# 16. TRACE ELEMENT GEOCHEMICAL HISTORY OF LATE MESOZOIC SEDIMENTATION IN THE SOUTHWEST ATLANTIC, FALKLAND PLATEAU, SITE 511<sup>1</sup>

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#### ABSTRACT

The distribution of paragenetic assemblages of trace and rare elements, as revealed by factor analysis (R-mode, Q-mode), the ratios of elements to Zr and the interpretation of these data in the context of the known mineralogy, lithology, and geology of the region, provide the bases for the outline of the geochemical history of sedimentation in the study area that forms the subject of this chapter. Two stages may be discerned.

1. Late-Middle Jurassic-Early Cretaceous (160-106? Ma). The sediments that accumulated in relatively shallow water (shelf) were predominantly clay, with dispersed sapropelic organic matter, plant fragments, pyrite, admixtures of acid-medium volcanic glass, and epigenetic crystals of gypsum. The bottom water layers of the basin are notably stagnant. The sediments are characterized by higher amounts of V, Zn, Cu, Cr, Rb, and Be associated with organic matter. Lower Cretaceous sediments, separated from those of the Upper Jurassic by a hiatus, accumulated in a deepened and enlarging basin. These Lower Cretaceous deposits are chemically similar to those of the Upper Jurassic, but contain diagenetic concentrations of Zn, Ni, and La.

2. Early-middle Albian (Unit 5)-middle Maestrichtian (106?-66.6 Ma). The prevailing regime was that of an open ocean basin that tended to expand and deepen.

During the second half of the early-middle Albian, the biogenic components Ba, Sr, and  $CaCO_3$  accumulated. By the end of this interval, Ti/Zr values had increased. In conjunction data on mineral composition, they testify to an outburst of basaltoid volcanism related to tectonic activity before an erosional hiatus (late Albian-Cenomanian).

At the end of the Cenomanian-Turonian, residual deposits of predominantly clay sediments with relatively high amounts of Ti and Zr and associated rare alkalis (Li, Rb) accumulated.

Clay sediments deposited during the Coniacian-Santonian were characterized by higher concentrations of Ti, Zr, Li, and Rb, by diagenetic carbonate phases of Ni, Zn, and La, and by sulphides and Fe-oxides with an admixture of Ni and Co. The latter half of the interval saw the deposition of fine basaltoid volcanoclastic material, diagenetically altered by zeolitization and carbonatization and enriched with Sc, Pb, Ti, Sr, Ba, Y, and Yb. Sediments with a similar chemistry accumulated in the Campanian-middle Maestrichtian.

Strong current activity preceding a global hiatus at the Mesozoic/Cenozoic boundary is reflected in both lower sedimentation rates and the presence of higher residual concentrations of Ti, Zr, Ba, Sr, and other elements studied in this chapter.

# INTRODUCTION

The upper Mesozoic section penetrated at DSDP Site 511 in the basin province of the Falkland Plateau is crucial for studying the paleogeographical and sedimentary development of the Southwest Atlantic Ocean. Data on the lithology of Middle-Upper Jurassic and Cretaceous sediments in this region are rather fragmentary; they are drawn mostly from Site 330, DSDP Leg 36, situated 10 km north of Site 511, and no information on the geochemistry is available (Barker, Dalziel, et al., 1977; Ludwig, Krasheninnikov, et al., 1980; Thompson, 1977).

The objective of this chapter is to study the late Mesozoic geochemical history of sedimentation in the Southwest Atlantic in the context of data on oceanic circulation, the climatic evolution of the Antarctic and the Southern Ocean, and the general process of sediment accumulation. The processes of sedimentation and postsedimentary transformations are assumed to have been registered in the chemical and mineral compositions of the sediments. Of special interest are changes in the chemical parameters of sedimentation for the major geochronological subdivisions and the nature of the factors controlling them during the Late Jurassic and Cretaceous.

#### MATERIALS AND METHODS

This study of the chemical and mineral composition and the lithological characteristics of late Mesozoic deposits penetrated at DSDP Site 511 was carried out at the Geological Institute of the U.S.S.R. Academy of Sciences. Determination of trace elements was carried out at the chemical laboratory of the All-Union Institute of Mineral Resources of the U.S.S.R. Ministry of Geology (M. A. Ritt, laboratory head) using emission spectroscopy and the international standards. Group determinations were made for Se, Pb, Nb, Ga, Mo, V, Cu, Zn, Ti, Co, Ni, Zr, Cr, Sr, Ba, Y, Yb, and La, and elements such as Li, Rb, Cs, and Be were identified from separate weight portions of samples with relatively high accuracy. CO2 was determined by routine methods and recalculated to CaCO3. Results are given in Table 1. The analytical data were processed by an EC-1022 computer at the mathematical research laboratory, GIN, U.S.S.R. Academy of Sciences (D. A. Kazimirov), using factor analysis (R-mode, Q-mode; Davis, 1973, Harman, 1967). Geochemical interpretations of factor analysis results have been considered, in the context of a similar project, in a previous paper (Varentsov, 1980). The absolute geochronogy is taken from works frequently used in DSDP investigations (Geological Society of London, 1974; Hardenbol and Berggren, 1978; Larson and Hilde, 1975; Van Eysinga, 1975; Van Hante, 1976).

#### PARAGENETIC ASSEMBLAGES OF ELEMENTS (TABLES 2, 3; FIG. 1)

The interpretation of paragenetic groups of chemical elements revealed by factor analysis (as just described) enables us to determine the geochemical character of as-

<sup>&</sup>lt;sup>1</sup> Ludwig, W. J., Krasheninnikov, V. A., et al., *Init. Repts. DSDP*, 71: Washington (U.S. Govt. Printing Office).

Table 1. Trace and rare elements and CO<sub>2</sub> in upper Mesozoic sediments, Site 511, Falkland Plateau, Southwest Atlantic.

