31. SOME TRACE ELEMENTS AND THEIR RELATION TO OXYGEN AND CARBON ISOTOPES IN THE CARBONATE SAMPLES RECOVERED FROM HOLE 400A OF DSDP LEG 48

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INTRODUCTION

Abundances of strontium, sodium, potassium, magnesium, manganese, and iron relative to the carbonate fraction were measured in 90 samples from Hole 400A. The age of the samples ranges from Aptian to Pleistocene. After crushing and washing in distilled water to eliminate pollution by sea water, the rocks were dissolved in acetic acid. Trace element analysis was carried out by atomic absorption according to the method described by Renard and Blanc (1971, 1972). X-ray diffraction methods reveal a constant carbonate mineralogy, i.e., low magnesian calcite. Oxygen and carbon isotope techniques are described by Létolle et al. (this volume). Results are summarized in Table 1.

RELATIONSHIP BETWEEN CONTENTS OF TRACE ELEMENTS AND INSOLUBLE RESIDUE

In this hole, in some zones such as the Eocene and Aptian, the percentage of carbonates is low (Figure 1). In using low-carbonate samples, great caution was exercised to assure that pollution was not introduced by flushing out the insoluble residue (i.e., interlayer cations in clay minerals).

Strontium concentrations in samples of Pleistocene to Oligocene age do not show any correlation with the insoluble proportion (Figure 2a). However, correlation appears in the pre-Oligocene sediments (see later explanation); results on carbonates from samples where the insoluble proportion is greater than 60 per cent are unreliable. A strong correlation is observed between the concentrations of sodium (Figure 2e), potassium (Figure 2f), and magnesium (Figure 2b) and the insoluble residue. These elements cannot therefore be used as geotechnical indicators because their variations are hidden by the non-carbonate phase pollution. For manganese (Figure 2c) there is no correlation, whereas for iron a more complex situation exists (Figure 2d); there is no correlation except in samples of Pleistocene and Aptian age (see later explanation).

STRONTIUM AND OXYGEN ISOTOPES

The distribution of strontium concentrations (Figure 3) is homogeneous throughout the Miocene sediments (average 1773 ppm) and in early Pliocene sediments (average 1778 ppm) showing the relative stability of the oceanic environment and the climate. During Pleistocene time, the concentration became lower (average 1536 ppm) and extremely variable, indicating deterioration of the climate. This alternation of high and low strontium content in the Pleistocene suggests a relationship to glacial and interglacial stages which cannot be better defined due to the small number of samples available for study.

From the Oligocene stratigraphically downwards, and particularly in the Eocene sediments, a continuous reduction in the amount of strontium is observed (only samples with more than 40 per cent of carbonate were used) (see Table 2).

This reduction is due to increasing diagenesis with depth in the hole, which has already been observed on Leg 44 and Leg 47B (Renard et al., 1978). It appears that the strontium lost during the carbonate dissolution was trapped rapidly by clay minerals. Indeed, the correlation between the amounts of strontium and the "insoluble proportion" appears only downward from the Oligocene interval, that is, when carbonate diagenesis becomes important.

The strontium concentration in the carbonate phase thus results from two phenomena: (1) syn-sedimentary processes (variation of strontium content due to environmental changes, climatic modifications, etc. . .), and (2) diagenetic processes.

Although the variations observed at the Oligocene/ Miocene boundary at this site may result from either of these two causes, the combined study of variations in amounts of strontium and the composition of oxygen isotopes in the carbonates enables this ambiguity to be removed.

For Pleistocene to Miocene values (Figure 4) there is a *negative* and strong correlation: (Correlation coeff. r = -0.6288; Student-Fisher test t = 4.24, although the value of t at a risk 0.001 for 36 samples is 3.646 > t > 3.551).

