Buried Pre-Illinoian-Age Lacustrine Deposits with "Green Rust" Colors in Clermont County, Ohio[1]

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Abstract. Buried, Pre-Illinoian-age lacustrine deposits found in at least two separate bedrock valleys in Clermont County, OH, exhibit brilliant colors of "green rust" that alter rapidly when exposed to oxygen. In these settings, the materials are leached of calcium carbonate but the iron has not undergone the redoximorphic depletion typically observed in gleyed hydric soils. Water movement has been exclusively through fractures and along varved bedding planes for approximately 700,000 years, indicating that in these settings, matrix flow is not occurring. The overlying Pre-Illinoian-age Backbone Creek glacial till also exhibits gleyed coloration but these materials are not leached of calcium carbonate. These materials also oxidize when exposed to air, indicating that again, the iron is not removed from the till. A possible correlation to similar permeability properties in northwest Ohio Late-Wisconsinan-age lacustrine materials and fine-grained tills is drawn. The "green rust" provides evidence for minimal to no matrix flow in fine-grained materials and supports the Ohio Fracture Flow Working Group recommendation that water movement along fractures, varved bedding planes, through sand stringers, and along paleosol unconformities be assumed unless matrix contributions have been documented and can be confirmed in these settings.

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INTRODUCTION

While the discoveries documented here are geologic and have hydrogeologic implications, the descriptions and analyses were conducted using soil science techniques. This choice of analysis tools allowed the authors to link the information developed for these sites to available published soils information worldwide. The use of the terms "green rust" and general mineral color descriptions used here follow the standard soil science applications as discussed in Bigham and others (2002). The use of the term "goethite" refers only to the yellowish-brown goethite color (Schwertmann 1993) that has been applied to the general color descriptions. It does not indicate laboratory crystallography confirmation of the actual presence of the goethite mineral.

The Discovery

Lacustrine deposits with unstable blue-green colors typical of "green rust" were discovered as part of ongoing investigations conducted by Clermont County and the Ohio Environmental Protection Agency (Ohio EPA). The investigations were related to the final closure and post-closure operations of the CECOS International Hazardous Waste Landfill (Fig. 1). "Green rust" deposits were found in the lowest, unconsolidated Clermont lacustrine unit at the CECOS site. Subsequently, discovery of similar materials as ripped up "clay balls" in the oldest Pre-Illinoian-age deposit at the Backbone Creek exposure near Batavia, OH, documented in Weatherington-Rice and others (2006), were made. These two discoveries are perhaps the first documentation of materials demonstrating such a brilliant "green-rust" coloration in Ohio's geologic and soils literature.

The "green rust" materials are older than the typical Late-Wisconsinan-age and Holocene-age lacustrine-derived soils of northwest Ohio that typically have gleyed (redoximorphic depletion) colors with Munsell (1947) chromas of 1 or 2. The Clermont County "green rust" is neither shallow nor young, and its coloration is richer with higher chromas than the typical gleyed soils. Munsell hues of blue, blue purple-blue, and purple-blue in the unoxidized state found at the two sites, are far more brilliant than the Munsell colors typically reported in the literature for "green-rust" pigmented materials.

Figure 1. Location map CECOS site and Backbone Creek till cut site, Clermont County, OH.

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The Clermont County materials demonstrate the usual rapid oxidation to yellowish-brown goethite color (Schwertmann 1993) when exposed to air. "Green-rust" pigmented iron compounds can be synthesized successfully in the laboratory but their stability is limited in an oxygen-rich environment (Genin and others 1998). This paper does not purport to fully explain the chemical parameters that allowed the "green-rust" pigmented lacustrine materials to form, but there is significant discussion relating to their survival.

CECOS Facility History

The CECOS facility was first opened as an independent sanitary waste operation in 1972, and began taking industrial hazardous wastes in 1976. This now-closed hazardous waste and solid waste landfill is located in Jackson Township, just south of US Route 50. The site is drained by Pleasant Run Creek, which flows into the East Fork Little Miami River just north of the Ohio Department of Natural Resources (ODNR) reservoir, Lake Harsha. The lake also serves as one of the primary water supplies for Clermont County. Contaminated leachate from the landfill has been documented entering the surface water supply for Williamsburg, OH, whose intake is just upstream from Lake Harsha.

