58. A GEOCHEMICAL NOTE: COMPARISON OF TECHNIQUES FOR OBTAINING $CaCO_3$, ORGANIC CARBON, AND TOTAL NITROGEN IN LIMESTONES AND SHALES[1]

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ABSTRACT

Contents of organic carbon and carbonate carbon were determined on the same set of Cretaceous samples from DSDP Hole 603B in three different laboratories in order to assess the degree of comparability of organic carbon and carbonate values obtained by different labs using the same or different methods. We report the results of analyses for organic carbon using two different CHN analyzers, LECO, and Rock-Eval II and for carbonate carbon by CHN (total C minus C after acidification), the carbonate bomb technique, and $CaCO_3$ calculated on the basis of total calcium obtained from X-ray fluorescence and induction-coupled plasma techniques. In addition, total nitrogen was obtained by two different labs using a CHN analyzer, but different bases for calculation were used.

The various techniques for organic carbon analysis yielded comparable results, with the exception of those obtained by one of the CHN analyses of acid-treated samples. The calculation of organic carbon values and comparison on a whole-rock basis is very sensitive to errors in determination of carbonate contents, and this factor explains most, but not all, of the disparities between the data sets. The carbonate bomb technique gives $CaCO_3$ values that correspond well with those calculated from total calcium concentrations (XRF and ICP analyses), whereas the $CaCO_3$ calculated from CHN total carbon minus acid-soluble carbon consistently overestimated $CaCO_3$. Total nitrogen and C/N results from the two different CHN analyses are not comparable and are subject to more error than the factor related to error in estimation of $CaCO_3$.

INTRODUCTION

Because we are collectively and individually engaged in comparative lithologic and geochemical studies of Cretaceous black shales and other units recovered in Deep Sea Drilling Project cores from all of the major ocean basins, we have used our own published and unpublished geochemical data and those of others in our research on relatively organic-carbon-rich strata. In particular, we are attempting to compile geochemical data sets that include analyses of both organic and inorganic constituents on the same samples. In this way we hope to infer relationships between carbonate content, organic richness (organic carbon content), organic preservation, and source (pyrolysis hydrogen and oxygen indexes or atomic H/C, O/C; total N; $\delta^{13}C$) and enrichments in trace metals, sulfur and phosphorus. We can thereby estimate the impact of widespread deposition of "black shales" on the geochemical cycles of various elements and understand the factors leading to such episodes of widespread deposition of organic carbon.

Different sample handling, treatment, and analytical methods potentially lead to widely different estimates of sediment composition, and, therefore, it is neither always wise nor possible to use results from different laboratories uncritically in comparative studies of sample sets from the same or different localities. During our geochemical studies of Leg 93 material, we had occasion to obtain carbonate (%$CaCO_3$) and organic carbon (%OC) values in three different laboratories using three essentially different methods on the same set of 63 samples of Cretaceous sediments collected on board ship. In addition, we obtained results on total nitrogen (TN) from two labs using the same techniques but different sample preparation. A second set of postcruise samples was analyzed by only two of the three laboratories. The results of our analyses are provided in Tables 1 and 2.

ANALYTICAL METHODS

Concentrations of total calcium (wt.% Ca) were measured on a set of shipboard samples of Cretaceous sediments and rocks from DSDP Hole 603B (63 samples plus six random duplicates) using both X-ray fluorescence (XRF) and induction-coupled plasma (ICP) techniques at the USGS in Denver as described in Dean and Arthur (this volume). A second set of 42 samples obtained postcruise from the DSDP repository at Lamont-Doherty Geological Observatory (LDGO) was analyzed by ICP only. One estimate for values of percent $CaCO_3$ in each sample was obtained by multiplying Ca (wt.%) values by 2.50. XRF values were used in the calculation for the shipboard sample set and ICP for the postcruise sample set. Measurements of $CaCO_3$ content in both sample sets were also obtained by the carbonate bomb technique (Müller and Gastner, 1971) at the University of Rhode Island (URI). For the shipboard samples carbonate-C—recalculated as percent $CaCO_3$—was also derived by difference from measurements of total carbon minus

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[1] van Hinte, J. E., Wise, S. W., Jr., et al., *Init. Repts. DSDP*, 93: Washington (U.S. Govt. Printing Office).

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Table 1. CaC0$_3$, organic C, and nitrogen in Hole 603B (shipboard samples).

