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Short-range vertical variation in organic carbon, carbonate carbon, total sulfur contents and Munsell color values in a core from the Upper Pennsylvanian Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas

by

M. R. Stanton, J. S. Leventhal and J. R. Hatch

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Abstract

Organic carbon, total sulfur, carbonate carbon and Munsell color value were determined for 21 successive samples from a 53-cm-thick section of drill core. These samples are from the Stark Shale Member of the Dennis Limestone of Upper Pennsylvanian age, Wabaunsee County, Kansas. The data confirm previous results (Hosterman and Whitlow, 1981) which showed that a limited relationship of color value to organic carbon exists for shales containing about 7 percent or less organic carbon. For samples with 7 percent or more organic carbon, color values are nearly all the same. The color value is useful in screening samples before trace element analysis and in estimating the organic carbon content and metal potential of the shale (Leventhal and others, 1982).

Introduction

Black shales are mudrocks with about 1 to about 20 percent by weight organic carbon. The organic matter is usually responsible for the dark-gray or black color of these shales; other shales may be lighter-colored because of different types and amounts of organic matter and minerals (Hosterman and Whitlow, 1981).

Perhaps the two most important constituents of a black shale are organic carbon and sulfur. The organic matter is a source of hydrocarbons and the organic matter and sulfur are also important "traps" for various metals, such as U, V, Mo, Hg, Zn, Cu, and Cr (Leventhal and others, 1981).

Color value may be used as an indicator of the organic carbon content and this relationship between color and organic carbon may have some use as a preliminary indicator of the hydrocarbon potential (Hosterman and Whitlow, 1981). Also, it may be possible to use color, organic carbon, and sulfur contents together to screen samples, prior to analysis, to estimate the trace-element metals content (Leventhal and others, 1981).

A previous study by Leventhal and Shaw (1980) showed variations on a 6-inch scale for shale samples; depending on the amount of organic carbon, these variations were sometimes not recognized.

Samples

The samples are from a core of the Stark Shale member of the Dennis Limestone (Upper Pennsylvanian age). The unit is 52.8 cm (21 in.) thick, and was collected from a depth of 567.8 - 568.3 m at SW 1/4, NE 1/4, SW 1/4 sec. 33., T. 13 S., R. 10 E., Wabaunsee County, Kansas.

The core was initially divided into 13 samples by the Kansas Geological Survey, based primarily on color differences. Eight of these samples were then subdivided by the authors into upper and lower portions, or multiple portions, based on color as well as the presence (or absence) of sulfides, phosphate nodules, fossils, and laminations. The down-hole positions and sample descriptions are shown on table 1.

Experimental techniques

Color designations were obtained by comparing the samples to the Munsell Rock and Soil Color Chart, (Munsell Color Co., Baltimore, Md. 1979), and are assigned on the basis of hue (color), value (lightness), and chroma (the degree of saturation). Neutral colors (indicated by an N), have color values only; no hue or chroma is associated with these colors. Neutral color values range from 0 (black) to 10 (white). For other colors having hue and chroma, color values range from 1 to 9. As color values increase, samples appear lighter-colored.

All samples (fresh, dry core) were first given a color designation based on field observations. One-fourth of each sample was then powdered, using a ceramic mortar and pestle, and given a color designation. The color designations for the intact and powdered samples are listed in table 1.

Total carbon analyses were obtained using a Leco WR-12* carbon determinator. This uses an induction furnace for combustion and a thermalconductivity detector. A weighed amount of the powdered sample is placed in a combustion crucible, along with copper and iron metal used to promote better combustion. Combustion (~1100°C) converts all carbon to CO_2 gas. The detector system measures the amount of CO_2 gas, based on thermalconductivity differences between this sample gas (CO_2) and the reference gas (O_2). The amount of carbon is displayed on the digital voltmeter, and this reading is converted to the weight-percent of carbon.

To determine organic carbon, samples were pretreated with warm 6N HCl for 15 minutes to remove carbonate carbon and then dried before being combusted. Carbonate carbon was determined by taking the difference between the total and organic carbon values.

Sulfur analysis also uses the induction furnace, but the Leco IR-32 determinator has an infrared cell detection system. The weighed sample, with tungsten and V_2O_5 (as "accelerators"), are combusted in a crucible in the induction furnace. All sulfur is converted into SO_2 gas; the amount of this gas is measured by the detector system and displayed on the digital voltmeter. Finally, the displayed reading is converted to percent sulfur.

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*Use of trade names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

Table 1.--Sample descriptions, Munsell color designation, and percent organic carbon. Samples are in order, from top [S-1] to bottom [S-13].

