39. STUDY OF GEOCHEMICAL DATA (EOCENE-SANTONIAN SAMPLES) FROM HOLE 516F (LEG 72) BY THE METHOD OF CORRESPONDENCE ANALYSIS[1]

Maurice Renard and Daniel Ambroise, Université Pierre et Marie, Curie, 75230 Paris Cedex 05, France

INTRODUCTION

This study involves samples of Santonian to Eocene age (Cores 516F-125 to 516F-38) taken from the Rio Grande Rise in the South Atlantic Ocean. These samples are from DSDP Site 516 occupied during Leg 72 of the *Glomar Challenger* (details given in site chapter, Site 516, this volume). Only Santonian to Paleocene cores have been well sampled, and analyses of the Eocene samples are preliminary results. Results of the trace element analyses (Mg, Sr, Mn, Ni, Fe, Na, K) of the carbonate fraction and $CaCO_3$ percentage for each sample can be found in Renard and others (this volume). Whole geochemical data are treated by the statistical method of correspondence analysis. Oxygen and carbon isotopic ratios measured on samples close to the Cretaceous/Tertiary boundary are not used in this study.

METHOD

The method of correspondence analysis is particularly well suited to interpretation of sedimentologic and geochemical data (Chenet and Teil, 1979; Rabussier, 1980; Ambroise et al., 1977; Tourenq, Ambroise, and Rohrlich, 1978). The mathematical theory is discussed in Benzecri (1973), Teil (1975), and Lebart and others (1980). In brief, correspondence analysis can be considered to be a variant of principal component analysis, in which the distance used for the calculation of the matrix is the metric χ^2 distance. Results are plotted on bivariate graphs representing two factorial axes. By means of the χ^2 distance, it is possible to project variable points and sample points simultaneously on the same graph. Thus, it is relatively easy to interpret the meaning of each axis and the relative positions of variable points and sample points. Each variable is "weighted" to have the same importance in the analytic results. Some of the variables show low "mass" values (numerous zero values, such as nickel and chromium) or are unreliable (such as potassium, which can be flushed out of clay minerals during acetic acid dissolution of carbonate) and are only used as illustrative variables (i.e., these variables are not included in the matrix but are plotted on the graph). Also, some doubtful samples (low carbonate content) and samples polluted by trace elements are used as extra samples. Table 1 shows only the samples used in the matrix calculation (62 samples).

RESULTS

In Figure 1, sample numbers and variable names are plotted in the first factorial space. The scale of coordinates and percentage inertia[2] of each axis are given. The first factorial plane explains 76% of the variability (Factor 1: 54.8%, Factor 2: 21.2%).

Table 2 contains the coordinates of variables relative to the first and second axes, and the coordinates of samples are listed in Table 3. Factor 1 (horizontal axis) is polarized both by manganese and strontium (and less by sodium). Factor 2 (vertical axis) is polarized, on the one hand, by magnesium, nickel, chromium, and iron. On the other hand, it is polarized by strontium and (in a less significant way) manganese. Part of the variability along Factor 2 is due to the inverse relationship of the magnesium and the strontium contents of the carbonates. This is probably caused by increasing diagenesis in the pelagic carbonates (Renard, 1979; Rabussier, 1980).

The correspondence analysis method is important for geochemical studies because it is possible to draw a curve that joins sample points in stratigraphic succession; the investigator, therefore, can follow the geochemical evolution of series during geologic time.

Coniacian to Santonian Samples

The first part of the series studied, Coniacian to Santonian samples, varies along a diagonal line from the manganese pole to the chromium, nickel, iron, and magnesium pole. From Sample 516F-125-1, 24–26 cm to Sample 516F-119-3, 85–87 cm (251 to 193, Fig. 1), there is a progressive displacement from the manganese pole.

