A New Graph for Understanding Colors of Mudrocks and Shales

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ABSTRACT

Empirical data on mudrocks and shales indicate that they exhibit two distinct color spectra: green-purple-red, controlled by the ratio of ferrous iron to ferric iron, and green-gray-black, controlled by total organic carbon content. Both the oxidation state of iron and the percentage of organic carbon are affected directly and indirectly by numerous physical and biological factors, the most important of which is oxidation potential - Eh.

The main controls and possible temporal changes in color of fine-grained sediments are summarized in a graph relating the color of the sediment, with the associated empirical data of organic content and oxidation state of iron (Y axis), to time (X axis). The color history of a sediment is traced out as a curve on the diagram starting at a point representing the initial conditions and ending with the termination of diagenetic reactions. Curves may be drawn for varying Eh conditions. Oxidative loss of carbon is nonreversible, so only positive slopes (lighter colors with time) are possible for the green-gray to black series. Changes in oxidation state are reversible, and therefore any number of temporal color changes between green and red are possible once the organic carbon is depleted.

Key words: Geology; petrology - sedimentary; review articles.

INTRODUCTION

The question of how sedimentary rocks acquire their color has been a long-standing question in geology. Much of the work has centered around explaining the red coloring of redbed sequences. There is consensus that color is almost always an early diagenetic phenomenon (Tomlinson, 1916; Downing and Squirrel, 1965; Walker, 1967; Thompson, 1970; Van Houton, 1973; McBride, 1974; Hubert and Reed, 1978; McPherson, 1980; Potter and others, 1980). The diagenetic reactions that lead to the development of color in mudstones and shales are controlled by the geochemical conditions and by biological activities. Understanding of these controls allows for the development of a graph that illustrates possible temporal changes in color as they relate to sediment compositions and geochemical conditions.

GREEN-GRAY TO RED COLORATION: ROLE OF OXIDATION-REDUCTION REACTIONS

The early work of Tomlinson (1916) demonstrated that the controlling factor in the development of color in shales is the Fe^{+3}/Fe^{+2} ratio and not the total percentage of iron. McBride (1974) postulated that as the Fe^{+3}/Fe^{+2} ratio in a rock varies from high to low values, the resulting colors would range from red to purple to gray. The colors are imparted by the types and amounts of various iron oxides. The less common yellows and browns are also derived from iron oxides. Yellow coloration is imparted by the mineral limonite, brown results from goethite, and red is due to the presence of hematite. Only a few percent hematite is needed to give a rock a deep red.

The green coloration of mudrocks and shales results from the presence of iron-bearing phyllosilicates such as chlorite, illite, and for some marine rocks, glauconite. Hematitic red coloration is imparted to sediments under oxidizing conditions by the early-postdepositional alteration of iron-bearing minerals, including: (1) dehydration reactions in which the limonite stain on detrital particles is altered to hematite, (2) dissolution of iron silicates and precipitation of the released iron, and (3) direct oxidation of magnetite and ilmenite grains (Hubert and Reed, 1978). Red sediments can later be converted to green by reduction of the iron (Hubert and Reed, 1978; Potter and others, 1980), which is then carried away in solution (Picard, 1965; Friend, 1966; McPherson, 1980) or reprecipitated as iron-rich clays such as chlorite (Thompson, 1970). Such is apparently the case for green reduction spots in red shales, which form under the locally reducing conditions around small accumulations of organic matter.

McBride (1974) noted that the *strength* of the red or green color, in a sediment or rock, is a function of grain size: fine-grained rocks have higher iron content and, therefore, more intense color. According to McPherson (1980), the high iron levels result from an amorphous or poorly crystalline iron oxide that attaches itself to clays. These are a precurser to the hematite found in red sediments. Diagenetic changes in the oxidation state of iron, and consequently in the color, occur as sediments are buried below the water table. It is common during burial for red sediments to be turned green due to interaction with reducing fluids. It is likely that where grain size and color are correlated, the controlling factor is permeability and flux of oxidizing or reducing fluids. For instance, in many sequences red shales will contain green sandstone beds (Myrow, 1987). The green color of the sandstones results from their high permeability relative to the muds, which in this case allowed for a greater flux of reducing fluids through the sands.