Sample	Thickness (cm)	Description of core sample	Color of core sample	Color of powdered sample	Hue	Value/Chroma	% Org carbon
S-1	2.5	Sulfides; Phosphatic; lenticular	N2	Brownish black	5 YR	2/1	21.7
S-2-2	1.7	Black, massive	N2	Brownish black to black	N	1	24.4
S-2-1	2.3	Black, massive	N2	Brownish black	5 YR	2/1	29.5
S-3-2	1.9	Dark-gray, laminated, sulfide nodules	N3	Dark yellowish brown	10 YR	4/2	2.0
S-3-1	1.8	Dark-gray, laminated, sulfide nodules	N3	Dark yellowish brown	10 YR	4/2	2.1
S-4-3	1.1	Massive	N2.5	Olive black	5 Y	2/1	7.5
S-4-2	1.3	Phosphatic, laminated	N2.5	Olive black	5 Y	2/1	10.8
S-4-1	3.1	Gray-black, laminated	N3.5	Olive black	5 Y	2/1	21.4
S-5	4.3	Phosphatic w/sulfides	N2	Brownish black	5 YR	2/1	14.4
S-6-2	1.8	Black, massive	N2	Olive black	5 Y	2/1	19.2
S-6-1	1.8	Black, massive	N2	Brownish black	5 YR	2/1	11.7
S-7	2.0	Fossiliferous, sulfides	N2	Dark gray	N	3	2.2
S-8-2	2.3	Phosphatic Debris .5mm thick and	N2	Olive black	5 Y	2/1	17.9
S-8-1	2.0	vitrinite band		Brownish black	5 YR	2/1	23.4
S-9-2	5.1	Reworked shale fragments, fossiliferous; bottom darker,	N2	Pale yellowish brown	10 YR	6/2	0.46
S-9-1	3.5	mottled reddish-gray		Olive gray	5 Y	4/1	0.91
S-10	4.8	4mm of phosphatic-sulfide lenses	N2	Brownish black	5 YR	2/1	17.8
S-11	3.0	Black	N2	Olive black	5 Y	2/1	13.5
S-12-2	2.0	Black, massive, sulfides	N2	Brownish black	5 YR	2/1	12.0
S-12-1	2.0	Black, massive, sulfides	N2	Brownish black	5 YR	2/1	23.6
S-13	2.5	Dark gray	N3	Olive gray	5 Y	4/1	1.6

Results

The results for the carbon and sulfur analyses are summarized in table 3 and plotted on figure 1.

The powdered samples were arranged in order from lightest to darkest without reference to a color chart. This was done to see if the arrangement would correspond to the organic carbon content. The results show that there is, in general, a correspondence for the lighter colored samples. The color lineup vs. organic carbon is shown in table 2.

The results for the color value vs. organic carbon show that the relationship is limited to the lighter colored samples with about 7 percent or less organic carbon. Up to about 7 percent organic carbon, color differences can be detected in a powdered sample; beyond 7 percent, all samples appear to be olive-black or brownish-black to black.

Darker samples that have the same value and chroma show widely varying amounts of organic carbon content. For example, samples S-2-1 and S-12-2 are both brownish-black (5 YR 2/1), yet S-2-1 has 29.5 percent organic carbon whereas S-12-2 has only 12.0 percent organic carbon. Thus, color is of little use in distinguishing samples that have chroma values of one.

Color differences are even less noticeable when comparing the whole rock core samples. Core samples all appeared to be neutral (gray and black with values from N2 to N3.5), but the organic carbon content varies from 0.46 percent to 29.5 percent. For example, S-9-1 appeared to be N2, as did sample S-10. However, S-9-1 has only 0.91 percent organic carbon while S-10 has 17.8 percent organic carbon. Thus, field identification of color value will not indicate organic content.

Total sulfur values appear to have no marked effect on color, whether or not the sample is light or dark. The organic carbon probably overwhelms any color contributed to the sample by FeS_2.

Discussion

The color values of a black shale are affected by the sample components. Organic and carbonate carbon are the two most important components. The relative amounts of these seem to affect the color more than the other sample components, such as sulfide. In turn, several factors (listed below) determine the final organic and carbonate values of a black shale.

Four major factors are the input of organic material into the depositional basin, rates of clastic and organic sedimentation, oxidation of organic matter, and any diagenetic processes, such as oil migration or cementation. These and other factors can all interact to alter the composition and the color of the shale (Leventhal and others, 1981).