There are several oscillations in between Sections 516F-119-1 and 516F-113-3. Between the manganese pole (Samples 516F-119-1, 119–121 cm; 516F-118-3, 14–16 cm; 516F-117-1, 132–134 cm; and 516F-114-1, 109–111 cm) and the iron-magnesium pole (Samples 516F-120-1, 36–38 cm; 516F-119-3, 85–87 cm; 516F-116-3, 31–33 cm; and 516F-117-6, 16–18 cm), manganese values are always less than in stratigraphically lower samples. These oscillations suggest that geochemical evolution during the Santonian was controlled principally by the opposing behavior of iron and manganese. Seafloor spreading (which produces volcanism and/or hydrothermal emission through sediments) and the removal of the site from the region of hydrothermal circulation are the main causes of variation in the geochemistry of sediments. Alternating iron-rich and manganese-rich periods during the Santonian may reflect variations in the chemical composition of oceanic hydrothermal exhalation. Such fluctuations are observed along mid-oceanic ridges today (Edmond et al., 1979).

Campanian to Eocene Samples

Beginning with Sample 516F-113-3, 51–54 cm (Campanian), samples are distributed primarily along the second factorial axis. The sharp break in the distribution of samples suggests that seafloor spreading did not play a leading role in the geochemistry of sediment after this time.

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[2] If λ_1 is the characteristic value of Axis 1, then $\lambda_1 + \lambda_2 + \lambda_3 + \ldots \lambda_p$ represents the total inertia of the cloud. The inertia percentage for Axis 1 equals

$$\frac{\lambda_1}{\sum_{i=1}^{p} \lambda_i}$$

For more details, see Teil (1975).

Table 1. Trace element content (in ppm) of Hole 516F samples used in the matrix calculation.

Code for Figure 1	Core-section (interval in cm)	CaCO₃%	Mg	Na	K	Mn	Sr	Ni	Cr	Fe
381	38-1, 98–100	92.07	1292	424	163	215	1185	7	3	1702
391	39-1, 42–44	87.34	1319	455	224	214	1266	7	3	1517
392	39-2, 37–39	86.31	1073	491	262	210	1347	5	3	1343
401	40-1, 95–97	89.03	1274	429	208	188	1305	3	3	1314
471	47-1, 18–19	89.67	1765	499	208	202	1160	5	5	1072
812	81-2, 101–103	94.01	1211	444	101	430	591	2	3	1144
831	83-1, 2–5	91.30	1687	523	190	370	652	5	2	1727
833	83-3, 10–12	87.45	1252	381	233	655	774	8	3	1204
835	83-5, 24–26	89.18	882	556	221	495	977	3	3	1079
843	84-3, 80–82	84.80	2294	623	225	688	990	3	2	2806
851	85-1, 51–53	87.40	770	569	180	790	1033	1	1	1052
855	85-5, 100–102	88.75	2473	389	122	547	1015	4	1	1919
863	86-3, 140–141	87.43	3195	593	209	567	1030	7	2	2734
866	86-6, 26–28	88.61	2695	396	112	545	1029	3	1	1987
873	87-3, 105–107	88.78	4316	383	109	636	838	4	1	2233
874	87-4, 3–5	89.66	3925	523	114	734	739	5	2	2387
875	87-5, 96–98	86.44	2698	441	140	651	723	3	1	1671
881	88-1, 102–103	88.44	1373	471	125	484	621	1	1	824
891	89-1, 55–57	78.80	1748	419	206	699	653	2	2	1227
896	89-6, 54–56	82.07	2506	330	198	850	804	3	4	1624
901	90-1, 66–68	79.04	1644	310	226	607	948	2	4	1290
902	90-2, 52–56	73.64	2354	322	303	679	945	4	4	1800
904	90-4, 99–100	81.61	2820	365	162	558	731	3	3	2032
905	90-5, 40–42	81.53	2477	401	172	696	724	3	4	1988
906	90-6, 14–16	82.53	2790	282	161	746	751	2	4	2050
911	91-1, 49–50	76.84	2551	311	209	643	728	3	4	1902
912	91-2, 145–147	81.49	2717	376	195	630	796	3	4	2079
913	91-3, 126–128	78.48	3733	356	238	582	737	3	4	2630
914	91-4, 51–53	81.42	3942	397	194	510	768	5	4	2822
933	93-3, 127–129	77.07	1305	629	267	810	747	1	4	1158
935	93-5, 12–14	42.20	2051	549	1197	761	884	7	6	834
972	97-2, 64–65	52.89	3128	473	938	1265	862	12	11	3225
982	98-2, 82–83	58.47	3419	404	742	1081	729	19	6	3595
042	104-2, 122–125	68.23	5366	339	292	835	933	7	5	4958
051	105-1, 42–44	68.54	4426	261	225	855	820	6	6	4086
055	105-5, 72–74	57.17	1010	240	322	978	861	4	6	1850
062	106-2, 65–67	71.65	766	242	168	855	818	2	4	1219
066	106-6, 68–70	67.28	1372	286	260	883	626	4	4	2016
077	107-7, 40–43	62.46	1197	270	290	804	736	4	5	1480
084	108-4, 44–45	63.08	2522	295	297	677	719	6	7	3070
093	109-3, 75–77	75.22	3679	251	235	636	684	7	6	4730
094	109-4, 41–43	71.63	2340	243	281	574	739	6	6	3234
133	113-3, 51–54	53.60	4779	456	428	672	567	14	14	5657
141	114-1, 109–111	82.62	1393	198	97	922	310	4	5	2055
146	114-6, 116–118	69.78	2908	262	172	773	383	7	8	3400
154	115-4, 27–29	69.40	2137	324	190	881	319	7	8	2888
161	116-1, 125–127	76.65	3187	315	127	770	314	9	8	4045
163	116-3, 31–33	40.83	4602	526	582	614	600	17	21	6268
166	116-6, 60–62	77.32	3219	274	161	758	371	8	8	4232
171	117-1, 132–134	79.04	1840	279	164	920	332	4	6	2665
174	117-4, 22–24	67.45	2626	359	260	685	466	7	11	3702
176	117-6, 16–18	63.01	3199	345	344	640	445	10	10	4678
181	118-1, 123–125	83.28	2893	230	120	769	260	5	6	3696
183	118-3, 14–16	85.38	1335	187	117	694	260	2	5	2122
191	119-1, 119–121	79.17	1334	254	165	800	353	3	7	2252
193	119-3, 85–87	70.94	3405	321	169	617	355	8	11	5339
201	120-1, 36–38	65.29	4084	371	126	773	384	9	18	5922
211	121-1, 61–63	68.47	2645	305	73	1126	270	4	12	3136
222	122-2, 120–122	56.36	3286	378	76	1935	317	4	17	3088
231	123-1, 53–55	56.71	1426	311	67	4538	393	6	19	1134
241	124-1, 20–22	76.23	4516	401	216	4171	162	2	5	4184
251	125-1, 24–26	39.96	3893	305	1246	3644	267	1	6	1563

