# 16. STRONTIUM, MANGANESE, AND IRON CONTENTS, AND OXYGEN ISOTOPES IN THE CARBONATE FRACTIONS RECOVERED FROM HOLE 398C, LEG 47B

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### INTRODUCTION

The strontium, manganese, and iron concentrations of the carbonate fraction were measured in samples from Hauterivian to Pleistocene sediments. The carbonate fraction was obtained by crushing the samples and then dissolving them in acetic acid. Trace element analysis was conducted by atomic absorption spectrometry using the method described by Renard and Blanc (1971, 1972). Mineralogically, the composition of the carbonate fraction always corresponded to low magnesian calcite. Exceptions were found in Aptian-Albian beds which contained no calcium carbonates in spite of a high weight loss when dissolved in acetic acid. For these samples, X-ray analysis showed the presence of quartz, opal, amorphous matter, and rhodocrosite. All data are summarized in Table 1.

#### **RELATIONSHIPS TO INSOLUBLE RESIDUE**

In some samples, the percentage of insoluble matter remaining after treatment with acetic acid was large enough to suggest contamination by the insoluble elements.

For strontium, the concentrations measured generally show no correlation with the levels of insoluble matter (Figure 1). However, a more detailed analysis shows a distinct positive correlation for all Hauterivian to Eocene samples. Therefore, the results are unreliable where the amount of insoluble matter is greater than 70 per cent. For manganese and iron content, no correlation was found with respect to the level of insoluble matter.

## STRONTIUM AND OXYGEN ISOTOPES

Strontium concentrations, which are quite high during the Pliocene, Miocene, and Oligocene (Figure 2), show a sharp decline in Eocene and older rocks. This decline continues gradually to the Hauterivian and is due to increasing diagenesis with depth (Renard et al., 1978). It appears that the strontium lost from the carbonates must be trapped readily by the argillaceous rocks since a positive correlation between the level of strontium and the percentage of insoluble matter is found only in Eocene and older rocks. It is difficult to pinpoint the exact cause for the strontium loss. Depth (hence temperature and pressure) may play a part. However, the graph comparing strontium levels at different depths (Figure 3) is irregular and the variations in the amount of subsidence may be a causative factor. The relationship to sedimentation rate (Figure 4) is also not obvious. The periods of extremely high sedimentation (Miocene-Pliocene and Barremian-Hauterivian) do not show particularly high losses of strontium.

The levels of strontium tend to increase during the Maestrichtian, a phenomenum shown quite clearly at Holes 390 and 390A of Leg 44 (Renard et al., 1978). One possible cause is the weakness of the diagenetic process during this time. It also could be simply that the original strontium levels were higher during this period.

A strong positive correlation is shown between the isotopic oxygen composition and strontium concentrations (Figure 5). Statistical analysis shows:

> Correlation coefficient "r" = 0.8235 Student, Fisher test t = 7.0055 (39 samples) Equation for correlation:

 $[SR] ppm = 398-93[\delta^{18}O] + 1273-74.$ 

We suggest that this positive correlation (already seen in Leg 44) is characteristic of diagenesis, a finding which agrees with those of Veizer (1977).

From Figure 5, it can be seen that regardless of which fractions are considered (Strontium levels of oxygen isotopes), the geochemical (diagenetic) division is situated between the Eocene and the Oligocene epochs. At present, we can offer no causal explanation for this.

## MANGANESE

The distribution graph for manganese concentrations (Figure 6) shows the following:

a) Two impoverished zones: (1) the Miocene and (2) the Hauterivian-Barremian;

b) One rich zone from the Maestrichtian to the early Oligocene (particularly the late Eocene).

The manganese level in a carbonate depends upon two principal factors. One factor is oxidation reduction conditions during deposition (Michard, 1969). In a reducing medium, the manganese coprecipitates with the carbonate which leads to manganese-poor limestones. In an oxidizing medium, manganese dioxide precipitates, leading to limestones rich in this element.