For the samples from Aptian to Oligocene the *positive* correlation is also strong¹. (r = 0.8698, t = 5.53 the value of t at a risk 0.001 for 19 samples being 3.992). For each group of samples a regression line of x/y and y/x has been drawn (Figure 4) as have correlation lines (droite inversible) whose equations are written:

¹Recently Veizer (1977) found the same positive correlations between strontium contents and $\delta^{18}O$ values for pre-Quaternary carbonates of various ages and locations.

Sample (Interval in cm)	CaCO ₃ (%)	Mg (ppm)	Na (ppm)	K (ppm)	Mn (ppm)	Sr (ppm)	Fe (ppm)	s ¹³ C (°/)	s ¹⁸ 0 (°/)	Lithology	Age
1-1, 48-50	44.34	4332	5561	2204	1156	1562	1004	+1.29	+2.01	Marly nannofossil ooze	Pleistocene
1-2, 16-18	23.28	15799	20984	5365	1252	1120	4211	+1.83	+2.07	Marly nannofossil ooze	Pleistocene
2-1, 54-56	8.6	32283	66015	18777	4839	1139	1356			Nannofossil ooze	Pleistocene
2-2, 54-56	50.8	5677	15540	3744	1038	1552	1207	+0.17	+3.04	Nannofossil ooze	Pleistocene
2-4 54-56	40.59	5724	10660	2007	1107	1405	1212	+1 29	+4 20	Nannofossil ooze	Pleistocene
2-5.54-56	57.1	3147	6277	1686	990	1725	476	+0.89	+2.17	Nannofossil ooze	Pleistocene
3-1, 84-86	59.46	2881	7544	1580	1081	1673	363	+0.67	+2.29	Nannofossil ooze	Pleistocene
3-2, 84-86	56.26	2844	9308	1780	968	1716	324	+1.08	+2.97	Nannofossil ooze	Pleistocene
3-3, 84-86	42.61	5132	2157	1629	1246	1534	1067	+0.24	+3.86	Nannofossil ooze	Pleistocene
3-4, 84-86	54.70	3358	1874	1467	1342	1744	297	+0.39	+1.61	Nannofossil ooze	Pleistocene
7-3, 30-32	56.72	1890	2398	736	1247	1915	576	+0.23	+1.49	Nannofossil ooze	Late Pliocene
8-3, 34-30	64.04	1/12	1233	736	938	1831	350	+0.49	+1.37	Nannotossil ooze	Late Pliocene
9-2 40-42	75 72	1317	1468	375	1150	1744	294	+0.50	+1.65	Nannofossil ooze	Late Pliocene
11-2, 18-20	64.96	1522	1435	675	756	1775	322	+1.08	+1.76	Nannofossil ooze	Early Pliocene
12-3, 47-49	57.80	1408	1008	666	680	1742	1118	+0.81	+2.02	Nannofossil ooze	Early Pliocene
13-4, 57-59	61.90	1605	2894	684	942	1815	881	+0.23	+1.77	Nannofossil ooze	Early Pliocene
14-1, 63-65	73.34	1179	3778	344	679	1587	353	+0.17	+1.45	Nannofossil chalk	Early Pliocene
15-2, 60-62	67.02	1457	899	452	740	1745	502	+0.12	+1.45	Nannofossil chalk	Late Miocene
17-2, 113-115	70.44	811	1295	361	729	1769	753	+0.94	+1.52	Nannofossil chalk	Late Miocene
18-3, 73-75	70.58	123/	985	364	659	1772	797	+0.78	+1.89	Nannofossil chalk	Late Miocene
20-3 95-97	62.07	1631	907	512	599	1701	613	+0.52	+1.50 +1.76	Nannofossil chalk	Late Miocene
21-4, 43-47	50.38	2857	1171	934	813	1741	901	+1.16	+1.74	Nannofossil chalk	Late Miocene
22-2, 65-67	55.67	2903	984	1067	1111	1703	583	+1.00	+1.42	Marly nannofossil chalk	Late Miocene
29-3, 90-92	52.35	2022	3100	1145	1119	1849	665	+0.77	+1.21	Marly nannofossil chalk	Late Miocene
24-4, 59-61	52.55	2061	1510	1022	1034	1720	317	+0.43	+0.97	Marly nannofossil chalk	Late Miocene
25-6, 109-111	55.78	1717	3339	994	536	1765	278	+0.63	+1.35	Nannofossil chalk	Middle Miocene
26-2, 139-141	66.39	1274	1255	522	576	1725	356	11-11-12-12-1	0.2.2622	Nannofossil chalk	Middle Miocene
29-1, 76-78	85.60	585	963	305	786	1735	377	+1.62	+1.61	Nannofossil chalk	Middle Miocene
31-1 50-52	27.30	1083	914	428	624	1609	310	+1.35	+1.42	Nannofossil chalk	Middle Miocene