Because of the historic contamination event(s), both Clermont County and Ohio EPA, through their Divisions of Drinking and Ground Water and Hazardous Waste Management, are working toward a final closure/post-closure program at the site that would include "in perpetuity" monitoring of the surface and ground water. Bennett & Williams Environmental Consultants Inc., Columbus, OH, have been involved in review and oversight of the site, first for Ohio EPA Southwest District Office (SWDO) and then for Clermont County, since the early 1980s. Concerns about contamination from the CECOS landfill entering the regional ground water flow were discussed by Greg Schumacher (1995), ODNR Division of Geological Survey.

Geologic Location

The CECOS facility is located on the south side of a segment of the ancestral East Fork Little Miami River drainage basin (Schumacher 1995), here represented by a deep, east-west trending, bedrock joint-controlled valley that has been cut into the Ordovician interbedded limestone and shale bedrock of the Fairview and Grant Lake (both the lowest Bellevue and middle Corryville members) formations of central Clermont County. The bedrock valley at this location appears to be floored just above the Kope Formation, but with depth to the west, the valley probably also intersects the Kope (Weatherington-Rice 2003). This valley is parallel with other joint-controlled east-west bedrock valleys that are part of the ancestral East Fork Little Miami River drainage system. These valleys were tributary valleys to the Manchester River, part of the Teays-Age Drainage System, which controlled most of Ohio's surface drainage before the advent of the Pleistocene Ice Ages (Ray 1974).

The bedrock valley under the site is filled and the surrounding uplands are blanketed with a series of lacustrine, alluvial, and glacially derived deposits that infilled the valley after the blockage and reversal of the Teays River drainage system in Ohio. The general stratigraphy of the unconsolidated material consists of the oldest Clermont Formation which include a lacustrine unit, the Pre-Illinoian-age Backbone Creek Till and the two Illinoian tills, the lower Batavia Till and the upper Rainsboro Till. All formation names are working names because these formations have not been described elsewhere and formally named in the literature, except for the covering Rainsboro Till name, which has been historically used in other counties in the glaciated south and southwest portion of Ohio.

Historical Review

Approximately 400 borings were drilled as part of the CECOS site development, monitoring, and closure efforts. Logs of borings to bedrock in the buried valley section of the site often would reference a "blue," "blue-green," or "green" clay or silty clay as the last deposit sampled before encountering bedrock. The color description was at odds with the typical "brown," "gray," and "tan" used to describe most of the other unconsolidated deposits encountered in the drilling efforts at the site (the pre-Illinoian-age Backbone Creek Till was often described as "olive," "olive green," or "olive brown"). The color description created puzzlement and was occasionally the source of discussion at Ohio EPA and at Bennett & Williams. No references could be found that identified such a color in unlithified materials in that portion of Ohio. Geologists speculated that the materials might be colored by deposits of glauconite ($K(Fe,Mg,Al)_2Si_4O_{10}(OH)_2$), which is a hydrous silicate of iron and potassium, or by vivianite ($Fe_2P_2O_8{\cdot}8H_2O$ or $Fe_3(PO_4)_2{\cdot}8H_2O$), a hydrous ferrous phosphate (Dana 1966; Carlson 1991). Since no samples were available for review, the unusual color remained a mystery until December 1998 and January 1999 when a subsurface investigation near the CECOS site, for the Clermont County Commissioners, encountered the unit in two borings.

MATERIALS AND METHODS

As part of a major re-evaluation of the CECOS site, the Clermont County Commissioners authorized the drilling of four geologic borings and the construction of one monitoring well on surrounding properties. Three borings and the monitoring well were constructed on the Rowan property to the east. One boring was undertaken at the Hartman historical cabin to the north of the intersection of US Route 50 and Aber Road. The borings were advanced by hollow stem auger and continuously sampled. Field notes were taken, and each core was placed into a wooden or cardboard core box and photographed in the field.