Table 2. Element coordinates relative to first and second factors.

Element	Factor 1	Factor 2
Magnesium	0.039	−0.317
Strontium	0.442	0.179
Sodium	0.254	0.051
Potassium	0.080	−0.020
Manganese	−0.495	0.134
Iron	0.005	−0.490
Nickel	0.140	−0.427
Chromium	−0.205	−0.431

Table 3. Coordinates of Hole 516F samples relative to first and second factors.

| Core-section (interval in cm)	Factor 1	Factor 2
38-1, 98–100	0.625	0.168
39-1, 42–44	0.640	0.197
39-2, 37–39	0.666	0.256
40-1, 95–97	0.682	0.260
47-1, 18–19	0.623	0.185
81-2, 101–103	0.251	0.160
83-1, 2–5	0.334	0.042
83-3, 10–12	0.163	0.173
83-5, 24–26	0.378	0.276
84-3, 80–82	0.146	0.016
85-1, 51–53	0.223	0.365
85-5, 100–102	0.319	0.133
86-3, 140–141	0.319	0.017
86-6, 26–28	0.324	0.126
87-3, 105–107	0.186	−0.025
87-4, 3–5	0.120	−0.026
87-5, 96–98	0.150	0.092
88-1, 102–103	0.267	0.252
89-1, 55–57	0.083	0.179
89-6, 54–56	0.041	0.133
90-1, 66–68	0.241	0.216
90-2, 52–56	0.193	0.115
90-4, 99–100	0.187	0.010
90-5, 40–42	0.105	0.058
90-6, 14–16	0.058	0.053
91-1, 49–50	0.119	0.042
91-2, 145–147	0.169	0.040
91-3, 126–128	0.165	−0.091
91-4, 51–53	0.226	−0.133
93-3, 127–129	0.107	0.237
93-5, 12–14	0.182	0.116
97-2, 64–65	−0.026	−0.028
98-2, 82–83	−0.015	−0.125