Core/Section	CO <sub>2</sub>								1	Trace Elem	ients (ppm	)						_				Rare Elem	ents (ppm	)
(interval in cm)	(wt.%)	Sc	Р	Pb	Nb	Ga	Мо	v	Cu	Zn	Ti	Co	Ni	Zr	Cr	Sr	Ba	Y	Yb	La	Li	Rb	Cs	Be
Campanian-Mae	estrichtian																							
27-2, 71-75	0.20	10	800	30	15	10	40	100	60	0	1500	70	150	70	40	200	600	20	2	40	28	82	< 9.4	1.8
Coniacian-Santo	onian																							
30-1, 50-52	3.83	15	800	15	15	15	1.5	100	40	100	1500	20	30	70	40	200	700	30	2	50	28	73	< 9.4	1.4
38-1, 46-50	4.22	15	1000	15	10	15	6	100	40	100	1500	20	40	70	40	200	600	30	2	40	32	82	< 9.4	1.4
38-3, 50-54	3.23	15	800	15	15	15	3	100	40	100	2000	20	50	70	40	300	700	30	3	40	37	82	< 9.4	1.8
39-1, 39-43	1.39	15	1000	15	15	15	3	100	40	100	1500	20	50	70	40	200	600	30	3	40	37	91	< 9.4	2.5
39-3, 39-43	9.90	15	700	15	15	15	3	100	40	0	1000	20	30	50	40	400	600	30	3	40	32	73	< 9.4	1.4
39-4, 39-43	3.97	20	1500	1000	10	15	3	100	40	100	4000	20	40	80	40	300	700	50	4	50	37	91	< 9.4	2.2
40-2, 40-44	5.77	20	700	15	10	15	1.5	100	40	150	4000	70	150	60	40	300	700	30	3	50	37	13	< 9.4	1.4
40-3, 40-44	19.01	15	700	15	10	15	1	40	40	150	100	20	40	50	30	500	1000	20	2	50	28	33	< 9.4	1.4
40-4, 40-44	0.49	15	800	20	10	20	5	100	60	100	4000	20	50	100	10	300	100	30	3	40	55	100	< 9.4	1.0
40-5, 40-44	9 44	15	700	20	10	20	2	100	20	150	2000	15	40	60	40	500	000	30	2	40	60	100	< 9.4	1.2
41-1 56-60	4 49	15	700	20	15	20	2	100	20	80	3000	20	20	70	40	400	700	30	3	50	64	100	< 9.4	2.2
41-2 28-32	5.81	20	700	15	10	20	3	100	30	150	3000	15	40	70	40	400	700	40	3	50	64	100	29.4	1.4
41-3 59-63	4 26	20	700	15	10	20	3	100	20	100	3000	15	40	70	40	400	600	30	3	50	87	109	< 9.4	2.2
42-1, 116-120	2.96	20	700	15	10	20	4	100	40	150	3000	20	60	100	50	300	300	30	3	50	74	109	< 9.4	1.8
42-2, 116-120	5.16	15	700	20	10	20	1.5	100	40	0	3000	20	40	100	50	300	300	30	3	50	60	91	< 9.4	1.8
42-3, 116-120	5.48	15	700	20	10	20	1.5	100	40	100	2000	15	30	70	40	300	300	30	3	50	55	91	< 9.4	1.4
42-4, 116-120	3.99	15	800	15	15	20	3	100	40	80	3000	15	30	100	40	150	200	30	3	50	51	109	< 9.4	1.4
42-5, 31-33	7.41	15	800	15	15	20	3	100	40	0	3000	15	30	60	40	300	200	30	3	50	51	91	< 9.4	1.4
43-1, 43-45	6.06	15	1000	15	10	15	3	100	30	0	3000	15	20	100	50	300	200	30	3	40	0	0	0	1.4
43-3, 43-45	2.06	15	1000	15	10	20	2	100	40	0	4000	15	20	100	40	300	200	30	3	40	41	91	< 9.4	1.8
44-1, 48-50	0.20	10	700	15	10	20	3	100	40	100	2000	100	100	70	40	70	150	15	2	0	32	109	< 9.4	2.2
47-2, 48-50	1.93	15	1000	20	15	20	2	100	50	100	3000	20	40	150	50	300	1000	30	3	40	37	82	< 9.4	2.2
47-3, 48-50	2.13	15	1000	20	15	20	3	100	40	100	3000	15	40	150	50	300	1000	30	3	40	32	91	< 9.4	1.8
47-4, 48-50	6.06	15	1000	10	15	20	3	100	40	70	3000	15	40	150	50	300	400	30	3	40	32	91	< 9.4	1.4
47-5, 48-50	8.50	20	800	20	15	20	2	100	50	0	3000	20	50	150	50	300	600	30	3	40	37	82	< 9.4	1.4
47-6, 48-50	7.52	15	800	30	15	20	2	100	70	0	3000	20	50	150	50	150	500	30	3	40	41	91	< 9.4	1.4
Turonian-upper	Cenomania	in																						
48-3, 46-48	0.20	20	700	30	15	20	2	100	30	100	3000	20	50	100	50	100	200	20	3	40	60	118	< 9.4	2.2
49-1, 36-38	0.20	15	800	30	15	15	3	100	60	150	3000	50	60	100	50	200	200	30	3	40	46	100	< 9.4	1.4
49-2, 36-38	0.27	15	800	30	15	15	3	100	50	100	3000	50	60	100	50	200	200	30	3	40	0	0	0	1.8
49-4, 36-38	1.46	15	800	30	15	15	2	100	40	70	3000	40	60	100	50	200	1500	30	3	40	37	109	< 9.4	1.8
49-5, 36-38	7.85	15	700	20	10	15	1	70	100	0	3000	40	60	100	40	300	5000	30	3	40	0	0	0	1.8
49-6, 36-38	10.10	15	800	20	10	15	1	70	30	0	3000	40	50	60	40	300	3000	30	3	40	37	91	< 9.4	1.8
Lower-middle A	lbian																							
50-1, 38-40	18.73	15	700	20	10	10	1	70	60	0	3000	40	40	70	40	300	4000	30	3	50	37	64	< 9.4	1.1
50-3, 58-40	11.72	15	700	20	15	15	3	60	50	0	3000	40	40	70	40	500	300	20	3	50	0	0	0	0
51-1, 02-66	10.58	15	700	20	10	15	1.5	60	40	0	3000	30	30	50	20	300	200	20	3	50	37	64	< 9.4	1.4
51-2, 62-66	14.81	15	700	20	10	15	1.5	70	30	70	3000	50	40	60	40	400	200	20	3	50	46	73	< 9.4	1.4
51-5, 02-00	10.18	15	700	20	10	15	1.0	70	30	0	3000	40	60	100	40	400	400	30	3	50	40	64	< 9.4	1.1
51 5 62 66	12.72	15	700	20	10	15	1.5	20	30	70	3000	40	60	150	40	400	1500	30	3	50	40	/3	< 9.4	1.4
51-5, 62-66	17.83	15	800	15	10	15	1.5	60	30	/0	2000	30	40	150	40	400	400	30	3	40	41	82	< 9.4	1.8
52-1 62-66	9.64	15	800	15	10	15	1.5	60	30	70	2000	40	50	150	30	200	2000	30	2	40	41	01	< 9.4	1.4
52-3, 62-66	11.67	15	800	20	10	15	1.5	70	30	0	2000	50	60	150	30	300	1000	30	3	40	51	77	-0 A	1.4
52-5, 62-66	0.90	10	700	15	10	15	1	300	20	100	1000	150	100	70	15	150	400	10	2	40	83	9	< 9.4	<0.9
52-6, 62-66	11.89	15	800	20	15	15	2	30	30	100	1500	60	60	100	40	300	8000	30	2	40	55	55	< 9.4	1.1
52-7, 16-20	2.74	15	800	20	10	15	1.5	50	30	100	2000	40	50	150	30	300	10,000	30	3	40	51	64	< 9.4	< 0.9
53-1, 76-80	15.60	15	800	20	10	15	1.5	50	30	0	2000	40	40	150	30	300	1000	30	3	40	37	64	< 9.4	1.1
53-2, 76-80	7.41	15	700	20	10	15	1	70	30	0	1500	70	100	50	40	300	800	30	2	40	92	55	< 9.4	1.1
53-3, 76-80	14.14	15	700	20	15	10	2	50	30	0	2000	40	40	70	40	300	1000	30	3	40	46	64	< 9.4	1.4
53-4, 76-80	11.44	15	700	20	15	15	2	60	40	0	2000	100	100	70	40	300	600	30	3	0	64	55	< 9.4	1.1
53-6, 76-80	17.16	15	700	10	15	10	1	100	15	0	1500	100	100	70	70	300	1000	20	3	40	55	36	< 9.4	< 0.9
54-2, 36-40	15.71	15	700	20	15	15	1	40	30	0	1500	40	50	60	30	200	1500	30	3	50	51	46	< 9.4	1.1

I. M. VARENTSOV

#### 54-3, 36-40 16.60 10,000 < 9.4 < 0.9 54-4, 36-40 10.32 < 9.4 1.5 < 0.9 54-5, 36-40 11.22 1.5 < 9.4 1.1 54-6, 36-40 11.11 < 9.4 1.1 55-1, 38-40 15.71 1.5 < 9.4 1.1 55-2, 38-40 12.00 < 9.4 1.4 55-5, 38-40 1.57 < 9.4 1.4 55-6, 38-40 17.95 56-2, 104-106 6.06 < 9.4 1.4 ্য 56-4, 99-101 8.62 10.000 < 9.4 1.1 57-2, 28-30 0.22 < 9.4 1.8 57-3, 28-30 6.60 < 9.4 1.8 57-4, 28-30 0.85 1.8 57-5, 28-30 1.01 < 9.4 1.8 9.40 57-6, 28-30 1.5 < 9.4 1.4 Aptian-Barremian 58-2, 40-42 1.21 9.4 0.9 58-3, 40-42 1.12 <94 1.5 58-4, 40-42 0.20 1.5 < 9.4 1.4 59-1, 9-11 15.15 < 9.4 < 0.9 59-2, 9-11 2.74 < 9.4 2.9 60-1, 144-146 25.36 < 9.4 < 0.9 60-2, 144-146 22.89 < 9.4 < 0.9 61-1, 57-61 0.20 9.4 1.1 61-2, 57-61 2.67 1.8 61-3, 57-61 0.20 9.4 1.8 61-4, 46-50 0.63 9.4 1.8 61-5, 32-34 3.48 < 9.4 1.4 62-2, 50-54 0.20 9.4 1.4 62-4, 116-120 0.20 9.4 2.2 62-5, 36-40 0.20 9.4 Upper Jurassic 63-1, 126-130 0.60 9.4 2.2 63-2, 68-72 0.64 9.4 2.2 63-3, 129-133 3.66 9.4 1.8 64-1, 26-30 1.21 9.4 1.4 64-2, 41-45 9.4 2.2 1.21 2.2 64-3, 26-30 1.00 9.4 2.5 64-4, 75-79 < 9.4 1.77 64-5, 51-55 1.13 9.4 2.5 64-6, 12-16 3.76 < 9.4 1.8 65-1, 52-56 2.00 18.8 2.2 65-2, 22-26 2.2 1.66 9.4 65-3, 63-67 1.81 < 9.4 2.2 65-5, 18-22 4.23 9.4 2.2 66-1, 34-36 4.34 9.4 2.2 66-2, 30-32 2.2 2.23 9.4 66-3, 34-36 3.78 9.4 66-4, 30-32 3.17 9.4 2.5 66-5, 34-36 2.2 2.15 9.4 66-6, 30-32 1.81 9.4 67-1, 85-87 1.92 9.4 2.2 67-2, 85-87 6.10 9.4 2.2 67-4, 85-87 2.2 0.89 9.4 1.1 67-5, 85-87 1.18 < 9.4 68-2, 65-67 1.11 9.4 1.4 69-2, 38-40 0.26 9.4 1.4 69-3, 38-40 0.26 9.4 2.5 69-5. 38-40 0.26 <9.4 2.2 - 5 70-1, 52-54 1.8 0.95 9.4 70-3, 52-54 0.22 9.4 2.2 70-5, 52-54 0.20 9.4 2.2

Note: 0 means "no information."