Sample (Interval in cm)	Carbona te Mineralogy	Solubility in Acetic Acid	Mn (ppm)	Sr (ppm)	Fe (ppm)	δ <sup>18</sup> 0 (°/)	δ <sup>13</sup> C (%)00)	Age
2-2, 60-67	Calcite	71.05	314	1710	508	0.73	-0.10	Pliocene
3-2,70	Calcite	76.07	404	1630	563	0.84	0.80	Miocene
4-2,60-62	Calcite	88.67	288	1897	314	0.94	0.96	Miocene
5-2, 40-42	Calcite	89.84	243	1858	176	1.35	1.53	Miocene
5-2, 60-62	Calcite	90.24	193	1820	177	1.08	1.63	Miocene
5-4, 44-46	Calcite	90.82	266	1621	196	1.44	1.60	Miocene
6-3, 40-42	Calcite	67.30	323	1935	269	1.32	2.40	Miocene
6-3, 60-62	Calcite	82.28	367	1747	222	1.52	2.60	Miocene
6-4, 31-33	Calcite	87.25	458	1781	275	1.68	2.65	Miocene
7-2, 58-60	Calcite	78.32	583	1433	304	1.03	1.54	Miocene
9-3, 99-101	Calcite	89.86	575	1539	321	1.42	1.73	Miocene
13-3, 62-64	Calcite	58.63	1620	1736	109	1.11	1.54	Oligocene
14-1, 35-37	Calcite	70.05	1094	1625	152	1.54	1.53	Oligocene
15-2, 45-46	Calcite	72.64	938	1695	112	1.30	1.37	Oligocene
20-3, 118-120	Calcite	20.96	5469	1952	274	-0.94	2.15	Eocene
21-2, 77-79	No calcium carbonate	7.23	6405	733	1332	-0.03	+1.66	Eocene
22-3, 23-25	Calcite	35.67	3700	1085	72	-0.03	+1.66	Eocene
23-2, 41-45	Calcite	16.79	3254	906	424	-0.62	+1.72	Eocene
25-1, 102-104	Calcite	16.29	6523	1462	258	-0.33	+1.61	Eocene
26-2, 39-41	Calcite	33.72	4008	1302	80	-0.02	+1.67	Locene
27-4, 89-91	Calcite	35.57	2723	1483	166	-1.27	+1.55	Eocene
28-2, 54-56	Calcite	27.97	1241	1450	209	-0.80	+1.75	Eocene
30-4, 132-134	Calcite	32.96	1943	1457	158	-1.12	+1.74	Eocene
32-1, 95-97	Calcite	19.40	2078	1112	253	\$251,6255	(1962) (1962)	Eocene
33-2, 141-142	Calcite	51.20	1855	841	67	-0.93	+0.71	Eocene
35-2, 77-79	Calcite	61.17	2532	1028	64	-0.75	+1.44	Eocene
36-2, 100-102	Calcite	41.93	3574	1139	89	-0.85	+2.55	Paleocene
38-2, 56-58	Calcite	39.29	3360	1102	29	-0.45	+2.15	Paleocene
39-2, 43-45	Calcite	37.15	3313	1140	55	-0.11	+1.63	Paleocene
40-1, 9-11	Calcite	41.05	3477	934	79			Paleocene
41-2, 8-10	Calcite	55.35	1529	1202	71	-0.25	+1.38	Paleocene
41-2, 31-33	Calcite	41.46	2336	1011	112	-0.26	+0.90	Paleocene
41-2, 38-40	Calcite	9.46	3000	1229	491	-1.08	+1.61	Paleocene
41-2, 45-47	Calcite	55.23	1813	803	42	-0.27	+2.19	Paleocene
41-2, 65-68	Calcite	59.97	2285	847	36	-0.37	+2.24	Paleocene
41-2, 131-133	Calcite	55.55	2316	749	39	-0.12	+2.38	Paleocene
42-2, 93-95	Calcite	48.26	2460	976	74	0.40	10.50	Maestrichtian
43-2, 16-18	Calcite	57.96	2028	1169	57	-0.48	+2.33	Maestrichtian
44-2, 65-67	Calcite	63.35	1565	1060	41	0.50	12.02	Maestrichtian
45-1, 18-20	Calcite	38.29	2803	1111	103	-0.59	+2.02	Maestrichtian
46-2, 28-30	Calcite	43.63	4214	1047	106	-0.43	+1.69	Maestrichtian
47-1,45-47	Calcite	24.56	3677	805	96			Maestrichtian
56-3, 12-14	No calcium carbonate	7.46	819	Neant	6920			Cenomanian
57-2, 101-103	Calcite	55.65	4958	863	439			Cenomanian
93-1, 86-87	No calcium carbonate	37.46	210.900	95	>50.000			Albian
111-3, 72-74	No calcium carbonate	33.37	195.000	125	29.940			Aptian
116-3, 80-82	No calcium carbonate	69.22	265.400	149	14.975			Aptian
130-4, /8-80	Calcite	23.55	622	1099	1938			Barremian
132-2, 108-109	Calcite	31.88	1108	416	6191		10121-14121-1	Barremian
133-2, 51-53	Calcite	54.38	1313	682	1876	-1.77	+1.31	Barremian
134-2, 78-80	Calcite	40.67	1450	771	1695	-1.47	+1.50	Hauterivian
135-2, 27-29	Calcite	44.70	864	662	1788	-1.74	+1.09	Hauterivian
137-2, 24-26	Calcite	75.41	960	486	2674	-1.50	+1.12	Hauterivian
138-1, 38-40	Calcite	87.10	1241	395	3843	-1.57	+1.08	Hauterivian