104-2, 122–125	0.100	−0.216
105-1, 42–44	0.033	−0.171
105-5, 72–74	−0.018	0.196
106-2, 65–67	0.012	0.298
106-6, 68–70	−0.070	0.110
107-7, 40–43	0.021	0.174
108-4, 44–45	0.088	−0.095
109-3, 75–77	0.082	−0.298
109-4, 41–43	0.144	−0.120
113-3, 51–54	0.063	−0.436
114-1, 109–111	−0.361	0.007
114-6, 116–118	−0.146	−0.261
115-4, 27–29	−0.224	−0.159
116-1, 125–127	−0.159	−0.361
116-3, 31–33	0.102	−0.477
116-6, 60–62	−0.132	−0.354
117-1, 132–134	0.271	−0.075
117-4, 22–24	−0.023	−0.261
117-6, 16–18	0.003	−0.382
118-1, 123–125	−0.241	−0.329
118-3, 14–16	−0.282	−0.078
119-1, 119–121	−0.223	−0.034
119-3, 85–87	−0.052	−0.507
120-1, 36–38	−0.106	−0.520
121-1, 61–63	−0.393	−0.162
122-2, 120–122	−0.561	−0.015
123-1, 53–55	−0.945	0.365
124-1, 20–22	−0.863	0.167
125-1, 24–26	−0.675	0.212
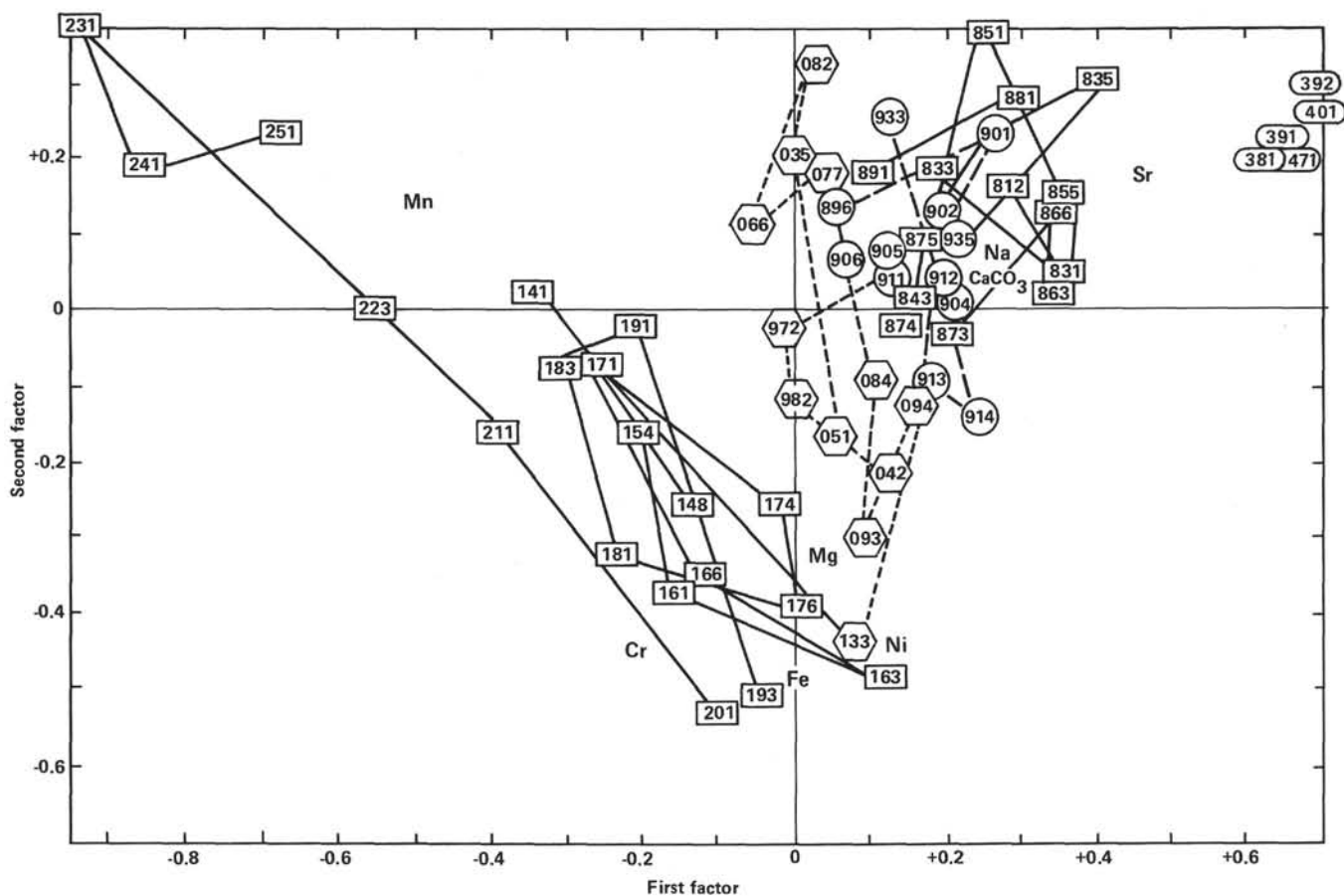
Figure 1. Analysis of samples from Cores 125 to 38 (Coniacian to Eocene samples) of Hole 516F. For sample number code, see Table 1. In Figure 2, these numbers are enclosed in different geometric figures corresponding to major time groups. Rectangles (141–251) = Coniacian to Santonian; hexagons = Campanian; circles = Maestrichtian; rectangles (812–891) = Paleocene; ovals = Eocene.