	$CaCO_3$ (wt.%)			OC (wt.%)			N (wt.%)		C/N	
Core-Section (interval in cm)	XRF-Ca (U.S.G.S.)	CHN (UM)	Bomb (URI)	CHN (UM)	CHN (URI)	RE (U.S.G.S.)	CHN (UM)	CHN (URI)	UM	URI
15-3, 128	1.66	0.0	0.0	0.19	0.09	—	0.011	0.033	18.0	2.7
15-3, 129	1.66	0.0	0.0	0.29	0.08	—	0.033	0.036	8.8	2.2
15-4, 087	0.98	0.0	0.0	0.16	0.14	—	0.007	0.020	24	7
15-5, 087	0.89	0.0	0.0	0.14	0.09	—	0.047	0.020	3	4.5
16-2, 020	0.8	0.0	0.0	0.23	1.42	—	0.019	0.047	12	30
28-1, 025	0.63	0.0	0.0	0.30	0.18	0.06	0.103	0.035	2.9	5.1
28-1, 026	0.64	0.0	0.0	0.11	0.17	—	0.058	0.035	1.9	4.9
28-3, 067	0.75	0.0	0.0	0.16	0.16	—	0.100	0.033	1.6	4.8
28-3, 068	0.75	0.0	0.0	0.19	0.14	—	0.048	0.031	4	4.5
28-3, 129	0.93	0.0	0.0	0.28	0.18	—	0.005	0.033	56	5.5
28-3, 130	0.93	0.0	0.0	0.84	0.19	—	0.175	0.032	4.8	5.9
28-8, 005	0.57	8.1	0.0	0.64	2.40	2.41	0.016	0.082	41	29
29-1, 142	0.57	4.3	0.0	0.30	0.92	0.87	0.025	0.051	12	18
29-1, 143	0.57	3.1	0.0	0.41	0.95	—	0.031	0.056	13	17
29-4, 103	0.68	0.0	0.0	0.16	0.11	—	0.019	0.029	8.4	3.8
29-4, 105	0.7	0.0	0.0	0.22	0.10	—	0.088	0.032	2.5	3.1
32-1, 045	0.61	0.0	0.0	0.30	0.12	—	0.058	0.034	5.2	3.5
32-1, 059	0.59	0.0	0.0	0.23	0.17	0.09	0.008	0.036	28	4.7
32-1, 061	0.55	6.2	0.0	1.52	3.33	3.00	0.103	0.140	15	24
32-1, 076	0.52	0.0	0.0	0.25	0.15	0.09	0.009	0.037	28	4.1
32-1, 115	0.64	0.0	0.0	0.14	0.10	—	0.082	0.033	1.7	3
34-2, 035	0.61	0.0	0.0	3.63	5.26	3.74	0.206	0.181	18	29
36-1, 115	0.84	0.0	0.0	0.28	0.38	0.25	0.014	0.029	20	13
36-1, 118	0.79	7.5	0.0	0.52	1.35	1.35	0.020	0.056	26	24
36-1, 121	0.84	0.0	0.0	0.14	0.21	0.12	0.007	0.025	20	8.4
38-1, 050	0.95	0.0	0.0	0.14	0.30	—	0.108	0.027	1.3	11
38-2, 052	0.84	0.0	0.0	0.40	0.46	0.33	0.167	0.032	2.4	14
38-3, 050	0.98	0.0	0.0	0.86	0.21	—	0.031	0.030	28	7
38-4, 050	0.89	0.0	0.0	0.21	0.13	—	0.029	0.020	7.3	6.5
38-5, 052	0.91	0.0	0.0	0.28	0.52	0.30	0.019	0.039	15	13
43-2, 030	0.95	0.0	0.0	0.14	0.11	—	0.006	0.020	24	5.5
43-2, 031	0.98	0.0	0.0	0.16	0.14	—	0.002	0.021	80	6.7
43-2, 054	0.93	1.4	0.0	0.71	0.08	—	0.057	0.20	14	4
43-2, 111	0.84	0.0	0.0	0.19	0.07	—	0.190	0.017	1	4.1