 TABLE 1

 Data Summary of Carbonate Fractions Analyses, Hole 398C

Secondly, the manganese level in a carbonate is influenced by the amount of manganese in the seawater, which introduces the problem of its origin. The manganese can be the result of either continental erosion or submarine volcanoes (an exhaustive bibliography dealing with this subject is in Cronan, 1974). Regarding Site 398, we believe that the high levels of manganese are due to submarine volcanic activity (hydrothermal and/or magmatic emanations). From the Maestrichtian to the early Oliogocene, there was a period of volcanic activity, reaching maximum intensity in the late Eocene.



Figure 1. Relationship between trace element concentrations and insoluble residue percentage after acetic acid dissolution.



Figure 2. Distribution curve for strontium concentrations.

500



Figure 3. Strontium concentration as a function of depth in the hole.

#### IRON

The distribution of iron (Figure 7) can be divided into three basic periods.

1) A high concentration zone in Barremian and Hauterivian time;

2) A low concentration zone in the Miocene-Pliocene;

 A very low concentration zone between the Maestrichtian and the Oligocene.

As was true for manganese, the problem is to determine the origin of these varying concentrations; once again, there can be either continental erosion or submarine volcanic activity.

For the Barremian to Hauterivian and the Miocene-Pliocene periods, we think that the iron originated from continental erosion. Given that the solubility products of iron and manganese oxides are very different, it normally would not be possible for the two elements to be co-precipitated. Figure 8 shows that those samples with a high concentration of iron have a correspondingly low concentration of manganese and vice versa. It becomes possible, therefore, to outline the basic characteristics of particular groups of samples, as we already have done for Leg 44 (Renard et al., 1978).

A group of samples from Site 398 with a high concentration of iron is characteristic of continental erosion sediments (Hauterivian, Barremian, and Miocene-Pliocene). Similarly, a group of samples with a high concentration of manganese is characteristic of volcanic sediments (Maestrichtian to Oligocene). The high concentrations of iron in the Hauterivian and Barremian samples imply a close proximity to the coastline.

There remains the problem of the Aptian-Albian samples. These were found to be totally lacking in calcium carbonates; however, they did contain high concentrations of both manganese (200,000 ppm) and iron compounds (20,000 to 40,000 ppm), when treated with acetic acid. The fact that these concentrations are always associated with the formation of new ocean floor leads us to postulate that the Aptian-Albian period was one of important oceanic expansion for this particular region, a finding which seems to agree with the geophysical data.

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Figure 4. Relationship between the sedimentation rates curve and the distribution curve of strontium concentrations.



Figure 5. Relationship between isotopic oxygen composition and strontium concentrations.

503



Figure 6. Distribution curve for manganese concentrations.



Figure 7. Distribution curve for iron concentrations.

505



Figure 8. Relationship between iron and manganese concentrations.