TRACE ELEMENT GEOCHEMICAL HISTORY

		Fa	ctor Loadin	ng (after r	otation)				
		I	1	I	Ш				
Component	IA(+)	IB(-)	IIA(+)	IIB(-)	IIIA(+)	IIIB(-)			
Sc		-0.07	0.23		0.57				
Pb		-0.13	0.13		0.39				
Nb		-0.02		-0.14		-0.02			
Ga	0.18		0.60		0.15				
Mo	0.75			-0.34		-0.06			
v	0.87			-0.06		-0.07			
Cu	0.51			-0.13	0.12				
Zn	0.67			-0.50		-0.03			
Ti	0.13		0.64		0.46				
Co		-0.68		-0.02		-0.17			
Ni	0.28			-0.52		-0.40			
Zr	0.09		0.63		0.27				
Cr	0.83		0.04		0.16				
Sr		-0.52	0.02		0.56				
Ba		-0.51	0.09		0.37				
Y	0.35			-0.02	0.73				
Yb	0.34		0.07		0.68				
La	0.04			-0.52	0.22				
Li		-0.19	0.48		0.05				
Rb	0.68		0.46		0.29				
Be	0.68		0.38			-0.05			
CaCO <sub>3</sub>		-0.60		-0.40	0.43				
Input									
Dispersion									
070	25.57		15.82		9.25				
Cumulative	25.57		41.39		50.64				

Table 2. Factor analyses (R-mode) of trace elements in upper Mesozoic sediments, Site 511, Falkland Plateau, Southwest Atlantic.

semblages such as compounds or specific forms of the groups of components that have been established by analysis. This determination proceeds by examining the mineral composition of sediments and the parameters of the processes that have the highest probability of yielding the elemental forms that actually occur.

#### Assemblage IA(+)

Ga (0.18)-Mo(0.75)-V(0.87)-Cu(0.51)-Zn(0.67)Ni (0.28)-Cr(0.83)-Y(0.35)-Yb(0.34)-Rb(0.68)-Be(0.68) Dispersion: 25.57%.

The well-understood association of this cluster of components with certain types of deposits and the peculiarities of its distribution within a section enable us to state that (1) the assemblage is clearly confined to the "black shales" (Unit VI); (2) the average factor scores of the assemblage regularly decrease over time, from the Upper Jurassic (1.15) through the Aptian-Barremian (1.07) to the lower-middle Albian (Unit VI) (0.41). The average content of  $C_{org}$  (wt. % Fig. 2) decreases in the same succession: in the Upper Jurassic it is 3.26, in the Aptian-Barremian 3.02, and in the lower-middle Albian (Unit VI) it is 1.10. Higher up the section Corg content abruptly decreases (Fig. 2). This assemblage may be related to the humified organic matter that is dispersed throughout the sediments of Unit VI and that is represented particularly by organometallic compounds of V, Zn, Cr, and Cu.

# Assemblage IB(-)

Pb(-0.13)-Co(-0.68)-Sr(-0.52)-Ba(-051)-Li(-0.19)-CaCO<sub>3</sub>(-0.60).

This group is an antagonist of Assemblage IA(+). The presence of CaCO<sub>3</sub>, with a relatively high factor

Table 3	3. 1	Stratigraphic	distri	bution	of	factor	scores	(R-1	node)	) for
cher	mic	al elements	of the	upper	M	esozoic	sedime	ents,	Site	511,
Fall	klar	d Plateau, S	Southw	est Atla	anti	c.				

		Fa	ctor Scores	s (after rot	ation)				
Core/Section	1	I	I	I	III				
(interval in cm)	IA(+)	IB(-)	IIA(+)	IIB(-)	IIIA(+)	IIIB(-)			
Campanian-Maes	trichtian								
27-2, 71-75		-0.29		-0.62		-1.78			
Coniacian-Santor	iian								
30-1, 50-52		-0.45		-0.18		-0.31			
38-1, 46-50		-0.27	0.11			-0.55			
38-3, 50-54	0.00	-0.21	0.34		0.04	0.20			
39-1, 39-43	0.09	-0.54	0.42	-0.38	0.17	-0.30			
39-4, 39-43		-0.05	0.04	0.00	3.30				
40-2, 40-44		-0.49		-0.20	0.38				
40-3, 40-44	0.05	-1.22	1.09	-1.38	0.69				
40-4, 40-44	0.05		1.08		0.62	-0.07			
40-6, 20-24	0.15	-0.53	0.73		0.42				
41-1, 56-60		-0.30	1.08		0.64				
41-2, 28-32		-0.28	0.57		1.23				
41-3, 59-63	0.07	-0.35	1.32		0.57				
42-2, 116-120	0.07	-0.18	1.05		0.45				
42-3, 116-120		-0.32	0.62		0.41				
42-4, 116-120		-0.02	0.92		0.18				
42-5, 31-33		-0.16	0.39		0.50				
43-1, 43-45		-0.55	0.65		0.65				
44-1, 48-50		-0.02	1.19		0.55	-3.14			
47-2, 48-50		-0.01	1.30		0.46				
47-3, 48-50		-0.01	1.14		0.54				
47-4, 48-50		-0.16	0.94		0.41				
47-6, 48-50		-0.33	1.01		0.85				
Coniacian-Campa	anian	0.29	0.96	0.54	0.64	0.97			
Average Turonian-upper	0.09	-0.28	0.85	-0.54	0.04	-0.87			
Cenomanian									
48-3, 46-48	0.13		2.16			-1.08			
49-1, 30-38	0.13		1.15			-0.32			
49-4, 36-38	0.09	-0.41	0.91		0.22	0.57			
49-5, 36-38		-0.72	0.63		0.85				
49-6, 36-38		-1.02	0.40		0.61				
Senonian average	0.12	-0.72	1.03	0	0.56	-0.59			
Lower/middle Al	bian								
50-1, 38-40		-1.23		-0.64	1.16				
50-3, 38-40		-1.12		-0.12	0.36				
51-1, 62-66		-1.18	0.21	-0.08	0.05				
51-2, 62-66		-1.19	0.02		0.76				
51-4, 62-66		-1.12	0.34		0.98				
51-5, 62-66		-0.82	0.54		0.73				
51-6, 62-66		-1.34	0.48		0.47				
52-1, 62-66		-1.15	0.59		0.57				
52-5, 62-66		-2.06	0.48		0.51	-3.92			
52-6, 62-66		-1.77	0.18		0.02				
52-7, 16-20		-1.52	0.67		0.60				
53-1, 76-80		-1.33	0.44		0.54	0.70			
53-2, 76-80		-1.57	0.21	-0.18	0.40	-0.70			
53-4, 76-80		-1.31		-0.31	0.21				
53-6, 76-80		-1.81		-0.49		-0.80			
54-2, 36-40		-1.53		-0.55	0.36				
54-3, 36-40		-1.76		-0.84	0.73				
54-4, 30-40		-1.45		-0.76	0.81				
54-6, 36-40		-1.31		-0.78	0.53				
55-1, 38-40		-1.26		-0.94	0.40				
55-2, 38-40		-0.94	0.19	-0.17	0.46	-0.12			
55-6, 38-40		-1.25	5.19	-0.20	0.52	0.15			

Table 3. (Continued).