GREENISH-GRAY TO BLACK COLORATION: ROLE OF ORGANICS

Potter and others (1980) combined the data on iron oxidation states and color (Tomlinson, 1916; McBride, 1974) with their own empirical data on the organic content of shales, which they found to be responsible for imparting a second color sequence from greenish-gray to black. This second sequence is independent of the oxidation state of iron and solely dependent on percent of organic carbon. Total organic carbon determines not only the greenish-gray to black color sequence, but ultimately the green to red sequence as well because the quantity of organic matter controls the Fe^{+3}/Fe^{+2} ratio by oxidation-reduction reactions (Potter and others, 1980; McPherson, 1980).

Levels of organic carbon in a sediment are controlled by many factors, most importantly: (1) sedimentation rate (S), (2) rate of supply of organic matter (P), and (3) rate of decay of

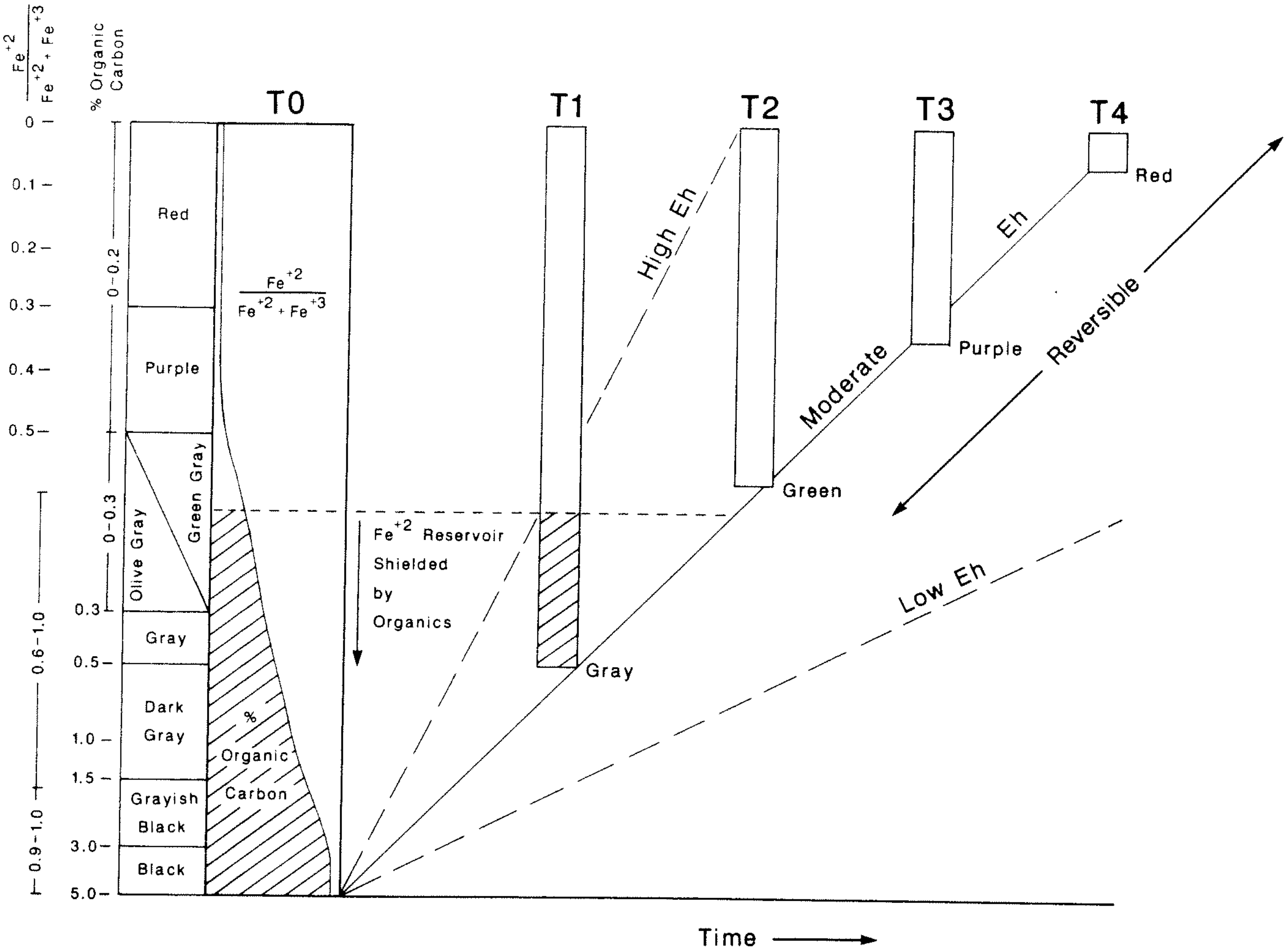

Figure 1: Graph relating color of rock, and the corresponding empirical data on organic content and oxidation state of iron (Y axis; modified from Potter and others, 1980; Figure 1.25), to Time (X axis). "Time" refers to the length of time that pore fluids interact with the sediment prior to lithification. The development of dark colors, olive gray to black, are primarily determined by organic content. For a given unit of sediment, the trend through time can only be toward lighter color with the oxidation of organic matter; this change is irreversible. The lighter colors, green-gray to red, are controlled by the mole fraction representing the proportion of iron in the +2 state (each unit in fraction represents the number of moles of iron per gram of rock); color changes are reversible through time, depending on Eh. Assuming that there is dissolved oxygen available in the sediment, the trend through time will be toward lighter color, first through the oxidation of organic carbon and later through the oxidation of reduced iron. The path taken through time is dependent on the Eh conditions. In this figure three representative paths are shown for an initial (T_0) black organic-rich sediment, corresponding to low, moderate and high Eh conditions. The color development is shown for pore waters of moderate Eh: at T_1 the sediment is gray, at T_2 it is green, at T_3 it is purple, and at T_4 it is red.