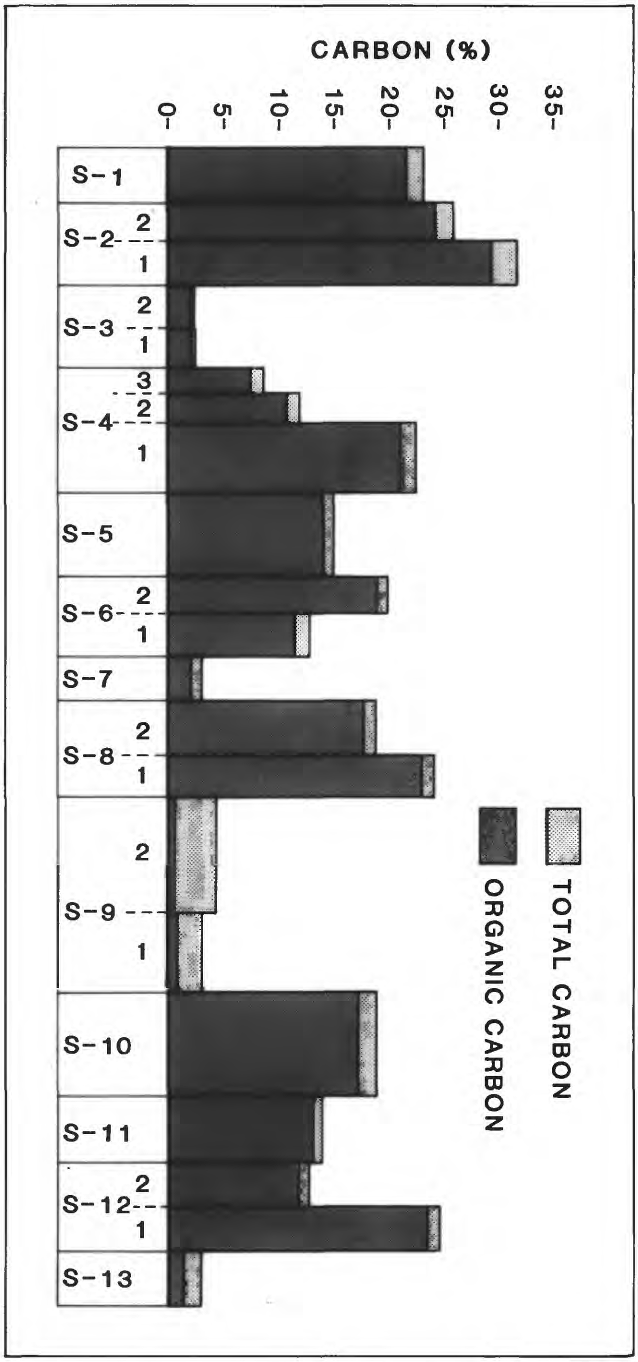

Figure 1.--Total carbon and organic carbon content with depth.

Table 2.--Relation of organic carbon to Munsell and observed color designations.

In order from lightest to darkest	% Org C	Color Value/Chroma
S-9-2*	0.46	6/2
S-3-2*	2.0	4/2
S-3-1*	2.1	4/2
S-13*	1.6	4/1
S-9-1*	.91	4/1
S-7*	2.2	N3
S-4-3*	7.5	2/1
S-12-2+	12.0	2/1
S-4-2+	10.8	2/1
S-6-1+	11.7	2/1
S-11+	13.5	2/1
S-5+	14.4	2/1
S-2-1+	29.5	2/1
S-10+	17.8	2/1
S-1+	21.7	2/1
S-12-1+	23.6	2/1
S-8-2+	17.9	2/1
S-4-1+	21.3	2/1
S-6-2+	19.2	2/1
S-2-2+	24.4	N1
S-8-1+	23.4	2/1

* - These 7 samples distinguishable on the basis of color.

+ - These 14 samples indistinguishable on the basis of color.

Table 3.--Percent total carbon, organic carbon, carbonate carbon, total sulfur, and Munsell color value.

Sample	Total carbon %	Organic carbon %	% Carbonate carbon (by difference)	% Sulfur (total)	Color value
S-1	23.2	21.7	1.5	4.1	2
S-2-2	26.1	24.4	1.7	2.7	1
S-2-1	31.8	29.5	2.3	3.3	2
S-3-2	2.27	2.0	0.27	1.96	4
S-3-1	2.43	2.1	0.33	2.0	4
S-4-3	8.7	7.5	1.2	2.5	2
S-4-2	12.0	10.8	1.2	2.25	2
S-4-1	22.7	21.4	1.3	2.55	2
S-5	14.98	14.4	0.58	2.10	2
S-6-2	20.14	19.2	0.94	3.8	2
S-6-1	12.9	11.7	1.2	4.95	2
S-7	3.18	2.2	0.98	1.65	3
S-8-2	18.9	17.9	1.0	1.85	2
S-8-1	24.29	23.4	0.89	1.7	2
S-9-2	4.36	0.46	3.9	2.0	6
S-9-1	3.31	0.91	2.4	1.0	4
S-10	19.1	17.8	1.3	3.8	2
S-11	14.24	13.5	0.74	2.25	2
S-12-2	12.88	12.0	0.88	3.6	2
S-12-1	24.8	23.6	1.2	3.8	2
S-13	3.2	1.6	1.6	1.45	4

Generally, a darker color would indicate rapid organic influx and deposition, slow clastic deposition (less color dilution), and little organic oxidation. This dilution effect can be seen for uranium and organic carbon in Devonian shales of the Appalachian basin (Leventhal and Kepferle, 1982).

Conclusions

At best, color value can be used to define two separate groups of black shale samples; high organic samples (>7 percent) and low organic samples (<7 percent).

Color values of about 3 or more (lighter) can semi-quantitatively indicate organic carbon contents. Above 7 percent organic carbon, however, the color value-organic carbon relation no longer holds, and samples are visually similar.

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