We can distinguish three groups in the Campanian section between Samples 516F-113-3, 51–54 cm and 516F-97-2, 64–65 cm. The first group (chiefly Campanian samples with high magnesium and iron content) occupies the lower part of the graph in Figure 2. Samples 516F-97-2, 64–65 cm to 516F-98-2, 82–83 cm (low iron values) comprise the second group, which shows up in the middle section of the graph. In the upper part of the graph is the third Campanian group, which consists of samples with low magnesium and iron values (Samples 516F-107-7, 40–43 cm; 516F-106-2, 65–67 cm; and 516F-105-5, 72–74 cm). Strontium values do not fluctuate and are not particularly high compared to other Campanian samples.

Maestrichtian samples (516F-93-5, 12–14 cm to 516F-89-6, 54–56 cm) are plotted near the strontium pole on Figure 2. The low positions of two samples (516F-91-3, 126–128 cm and 516F-91-4, 51–53 cm) are chiefly the result of a high magnesium content (perhaps contamination by interlayer magnesium of clay minerals) and seem atypical. The extreme position of Sample 516F-90-1, 66–68 cm, however, which is related to high strontium and to low magnesium and iron values, suggests a special geochemical condition during the Paleocene. Very close to the strontium pole in Figure 2 are the symbols for Paleocene Samples 516F-89-1, 55–57 cm to

516F-81-2, 101–103 cm. The lower positions of five samples (Samples 516F-84-3, 80–82 cm; 516F-87-4, 3–5 cm; 516F-87-3, 105–107 cm; 516F-87-5, 96–98 cm; and 516F-89-1, 55–57 cm) are related to high iron and relatively low strontium contents. Samples very close to the Cretaceous/Tertiary boundary have not been plotted; the results of their analyses are particularly unreliable because of their low carbonate content. Although Danian samples are distinguished from Thanetian samples by their strontium values (Renard, this volume), they are not identified by the correspondence analysis method, even on Axis 3 (perpendicular to the plane defined by Axes 1 and 2, and not shown on our projection). Apparently, iron variability camouflages other geochemical variations in the Tertiary series.

Eocene Samples 516F-47-1, 18–19 cm to 516F-38-1, 98–100 cm are plotted as preliminary data and are located beyond the strontium pole. This location indicates that they are different from the other samples discussed.

