Colored Clays in a Groundwater Stream, Correlating Fiber-optic Reflectance with Electrical Impedance

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Abstract

A bifurcated fiber-optic light guide was used to measure the colors of clays in a groundwater stream over the Upper Ordovician Queenston Formation of the Niagara Escarpment (Ontario, Canada). One branch of the light guide illuminated the samples, and the other branch gathered reflected light for spectrophotometry. Measuring Munsell rock color chips, and using the weighted-ordinate method to calculate chromaticity coordinates from reflectance spectra, the dominant chemically reduced clay was greenish-gray (Munsell 5G 6/1, x=0.348, y=0.352, Y%=62.3) while the dominant oxidized clay was grayish-red (Munsell 5R 4/2, x=0.388, y=0.338, Y%=23.8). The electrical impedance of clays were correlated with x (r=-0.92 for capacitance and r=0.96 for resistance, P<0.001 at 10 kHz).

The peak wavelengths for correlations were around 500 to 540 nm. The matrix between the corallites of a Devonian fossil coral above the collection site (Eridophyllum seriale) was within the statistical range of oxidized grayish-red Ordovician shale. There was no evidence that low pH in the groundwater stream had caused the variation in clay color, thus, leaving conditions when the source shale was deposited as the most likely cause of color variation.

Keywords: Groundwater; Clay color; Fiber-optic reflectance; Electrical impedance

Introduction

Clay is a well-known aquitard whose distribution often determines the geographical location of groundwater springs, which may then cascade over the clays to produce bright colors. Clay color is important in geological stratigraphy and depositional analysis [1], and the Queenston Formation shales exposed on the Niagara Escarpment in Ontario, Canada, produce clays of different hues [2-5], variously reported as brown, red, green, gray, or blue. While the mineral basis of clay color can be contentious [6], it has been suggested that the acidity of groundwater may cause color variations in clay [7]. Subjective descriptions of clay colors are often confusing, and there is much to be gained by using objective colorimetry [8-10], or Munsell rock color standards for subjective evaluation [11].

With geological samples, it is very difficult to follow the strict protocols of CIE (Commission International de l’Eclairage) colorimetry with regard to illuminator emission spectrum, sample size and viewing angle [12]. But using a Y-shaped or bifurcated fiber-optic light guide, it is possible to illuminate small areas and collect reflected light for spectrophotometry [13]. Spectral data may be processed using the weighted-ordinate method on which the CIE system is founded; at maximum reflectance (sterance) at 550 nm. Color coordinates were calculated using the 1931 weighted ordinates [12]. Spectra were tested using t-tests and simple correlation coefficients at each wavelength.

Electrical impedance

For electrical measurements, clay samples were impaled with parallel needles (gauge 18, axial separation 17 mm) and measured with a Hewlett Packard 4262A LCR meter (Palo Alto, California) using a capacitors, and their alternate charging and discharging further impedes the current. Thus, electrical impedance with an alternating current is a triangular function of what, for the sake of simplicity in this report, will be termed resistance (ohms) and capacitance (farads). Resistance in clays depends on alternating current frequency and is an indication of cation-exchange capability [14].

Materials and Methods

Fiber optics

The common trunk of the fiber-optic light guide had a single illuminating fiber surrounded by six fibers to gather reflected light. The illuminator was a 100 W halogen source powered from a stabilized transformer. Reflected light passed through a grating monochromator and onto a side-window photomultiplier. Complete details of the apparatus are reported elsewhere [15]. The system was standardized against a white oral glass plate from a Zeiss Elrefo colorimeter, adjusting the distance between the probe tip and the plate to give maximum reflectance (sterance) at 550 nm. Color coordinates were calculated using the 1931 weighted ordinates [12]. Spectra were tested using t-tests and simple correlation coefficients at each wavelength.

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parallel circuit mode at 120 Hz, 1 kHz and 10 kHz. Depth of penetration was standardized to 4 cm by insulating sleeves on the electrodes.

**Clay samples**

Wet clay samples were collected from a groundwater stream on the Niagara Escarpment north of Niagara Falls, where the Mad River runs through a preglacial notch in the escarpment, then joins the Nottawasaga River to empty eastwards into the Georgian Bay of Lake Huron (Figure 1). The full stratigraphic column of the escarpment (Cambrian, Ordovician, Silurian and Devonian) has been eroded here, so that the top layer in situ in the headwaters of the Mad River Valley is the Amabel formation of the Lower Silurian, although Devonian rocks and fossils are scattered above the top layer. As the Mad River cuts eastwards down the escarpment, the lower levels of the Clinton and Cataract Groups (Middle and Lower Silurian, respectively) are exposed above the colored shales of the Queenston Formation (Upper Ordovician). Weathering of the colored shales gives rise to colored clays. The clay samples were wrapped to maintain their original stiff, damp texture and were measured at approximately 18° C.

**Hydrology**

Water temperature and pH were measured with a water-proof meter calibrated before each set of measurements (PC300, Oakton Instruments, Vernon Hills, IL) for a period of two years. The pH electrode was cleaned regularly with pepsin and HCl (Oakton 653-06) and stored in an appropriate medium (Oakton 653-04). During cold weather, the meter was kept warm. Measurements were made 20 secs after the ready indicator appeared.