43-3, 135	0.75	0.0	0.0	0.10	0.11	—	0.008	0.015	13	7.3
43-4, 015	0.64	0.0	0.0	0.11	0.08	—	0.020	0.012	5.5	6.7
43-6, 025	0.84	0.0	0.0	0.67	0.36	0.23	0.018	0.028	37	13
44-3, 053	2	10.0	0.0	0.92	3.21	3.10	0.012	0.118	78	27
53-5, 028	18.8	22.5	17.2	0.67	2.58	2.71	0.024	0.098	28	26
53-5, 032	13.6	24.2	13.6	0.45	1.70	2.16	0.012	0.058	37	25
57-1, 080	78.9	63.8	80.5	1.70	1.41	2.01	0.041	0.056	41	25
57-1, 086	17.7	24.2	16.0	0.47	2.06	1.77	0.019	0.077	25	27
57-1, 093	75.9	76.0	75.1	0.93	1.57	2.43	0.031	0.061	30	26
58-4, 102	22.9	32.4	20.4	0.43	1.85	—	0.027	0.063	16	29
58-4, 104	74.8	85.5	76.0	0.10	0.44	—	0.005	0.015	22	29
58-4, 106	32.5	45.8	29.9	0.33	1.73	—	0.011	0.062	30	28
63-5, 128	14.2	23.2	11.4	0.52	2.74	2.66	0.037	0.088	14	31
63-5, 132	52.9	61.3	52.4	0.57	1.50	2.11	0.034	0.046	17	33
64-5, 043	84.5	44.0	85.1	0.06	0.21	0.37	0.005	0.006	13	35
64-5, 046	18.6	26.2	16.8	0.40	1.61	1.87	0.024	0.053	16	30
64-5, 048	82.9	95.4	84.3	0.04	0.43	0.53	0.001	0.012	31	36
65-1, 017	61.1	65.2	61.6	1.49	3.08	3.49	0.031	0.086	48	36
65-4, 100	78.9	86.3	79.7	0.07	0.28	0.36	0.008	0.011	8.6	25
65-4, 107	11.2	18.4	8.5	0.44	1.81	2.08	0.041	0.062	11	29
65-4, 113	82	81.2	83.3	0.09	0.19	0.37	0.002	0.006	53	32
66-3, 025	90.4	98.2	89.4	0.01	0.12	—	0.001	0.005	19	24
66-3, 032	72.1	81.9	72.4	0.11	0.54	0.96	0.006	0.016	17	34
66-3, 035	24.8	34.2	22.2	0.99	2.24	2.79	0.381	0.086	2.6	26
66-3, 044	89.5	99.0	89.5	0.02	0.71	—	0.001	0.024	18	30
66-3, 059	75	92.9	74.6	0.04	0.18	—	0.005	0.008	8.5	23
67-4, 126	18.6	23.7	16.5	0.73	2.45	2.82	0.052	0.089	14	28
75-2, 034	70.7	80.0	70.3	0.08	0.24	44.00	0.003	0.010	32	24
75-2, 048	24.6	31.2	15.3	0.33	1.58	1.48	0.012	0.048	27	33
75-2, 049	24.5	30.1	21.6	0.30	1.27	—	0.029	0.045	10	28
75-2, 061	25.9	33.6	22.4	0.35	1.43	2.10	0.020	0.048	17	30
75-2, 070	66.2	79.7	65.3	0.08	1.07	1.59	0.002	0.029	52	37
75-2, 086	69.6	86.6	68.9	0.05	0.47	0.68	0.004	0.014	13	34
75-2, 099	56.4	60.6	54.4	0.90	2.05	2.61	0.028	0.068	32	30
75-2, 114	14.5	20.4	13.2	0.72	1.7	2.30	0.026	0.047	27	36