	Factor Scores (after rotation)												
Core/Section		I	1	I	III								
(interval in cm)	IA(+)	IB(-)	IIA(+)	IIB(-)	IIIA(+)	IIIB(-)							
56-2, 104-106		-0.63		-0.42		-0.03							
56-4, 99-101		-0.19		-1.98	1.35								
Lower-middle													
Average	0	-1.24	0.39	-0.57	0.54	-1.12							
Lower/middle Al	hian		0107	0.0.1	0.01								
Lower/ initiale Ai	olan												
57-2, 28-30	0.21	0.10		-0.76		-1.53							
57-3, 28-30	0.24	-0.19		- 2.01		-0.69							
57-5, 28-30	0.69			-1.17		-0.67							
57-6, 28-30		-0.53		-2.68		-0.68							
Lower/middle													
Albian (Unit VI)													
Average	0.41	-0.36	0	-1.44	0	-0.86							
Aptian-Barremia	n												
58-2, 40-42		-1.68		-1.24		- 3.99							
58-3, 40-42		-0.02		-0.27		-2.60							
58-4, 40-42	0.20		0.12		2.21	-0.75							
59-1, 9-11	1.32			- 3.66	2.31	-0.24							
60-1, 144-146	1.14	-0.64		-3.69		-1.69							
60-2, 144-146		-0.04		-2.56		-0.33							
61-1, 57-61	0.99		0.07			-0.16							
61-2, 57-61	1.05		0.37	-0.29	0.10	0.21							
61-3, 57-61	1.12		0.37		0.00	-0.31							
61-5, 32-34	1.11		0.30	-0.54	0.71								
62-2, 50-54	0.98		0.31		0.31								
62-4, 116-120	1.27		0.67		0.39								
62-5, 36-40	1.20		0.80		0.11								
Aptian-Barrem. Average	1.07	-0.59	0.38	-1.55	0.70	-1.26							
Upper Jurassic													
63-1, 126-130	1.11		0.27			-0.20							
63-2, 68-72	1.18		0.42			-0.14							
63-3, 129-133	1.27			-0.72	0.75								
64-1, 26-30	1.40		0.50	-0.45	1.06								
64-3, 26-30	1.12		0.39		0.17								
64-4, 75-79	1.24		0.24		0.40								
64-5, 51-55	1.40			-0.24	0.27								
64-6, 12-16	1.22			-0.86	0.49								
65-1, 52-56	1.05			-0.15	0.11	0.20							
65-3, 63-67	1.23			-0.56		-0.02							
65-5, 18-22	1.23			-0.85		-0.15							
66-1, 34-36	1.39			-1.06	0.07								
66-2, 30-32	1.61			-1.01	0.57	0.00							
66.4 30-32	1.10			-0.38		-0.50							
66-5, 34-36	1.34			-0.67		-0.32							
66-6, 30-32	1.14			-0.39		-0.69							
67-1, 85-87	1.05			-0.22		-1.06							
67-2, 85-87	0.77			-0.96		-0.71							
67-5 85-87	0.97			-0.60		-0.65							
68-2, 65-67	1.31			-0.76		-0.13							
69-2, 38-40	0.87		0.28	0.10		-0.52							
69-3, 38-40	0.82		1.80			-2.24							
69-5, 38-40	1.02		1.34		1.00	-0.45							
70-1, 52-54	0.98		1.80		1.38	-0.89							
70-5, 52-54	0.98		1.72			-1.13							
Upper Jurassic													
Average	1.15	0	0.85	-0.59	0.48	-0.58							

Note: Blanks indicate assemblage not present.

loading, suggests that this group is represented by a carbonate phase containing elements in the form of an isomorphous admixture. The data show that the association can incorporate Mn. The assemblage is best developed in lower-middle Albian (Unit V) and Turonianupper Cenomanian deposits (Fig. 1, Table 3). Worth noting is the biogenic mode of accumulation of most components of the cluster.

#### Assemblage IIA(+)

Sc(0.23)-Pb(0.13)-Ga(0.60)-Ti(0.64)-Zr(0.63)-Li(0.48)-Rb(0.46)-Be(0.38).

Dispersion: 15.82%

The presence in this group of such characteristic elements as Ti, Zr, and Ga with relatively high factor loadings (>0.60) suggests that the assemblage is represented by clastic material, along with clay minerals that developed after deposition. The presence of rare alkalis (Li, Rb) is indicative of mica; this finding is consistent with X-ray diffraction data. This association is best developed in upper Cenomanian-Turonian and Coniacian-Santonian deposits represented mostly by smectite-hydromicaceous clays—frequently zeolite of the heulandite type (see Table 3, Fig. 1).

#### Assemblage IIB(-)

Nb(-0.14)-Mo(-34)-Cu(-0.13)-Zn(-0.50)-Ni(-0.52)-La(-0.52)-CaCO<sub>3</sub>(-0.40).

The group is represented by an authigenic (postsedimentary) carbonate phase that includes elements with significant factor loadings (>0.30) as isomorphous admixtures and, to a lesser extent, as adsorbed components (Mo, for instance).

The assemblage is most pronounced in the lower and middle Albian, Unit VI (factor score -1.44) and the Aptian-Barremian (-1.55), somewhat less so in Upper Jurassic deposits (-0.59). Aggregates of microspherolitic patches (0.007-0.02 mm) of complex carbonates (Fe, Mg, Ca, Mn) are visible under the microscope. The concentrated development of this group, very different from Upper Jurassic to Lower Cretaceous deposits, can be related to the extensive development of marine sedimentary environments in the Early Cretaceous.

# Assemblage IIIA(+)

Sc(0.57)-Pb(0.39)-Ga(0.15)-Cu(0.12)-Ti(0.46)-Zr(0.27)-Cr(0.16)-Sr(0.56)-Ba(0.37)-Y(0.73)-Yb (0.68)-La(0.22)-Rb(0.29)-CaCO<sub>3</sub>(0.43)

Dispersion: 9.25%

The composition of this assemblage, its distribution within the section, and data on the mineral composition of the sediments suggest that it is related to at least two major phases: (1) volcanoclastic matter of basic composition transformed into clay, mostly smectitic material; the major element of this volcanogenic phase is Ti. (2) Carbonate developed during diagenesis/epigenesis after elements from the basic volcanoclastic material had dispersed into the silicate material. Figures 3, 4, and 5 show that the relatively high values of Ti/Zr correspond to intervals when basaltoid volcanoclastics were accu-



Figure 1. Distribution of average factor scores (R-mode) for paragenetic assemblages of trace and rare elements in upper Mesozoic sequences, Site 511, Falkland Plateau, Southwest Atlantic.

mulating. High factor scores are recorded in the same intervals for this assemblage (see Table 3).

# Assemblage IIIB(-).

Co(-17)-Ni(0.40). This group is antagonistic to Assemblage IIIA(+). Relatively high factor scores (see Table 3) are observed mostly in Upper Jurassic, Barre-

mian-Aptian, lower and middle Albian (Unit VI and to a lesser extent Unit V) sediments and sporadically in higher horizons (upper part of the Turonian-upper Cenomanian, see Table 3). Ni and Co make up part of sulphide patches and Fe hydroxides. The association is clearly diagenetic, a product of postsedimentary concentration of dispersed metals.

# DISTRIBUTION OF THE INDICATOR RATIOS OF ELEMENT EI/Zr

Elemental ratios are given in various papers that assess the geochemical parameters of sedimentation, the role of biological activity, hydrogenous deposition, hydrothermal inflow, supply of volcanoclastic components, terrigenous, glacial, and eolian constituents, and the products of authigenic mineral formation (Angino, 1968; Angino and Andrews, 1968; Chester, 1965; El Wakeel and Riley, 1961; Goldberg and Arrhenius, 1958; Turekian, 1968). For a ratio of elements to characterize well a geochemical process, one needs a relatively inert element that is rather evenly distributed in the phases under study. Zr is such an element under conditions of sediment lithogenesis. The Zr content in basalts and granites rich in Ca is 140 ppm. Similar values are recorded for clay rocks of the earth's crust (160) and deep sea clayey sediments (150; see Table 4; Turekian and Wedepohl, 1961). The data obtained by other authors differ only insignificantly from these values. Analysis of the distribution of such ratios makes it possible to compare lithologically different and heterofacial deposits.

# Ti/Zr (Figs. 2-5; Table 4)

### The Geochemical Significance of the Ti/Zr Ratio

Goldberg and Arrhenius (1958), referring to earlier studies of the Atlantic carried out by Correns, showed that relatively high Ti concentrations in Pacific Ocean sediments are related mostly to the presence of basaltic volcanoclastic material. The concentration of Ti in clays



Figure 2. Distribution of average CaCO<sub>3</sub> and C<sub>org</sub> contents and average values of Ti/Zr, Pb/Zr, Cu/Zr, Zn/Zr, Co/Zr, Sr/Zr, and Ba/Zr within upper Mesozoic sediments, Site 511, Falkland Plateau, Southwest Atlantic.





and deep sea clayey sediments—4600 ppm, or Ti/Zr  $30,670 \times 10^{-3}$  (Turekian and Wedepohl, 1961)—is a critical value above which the occurrence of basaltoid material can be considered probable. This value is somewhat higher than the average content of Ti in Atlantic sediments—3100 ppm (Emelyanov, 1974). This has been repeatedly mentioned by many researchers as a feature resulting from a relatively high continental runoff.

#### Distribution of Ti/Zr

#### Average Values (Fig. 2)

From Upper Jurassic through middle Albian sediments Ti/Zr values gradually decrease from  $25,000 \times$   $10^{-3}$  to  $21,277 \times 10^{-3}$ . This suggests a significant input of decomposition products of continental sialic material and of medium/acid volcanoclastics. From the end of the Cenomanian to the Santonian, higher values of Ti/ Zr (to  $32,258 \times 10^{-3}$ ) testify to an increase in basaltoid volcanoclastics. This conclusion agrees with data on the mineral composition of sediments presented in other chapters of these *Reports*. On the whole, average values of the Ti/Zr ratio for the major geochronological intervals in the Falkland Plateau region reveal that fine silty and clay sediment products derived from continental decomposition predominate (see Table 4). The data on upper Cenozoic deposits (DSDP Site 329; Tarney and Donnellan, 1977) show that in the interval from Oligo-



Figure 4. Distribution of Ba/Zr, Sr/Zr, Zn/Zr, Pb/Zr, and Ti/Zr ratios in Lower Cretaceous sediments, Hole 511, Cores 58-50 (432-556 m sub-bottom; Units V and VI Falkland Plateau, Southwest Atlantic. Arrows indicate average ratios of elements for lower-middle Albian sediments, Unit VI (ALB 6) and Unit V (ALB 5), average Aptian-Barremian sediments (AB), CLAY, DSCS, CALC S. (For explanations of other symbols see Fig. 3.)

cene to Holocene the average values of Ti/Zr did not exceed  $11,261 \times 10^{-3}$ . This may indicate a relatively high silty sandy content in the product of continental runoff (Table 4).

chemical phenomena within the geochronological intervals under study.

