0.41	-	-									
La	-	-	0.80	-	-	-0.45	0.42	-	-	-	0.45	-	0.67								
Ce	-	-	0.75	-	-	-0.40	-	-	-	-	0.35	-	0.64	-							
Pb	-	-	0.36	-	-	-	-	-	-	-	0.54	0.37	-	-	-	-					
Th	-	-	-	-	-	-	-	-	-	-	0.35	-	-	-	-	-	-				
Cr/Ni	0.95	0.89	-0.62	-	0.85	-	0.99	0.91	-	0.54	0.95	0.62	-	-	-	-	-				
Fe/Mn	0.69	0.61	-1.03	-	-0.93	-	-1.15	1.07	-	0.64	1.09	0.52	-	0.43	-	0.42	-	-			
Rb/Sr	-	-	-	-	-	-0.60	0.38	-	-	-	0.96	0.88	-	-	-	-	-0.37	0.66	0.77		
Ba/Rb	-	-	-	-	-	-0.76	-	-	-0.37	-	0.65	-	-	-	-	-	-	-	-	-	-
Ba/Sr	0.38	0.60	-	-	-	-	0.35	0.38	1.08	-	0.48	0.74	-0.46	0.55	0.40	0.42	-	0.78	0.97	0.73	-0.92

Note: Positive values indicate an increase in correlation coefficient (whether positive or negative correlation) in Site 329 sediments while negative values indicate a decrease in degree of correlation. Only changes significant at better than 99.5% confidence level, on the basis of student T test, are included.

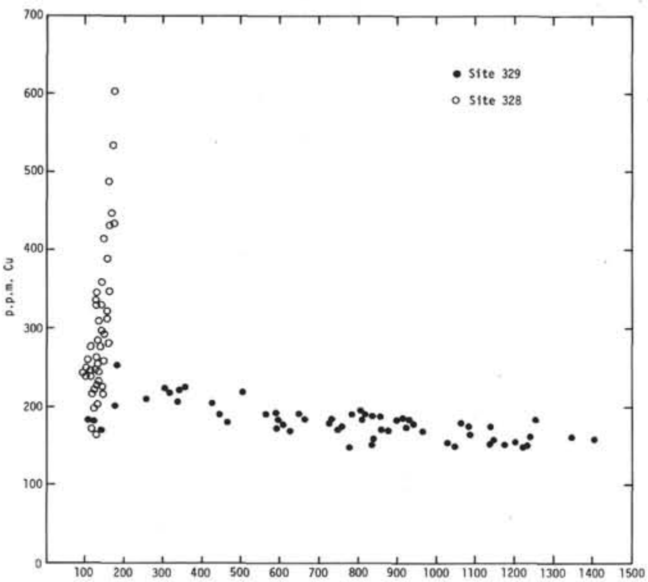

Figure 8. *Cu versus Sr for Site 328 and Site 329 sediments.*

situation of Site 328 allows the possibility of sediments being derived from either the Antarctic continent, or from southernmost South America via the long narrow Falkland Trough. In either case transport may have been largely through the agency of bottom currents. The downhole variability of Site 328 sediments may reflect this variable sediment source. On the other hand, if transport of terrigenous clay components was largely by bottom currents, it is unlikely that much of the clay would find its way onto the shelf environment of the Falkland Plateau. This would concur with the geochemical findings.

Finally, short-, medium-, and long-term trends are evident in the downhole geochemical patterns. While some of these trends can be correlated directly with changing lithology and breaks in sedimentation, the significance of other trends is more obscure and may be related to variations in sediment source, gradual changes in the nature of biogenic components, or to varying *p*H and Eh conditions connected with changes in bottom-current activity.

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