Note: Dash indicates sample not analyzed by that particular technique.

Table 2. $CaC0_3$, organic C, nitrogen in Hole 603B (postcruise samples).

	$CaCO_3$ (wt.%)		OC (wt.%)			N (%; raw)	N (%; w.r.)	
Core-Section (interval in cm)	ICP-Ca (U.S.G.S.)	Bomb (URI)	CHN (URI)	LECO (U.S.G.S.)	RE (U.S.G.S.)	CHN (URI)	CHN (URI)	C/N (URI)
35-1, 23	<1	0.0	0.14	0.09	—	0.001	0.001	140
35-1, 30	<1	0.0	1.52	1.46	1.29	0.052	0.052	29
35-1, 49	<1	0.0	1.67	1.39	—	0.058	0.058	29
35-2, 18	<1	0.0	4.25	3.73	4.05	0.147	0.147	29
35-2, 47	<1	0.0	0.82	0.78	—	0.031	0.031	26
35-2, 128	<1	0.0	0.17	0.22	0.13	0.014	0.014	12
36-3, 8	<1	0.0	0.41	0.41	—	0.016	0.016	26
36-3, 13	<1	0.0	0.28	0.29	0.23	0.019	0.019	15
36-3, 17	<1	0.0	1.71	1.63	—	0.073	0.073	23
36-3, 21	<1	0.0	1.15	1.01	—	0.051	0.051	23
36-3, 27	<1	0.0	1.72	1.59	—	0.076	0.076	23
36-3, 35	<1	0.0	2.02	1.79	—	0.086	0.086	23
36-3, 49	<1	0.0	4.24	4.06	4.18	0.174	0.174	24
36-3, 57	<1	0.0	3.96	3.52	3.72	0.159	0.159	25
36-3, 70	<1	0.0	1.46	1.39	1.42	0.062	0.062	24
37-1, 30	<1	0.0	0.95	0.88	—	0.048	0.048	20
37-1, 33	<1	0.0	1.08	1.03	—	0.051	0.051	21
37-5, 104	<1	0.0	0.47	0.52	0.42	0.026	0.026	18
37-5, 107	<1	0.0	1.87	1.83	1.76	0.072	0.072	26
37-5, 111	<1	0.0	1.48	1.49	—	0.064	0.064	23
38-1, 146	<1	0.0	5.49	5.23	5.48	0.218	0.218	25
38-2, 8	<1	0.0	0.22	0.21	0.20	0.020	0.020	11
38-2, 18	<1	0.0	2.58	2.47	—	0.101	0.101	26
38-2, 22	<1	0.0	1.46	1.49	1.45	0.066	0.066	22
38-2, 25	<1	0.0	0.25	0.30	0.20	0.031	0.031	8
66-3, 3	<1	0.0	0.15		—	0.050	0.050	3
66-3, 40	87.5	87.8	0.90	0.68	—	0.305	0.037	24
66-3, 51	87.5	91.6	0.19		—	0.069	0.006	32
66-3, 68	15.0	12.4	1.53	1.23	—	0.066	0.058	26
69-2, 133	20.0	18.5	1.59		—	0.057	0.046	35
69-2, 143	18.8	16.0	1.57		—	0.053	0.045	35
69-3, 7	87.5	91.5	0.17	0.11	—	0.047	0.004	43
69-3, 19	85.0	90.8	0.10		—	0.037	0.003	33
69-3, 27	85.0	89.5	0.14	0.11	—	0.048	0.005	28
69-3, 42	80.0	83.1	0.90	0.83	—	0.193	0.033	27
69-3, 48	80.0	84.9	0.07	0.49	—	0.104	0.016	4
69-3, 57	77.5	89.7	0.23	0.19	—	0.058	0.006	38
69-3, 66	87.5	90.5	0.13		—	0.042	0.004	33
69-3, 71	83.9	88.8	0.13	0.11	—	0.038	0.004	33

Note: Dash indicates sample not analyzed by that particular technique.

carbon in an acidified sample using a Hewlett-Packard CHN analyzer at the University of Michigan (UM) (see Dunham et al., this volume).

Concentrations of OC were determined in some of the samples by four different techniques. All samples were analyzed at URI using a Carlo Erba 1106 CHN analyzer after the samples had been acidized with 3*N* HC1 (residues of carbonate bomb technique), rinsed with distilled water six times, centrifuged, decanted, and freeze-dried. Selected samples of both sets were analyzed for OC by standard LECO combustion (on acidified and dried samples) and the Rock-Eval II (RE) pyrolysis method (see Dean and Arthur, this volume). Percent OC was determined for the shipboard samples at UM on acidified samples using a Hewlett-Packard 185B CHN analyzer (see Dunham et al., this volume). The samples were freeze-dried and residual carbon was measured after HC1 (3*N*) dissolution of carbonates; this carbon was considered to represent the total OC content. Percent $CaCO_3$ was calculated from the difference between the whole-rock and residual carbon contents. Percent OC of the samples was calculated on a dry-weight basis for the original, carbonate-containing sediment in all techniques. TN was determined on the shipboard acidified (carbonate-free) samples by CHN at both UM and URI and recalculated as weight percent whole rock. C/N ratios for each sample were determined from residual (carbonate-free) OC and TN values for the UM data and whole-rock values for the URI data.