35-2 62-64	50.95	2072	1470	1105	1506	1870	605	+1.74	+1.16	Nannofossil chalk	Middle Miocene
36-1, 45-47	82.71	689	1016	245	1340	1679	647	+1.54	+0.53	Marly nannofossil chalk	Middle Miocene
37-1, 31-33	73.36	1059	1232	457	2028	1712	320	+1.49	+0.85	Marly nannofossil chalk	Middle Miocene
39-1, 135-137	66.14	1235	1023	652	2988	1738	361	+1.36	+0.94	Marly nannofossil chalk	Early Miocene
40, CC, 71-76	60.07	1334	1461	606	2063	1894	318	+1.47	+0.98	Siliceous nannofossil chalk	Early Miocene
41-1, 16-18	35.01	2686	3027	1734	1893	2177	365	+1.29	+0.49	Siliceous nannofossil chalk	Early Miocene
43-3, 104-106	64.07	1302	1218	449	2416	1530	188	+1.27	+0.29	Marly nannofossil chalk	Oligocene
44-1, 85-87	36.63	2802	7091	1285	2116	1773	73	+1.06	+0.31	Marly nannofossil chalk	Oligocene
44-1, 105-107	20.03	1800	1414	/91	1848	1614	48	+0.92	+0.85	Marly nannolossil chalk	Oligocene
45-3 110-112	59 59	1423	4574	1351	2381	1525	40	+0.90	+1.74 +0.79	Narry nannotossil chaik	Oligocene
46-4. 71-73	57.04	1224	1908	486	3312	1591	27	+1.09	+0.98	Nannofossil ooze	Oligocene
46-5, 140-142	61.42	1307	1810	822	3881	1739	20	+2.13	+0.87	Nannofossil ooze	Oligocene
47-1, 15-17	21.9	5363	10876	4841	4639	1945	127			Nannofossil ooze	Oligocene
47-6, 106-108	30.76	3526	5568	2639	3641	1305	80	+1.66	-0.22	Marly nannofossil chalk	Middle Eocene
47-6, 124-126	9.52	5335	32527	10581	5634	2898	499			Marly nannofossil chalk	Middle Eocene
48-2, 109-111	6.00	19014	41812	19908	12950	3536	1022	+1.72	+0.20	Conglomerate chalk	Middle Locene
49-3, 44-47	7.09	15826	37040	18506	15506	2711	678	11 (2	0.70	Siliceous marly chalk	Middle Eocene
51.4 137.141	29.50	3148	0563	3810	/169	1507	208	+1.03	-1.00	Siliceous mudstone	Middle Eocene
53-1 69-73	18 44	5955	8394	5181	8398	1533	172	+2 17	-1.05	Siliceous mudstone	Early Eocene
54-3, 103-105	35.63	2378	12965	2636	7047	1072	19	+1.62	-1.70	Siliceous mudstone	Early Eocene
55-2, 84-86	52.04	1633	8275	1751	3577	1014	26			Calcareous claystone	Early Eocene
55-2, 89-91	48.91	1219	5668	1622	3754	1049	21	+1.01	-1.34	Marly nannofossil chalk	Early Eocene
57-2, 17-19	26.1	5588	6421	2945	3307	1439	111	+1.21	-1.91	Marly nannofossil chalk	Early Eocene
59-1, 23-24	58.84	1417	2007	1574	3676	1245	23	+2.96	-0.52	Marly nannofossil chalk	Late Paleocene
59-1, 68-71	58.34	1810	4109	1939	3669	1078	33	+2.90	-0.54	Marly nanno lossil chalk	Late Paleocene Meastrichtian
60-7, 19-21	58 77	829	957	1280	1/40	630	182	+2.43	-0.25	Interbedded marly calcareous	I ate Albian
02-1, 13-17	30.11	1439	6039	1209	2142	039	102	12.05	-1.05	chalk and santopelic chalk	Late mount
62-1, 49-51	67.13	2249	4093	768	4571	681	1111	+1.84	-2.27	Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
62-1, 116-117	49.55	3100	4627	1377	3561	760	822			Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
62-2, 24-25	57.08	1537	5050	1197	4060	680	796	+1.80	-2.31	Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
62-2, 149-150	49.82	4958	1505	1739	4347	869	924			Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
62-4, 21-22	47.74	1512	5377	1001	4157	867	930			Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
62-5, 24-27	41.06	1852	5921	1120	3958	810	917	+2.11	-2.10	Interbedded marly calcareous chalk and sapropelic chalk	Late Albian