organics in the upper few centimeters of the sediment column, which is closely tied to oxygen levels (O) (Potter and others, 1980). Although the relationships among these variables are not well understood or necessarily predictable, Potter and others (1980) have suggested that C=(P-O)/S, where C is percent carbon.

Sedimentation Rate

It is difficult to evaluate the effect of sedimentation rate on final organic carbon content, although, as Potter and others (1980) point out, according to the above relationship, higher rates of sedimentation would reduce the value of C simply because inorganic detritus dilutes the sediment with regard to organic carbon. One might intuitively expect, however, that higher sedimentation rates would result in *greater* preservation of carbon through removal of the carbon from the upper few centimeters of sediment by progressive burial, the zone directly below the sediment-water interface having greater levels of oxidation and bacterial decomposition. Rapid burial would also decrease the amount of time that deposit-feeding organisms, which rework the upper oxidized layers of sediment, would have to remove organic carbon.

Berner (1978), using data from widespread sites with varying depositional rates, concludes that bacterial decomposition of organic matter increases with *increasing* sedimentation rate. This relationship is complicated by the availability of sulfate, which controls the activity of sulfate-reducing bacteria. Further complications arise because of our lack of understanding as to how rates of breakdown by methanogenic bacteria vary with sedimentation rate. Berner's (1978) findings make the situation more complicated, because he found that different types of organic matter are more reactive to one or