RESULTS

Calcium Carbonate and Total Carbon

Results of our analyses are provided in Tables 1 and 2. Figure 1 illustrates the correspondence of $CaCO_3$ values on shipboard samples obtained by the carbonate bomb technique versus those calculated from XRF-Ca values. The precision for replicate analyses by the bomb technique is ±5% and for the XRF-Ca values ±3%. With the exception of one point, the data fall neatly along the line representing 1:1 correspondence, and there is therefore excellent correlation ($r = 0.99$) between the two methods. Dean and Parduhn (1984), in agreement with this study, have shown for another Cretaceous and Tertiary sample set that the percent $CaCO_3$ determined by carbonate bomb, XRF-Ca and ICP-Ca values are all in

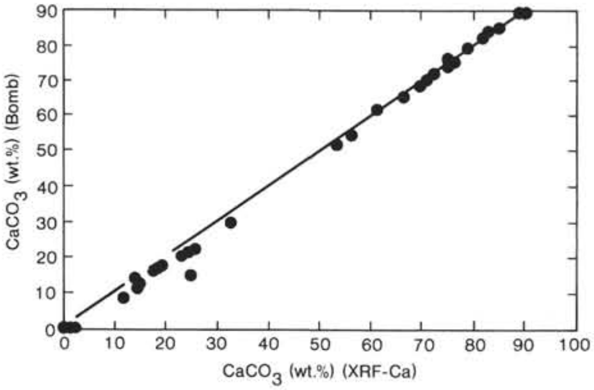

Figure 1. $CaCO_3$ (wt.%) determined by the carbonate bomb method (URI) vs. $CaCO_3$ (wt.%) calculated from XRF-Ca values on shipboard samples (69 points; $r = 0.99$). Line represents 1:1 correspondence. Note that the cluster of points near the origin actually represents 37 points where $CaCO_3$ was $<1\%$ in both data sets.

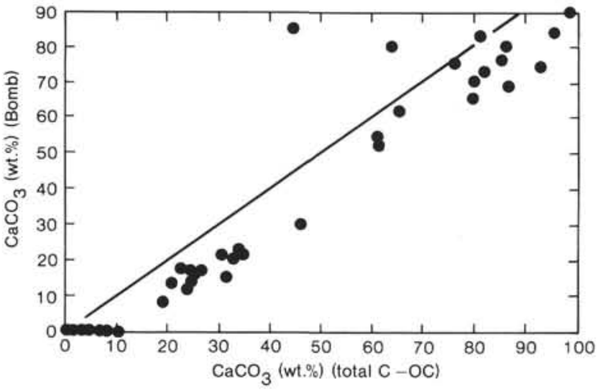

Figure 2. $CaCO_3$ (wt.%) from carbonate bomb (URI) determinations vs. that resulting from CHN analysis of total C minus OC (on insoluble residues; UM) on shipboard samples (69 points; $r = 0.97$). Line represents 1:1 correspondence.

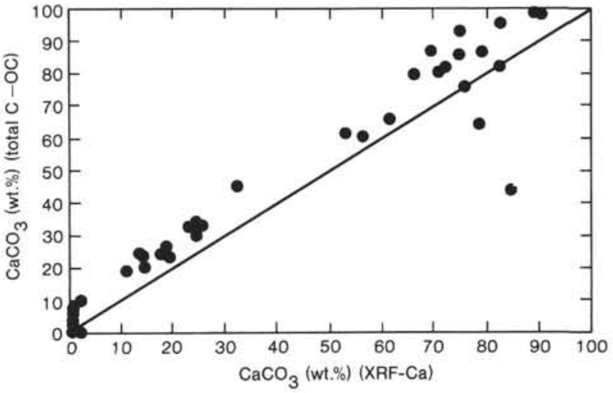

Figure 3. $CaCO_3$ (wt.%) from CHN (see Fig. 2 caption; UM) vs. that from XRF-Ca analyses (×2.50) (69 points; $r = 0.97$). Line represents 1:1 correspondence.

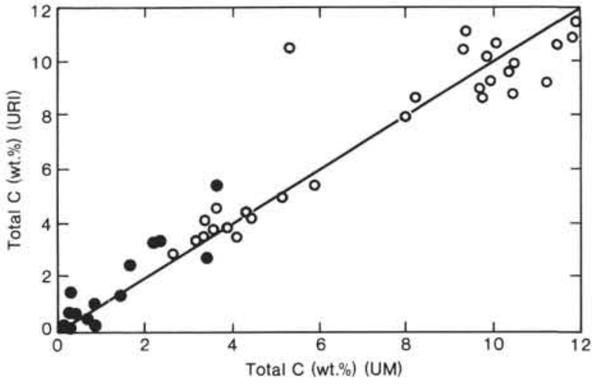

Figure 4. Total C (wt.%) (bomb $CaCO_3$ × 0.12 + organic C from CHN analyses; URI) vs. percent total C by CHN only (UM); (69 points; $r = 0.95$). Line represents 1:1 correspondence. Solid symbols are black shales; open symbols are carbonate-containing samples.

good agreement, but that XRF analyses give the optimum values of Ca and are in best agreement with carbonate bomb $CaCO_3$.