# Upper Jurassic (Fig. 3)

Average figures, however, frequently flatten out sharply contrasting values that signal interesting geoThese deposits are characterized by a pronounced tendency toward an increasing Ti/Zr ratio in the upper



Figure 5. Distribution of Ba/Sr, Sr/Zr, Zn/Zr, Pb/Zr, and Ti/Zr ratios in Upper Cretaceous sediments, Hole 511, Cores 28-49 (sub-bottom depth 223.5-432.5 m; Units IV and V) Falkland Plateau, Southwest Atlantic. Arrows indicate average ratios of elements for average Coniacian-Santonian sediments (CS), average upper Senonian-Turonian sediments (ST), CLAY, DSCS, Ca-GRAN. (For explanations of other symbols see Fig. 3.)

part of the interval (higher than Sample 511-65-1, 52-56 cm). This can be related both to an increase in the relative amounts of basaltoid hyalopelitic material and to an increase of residual titanium components near the boundary of a large erosional gap. (Hauterivian-Portlandian, about 20 m.y.)

# Barremian/Aptian to Albian (Fig. 4)

A relatively monotonous distribution of Ti/Zr slightly deviating from the average values, is observed.

### Second Half of the Lower-Middle Albian (Fig. 4)

In the interval from Samples 511-50-1, 38-40 to 511-53-3, 62-66 cm, Ti/Zr reaches  $50,000 \times 10^{-3}$ , a high value that is explained by the presence of basaltoid volcanoclastic material and the appreciable enrichment of sediments with residual titanium in finely dispersed minerals near the boundary, with a considerable stratigraphic hiatus ( $\sim 10-12$  m.y., late Albian–Cenomanian).

# Upper Cenomanian/Turonian-Upper Santonian (Fig. 5)

There are two intervals with relatively high Ti/Zr values: (1) A basal layer (Sample 511-49-6, 36-38 cm) resting directly above the erosional gap just noted (Ti/Zr 50,000  $\times 10^{-3}$ ); higher concentrations of Ti in these sediments are of a residual, relic character. (2) The upper part of the Coniacian-upper Santonian (Samples 511-39-4, 39-43 cm to 511-42-5, 31-33), characterized by Ti/Zr values up to 66,667  $\times 10^{-3}$ . These sediments have a higher content of fine silty-pelitic, basaltic volcanoclastic material strongly zeolitized.

Thus, the distribution of the Ti/Zr values reveals both residual accumulations near erosional contacts and

Sediment		Contents <sup>a</sup>											Ratios $(\times 10^{-3})$						Data
Lithology	Age	Pb	Ti	Zr	Cu	Zn	Co	Ni	Sr	Ba	Yb	La	Ti/Zr	Ba/Zr	Cu/Zr	Zn/Zr	Sr/Zr	Pb/Zr	Source
Silty sand, enriched in siliceous sedi- ment, ooze	Holocene	11	0.145%	165	176	131	200	29	126	516		14	8788	3127	1067	794	764	67	DSDP Site 329
Nannofossil diatomaceous oozes	Pleistocene-upper Pliocene	10	0.125%	112	180	80	-	23	491	545	-	12	11,261	4866	1607	714	4384	89	DSDP Site 329
Diatomaceous nannofossil chalk	upper Miocene	3	0.077%	85	185	64	_	25	739	413	_	7	9059	4859	2176	753	8694	91	DSDP Site 329
Diatomaceous nannofossil chalk	middle-upper Miocene	5	0.068%	80	189	56	_	18	777	431		5	8500	5388	2363	700	9713	63	DSDP Site 329
Diatomaceous nannofossil chalk	lower-middle Miocene	8	0.062%	77	152	33	_	10	1205	997		8	8052	12,948	1974	429	15,649	104	DSDP Site 329
Diatomaceous nannofossil chalk	Oligocene	5	0.068%	43	154	43		26	1120	458	-	8	8293	5585	1878	524	13,659	61	DSDP Site 329
Claystones zeolitic claystones	Campanian-Maestrichtian	30	1500	70	60	_	70	150	200	600	2	40	21,429	8571	857		2857	429	DSDP Site 511
Claystones, reolitic clays	Conjacian-Santonian	54	2674	89	41	17	23	46	306	554	3	41	30.045	6225	461	865	3438	607	DSDP Site 511
Claystones, marls, muddy nannofossil chalks	Turonian-upper Cenomanian	27	3000	93	52	70	40	57	217	1683	3	40	32,258	18,097	559	753	2333	290	DSDP Site 511
Claystones, marls, muddy nannofossil chalks	lower-middle Albian (Unit V)	21	2000	94	34	28	46	58	291	1852	3	37	21,277	19,702	362	298	3096	223	DSDP Site 511
"Black shales," mudstones, nannofossil mudstones	lower-middle Albian (Unit VI)	17	1260	62	58	330	380	250	110	190	3	50	20,323	3065	935	5323	1774	274	DSDP Site 511
"Black shales," mudstones, nannofossil mudstones	Aptian-Barremian	15	1807	78	49	263	11	81	170	337	3	35	23,167	4321	628	3372	2179	192	DSDP Site 511
"Black shales," mudstones, nannofossil mudstones	Upper Jurassic	16	2150	86	46	345	15	79	157	320	3	27	25,000	3721	535	4012	1826	186	DSDP Site 511
Average values																			
Clays (AVG)		20	4600	160	45	95	19	68	300	580	2.6	92	28,750	3620	281	594	1875	125	Turekian and Wedepohl, 1961
Deep sea carbonate sediments (AVG)		9	770	20	30	35	7	30	2000	190	1.5	10	6820		-	73	91	32	Turekian and Wedepohl, 1961
Deep sea clayey sediments (AVG)		80	4600	150	250	165	74	225	180	2300	1.5	115	3850	9500	1500	1750	100,000	450	Turekian and Wedepohl, 1961
Basalt (AVG)		6	1.38 %	140	87	105	48	13	465	330	2.1	15	30,670	15,330	1666	1100	1200	533	Turekian and Wedepohl, 1961
Ca = rich granite (AVG)		15	0.34 %	140	87	105	7	15	440	420	3.5	45	98,570	2360	621	621	3321	43	Turekian and Wedepohl, 1961
Oceanic sediments																			
Carbonates		150	_	140	338		91	232	1110	1360		100	24,286	30,000	621	750	31,430	107	El Wakeel and Riley, 1961
Clavey		175		126	400	_	100	300	450	2000	-	90	-	9714	2414		7929	1072	El Wakeel and Riley, 1961
Siliceous		180		170	370		200	330	230	1050	-	80	-	15,873	3175		3571	1389	El Wakeel and Riley, 1961
Pelagic clay sediments, Pacific Ocean		150	—	180	740		160	320	710	3900	-	140	$\sim - \sim$	6176	2176		1353	1059	Goldberg and Arrhenius, 1958
Deen sea clays. Atlantic Ocean		52	-	-	115	129	39	79	-			-	-	21,667	4111	-	3944	833	Turekian and Imbrie, 1966
Marine glacial sediments (AVG), Weddell Sea		-	2600	238	70	-	20	46	_	-	_	_	10,924	<u></u>	<u></u> -	-	-	-	Angino, 1966

Table 4. Average contents of trace elements and element/Zr ratios for the main stratigraphic subdivisions of upper Mesozoic sediments, Sites 329 and 511, Falkland Plateau, Southwest Atlantic.

Note: Contents and ratios of elements in the sediments from Hole 329, after Tarney and Donnellan, 1976. Contents and ratios of elements in sediments from Hole 511 calculated from the data in Table 1. Values for element contents in ppm unless otherwise indicated.

intervals of accumulation of basaltic volcanoclastics. It is notable that manifestations of basaltic explosive volcanism shown in the Ti/Zr ratios preceded, as a rule, large erosional gaps. The latter can result from tectonic activity in the areas adjacent the Falkland Plateau.

### Ba/Zr (Figs. 2-5; Table 4)

#### Geochemical Significance of the Ba/Zr Ratio

The average content of Ba in suspended river matter (400 ppm; Gurvich et al., 1978), is somewhat lower than the Ba concentration in clays (580 ppm or Ba/Zr 3620  $\times$  10<sup>-3</sup>; Turekian and Wedepohl, 1961). Maximum concentrations of Ba can be observed in deposits related to high biological productivity and in hydrothermal metal-liferous sediments (Chester, 1965; El Wakeel and Riley, 1961; Goldberg and Arrhenius, 1958; Turekian, 1968; Turekian and Imbrie, 1966). In deep sea clay sediments the concentration of Ba is 2300 ppm or (Ba/Zr 15,330  $\times$  10<sup>-3</sup>; Turekian and Wedepohl, 1961). This value is tentatively accepted as critical; when it is higher, the causes of the relatively high Ba content in the sediment should be considered.