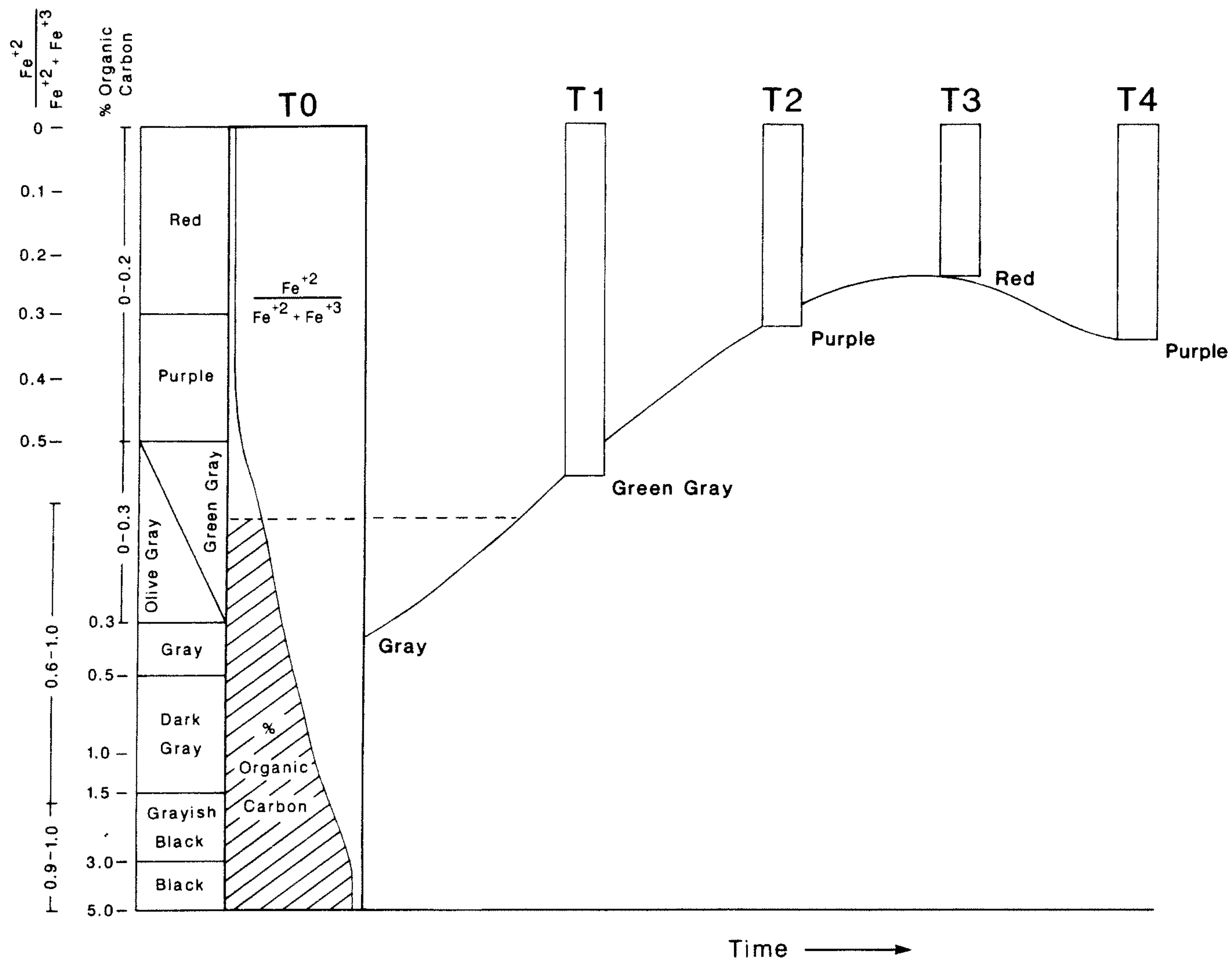

Figure 2: The temporal evolution of a sample is shown with initial conditions that plot along the Y axis in field of gray color. Through the oxidative loss of organic carbon and then through the oxidation of reduced iron, the color changes from gray (T_0) to green-gray (T_1), purple (T_2) and red (T_3). Later reduction of a portion of the oxidized iron, under reducing conditions, changes the color back to purple (T_4). Arresting the diagenesis of the sediments anywhere along the path would also arrest the color development, and the resulting color would depend on the nature of the sediment at that time.

the other bacterial decomposition process, and the abundance of reactive and refractory organic matter for each process is apparently controlled in part by sedimentation rate. It is unfortunate that " . . . studies combining carbon content, color, and sedimentation rate are lacking" (Potter and others, 1980, p. 57).

Eh Conditions

Rates of oxidation of organic matter appear to be most closely tied to Eh conditions. Environments as disparate as arid fluvial settings and abyssal oceanic depths, with vastly, different accumulation rates, may have sediment with low organic carbon due to high levels of oxygen. Oxidation rate is, of course, highly variable from setting to setting. Such variation on a regional scale in modern and ancient oxygen-deficient basins is due to bottom-water oxygen levels (Rhodes and Morse, 1971; Byers, 1977; Cluff, 1980; Savrda and others, 1984; Thompson and others, 1985). However, it should be noted that there is tremendous variation in oxygen gradients both within and between lower bottom waters and the upper sediment column. Oxygen levels may show a dramatic reduction from the lower bottom waters across the upper few centimeters of sediment. More gradual reductions in oxygen are possible between and within the upper sediment column and would have important consequences on the level of preserved organic matter and, therefore, the color.

DESCRIPTION OF GRAPH

Figure 1 attempts to summarize the possible temporal changes in color as they relate to changing environmental conditions (in particular, oxidation potential) by relating color (shown on the Y axis) along with organic content and the oxidation state of iron to time (shown on the X axis). The data on oxidation state are presented as a mole fraction expressing the proportion of reduced iron ($Fe^{+2}/Fe^{+2}+Fe^{+3}$); units for each variable in the fraction are the number of moles of iron per gram of rock. The left side of this graph is modified from Potter and others (1980, Figure 1.25). Time refers to the length of time that pore fluids interact with the sediment prior to lithification.