A comparison of $CaCO_3$ values from the bomb method versus total carbon minus OC on acidified samples from CHN (UM) in Figure 2 illustrates a somewhat poorer correlation ($r = 0.97$) with more scatter at higher values. The plot suggests that the latter method typically overestimated the $CaCO_3$ content. A similar relationship is shown in Figure 3, which compares the UM $CaCO_3$ results with those resulting from the U.S.G.S. XRF-Ca determinations.

However, Figure 4 illustrates that the total carbon determined by CHN on unacidified samples (UM) and that obtained by summing carbonate carbon ($CaCO_3$ by bomb × 0.12, URI) and OC (CHN-URI) on bomb residues are more similar ($r = 0.95$) than $CaCO_3$ values. This suggests that the disagreement is not caused by incomplete dissolution of $CaCO_3$ during acid treatment of samples at UM (that would lead to underestimates of $CaCO_3$ content by that method), but is perhaps caused by some preferential loss of the organic fraction during acid treatment. However, the latter explanation seems unlikely because the acid molarity used to obtain insoluble residues was the same in both laboratories.

Figure 5 shows that the loss-on-ignition (U.S.G.S.) prior to XRF analysis also exhibits a linear correlation ($r = 0.95$) with total carbon (URI). The relationship suggests that these samples consistently contain about 10% water and other volatiles in addition to $CaCO_3$ and OC.

Organic Carbon

Comparison of the percent OC determined by CHN (URI) on acidified samples with the percent OC obtained by RE analyses on 51 shipboard and postcruise samples shows a surprisingly good correlation (Fig. 6; $r = 0.96$). The replicability of percent OC for a given sample determined by RE is ±7%. Figure 7 shows that there is also a good correlation ($r = 0.99$) between the percent OC determined by CHN (URI) and percent OC determined on 33 samples by LECO (U.S.G.S.). Figure 8 is a plot of OC from shipboard samples analyzed by CHN on acidified samples at UM versus the same technique at URI. There is poor agreement ($r = 0.77$) in the results, and the CHN analyses from UM apparently underestimated the amount of organic carbon, but not in a

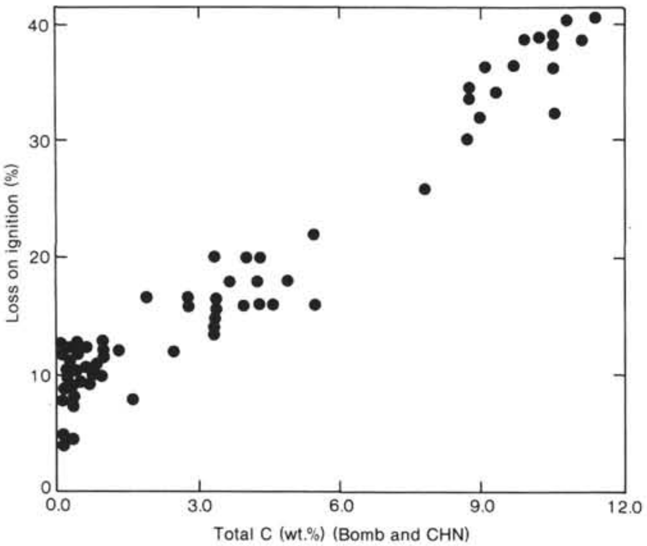

Figure 5. Percent weight loss on ignition (1000°C) prior to XRF analyses plotted against total C (wt.%) (URI); (all data including duplicates; 103 points; $r = 0.95$).

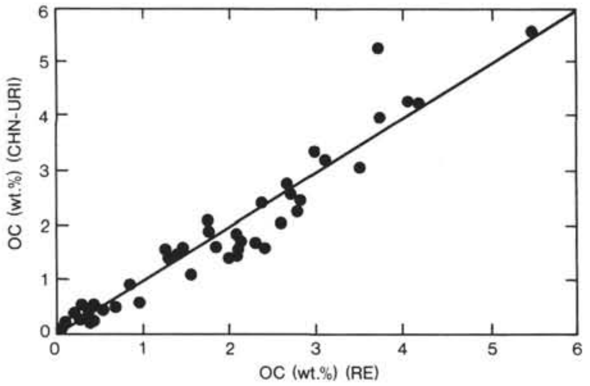

Figure 6. OC (wt.%) determined on insoluble residues by CHN (URI) vs. that determined by the RE method (51 points; $r = 0.96$). Line represents 1:1 correspondence.