#### Distribution of Ba/Zr

#### Average values (Fig. 2)

Three stages identified in the distribution of average Ba values in the upper Mesozoic section are (1) Upper Jurassic-lower/middle Albian (Unit VI; 3065-4321 ×  $10^{-3}$ ); where the range of values remains within the values established by typical suspended river matter and relatively shallow water terrigenous sediments. (2) Lower-middle Albian (Unit V, upper Cenomanian-Turonian;  $18,097-19,702 \times 10^{-3}$ ), high values representative of essentially clay nanno-micritic sediments affected by such factors as relatively high biological productivity, volcanogenic emanations, and authigenic concentration of Ba by hydroxides of Fe or Mn. (3) Coniacian-Santonian—Campanian-Maestrichtian;  $6252-8571 \times 10^{-3}$ , values similar to the indices for the late Cenozoic (see Table 4), and characteristic of relatively deep water, open-ocean environments.

Again, average values level out extremes that are of interest for understanding the geochemical history of the basin.

#### Upper Jurassic (Fig. 3)

This interval is characterized by accumulation of sediments with a relatively monotonous distribution of Ba/Zr, deviating only slightly from the average values.

#### Barremian-Aptian—Albian (Unit VI; Fig. 4)

The distribution of Ba/Zr differs only insignificantly from that shown for Upper Jurassic sediments.

### Lower-Middle Albian (Unit V; Fig. 4)

Clay nanno-micritic sediments accumulated, with an appreciable admixture of basic volcanoclastic material and abnormally high values of Ba/Zr (to  $66,667 \times 10^{-3}$ ). Basaltic volcanoclastics were recorded in the upper part

of this interval with high Ba/Zr values (Samples 511-51-4, 62-66 cm to 511-55-1, 38-40 cm), as was noted in considering Ti/Zr ratios. In interpreting the Ba/Zr distribution, it should be borne in mind that in Recent diatomaceous sediments of the near Antarctic zone of high biological productivity, the Ba/Zr ratio reaches  $\sim 30,000 \times 10^{-3}$ , somewhat higher than a similar ratio for carbonate varieties of metalliferous sediments (Gurvich et al., 1978). Along with the Fe- and Mn-hydroxides dispersed in the ground mass of the clay nannomicritic sediments are authigenic collectors (concentrators) of Ba, initially volcanogenic and later transformed by biological concentration.

### Upper Cenomanian–Turonian–Upper Santonian (Fig. 5)

Two intervals of high Ba/Zr values are distinguished: (1) basal (Upper Santonian-Turonian) resting directly under a rather extensive erosional hiatus (Ba/Zr 50,000  $\times 10^{-3}$ ). The residual, relic nature of barite accumulations is obvious in this case. (2) A zone of relatively high Ba/Zr values (up to 20,000  $\times 10^{-3}$ ) distinctly distinguished in the Coniacian-Upper Santonian (Samples 511-30-1, 50-52 cm to 511-41-3, 59-63). As already mentioned, observation by microscope and high values of Ti/Zr (Fig. 5) testify to a significant role of hyalopelite-silty basaltic matter and of possible products of hydrothermal exhalations.

# Sr/Zr (Figs. 2-5; Table 4)

#### Geochemical Significance of the Sr/Zr ratio

In marine sediments the biogenic carbonate components are the main carriers of Sr. To a lesser extent this function is assumed by clay matter, Fe- and Mn hydroxides, and authigenic phosphates (Chester, 1965; El Wakeel and Riley, 1961; Goldberg and Arrhenius, 1958). Concentrations of Sr in deep sea carbonate sediments (2000 ppm; Sr/Zr 100,000  $\times$  10<sup>-3</sup>) and in deep sea clay sediments (180 ppm; Sr/Zr 1200  $\times$  10<sup>-3</sup>) are considered critical values (Turekian and Wedepohl, 1961). An Sr concentration of 2000 ppm is regarded by most researchers (Chester, 1965) as abnormally high, peculiar to Recent sediments of the equatorial zone of high biological productivity of the Atlantic Ocean.

#### Distribution of Sr/Zr

# Average Values (Fig. 2)

The following intervals have distinctive distribution of Sr/Zr average values: (1) the Upper Jurassic—lowermiddle Albian (accumulation time of Unit VI; Sr/Zr 1774-2179 × 10<sup>-3</sup>); these values are close to the Sr/Zr ratios for continental clays (1875 × 10<sup>-3</sup>) and shallowwater marine terrigenous sediments. (2) Lower-middle Albian (Unit V)—Campanian-Maestrichtian; during this interval the Sr/Zr ratios varied slightly from 2333-3438 × 10<sup>-3</sup>, corresponding to values characteristic of carbonate-clay sediments of the open ocean. Worth noting are Oligocene-lower-middle Miocene sediments (see Table 5; Sr/Zr 13,659-15,649 × 10<sup>-3</sup>. An outburst of biological productivity then occurred as a result of the northward penetration of Antarctic waters rich in nutrient components in conjunction with the opening of the Drake Passage.

# Upper Jurassic (Fig. 3)

Sediments are characterized by a relatively even distribution of Sr/Zr, slightly differing from the values earlier considered average.

# Barremian-Aptian-Albian (Unit VI)

The distribution of Sr/Zr was close to that observed for Upper Jurassic sediments (see Fig. 4).

# Lower-Middle Albian (Fig. 4)

In this interval, the same general patterns of distribution hold for Sr/Zr, Ba/Zr, and Ti/Zr: an abrupt increase in the values of the ratios in the upper part of the interval as the explosive-hydrothermal activity of basaltoid volcanism intensified. In the process, such elements as Ba and Sr could be appreciably transformed by biological factors. Worth noting is the outburst of volcanism that preceded the erosional hiatus (late Albian-Cenomanian, about 12 m.y.) and was related to tectonic activity.

# Upper Cenomanian-Turonian—Coniacian-Upper Santonian (Fig. 5)

Sr/Zr is distributed with the same regularity as Ba/Zr and, in general, Ti/Zr. This similarity is attributed to common causes: residual basal accumulations (Sample 511-49-6, 36-38 cm) and effects of biological transformations of volcanogenic products (Samples 511-38-3, 50-54 cm to 511-41-3, 59-63 cm).

# Pb/Zr (Figs. 2-5; Table 4)

#### Geochemical Significance of the Pb/Zr Ratio

An important feature of Pb in sedimentary processes is its tendency toward accumulation in authigenic phases from sea water, mostly in Mn and Fe hydroxides and in organic matter but to a lesser extent in clayey components. The result is a greater Pb enrichment of pelagic than of shallow-sea sediments. This difference is more obvious for pelagic sediments in oceanic basins where continental runoff predominates (the Atlantic, for instance, where Pb is 52 ppm, Pb/Zr is  $347 \times 10^{-3}$ ; Turekian and Imbrie, 1966) and volcanogenic-hydrothermal sources exist (the Pacific Ocean, for instance, where Pb is 150 ppm and Pb/Zr is  $1000 \times 10^{-3}$ ; Goldberg and Arrhenius, 1958). In coastal sea sediments the Pb content does not as a rule exceed the concentration of this element in clays (see Table 4: Pb/Zr,  $125 \times 10^{-3}$ ; Chester, 1965; El Wakeel and Riley, 1961; Goldberg and Arrhenius, 1958; Turekian and Imbrie, 1966). These Pb/Zr values enable one to understand the genesis of the deposits when they are analyzed in the context of data on lithology, mineralogy, and geochemistry of the major and trace elements.

#### Distribution of Pb/Zr

#### Average Values (Fig. 2)

Average Pb/Zr values may be subdivided into four main intervals:

1) Upper Jurassic—Barremian–Aptian: Sediments are characterized by Pb/Zr values up to  $192 \times 10^{-3}$ , peculiar to shallow-water sea deposits.

2) Lower-middle Albian (Unit VI): Relatively higher values of Pb/Zr ( $290 \times 10^{-3}$ ) testify to deepening of the basin and an appreciable contribution of volcanogenic products.

3) Lower-middle Albian (Unit V)—late Cenomanian-Turonian: Average Pb/Zr values approximate those characteristic of Recent pelagic sediments of the Atlantic—290  $\times 10^{-3}$ .

4) Upper Coniacian–Santonian–Campanian–Maestrichtian: Pb/Zr values increase to  $607 \times 10^{-3}$ . These data and data on the mineral composition of sediments indicate that volcanogenic exhalation components play an appreciable role.

In Tertiary sediments of this region (Site 329, DSDP Leg 36), Pb/Zr values vary from  $61 \times 10^{-3}$  (Oligocene) to  $104 \times 10^{-3}$  (early/middle Miocene), testifying mostly to the accumulation of products of continental runoff that is considerably diluted by siliceous calcareous biogenic remains.