The complete cores, including the portions exhibiting "green rust" characteristics, were then carefully logged and photographed in the lab. Because of the number and respective ages of the Pleistocene units encountered, with the potential for intervening paleosols, the core descriptions were developed and written to establish the soils record, the glacial and bedrock geologic record, and the geotechnical record. Representative samples were collected and subjected to typical laboratory analyses, including bulk density, grain-size analyses, textural classification, and several saturated hydraulic conductivity tests (see Tables 1 and 2). Tables referenced here are abbreviated to contain only the information for the Clermont lacustrine unit section of the whole cores. These analyses were performed to match the historical geotechnical analyses that had been conducted on other samples from the site.

In addition, seven of the samples were tested for total organic carbon content, percent calcite and dolomite to establish calcium carbonate equivalence (CCE), and clay mineralogy (see Tables 3 and 4). One sample was sent to the Calmar Soil Testing Labs in Westerville, OH, for a full agronomic analysis (see Table 5). A sample of the "green rust" portion of the Clermont lacustrine zone was left whole and undisturbed, wrapped tightly in clear plastic wrap, and frozen for additional mineralogical analyses and future research. A portion of that sample was later forwarded to Denmark for analyses of the

Table 1

"Green Rust" laboratory analysis sample summary.

Sample Summary		USDA ARS Soils Lab				OSU Soils Lab			Other Labs	
Boring Run Sample #	Depth of Run	Depth of Sample	Grain Size Texture	Bulk Density	Sieve (subset)	Clay Mineralogy	Total Carbon	% CCE*	Other Tests	Run By
#3-12	52.5-57.5'	grab, 54'	X	X						
#3-12	52.5-57.5'	55'	X	X			X	X		
#3-12	52.5-57.5'	56.6'	X						Polarity-age	U of Akron
#3-13	57.5-62.5'	58.5-58.75'	X	X						
#3-13	57.5-62.5'	58.6'			X	X				
#4-29	125.5-130.5'	126-126.5'	X							
#4-29**	125.5-130.5'	127.5'	X						Agronomic	CALMAR Labs
#4-29	125.5-130.5'	128.6-129'	X	X	X	X				
#4-29	125.5-130.5'	130'	X							

* %CCE = Percent Calcium Carbonate Equivalent
** Boring Run Sample # 4-29, 127.5' is a thin buried paleosol of Plesitocene age, approximately 700,000 yrs Before Present.

Table 2

Results of samples analyzed by the USDA ARS soils lab.

Boring Run Sample #	Depth of Run	Depth of Sample	Grain Size % Clay	Grain Size % Sand	Grain Size % Silt	USDA Texture	Bulk Density g/cm^3
#3-12	52.5-57.5'	grab, 54'	20	7	73	silt loam	
#3-12	52.5-57.5'	55'	67	1	32	clay	1.69
#3-12	52.5-57.5'	56.6'	49	7	44	clay	
#3-13	57.5-62.5'	58.5-58.75'	22	8	70	silty clay	1.88
#4-29	125.5-130.5'	126-126.5'	4	87	9	loamy sand	
#4-29*	125.5-130.5'	127.5'	29	13	59	silty clay	
#4-29	125.5-130.5'	128.6-129'	46	5	48	silty clay	1.87
#4-29	125.5-130.5'	130'	11	59	30	sandy loam	

* Boring Run Sample # 4-29, 127.5' is a thin buried paleosol of Plesitocene age, approximately 700,000 yrs Before Present.

TABLE 3

Samples analyzed by the OSU soils characterization lab for grain size and clay mineralogies.

Boring Run Sample #	Depth of Run	Depth of Sample	Sample Weight (g)	Grain Size*			USDA Texture	OSU Lab Sample #	Clay Mica (Illite)	Kaolinite	Chlorite	Vermiculite	Quartz	Feldspar
				Clay	Sand	Silt								
#3-13	57.5-62.5'	58.6'	12.05 g	24.1	21.1	54.8	silt loam	309	40-55%	10-25%	10-25%	10-25%	<10%	<10%
#4-29	125.5-130.5'	128.6-129	8.81 g	24.1	8.2	67.7	silt loam	475	40-55%	10-25%	10-25%	10-25%	<10%	<10%

* Grain Size = The materials analyzed at this part of the process are a subset of the original, so grain size and texture will vary from the original sample.

"green-rust" mineralogy. The paleomagnetic signature of an oriented sample was measured for age dating by polarity.