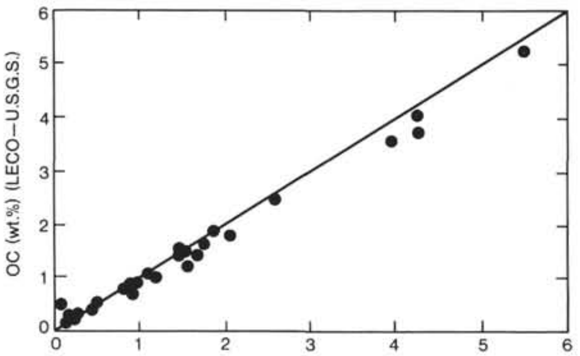

Figure 7. OC (wt.%) determined by CHN (URI) and by LECO carbon analysis after acidification (U.S.G.S.) (33 postcruise samples; $r = 0.99$). Line represents 1:1 correspondence.

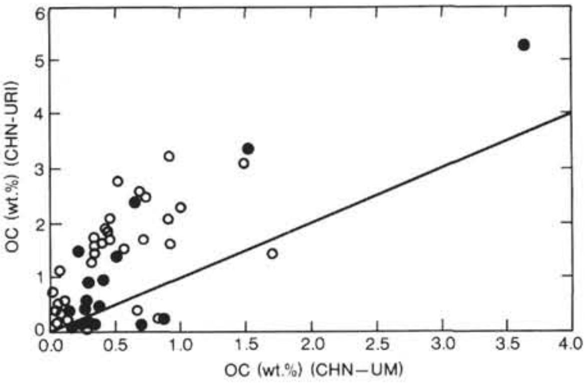

Figure 8. OC (wt.%) determined by CHN at URI plotted against that determined by CHN at UM. Filled symbols are values from black shales that contain less than 10% $CaCO_3$; open symbols are all other carbonate-containing samples; (69 points). Line represents 1:1 correspondence.

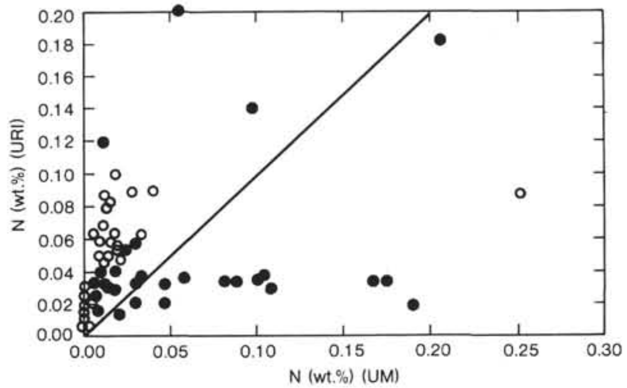

Figure 9. Nitrogen (wt.%) determined by CHN at URI vs. the same parameter analyzed at UM. Symbols and line same as in Figure 8 (69 points).

systematic way. Carbonate content does not seem to be a factor because the fields for carbonate-free claystones and for carbonate-containing sediments overlap. Table 1 reveals that there is frequent disagreement between OC contents as determined by the CHN (UM) analyses and those by RE (U.S.G.S.). Considering the good agreement between the CHN (URI) and the RE and LECO determinations, we suspect that the CHN (UM) OC determinations are in error.

Earlier comparison of shipboard OC determinations on Leg 75 samples with those done by CHN analyzer at the University of Michigan showed generally good agreement (relative standard deviation ±8.87%, Meyers et al., 1984). These comparisons, however, used shipboard bomb $CaCO_3$ values and hence avoided possible errors from carbonate C measurement by differences that are evident in the present comparison of procedures.

