

30. NOTES ABOUT THE SPECIFIC CHEMICAL COMPOSITION OF "BLACK SHALES" FROM SITE 367 (LEG 41)

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Six samples of gray shale were analyzed from Leg 41, Site 367, Cores 17, 18, 21, and 22 drilled in the Cape Verde Basin southeast of the Cape Verde Islands. According to the Initial Core Descriptions, Cores 17, 18, and 21 are Cenomanian and Core 22 is Albian in age. The four Cenomanian aged samples are darker and more fissile than the clay from Core 22. The chemical composition of Core 22, Section 3 approaches that of a normal noncarbonaceous shale. The analytical methods employed with relative standard deviation in square brackets are: coulometry (C_{org} , CO)² [2%], AAS-flame (Fe, K, Na, Mn, Cu, Ni, Zn, Cr, Ba) [$\leq 10\%$], γ -spectrometry (U, Th) [25%], optical emission spectrography (V, Mo) [20%], and AAS-flameless after separation (Cd, Pb, Tl, Bi, Hg) (Heinrichs and Lange (1973; Heinrichs (1975a)) [15%]. Systematic errors have been excluded by the use of several sets of international standard reference rocks.

Our analytical results are compiled in Table 1. The content of C_{org} of the Cenomanian samples is high compared with black shale from other than oceanic occurrences. Several elements are well correlated with the concentration of C_{org} and are far beyond the ranges in which these elements often occur in black shales (V, Mo, Ba, U). The elements Zn, Cd, Cu, Ni, and Tl are also correlated with C_{org} . Their concentrations are less pronounced than those of the above-mentioned constituents. A correlation of Tl with C_{org} has not been reported before. No correlation with C_{org} could be observed for the following minor elements: Cr, Pb, Th, Hg, and Bi. The concentrations of Cr and Th in our samples are higher than in noncarbonaceous shales however. Vine and Tourtelot (1970) have compiled data on 21 minor elements in 20 sets of 779 individual black shales from North America. We have included their median values in our Table 1 for comparison. Wedepohl (1964) published a similar compilation of European black shales considering a smaller number of elements. He demonstrated that black shales often contain about 1000 ppm V and 100 ppm Mo. Both compilations mention manganese as the only element being lower in typical black shale than in shale and clay with subordinate concentrations of C_{org} . Diagenetic mobilization of manganese after reduction of Mn^{4+} can explain the low concentrations in the reducing environment.

Another reference used in Table 1 is a set of average concentrations in shales low in C_{org} as compiled by two of us (H.H. and K.H.W.).

The processes and the sources by which the abnormal concentrations of several minor elements in the black

shales under investigation have accumulated are unknown. The Cretaceous Proto-North Atlantic was large enough to provide normal concentrations of these elements in seawater. Hence, the process of extraction of metals from seawater or pore water solutions is of importance.

The organic marine primary production (plankton, seaweeds) and land plants are usually low in minor elements. Yamamoto and Fujita (1966), in their compilation of chemical data on seaweeds (for the majority of elements more than 70 samples), report the following averages in dry matter for elements considered in this investigation: 591 ppm Fe, 150 ppm Zn, 94 ppm Mn, 14 ppm Cu, 3.1 ppm V, 2.8 ppm Ni, 1.2 ppm Cr, 0.3 ppm Mo. Several authors have published additional data on algae, plankton and higher animals in comparable ranges of minor element concentration. Riley and Roth (1971) mention slightly higher vanadium values. Martin and Knauer (1973) observed 38 ppm Ba, 3.2 ppm Cd, and 0.15 ppm Hg in dry plankton from the northeast Pacific (average of 45 samples). If we extrapolate those elements which correlate with C_{org} in our samples to 80% C as the potential carbon content of the organic residues, we get about 3000 ppm Zn, 1200 ppm Cu, 8100 ppm V, 4700 ppm Ba, 1100 ppm Ni, 550 ppm Mo, 110 ppm U, and 12 ppm Cd. These accumulations are much too high (factors in the range of 1000 for V, Ni, and Mo) to be explained by the composition of original marine organic substances. Higher concentrations of minor elements could be attained if a large fraction of the dead organic matter has been oxidized in an oxic water column. This assumption requires closed system conditions for the metals exclusively. Using the above-listed data on seaweeds and plankton, the sequence of minor element concentration should be: Zn > Ba > Cu > V ~ Cd ~ Ni >> Mo. We observe the following order of abundances instead: V > Ba > Zn > Cu = Ni > Mo >> Cd. The fractionation could be a function of the stability of organic complexes formed during diagenesis of the organic matter or of supply from different sources. Porphyrin complexes of V and Ni are more stable than those of Cu and Zn (Hodgson et al., 1967). The ranges of concentration of porphyrin vanadium and porphyrin nickel complexes in American crude oils are equivalents of 20 to 900 ppm V and 5 to 130 ppm Ni, respectively (Dunning et al., 1960). Terrestrial plants could be an additional source for the organic residues in our shales. Using data reported by Bowen (1966), the following sequence of minor elements are expected in plant matter: Zn > Ba ~ Cu >