CONCLUSION

Correspondence analysis allows a simultaneous global treatment of all geochemical parameters of Coniacian-Eocene sediments from Hole 516F. The synthesis graph (Fig. 2), which summarizes the geochemical evolution of the series, leads to the following conclusions.
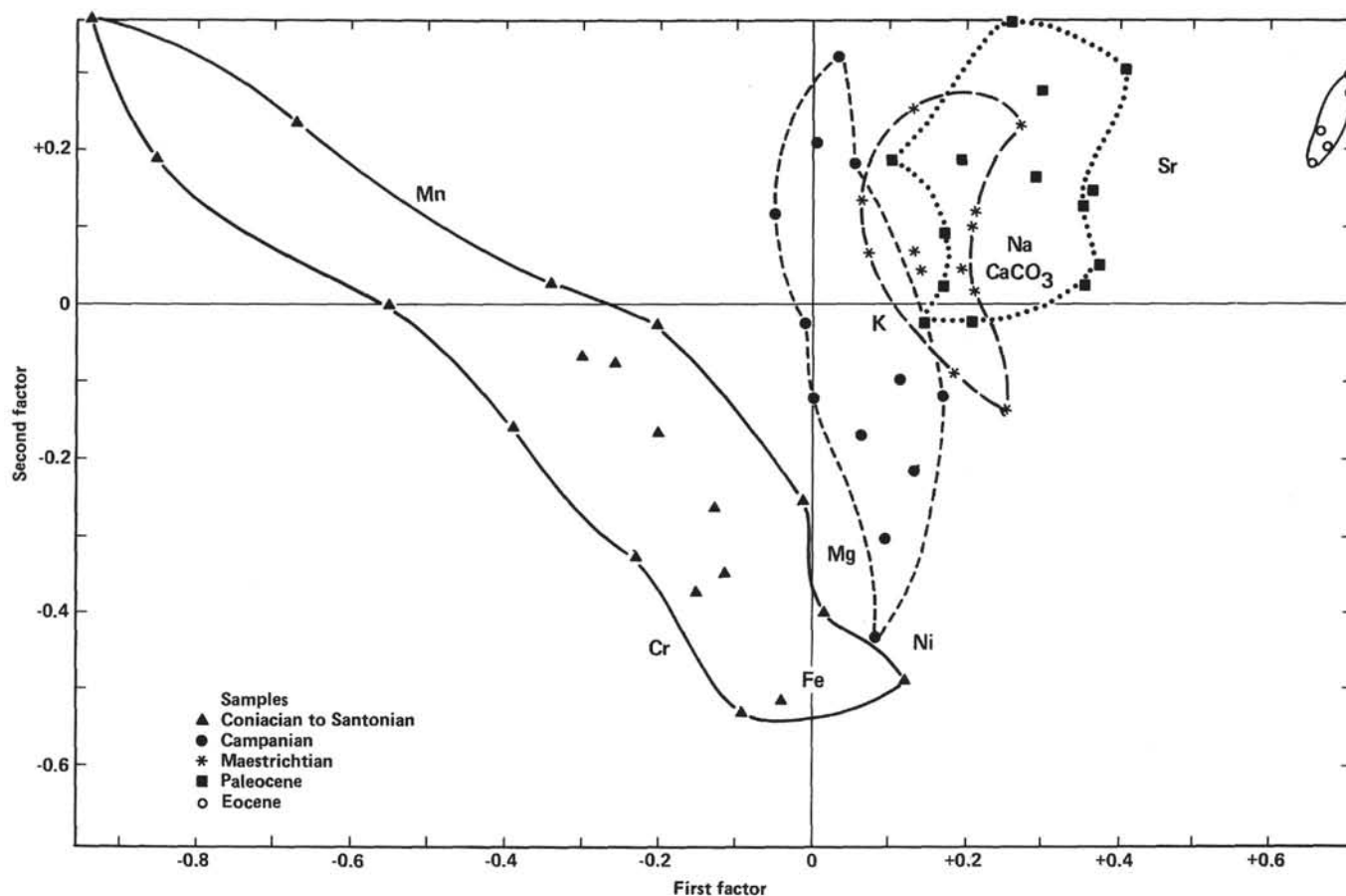
Figure 2. Schematic evolution of Coniacian to Eocene sedimentary geochemistry (Hole 516F). For sample identification, refer to Figure 1.

1) Each time stage has a very well defined area; each can be easily characterized by its geochemistry.

2) During the Coniacian to Santonian, manganese was the dominant geochemical constituent; this suggests that the geochemical evolution of sediments from that interval is mainly controlled by seafloor spreading;

3) After the Campanian, there was a sharp change in the control of the geochemical evolution of sediments. This evolution is now mainly controlled by chemical variations of the sedimentary environment and by diagenetic phenomena.

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