**Results**

**Fiber-optic reflectance**

Reduced clay samples were greenish-gray (Munsell 5G 6/1, x=0.348, y=0.352, Y%=62.3) while oxidized clay samples were grayish-red (Munsell 5R 4/2, x=0.388, y=0.338, Y%=23.8), with color coordinates calculated from fiber-optic measurements of Munsell Rock Colors (Figure 2). Fiber-optic measurements of actual clay samples produced spectra similar in shape to the Munsell Rock Colors of Figure 2. Reduced (Figure 3) and oxidized clays (Figure 4) both showed considerable differences in luminosity.

**Electrical impedance**

From 120 Hz to 10 kHz, reduced clay had higher electrical capacitance and lower resistance than oxidized clay (Table 1). Correlations of color coordinates and electrical parameters were strongest in the x-axis (blue-green to orange-red), as shown in Table 2. However, significant correlations of electrical parameters with Y% were also detected (Table 2). This gets complicated because, not only was the green to red hue indicative of the basic physical properties of the clay, but there was also some connection with luminosity. This may have been because oxidized clay was darker than reduced clay, as shown in Figure 2 for Munsell Rock Colors, and by noting the y-axis data in Figures 3 and 4. In summary – where was the information, in the shape of the spectrum, in the luminosity, or both?

**Correlations**

To work on this problem, the correlations of reflectance with electrical parameters were plotted across the spectrum. Capacitance was positively correlated with reflectance (Figure 5C) while resistance was negatively correlated with reflectance (Figure 5R). The strong negative correlations of x with capacitance (Table 2, column 2) had only a small effect from the frequency of the test current (120 to 10 kHz) and were strongest from 500 to 540 nm (P<0.005). The strong positive correlations of x with resistance (Table 2, column 2) also showed little effect from the frequency of the test current, and correlations were strong from 500 to 540 nm (P<0.005). Thus, reflectance from blue (500 nm) to green (540 nm) was the dominant sources of the strong correlations of x with electrical parameters seen in Table 2, column 2.
Table 1: Capacitance (C, farads) and resistance (R, ohms) in parallel at three different frequencies (Hz) for reduced and oxidized clays.

|       | Reduced          | Oxidized         |
|-------|------------------|------------------|
| 120 Hz C | 6.24 E-7 ± 9.35 E-8 | 2.99 E-7 ± 8.91 E-9 |
| 120 Hz R  | 447.2 ± 22.6     | 631.3 ± 23.7     |
| 1 kHz C   | 2.18 E-8 ± 2.40 E-9 | 1.00 E-8 ± 4.24 E-10 |
| 1 kHz R   | 400.6 ± 20.5     | 591.6 ± 21.3     |
| 10 kHz C  | 1.02 E-9 ± 1.23 E-10 | 5.68 E-10 ± 2.52 E-11 |
| 10 kHz R  | 386.5 ± 19.8     | 576.6 ± 21.3     |

Differences between reduced and oxidized clays, all P<0.001

Table 2: Correlations of capacitance (C) and resistance (R) in parallel with chromaticity coordinates at three different frequencies (Hz).

|       | x       | y       | Y%       |
|-------|---------|---------|----------|
| 120 Hz C | -0.916*** | 0.427*  | 0.559*   |
| 120 Hz R  | 0.956***  | -0.427* | -0.677*  |
| 1 kHz C   | -0.947*** | 0.42*   | 0.617*   |
| 1 kHz R   | 0.963***  | -0.428* | -0.681***|
| 10 kHz C  | -0.92***  | 0.352   | 0.594*   |
| 10 kHz R  | 0.964***  | -0.427* | -0.681***|

P<0.05*, 0.01**, 0.001***, and 0.0005**** with n=20, 1-tailed t-test

Discussion

The suggestion that groundwater might be responsible for variations in clay color [7] deserves serious attention because colorful banded shales and clays are a conspicuous feature of many badlands and escarpments. Even the Munsell Rock Color book [11] displays...
them as an attractive feature, and they appear in countless tourist images on the internet. The original suggestion by Vos [7] was continued by Rutka and Voss [17], and appears in Wikipedia [18] for all to see. But taking a critical approach, look at the acidity of groundwater (Figure 8) passing over alternating strata of greenish-gray and grayish-red clays (Figures 3 and 4). If acidity was the primary cause of color change, how could superficial color changes persist to create banded clays in a single stream? Also, the electrical impedance data (Table 1) showed that clay colors were not merely a surface effect caused by groundwater pH—there were deep difference in the clays. Thus, the superficial effects of groundwater acidity may be dismissed, which leaves the possibility that groundwater might have acted deep within strata over the long period of geological time. But this would require that various strata of shales and clays do not function as a blanket aquitard, and that they allow groundwater to penetrate through seams within clay strata. This is possible, but requires a proof.

Hence, at present, it seems more likely that color differences in the source shales and their derived clays were produced by depositional conditions during and after the Taconic Orogeny, when volcanic ash deposited along the eastern coast of North America was the dominant source of sediments [5]. Oxidized grayish-red shale in the matrix of a fossil coral (Figure 6) suggests that the grayish-red color originated in aerobic conditions, with the corollary, that greenish-gray shale originated in anaerobic conditions.

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