### Upper Jurassic (Fig. 3)

Sediments are characterized by relatively even distribution of Pb/Zr, slightly deviating from average values; their genetic nature has already been discussed.

# Barremian-Aptian—Lower-middle Albian Unit VI (Fig. 4)

Sediments show a clear tendency toward increasing Pb/Zr values by the end of the interval, indicating an appreciable deepening of the basin, relatively marked patterns of marine sedimentation, and the presence of volcanogenic products. The gradual character of this transition is noteworthy.

#### Lower-Middle Albian (Unit V)

Higher values of Pb/Zr prevail in the upper part of the interval. Approximately within the same limits, an increase of Ba/Zr, Sr/Zr, and particularly Ti/Zr was mentioned. Volcanogenic processes played a significant role in such changes of sediment geochemistry along with the development of an open marine sedimentary regime.

# Upper Cenomanian-Turonian—Coniacian-Santonian (Fig. 5)

The distribution of the Pb/Zr values in this interval cannot be so clearly distinguished as that of Ti/Zr, Ba/Zr, and Sr/Zr (upper half of the Coniacian-upper Santonian; Fig. 5). The noticeable changes in the geochemistry indicate both normal oceanic conditions and volcanic phenomena.

# Zn/Zr (Figs. 2-5; Table 4)

#### Geochemical Significance of the Zn/Zr Ratio

The geochemical features of zinc in relation to the sedimentary process have been poorly studied. When river runoff enters a sedimentation basin, a considerable part of the suspended Zn (up to 70–90% total Zn) is detrital and metallo-organic. Further distribution of Zn in a basin is controlled by hydrodynamic conditions. In the succession river-estuary-sea, the role of dissolved metallo-organic forms of Zn abruptly increases. Under open-ocean conditions the main factor controlling the distribution of Zn is the biological activity of plankton (Leinen and Stakes, 1979). The ratios of Zn/Zr for clays (594 × 10<sup>-3</sup>) and deep sea clay sediments (1100 × 10<sup>-3</sup>) can be taken as critical values (Turekian and Wedepohl, 1961).

### Distribution of Zn/Zr

### Average Values (Fig. 2)

The average values of Zn/Zr may be subdivided into three main intervals:

1) Upper Jurassic—lower-middle Albian (Unit VI): Sediments are characterized by abnormally high Zn/Zr values:  $3372-5323 \times 10^{-3}$ . The intense accumulation of Zn in "black shales" (Unit VI) is due to a relatively high content of humified organic matter (up to 3-5% C<sub>org</sub>) and to a lesser extent of dispersed sulphides. Thus the accumulation of plant detritus and sapropelic, suspended, organic matter in the relatively shallow water sea basin of the Southwest proto-Atlantic controlled the accumulation of Zn as well as the subsequent diagenetic redistribution of this element.

2) Early/middle Albian (Unit V): Sediments are characterized by a sharp decrease in the average Zn/Zr value (298 × 10<sup>-3</sup>), compared to preceding deposits. Such a large change is related to the development of a normal marine, well-aerated sedimentary regime, in which the average  $C_{org}$  content in sediments decreased to 0.20%, and the amount of nanno-micritic CaCO<sub>3</sub> (the diluting material) increased to 28%.

3) Upper Cenomanian-Turonian—Coniacian-Santonian. Average Zn/Zr values ( $753-865 \times 10^{-3}$ ) in these sediments are rather close to the ratios in the middle-upper Miocene—Holocene sediments (see Tarney and Donnellan, 1977, Table 5, DSDP Site 329). Taking into consideration the peculiarities of the geochemistry and mineral composition of sediments in this interval, we can state that Zn owes its accumulation mostly to biological transformation of dissolved forms supplied from the continental runoff and from endogenic sources.

# Upper Jurassic (Fig. 3)

Sediments are characterized by an uneven distribution of Zn/Zr that tends to increase upsection. The genetic interpretation has already been given.

# Barremian-Aptian—Lower/middle Albian (Unit VI; Fig. 4)

Despite considerable fluctuations, Zn/Zr values in these sediments tend to increase. Such an uneven distri-

bution of Zn/Zr is related, as already mentioned, to peculiarities in the occurrence of the organic matter that is the main carrier of Zn.

# Lower-middle Albian (Unit V; Fig. 4)

The Zn/Zr values, rather unevenly distributed in the section, decrease in these sediments. Rather large values of Zn/Zr are recorded in the upper part of the interval, which is characterized by high values of Ti/Zr, Ba/Zr, Sr/Zr, and Pb/Zr that result from manifestations of basic volcanism. The factors causing the general decrease in Zn/Zr in this interval have been described already.

### Upper Cenomanian–Turonian–Coniacian–upper Santonian (Fig. 5)

Zn/Zr is unevenly distributed but shows a tendency to increase in the upper Coniacian-upper Santonian. This interval (see Fig. 5) is also characterized by higher values of Ti/Zr, Ba/Zr, Sr/Zr, and Pb/Zr that reveal intensified basaltoid volcanism.

# DISCUSSION: GEOCHEMICAL HISTORY OF LATE MESOZOIC SEDIMENTATION

DSDP Site 511 is located in the basin province of the Falkland Plateau, approximately 10 km south of DSDP Site 330, Leg 36. The oldest deposits, occurring on weathered granitoids of the continental basement, are Middle-Upper Jurassic sediments (Barker, Dalziel, et al., 1977). The location of Site 511 was chosen to study the history of sedimentation in the late Mesozoic and Cenozoic, the role of erosional phenomena, and the general development of the Southwest Atlantic basin. Even though the geochemical aspects of Cenozoic sedimentation of this region have been elucidated (Tarney and Donnellan, 1977), there is no information on the geochemistry of upper Mesozoic sediments.

The main stages and phases of the geochemical history of sedimentation in the late Mesozoic are:

# Stage 1: Late-Middle Jurassic—Early Cretaceous (160-106 m.y.); Sedimentation in a Relatively Shallow Water Stagnant Basin

# Late Jurassic (140-160 m.y.)

During the Late Jurassic (and Middle Jurassic according to some DSDP Leg 36 reports) relatively shallow water (shelf), mostly clayey sediments with a small admixture of silty glassy particles of medium-acid composition (up to 10%) accumulated. The presence of dispersed sapropel-like organic matter and plant fragments (up to 7%), pyrite-marcasite patches (to 7%) and quartz is notable, and epigenetic rosettes and gypsum crystals are also present (see Fig. 3.). The clay matter is represented mostly by mixed-layer Na-montmorillonite with a small amount of micaceous packets, hydromica, and an admixture of chlorite and kaolinite. Sediments accumulated in a basin characterized by pronounced stagnation and an oxygen-free regime in bottom waters (Barker, Dalziel, et al., 1977; Ludwig, Krasheninnikov, et al., 1980; Thompson, 1977). A characteristic geochemical feature of the sediments is the accumulation of dispersed organic matter (average  $C_{org}$  3.26%), closely related to Zn, Cu, Cr, Rb, and Be (Assemblage IA[+]; see Tables 2, 3, and Fig. 1). These are organometallic compounds. The concentration of other elements does not exceed, as a rule, the average contents in clays (see Table 4 and Figs. 1–5).

# Late Jurassic (Portlandian)-Early Cretaceous (Hauterivian) (142-121 m.y.); Hiatus in Sedimentation

This extensive hiatus is associated with the initial break-up of the Gondwanaland supercontinent and the embryonic stage in the formation of the South Atlantic (Barker, Dalziel et al., 1977; Ludwig, Krasheninnikov, et al., 1980).

# Early Cretaceous (Barremian-Aptian-Early-Middle Albian (Unit VI) (121-106? m.y.)

During this time sediments similar to those of Late Jurassic times accumulated. However, deepening of the basin manifested itself in the accumulation of relatively smaller amounts of organic matter and an increase in the carbonate content of the sediments (see Fig. 2), whereas the regime of oxygen-poor bottom waters and restricted water exchange persisted in the basin. These insignificant changes in sedimentation conditions were represented geochemically by a smaller accumulation of components related to organic matter: V, Zn, Cu, Cr, (Assemblage IA[+]; see Figs. 1, 2, Tables 2–4) and diagenetic concentrations of Zn, Ni, La, and perhaps Mo in the carbonate phase (Assemblage IIB[-], see Figs. 1, 2, Tables 2–4).

#### Stage 2: Early-Middle Albian (Unit V)—Middle Maestrichtian (106?-66.6 m.y.); Sedimentation in an Open Oceanic Basin

#### Early-Middle Albian (Unit V), 106?-104 m.y.

In the second half of the early-middle Albian sedimentation conditions changed significantly. During this time there accumulated variegated (later red), mostly clayey nannofossil oozes represented by nanno-micritic (average  $CaCO_3 = 28.03\%$ ) clay matter (up to 50-70%), dispersed Fe-hydroxides (up to 5-7%), and an admixture of medium to basic volcanoclastic material (up to 10%). The clay matter is composed of a range of mixedlayer montmorillonite-mica, hydromica, and an admixture of kaolinite.