TABLE 1 Summary of Results

TABLE 1 - Continued

Sample (Interval in cm)	CaCO ₃ (%)	Mg (ppm)	Na (ppm)	K (ppm)	Mn (ppm)	Sr (ppm)	Fe (ppm)	S ¹³ C (°/)	s ¹⁸ o (°/)	Lithology	Age
63-1, 104-105	20.35	2441	11879	2159	3254	1105	1125	+1.98	-2.31	Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
63-3, 24-27	51.35	1639	5385	835	3870	801	1088	+2.33	-2.28	Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
63-4, 109-110	32.10	2733	12686	2003	2002	948	1312	+1.94	-1.38	Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
64-2, 63-64	38.26	3398	8610	2025	1871	973	440			Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
64-3, 23-24	39.17	2850	5895	1820	2211	934	573			Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
64-4, 26-27	35.33	2660	7956	1590	1926	915	578			Interbedded marly calcareous chalk and sapropelic chalk	Late Albian
64-5, 70-71	23.18	4646	14146	2075	896	1095	433	+2.25	-2.51	Interbedded marly calcareous chalk and sapropelic chalk	Early to middle Aptian
66-1, 13-15	7.20	12719	78604	8710	679	1807	3818	+2.60	-1.96	Interbedded marly calcareous chalk and sapropelic chalk	Early to middle Aptian
66-1, 33-35	9.40	12599	28663	14683	876	2728	2322	+3.01	-1.69	Interbedded marly calcareous chalk and sapropelic chalk	Early to middle Aptian
66-1, 90-92	21.57	7019	7481	4296	517	1400	613			Interbedded marly calcareous chalk and sapropelic chalk	Early to middle Aptian
68-1, 111-112	32.08	3381	3388	1955	733	1100	533			Marly nannofossil chalk	Early to middle Aptian
68-3, 9-10 69-1	20.78	7522	11526	4044	505	1534	1524	+2.90	-2.25	Marly nannofossil chalk Calcareous mudstone	Early to middle Aptian Late Aptian
71-1, 98-99	22.26	7295	10819	3988	2017	1616	1564	+2.34	-1.48	Calcareous mudstone	Late Aptian
71-2, 36-37	6.66	23566	33066	13064	3462	4480	1909	+2.03	-1.08	Calcareous mudstone	Late Aptian
72-3, 94-96	28.26	3854	15437	2559	745	934	346			Calcareous mudstone	Late Aptian
72-4, 1-2	18.89	5106	6081	3141	680	1219	942	+2.51	-1.43	Calcareous mudstone	Late Aptian
72-4, 18-19	25.49	4355	14451	3011	757	1009	295			Calcareous mudstone	Late Aptian
74-1, 22-25	57.8	1835	1464	269	6986	389	396	+2.10	-2.91	Calcareous mudstone	Late Aptian