TABLE 1
Chemical Composition of Samples from Site 367 and Averages of Shale References

| Sample (Interval in cm) | Fe (%) | Na (%) | K (%) | S (%) | C _{org} (%) | CO ₂ (%) | V (ppm) | Cr (ppm) | Mn (ppm) | Ni (ppm) |
|---|--------|--------|-------|-------|----------------------|---------------------|---------|----------|----------|----------|
| 17, CC | 4.53 | 0.77 | 1.64 | 3.72 | 9.96 | 1.55 | 1070 | 240 | 610 | 200 |
| 18-1, 104-105 | 2.65 | 0.74 | 0.80 | 6.48 | 22.72 | 17.55 | 1480 | 100 | 300 | 310 |
| 21-2, 80-82 | 4.15 | 0.92 | 2.34 | 2.36 | 6.46 | 1.58 | 800 | 240 | 280 | 180 |
| 21-4, 56-58 | 4.53 | 0.76 | 2.50 | 2.80 | 10.16 | 0.92 | 1700 | 260 | 340 | 210 |
| 22-3, 10-12 | 4.90 | 0.92 | 2.36 | 2.35 | 1.57 | 7.07 | 275 | 130 | 600 | 70 |
| 22-4, 83-85 | 5.25 | 0.99 | 2.46 | 3.63 | 5.04 | 0.81 | 500 | 250 | 580 | 110 |
| Average shale low in C _{org} | 4.8 | 0.9 | 3.0 | — | 0.6 | 6.1 | 130 | 90 | 600 | 68 |
| Black shales (Vine and Tourtelot, 1970) | 2.0 | 0.7 | 2.0 | — | 3.2 | 1.0 | 150 | 100 | 150 | 50 |

TABLE 1 Continued

| Sample (Interval in cm) | Cu (ppm) | Zn (ppm) | Mo (ppm) | Cd (ppm) | Ba (ppm) | Hg (ppm) | Tl (ppm) | Pb (ppm) | Bi (ppm) | Th (ppm) | U (ppm) |
|---|----------|----------|----------|-------------------|----------|---------------------|-------------------|----------|-------------------|----------|---------|
| 17, CC | 250 | 680 | 117 | 1.9 | 1280 | 0.76 | 3.5 | 20.0 | 0.22 | 34 | 18 |
| 18-1, 104-105 | 240 | 580 | 133 | 2.4 | 2350 | 0.16 | 4.9 | 5.8 | 0.11 | 15 | 35 |
| 21-2, 80-82 | 200 | 380 | <30 | 3.0 | 780 | 0.29 | 2.3 | 11.8 | 0.25 | <10 | 15 |
| 21-4, 56-58 | 190 | 410 | 88 | 1.6 | 620 | 0.29 | 2.0 | 15.7 | 0.22 | <3 | 9 |
| 22-3, 10-12 | 35 | 88 | 6 | 0.65 | 580 | 0.11 | 0.72 | 16.2 | 0.15 | <13 | <5 |
| 22-4, 83-85 | 65 | 210 | <30 | 0.86 | 830 | 0.13 | 0.95 | 12.3 | 0.13 | <10 | <4 |
| Average shale low in C _{org} | 39 | 110 | 2.6 | 0.69 ^a | 628 | 0.48 ^{a,b} | 0.99 ^a | 23 | 0.35 ^a | 12 | 3.7 |
| Black shales (Vine and Tourtelot, 1970) | 70 | <300 | 10 | — | 300 | — | — | 20 | — | — | — |

^aHeinrichs (1975b).

^bCan be influenced by contamination during laboratory storage.

$Ni \geq V = Mo > Cd$. Again, this order cannot explain the observed accumulation, especially the prevalence of vanadium in the black shales.

Pyrite is common in the neighboring layers of several of our samples according to the Initial Core Descriptions. This mineral is a typical product of bacterial sulfate reduction and diagenesis. Additional sulfides were not observed. At seawater NaCl concentrations, the solubility of Hg, Cu, Cd, and Zn sulfides is still less than the normal abundance of these elements in seawater. A correlation between these metals and sulfur does not exist. Spencer and Brewer (1971) observed 0.7 ppb Zn and 0.4 ppb Cu in the anoxic Black Sea deep water which is distinctly less than in oxic seawater (3 ppb Zn, 1 ppb Cu). Therefore, these sulfides could have been precipitated in anoxic bottom waters or pore water solutions of the Cretaceous North Atlantic. Because of the moderate accumulation of Hg and Cu in our samples, this process could not have contributed much to our black shales.

Additional investigations of the black shale as a characteristic sediment type in the Cretaceous Atlantic Ocean are needed for an understanding of the environment of deposition and the processes of element accumulation.

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