RESULTS

Full results of analyses for all the units encountered in the four borings are presented in Appendix E of Weatherington-Rice (2003). The results for the Clermont lacustrine unit are summarized and presented in Tables 1 through 5. The most surprising discovery involved sections of the Clermont lacustrine deposit that exhibited a strong turquoise blue color not found on Munsell soil or rock charts (Munsell 1947). The most common color observed was the Munsell color 10BG (Blue Green-Blue) 5/6, with colors darkening to 3/6 at the base of the Hartman No. 4 boring. This material oxidized quickly to a yellow-brown color when exposed to air. It was clear that this must be the elusive "blue," "blue-green," and "green" of the historic CECOS boring logs dating back to the early 1970s. The unusually colored section of the Clermont unit was encountered in the Rowan No. 3 boring (Appendix D of Weatherington-Rice 2003) at 57.5 feet below the surface. The color persisted to 62 feet in depth.

The core sample shown in Figure 2 came from the upper portion of sample 3-13, 57.5 to 61.25 feet. The most vividly blue-green of the samples (keyed to 10BG (Blue Green-blue) 4/6), oxidized very quickly. Within a few hours, fresh surfaces changed to colors more representative of the yellowish-brown goethite color typical in oxidized soils (Schwertmann 1993; Dana 1966). Where the lowest Clermont unit is encountered at the Hartman No. 4 boring location, it is much deeper in the main buried valley, and the setting produces a different set of conditions. While some of the unit exhibits the "green rust" characteristics found at Rowan No. 3, the colors are slightly different and the total thickness is much less.

The original core samples from a number of the CECOS borings drilled while the site was still in operation were also observed. The samples had been in core boxes for some period of time, in some cases 20 years or more, and were dried out. All samples from the Clermont deposits had lost their gleyed or "green rust" coloration, due to oxidation. However, with the passage of time, the remaining "cornflower blue" mineral inclusions also found in these units, which may be vivianite crystals, retained their coloration and, if anything, had only deepened in color. This identification of vivianite must be considered a field verification only. No samples of the "cornflower blue" crystals were available for laboratory analysis so the exact composition cannot be confirmed at this time.

While there have been no other noted references to vivianite in Clermont County, Carlson, in his standard reference, *Minerals of Ohio* (1991), lists vivianite crystals as having been found in Brown, Hamilton, Montgomery, and Warren counties in southwestern Ohio. The setting for Hamilton County is not dissimilar from the one here where "small globular masses of vivianite in sand and loam" was noted. Carlson's mineral reference was Orton and Peppel who published their observations in 1906.

DISCUSSION

The Critical Discovery

The most significant finding from this set of observations is the discovery of what appears to be unstable "green rust" deposits at two different locations (in borings

TABLE 4

Sample analyzed by the OSU soils characterization lab for C and CO^3.

Boring Run Sample #	Depth of Run	Depth of Sample	% Total Carbon	% Organic Carbon	% Calcite	% Dolomite	% Calcium Carbonate Equivalence (CCE)
#3-12	52.5-57.5'	55'	2.83	2.6	0	1.7	2

Table 5

Sample analyzed by the CALMAR soil testing labs.

Boring Run Sample #	Depth of Run	Depth of Sample	% Organic Matter	Bray P1 Lbs/A*	K Lbs/A*	Mg Lbs/A*	Ca Lbs/A*	Soil pH	CEC**	% Base Saturation			S Lbs/A*	Zn Lbs/A*	Mn Lbs/A*	B Lbs/A*	Cu Lbs/A*	Fe Lbs/A*
										% K	% Mg	% Ca						
#4-29	125.5-130.5'	127.5'	3.7	68	239	820	5018	7.3	16.3	1.9	21	77	176	2.9	10	0.7	14.7	185

* Lb/A = Pounds per Acre. This is an agronomic unit and it represents the amount of the element already available for plant uptake in the soil profile.
Bray P1 is a test for phosphorus.
** CEC = Cation Exchange Capacity