$$[Sr]_{ppm} = -158.87 [\delta^{18}0] + 2014.77$$

and

$$[Sr]_{ppm} = 289.69 [\delta^{18}0] + 1352$$

This correlation determines the approximate boundary between syn-sedimentary and diagenetic phenomena which occurs at the point where the correlation is reversed, that is between the Miocene and the Oligocene.

MANGANESE

The distribution of manganese content (Figure 5) shows two zones to be particularly rich: late Albian, and Eocene to early Miocene (but particularly the Eocene).

The amount of manganese in the carbonate depends in main on two factors: (1) the oxidation-reduction conditions of the environment (Michard, 1969) and (2) the manganese concentrations in seawater. In a reducing medium, manganese co-precipitates with carbonates to produce manganese-poor carbonate. In an oxidizing medium, manganese dioxide precipitates to produce manganese-rich carbonate. With regard to the question of the origin of supply, manganese can come from either the erosion of continental material or submarine volcanism — either directly by hydrothermal solutions (Böstrom and Peterson, 1966) or indirectly by leaching of newly extruded basalt (Corliss, 1970). A comprehensive bibliography can be found in Cronan (1974).

At Hole 400A, there is no relationship between the detrital clay mineral content and the amount of manganese (Figure 2c), and it is therefore concluded that the

manganese probably originated from submarine volcanism. It follows that there were two principal periods of volcanic activity near this area, the first in late Albian and the second in the Eocene (Albian volcanism is described in a following chapter). The influence of Eocene volcanism seems to be fairly general: traces of it occur in Site 398C of Leg 47B (Renard and Létolle, in press). The exact location of the volcanism lies probably in the north, perhaps from the Reykjanes Ridge, because, at Rockall Plateau, Eocene volcanic tuffs were found at Sites 403 and 404 (see Harrison, this volume). However, manganese contents in the carbonate fraction cannot be explained by only one cause; it appears that oxidation-reduction conditions also play a role. For instance, a rather positive correlation is observed between the amounts of manganese and the carbon isotope composition of carbonate (Figure 6). The correlation coefficient r is equal to 0.3654 and the t value is 2.7895 (the value of t for this case being <3.551 at the risk 0.001 and <2.704 at the risk 0.01). Regression lines of x/y and y/x and also the correlation line [Mn] ppm = 2872.13 $\delta^{13}C - 1605.98$ are shown.

If the carbon isotope composition depends on the depth of formation of the carbonate (Duplessy, 1972) it may correspond approximately to the oxidation state of the environment. If this hypothesis holds true, the late Albian and Eocene are not only the periods when the manganese supply was at a maximum, but also when the environment was most suitable for manganese deposition. Supply and oxidation-reduction conditions are thus equally important. For example, during the early Albian although the environment was strongly oxidizing ($\delta^{13}C$ between +2.5 and +3%), the amount of manganese remained less than 1000 ppm because supplies were lower.





Figure 1. Repartition curve of carbonate contents.

IRON

The distribution curve of iron concentrations (Figure 7) shows three enrichment zones, late Albian, late Miocene to early Pliocene, and Pleistocene; a particularly poor episode occurred between Paleocene and Oligocene time.

The problem of the origin and supply of iron is similar to that of manganese. In Mio-Pliocene and Pleistocene times iron came from continental erosion; during these two periods there is a strong correlation between the amount of iron and the clay mineral content which is not observed for the Albian (Figure 2d). Because the solubility products of iron oxides and manganese oxides are very different, their precipitation together is prohibited. Figure 8 shows that iron-rich samples are low in manganese content and vice-versa. Thus, it is possible to distinguish iron-rich samples characteristic of continental supply (of Pleistocene and late Miocene to early Pliocene age) from manganese-rich samples, characteristic of volcanic origin (Paleocene to Oligocene age).