According to Sliter (Barker, Dalziel et al., 1977) who studied benthic foraminifers, the depth of the basin does not exceed values typical of the shelf (100–400 m). The geochemical signature of this time interval is reflected in its biogenic components—Ba, Sr, CaCO<sub>3</sub>, and Co (diagenetically bound into a carbonate form) (Assemblage IB[-]; see Figs. 1, 2, Tables 2–5). Worth noting in the second half of this interval are the abruptly increased values of Ti/Zr, interpreted as evidence of an outburst of basaltoid volcanism associated with tectonic activity before a sedimentation hiatus. This conclusion was confirmed by microscope observations. Rather high concentrations of Pb, Zn, Ba, Sr and other metals are related to this volcanic activity (see Fig. 4).

# Late Albian-Late Cenomanian (104-94? m.y.); Hiatus in Sedimentation

This hiatus is related to the ongoing expansion and deepening of the basin and to activation of currents between the eastern and western parts of the Antarctic in the Late Cretaceous and Cenozoic that is confirmed by paleomagnetic data (Barker, Dalziel, et al., 1977).

### Late Cenomanian-Turonian (94?-86 m.y.)

This time interval is characterized by the accumulation of mostly clay sediments (mixed-layer montmorillonite-mica, hydromica, and chlorite admixtures), frequently with appreciable amounts of nanno-micrite, remains of foraminifers (up to 30%), dispersed Fe-hydroxides, admixtures of basic volcanoclastic materials, and fragments of pelecypods (up to 20%). The rate of sedimentation is extremely low (below 3.2 mm/10<sup>3</sup> y.). These data enable one to regard these sediments as residual products preserved despite the strong bottom currents active since the preceding hiatus.

Extension and deepening of the open oceanic basin continued. Sedimentation was characterized by intense accumulation of components such as Ti, Zr, and the related rare alkalis Cs, Li, and Rb (Assemblage IIA[+]; see Tables 2, 3, Figs. 1-5) that indicate the residual nature of the clay sediments. Ni and La, incorporated into a postsedimentary carbonate phase (Assemblage IIB[-], see Tables 2, 3, and Fig. 1), were recognized in lesser amounts. High values of Ti/Zr and Ba/Zr, Sr/Zr as products of residual, relic enrichment (Fig. 5) in the basal layer of the sediments mark the boundary of the hiatus.

#### Coniacian-Santonian (86-78 m.y.)

This time interval witnessed a rather intense accumulation (23.7 mm/ $10^{-3}$  y<sup>-1</sup>) of mostly clay sediments represented by montmorillonite with small amounts of mica interlayers (up to 10-20%), hydromica, chlorite admixtures, and sometimes kaolinite, quartz, and feldspar. In the later sediments there are appreciable amounts of zeolites (from the heulandite group), formed after finely dispersed basic volcanoclastics. Sedimentation took place in a relatively deep water (not less than 2000 m), open ocean basin below the carbonate compensation depth, during active circulation of meridional currents (Barker, Dalziel, et al., 1977). The sediments are characterized by the accumulation of rather high amounts of Ti and Zr, the bound rare alkalis Li and Rb (Assemblage IIA[+]; see Tables 2, 3, and Fig. 1), lesser amounts of diagenetic carbonate phases of Ni, Zn, La (Assemblage IIB[-]), and sulphide and oxide phases of Fe with an admixture of Ni, Co (Assemblage IIIB[-]). Of special interest are accumulations of fine basaltoid volcanoclastic material, partly transformed diagenetically into carbonates recognized as groups of Sc, Pb, Ti, Sr, Ba, Y, Yb, and CaCO<sub>3</sub> (Assemblage IIIA[+]) in sediments of the later half of the interval. Such intense enrichment of these sediments with Ti, Ba, Sr, and other elements in connection of the volcanic outburst is evident in increased values of the Ti/Zr, Ba/Zr, Sr/Zr, and other ratios (see Fig. 5).

# Campanian-Early Maestrichtian (78.0-68.3 m.y.)

Clay sediments with an admixture of fine volcanoclastics accumulated during this interval and were subsequently transformed into essentially zeolitic minerals (up to 70%). The clay matter is represented by mixedlayer montmorillonite-mica, hydromica, and zeolite from the heulandite group. The sedimentation rate was rather low:  $1.5 \text{ mm}/10^3 \text{ y}$ . This can be interpreted as evidence of the beginning of intense bottom currents preceding the development of a large global hiatus at the Mesozoic/Cenozoic boundary.

Data on the geochemistry of these sediments are rather fragmentary. Chemically, they can be considered to resemble the deposits accumulated at the end of the preceding interval.

### Middle Maestrichtian (68.3-66.4 m.y.)

Mostly clay sediments accumulated, with clastic glauconite (up to 30%) and frequently with an admixture of nanno-micrite and basic volcanoclastics (up to 10%), variously zeolitized. The clay matter is represented by mixed-layer montmorillonite-mica, hydromica, and zeolite from the heulandite group. Sedimentation took place in deep-water, open-ocean environments at rather low rates: 7.3 mm/10<sup>3</sup> y.

#### Late Maestrichtian-Late Eocene (66.4-57? m.y.): Hiatus in Sedimentation

The paleoceanographic nature of this almost global hiatus has been reviewed in numerous works (for instance, Barker, Dalziel, et al., 1977; Ciesielski and Wise, 1977; Ludwig, Krasheninnikov et al., 1980; Thiede and van Andel, 1977;).

#### CONCLUSION

The section of late Mesozoic sediments penetrated at DSDP Site 511 in the basin province of the Falkland Plateau is crucial for studying the early stages of the geochemical history of sedimentation in the Southwest Atlantic Ocean.

The major phases of development are delineated in this chapter through study of the distribution of paragenetic assemblages of trace and rare elements in the section; these are revealed by factor analysis (R-, Q-mode), peculiarities of the element/Zr ratios, and interpretations of the data in the context of information on the mineralogy, lithology, and geology of the region.

# Stage 1: Late-Middle Jurassic—Early Cretaceous (160-106? m.y.)

Relatively shallow water (shelf), mostly clay sediments accumulated at that time, with appreciable amounts of dispersed sapropel-like organic matter and plant fragments, pyrite, marcasite, quartz, volcanic glass, and epigenetic crystals of gypsum. Sedimentation occurred in a markedly stagnant environment, with oxygen-poor bottom water layers. Sediments are characterized by higher concentrations of V, Zn, Cu, Cr, Rb, and Be associated with dispersed organic matter ( $C_{org}$  up to 3.26%). In the Early Cretaceous, following a significant erosional hiatus, the basin tended to deepen and expand. Sediments chemically similar to those of Late Jurassic times accumulated here. These were distinguished, however, by diagenetic concentrations of Zn, Ni, and La in the carbonate phase.

# Stage 2: Early-middle Albian (Unit V)—Middle Maestrichtian (106?-66.6 m.y.)

This stage is characterized by sedimentation in an open ocean basin, normally oxygenated and with a pronounced tendency toward expansion and deepening.

During the early-middle Albian biogenic components accumulated (Ba, Sr, and  $CaCO_3$ ). At the end of this interval Ti/Zr values increase, testifying to an outburst of basaltoid volcanism related to tectonic activity before the erosional hiatus (late Albian-late Cenomanian).

At the end of the late Cenomanian-Turonian mostly clay sediments accumulated, with rather high Ti and Zr and related rare alkalis (Li, Rb) that reveal the residual nature of the clays. During the Coniacian-Santonian, clay sediments accumulated, characterized by higher concentrations of Ti, Zr, Li, Rb, diagenetic carbonate phases of Ni, Zn, La, sulphides, and Fe-oxides with admixtures of Ni and Co. The latter half of this interval shows the accumulation of fine basaltoid volcanoclastic material diagenetically altered by zeolitization and carbonitization and enriched with Sc, Pb, Ti, Sr, Ba, Y, and Yb. Chemically similar sediments accumulated during the Campanian-middle Maestrichtian.

Activation of currents preceding a large global erosional hiatus at the Mesozoic/Cenozoic boundary is reflected in both the lower rates of sedimentation and the residual higher concentrations of Ti, Zr, Ba, Sr, and others.

#### ACKNOWLEDGMENTS

I am grateful to colleagues of the Geological Institute of the U.S.S.R. Academy of Sciences: D. A. Kazimirov, N. I. Kartoshkina, and N. Y. Vlasova, for their help in computer processing of the analytical data, recalculation, and presentation of the results; B. A. Sakharov and T. G. Eliseeva, for X-ray structural analysis and assistance in interpretation of the data obtained; V. A. Krasheninnikov, for the study materials and consultation on stratigraphy; E. I. Pyatigorskaya, O. D. Smirnova, and O. P. Kachan for help in graphic work, and G. N. Surovtseva and I. G. Sheremet for translation of the paper.

Critical review of the paper and comments by N. G. Brodskaya and A. G. Kossovskaya improved the work.

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