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 was 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'Éclairage) 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 regular intervals across the spectrum, the data are weighted by their appearance to the human eye, to give two chromaticity coordinates (x and y) and a measure of luminosity (Y%). Thus, by measuring both clays and their matching rock color standards, it is possible to minimize subjectivity. But do the color data have any real meaning?

The idea of this research was to look for relationships between fiber optic reflectance data and an independent physical property of clay – electrical impedance. Electrical resistance to a direct current is measured in ohms. But if we attempt to measure the resistance of a complex system like clay using a direct current and metal electrodes, then electrochemical reactions occur on the electrode surfaces to create miniature batteries, so now the sample is between two slowly changing resistances. This can be avoided by using an alternating current whose frequent changes of current direction cancel electrochemical changes, but now any insulating components in the system act as storage 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 opal glass plate from a Zeiss Elrepho 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.

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

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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
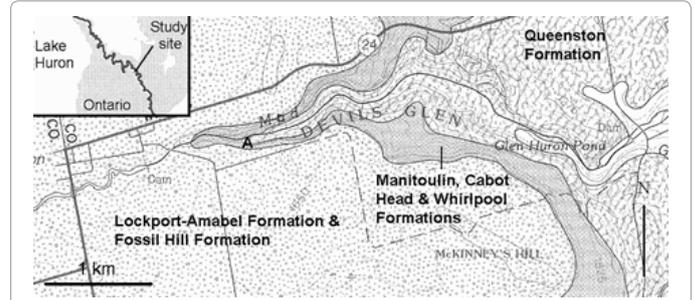

Figure 1: Location of the groundwater stream (site A), adapted from Tovell's map F-2 [3].
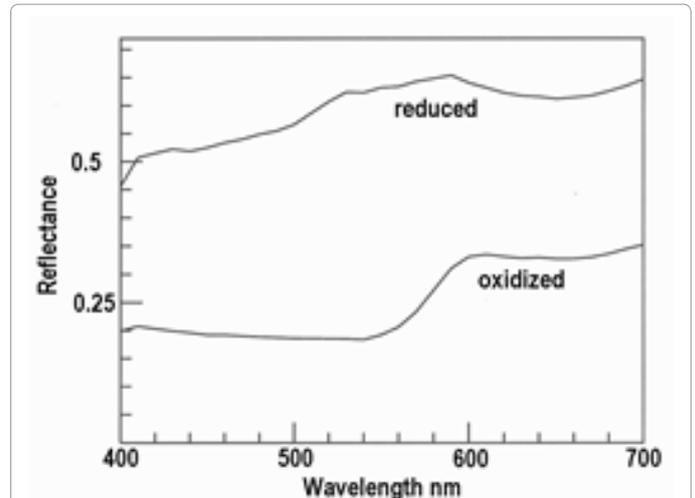

Figure 2: Fiber-optic reflectance spectra measured from the Munsell rock color chips for reduced clay (greenish-gray, Munsell 5G 6/1) and oxidized clay (grayish-red, Munsell 5R 4/2).
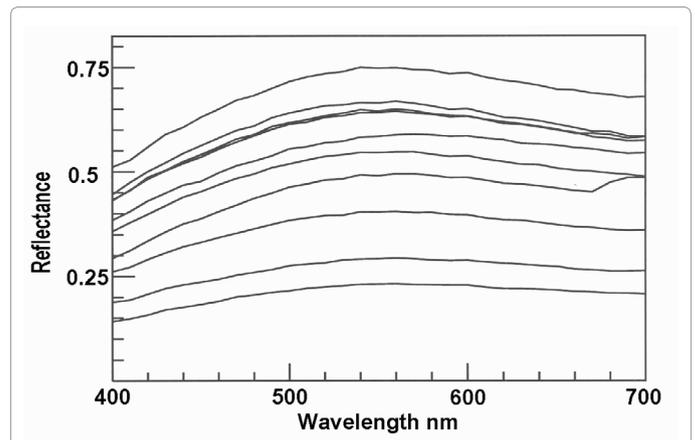

Figure 3: Fiber-optic reflectance spectra of reduced clay.

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.
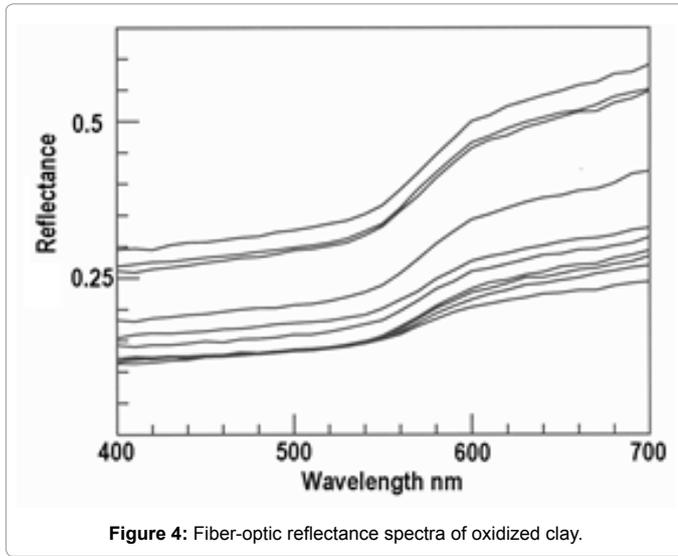
Figure 4: Fiber-optic reflectance spectra of oxidized clay.