The late Albian samples which are enriched in both iron and manganese remain a problem. Possible origins of iron and manganese oxide-rich sediments have been summarized by Cronan (1974), who concluded that these sediments appear to be a common feature associated with the generation of new ocean floor. If that conclusion is correct, then, in the late Albian, Hole 400A was near to the iron and manganese source which was volcanic. This indicates that an important hydrothermal (or volcanic) event occurred in the late Albian, probably related to the opening of the Bay of Biscay. If the actual opening did not occur in late Albian time, then at least it was a very active period in its opening history; geophysical data (Williams, 1975) supports this contention.

In summary, we propose that during late Albian time Hole 400A was close to a volcanic source and received supplies of both iron and manganese. Later, in Eocene time, the site was further removed from the volcanic source and received only manganese. Either the site was removed from the vicinity of the Albian source, or the source was transferred to a more distant location as, for example, the Reykjanes Ridge.

The possibility exists that, as in the case of manganese, oxidation-reduction conditions played an important role in iron deposition. Correlation between amounts of iron and the composition of carbon isotopes in the carbonates is poor (Figure 9); calculation shows that r=0.1103 and t=0.8861. Iron concentrations would therefore be less sensitive than the manganese ones to oxidation-reduction conditions. Such a conclusion must be moderated because (1) the iron is volcanic in origin for the Albian and of continental origin for the Mio-Pleistocene (which may suggest its transport to the basin in the form of micro particles associated with clay-minerals; (2) the range in iron content is smaller than for manganese, which reduces the weighting in statistical calculations.

A better way of examining the problem is to study the correlation between the sum of amounts of iron and

manganese and the carbon isotope composition of the carbonate. The correlation (Figure 10) is better than that for manganese alone;

$$r = 0.5280$$

 $t = 4.7365$

the equation of the correlation line being [Mn + Fe] ppm = $2349.87 \delta^{13}C - 510.76$.

The respective roles of supply and the environment may now be better understood. An oxidizing medium is necessary but not sufficient to precipitate iron and/or manganese. Removal of the source results in precipitation of iron or manganese or both.

ACKNOWLEDGMENTS

We are grateful to Dr. Y. Lancelot, who read several versions of the manuscript and to Michel Petzold for preparation of the figures. Thanks are also due to Mrs. Anne Demond for typing the manuscript and to Mrs. Jennifer Limond for correction of the English text. Centre National de la Recherche Scientifique provided financial support through Action Thematique Programmée "IPOD."

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Figure 2. Relationship between carbonate percentage and trace element concentration. (a) Strontium, (b) Magnesium, (c) Manganese, (d) Iron, (e) Sodium, (f) Potassium.



Figure 2 – Continued



Figure 3. Repartition curve of strontium concentrations.



Figure 4. Relationship between strontium concentration and oxygen isotope composition of carbonates: continuous line is the correlation line (see explanation in text) and dotted lines are regression lines of x/y and y/x.



Figure 5. Repartition curve of manganese concentrations.



Figure 6. Relationship between manganese concentration and carbon isotope composition of carbonates: continuous line is the correlation line and dotted lines are regression lines of x/y and y/x.





Figure 7. Repartition curve of iron concentrations.

TRACE ELEMENTS



Figure 8. Relationship between manganese and iron concentrations: circle dotted line shows late Albian samples which are enriched in both iron and manganese.



Figure 9. Relationship between iron concentration and carbon isotope composition of carbonates.



Figure 10. Relationship between iron-manganese concentration and carbon isotope composition of carbonates. Continuous line is the correlation line and dotted lines are regression lines of x/y and y/x.