Nitrogen

Figure 9 illustrates TN concentrations expressed as weight percent of the whole rock determined by CHN at the UM and URI laboratories. The values are not at all comparable, suggesting an analytical problem with one or both labs. The plot suggests that the URI analyses usually underestimated TN in claystones and that the UM analyses almost always underestimated TN in carbonates. The disparity in the analyses goes beyond the difference in $CaCO_3$ used by each laboratory in calculating TN. This point is emphasized by the broad scatter in C/N ratios (Fig. 10), which are independent of $CaCO_3$ content. The differences also are not simply related to differences in OC content determinations between the two labs. At this time we do not understand the reason for the great disparity between the two data sets, but the C/N ratios calculated from the URI data set are more consistent and within a narrower range. As an independent check, we have values of atomic C/N ratio for 11 of our samples of Neocomian carbonates calculated by G. H. Rau (San Francisco State Univ. and NASA-Ames Research Center, personal communication, 1984) from percent N yield during sample preparation for N-isotope analysis and percent OC determined by RE pyrolysis (U.S.G.S.). The atomic C/N ratios (NASA) are plotted versus C/N from CHN data (UM and URI) for the 11 Neocomian samples in Figure 11. We did not recompute the atomic C/N ratio (NASA) to a weight percent C/N ratio because we wanted only to compare the URI and UM results against some independent baseline, and the difference between a weight percent and an atom C/N ratio is small because of the similar atomic weights of C and N. The correlation coefficients between the atomic C/N ratio (NASA) and C/N weight ratios for UM and URI data are -0.06 and $+0.57$, respectively.

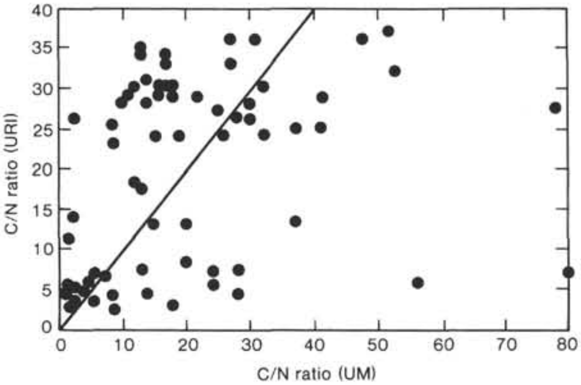

Figure 10. C/N ratio (organic C/total N) for URI and UM data sets (69 points).

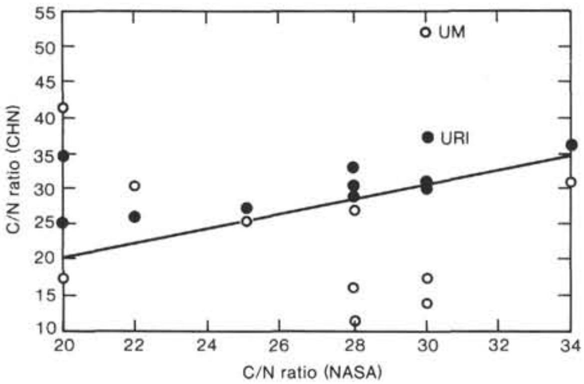

Figure 11. C/N ratio determined by CHN (URI and UM) vs. atomic C/N ratio calculated from percent OC (RE-U.S.G.S.) and TN determined on 11 points by N yield in preparation for N isotope analyses (NASA).

SUMMARY AND CONCLUSIONS

This comparison of the results of different analytical procedures for determination of percent $CaCO_3$ and OC shows that some procedures give comparable values whereas others clearly do not. The conclusions of this comparison can be summarized as:

1. $CaCO_3$ determinations by carbonate bomb and calculated from percent Ca determined by XRF and ICP agree well. Data from such procedures are comparable with each other unless significant amounts of siderite, dolomite or manganoan carbonate, or noncarbonate Ca minerals are suspected in samples to be analyzed.
2. $CaCO_3$ determinations based on the difference between total carbon and organic carbon can be in error, possibly because of a nonlinear response of CHN analyzers over the wide range of carbonate concentrations common in DSDP samples relative to the standards routinely analyzed for calibration. Sample size may be a determinant in obtaining accurate values.
3. Organic carbon concentrations measured by one CHN analyzer, LECO, and RE are surprisingly similar.
4. When organic carbon values are expressed on a whole-rock, dry-weight basis, it is important to have accurate determinations of carbonate concentrations. Small errors in either of the two determinations involved in the carbonate-by-difference procedure become magnified and result in possible major errors in whole-rock OC data. In view of this potential source of error, we recommend that carbonate be either determined by carbonate bomb or calculated from a reliable (accurate and precise) measurement of total Ca.
5. C/N ratios are significantly biased by errors in determination of both OC and TN and must be used carefully. We do not, at this time, understand the large differences in the two data sets presented here, but based on a few independent determinations of atomic C/N ratios it appears that the URI C/N values represent a more reasonable range of TN concentrations.

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