	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	5.88 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 1: Capacitance (C, farads) and resistance (R, ohms) in parallel at three different frequencies (Hz) for reduced and oxidized clays.

	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

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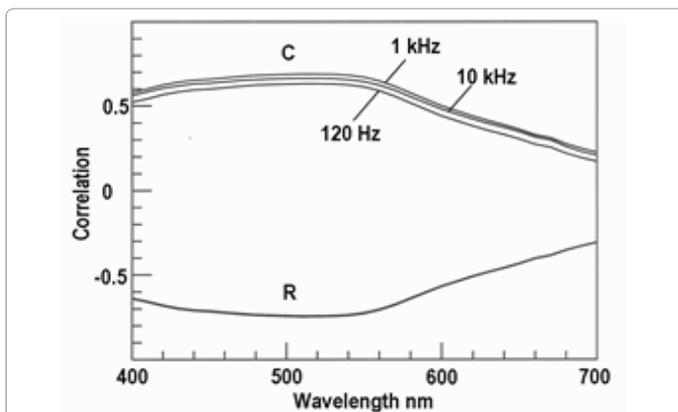

Figure 5: Correlations of fiber-optic reflectance with capacitance (C) and resistance (R) at three frequencies (Hz), all three frequencies for R gave the same result.

Shale color

Above the clay collection site was an erratic reef of Devonian fossil coral, *Eridophyllum seriale* [16]. The matrix between the corallites was only several millimeters in width and contained colored shale (Figure 6). As seen in Figure 7, the matrix permeating this ancient coral was within the statistical range of oxidized grayish-red shale.

Groundwater stream hydrology

The groundwater entering the stream above the colored clays tended to have a low pH in the winter and a high *p*H in the summer (Figure 8). The mean pH in the stream above the clay site was 7.24 ± 0.23 but increased (P<0.001, n=70) as water passed over the clay site to pH 7.84 ± 0.21 as a consequence of CO_2 degassing. Degassing was affected by water temperature through the year, so that water temperature was correlated with pH (r=0.30, P<0.01, n=70).

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

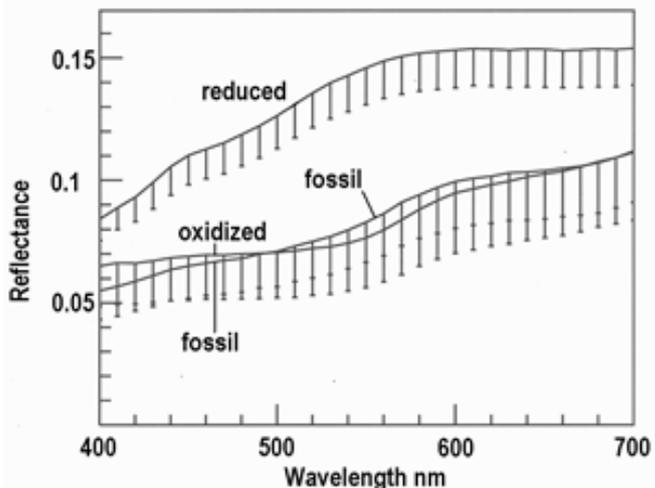**Figure 6:** Shale matrix permeating the Devonian coral, *Eridophyllum seriale*.

Figure 7: Fiber-optic reflectance spectra of reduced and oxidized Queenston Formation shales compared with the shale matrix between the corallites of the Devonian fossil coral, *Eridophyllum seriale*. Error bars show standard deviations.
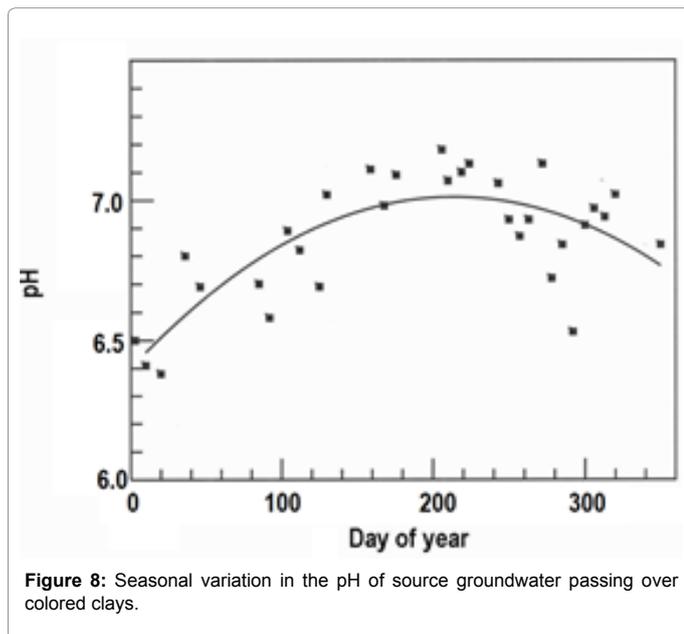
Figure 8: Seasonal variation in the pH of source groundwater passing over colored clays.

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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