Any particular sediment will have initial values for the $Fe^{+2}/Fe^{+2}+Fe^{+3}$ ratio and percentage of organic carbon. Evolution of the sediment can be traced out as a curve on the diagram with Eh as a parameter. Other parameters, such as sedimentation rate or degree of bioturbation, were not selected, because it is clear from the above discussion that Eh is the primary factor in controlling both organic-carbon content and iron-oxidation states. Because the loss of organic carbon by oxidation is a nonreversible process, only curves with positive slopes are possible in the lower portion of the graph. Therefore, for dark sediments – olive gray to black – the only possible trend through time is toward lighter colors.

The change in iron-oxidation state is reversible, however, so that both positive and negative slopes are possible; in other words, the sediment may change from red to green or vice versa. This means that an infinite number of curves are possible in the upper portion of the graph through redox reactions. These redox reactions will take place only after a considerable portion of the organic carbon in the sediment has been oxidized so that it no longer acts to depress the Eh by removal of free oxygen. The Fe^{+2} reservoir is, therfore, 'shielded' by organics, as shown in Figure 1.

In Figure 1, I have chosen, for simplicity, three linear curves all of which start (at T_0) with very high levels (5%) of organic carbon. The three lines illustrate the path taken for nonvarying conditions of low, moderate, and high Eh, with the sequence of colors illustrated for conditions of moderate Eh shown for times T_1 to T_4. These curves indicate that, if there is dissolved oxygen available in the sediment, the trend through time will be toward lighter color, first through the oxidation of organic carbon and later through the oxidation of reduced iron.

The sediment at time T_0 may have any value of organic carbon and any mole fraction of reduced iron, so the initial sediment may plot anywhere along the Y axis. Figure 2 shows the history of a sample that had a relatively low organic content, and was therefore gray, at the time of deposition. This sample is shown to proceed with the oxidative loss of organic matter and then the oxidation of reduced iron to the point where the color was red. Later reduction of some oxidized iron, presumably under decreasing Eh conditions, resulted in the final purple color.

OTHER ASPECTS OF COLOR

The diagram described above summarizes what are thought to be the most important controls on the development of color in the majority of mudrocks and shales. There are other factors that may also be important in the coloration of shales and mudstones. It is common among field geologists to attribute the darkness of black shales to the presence of disseminated pyrite, but this may not be correct. Holocene marine sediments that are black at the surface get lighter with depth. According to Berner (1971) this is due to the transformation, with burial, of the metastable minerals mackinawite (FeS) and greigite (FeS4) to aggregates of submicron-sized crystals of pyrite called framboids. These may impart a gray color to the sediments and later the mudrock or shale, but presumably will not result in a black coloration.

Another potentially important factor in determining color is thermal maturity. Lyons (1988) shows that the black color of some limestones is due to the carbonization of minute quantities of organic matter (<0.06% total organic carbon). His laboratory studies also indicate that thermal maturation of small quantities of organic carbon, perhaps with additional manganese oxidation (formation of pyrolusite), could impart a dark color to light colored rocks. Whether this is an important factor in the color of thermally mature shales is not clear.

Parameter	Effect
Total Iron Content	Little or no effect other than intensity of color
$Fe^{+2}/Fe^{+2} + Fe^{+3}$	Determines color spectrum: green-purple-red
Total Organic Carbon	Determines color spectrum: gray-black
Grain Size	1. Fine grain size = more intense color 2. Indirectly through permeability: allowing for greater or lesser flow of reducing or oxidizing fluids
Oxidation Potential	Oxidation of organic carbon; Incorporated into biofacies models for modern and ancient dysaerobic basins
Sedimentation Rate	*Unclear:* 1. High sedimentation rate results in dilution of organic carbon fraction 2. Higher rate removes sediment more quickly from shallow oxidizing environment and deposit-feeding organisms 3. Bacterial breakdown may proceed more quickly with higher rate
Availability of SO_4	Limiting factor for sulfate-reducing bacteria in reduction of organic carbon
Disseminated Pyrite	Promotes dark gray color
Thermal Maturation	Unclear

Table 1: Summary of various parameters that directly and indirectly control the color of mudstones and shales and their respective effects.

DISCUSSION

The question of what imparts color to shales and mudrocks is not yet fully answered (Table 1). The controlling factors appear to be the presence of organic carbon and the ratio of reduced to oxidized iron, both of which appear to be controlled by diagenetic conditions. Some questions remain, particularly as to the role of disseminated pyrite or other sulfides and oxides. More importantly, it is necessary to firmly establish the relationships among color development and both biological and sedimentary processes. The graph presented here shows the possible temporal changes in color as they relate to initial sediment composition and variable Eh. The value of the graph lies in its clear depiction of both the controls on color and the kinds of changes that can and do occur during diagenesis.

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