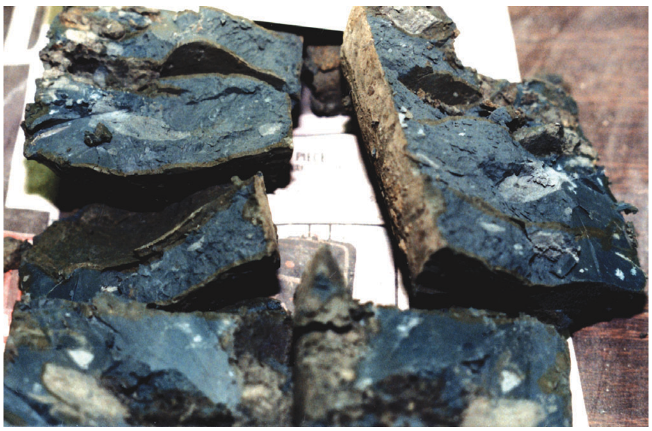

Figure 2. Sections of the Clermont oldest lake deposit from Rowan No. 3. The matrix materials of the lacustrine varves are colored a deep turquoise blue (10BG (Blue Green-Blue) 4/6) (Munsell 1942) by iron pigmentation in its "Green Rust" stage. The matrix materials have remained in suspended partial oxidation hydrolysis for up to 700,000 years. Faces of the varves, which have been exposed to the flow of ground water, have continued to slowly oxidize to magnetite. Picture taken by Julie Weatherington-Rice, Winter 1999.

at the CECOS site and in the stream cut at Backbone Creek) in Clermont County. While co-author Bigham has been unable to stabilize the mineral deposit long enough to obtain a chemical signature in the laboratory, the color and behavior of the materials parallel synthetic preparations of "green rust" in his laboratory and in his observations of the mineral in industrial settings. The brilliant colors associated with "green rust" are caused by the presence of iron in mixed valence states in a so-called double hydroxide structure $[Fe(II)_{1-x}Fe(III)_x(OH)_2(Cl^-,SO_4^{2-},CO_3^-)_x]$ (Bigham and others 2002). Due to the presence of (Fe ll), "green rust" must be maintained in an oxygen-free environment to prevent its oxidation and conversion to goethite, lepidocrocite, maghemite, or magnetite (Genin and others 1998; Bigham and others 2002). Possible reaction pathways are shown on Figure 3.

The samples identified were buried in the bedrock valley that transects the CECOS Hazardous Waste Landfill, representing potentially hundreds and possibly thousands of hectares of deposits in the bottom of this east-west valley. Additionally, there were samples identified at the Backbone Creek till cut, the next east-west buried valley south (Weatherington-Rice and others 2000a,b) as seen on Figures 4-A and 4-B. There, the samples were found as ripped-up "clay balls" or "till balls," derived from buried valley lacustrine clays which must have been exposed further up the buried valley during outwash deposition. These lacustrine clays were incorporated into the Pre-Illinoian-age sand and gravel deposit at the base of the Backbone Creek cut in which a thick paleosol has developed (Teller 1970). The CECOS site is approximately seven miles northeast of the Backbone Creek till cut and is situated over a completely separated east-west pre-glacial drainage channel in Clermont County. Consequently, this second discovery must indicate the existence of two different sources of similar depositional conditions and history (Fig. 1).

The materials at Backbone Creek, first deposited in a Pre-Pre-Illinoian-age lake and then reincorporated into a Pre-Illinoian-age outwash deposit that weathered to a paleosol before being covered by Illinoian-age tills, have maintained their "turquoise blue" coloration for over 700,000 years until exposed to air during site excavations. The approximate age of the materials was determined by the paleomagnetic signature of an oriented sample from one of the Clermont County borings installed near CECOS. The unit was found to have only a very weak normal polarity paleomagnetic signature, thereby indicating that the lacustrine materials were deposited either just after the time of the last polar reversal approximately 730,000 years ago (Harland and others 1990), or during a much older reversal. Given that the lacustrine infill of the buried valley did not occur until after the blockage of the Teays drainage (which is first filled with the reversed polarity Minford silts), a glacial and stratigraphic relationship can also be applied to the age of the lacustrine unit (Teller 1970). These two pieces of information bracket the age of the deposit between the deposition of the Minford Silts and the deposition of Pre-Illinoian-age glacial advances over the area. Therefore, water and air have traveled around and through fractures and bedding planes in these lacustrine materials for approximately 700,000 years or more without disturbing the chemically unstable "green rust" compounds within the preserved matrix of the formation.

This complete separation of the matrix from the regional ground-water flow system can be observed in a

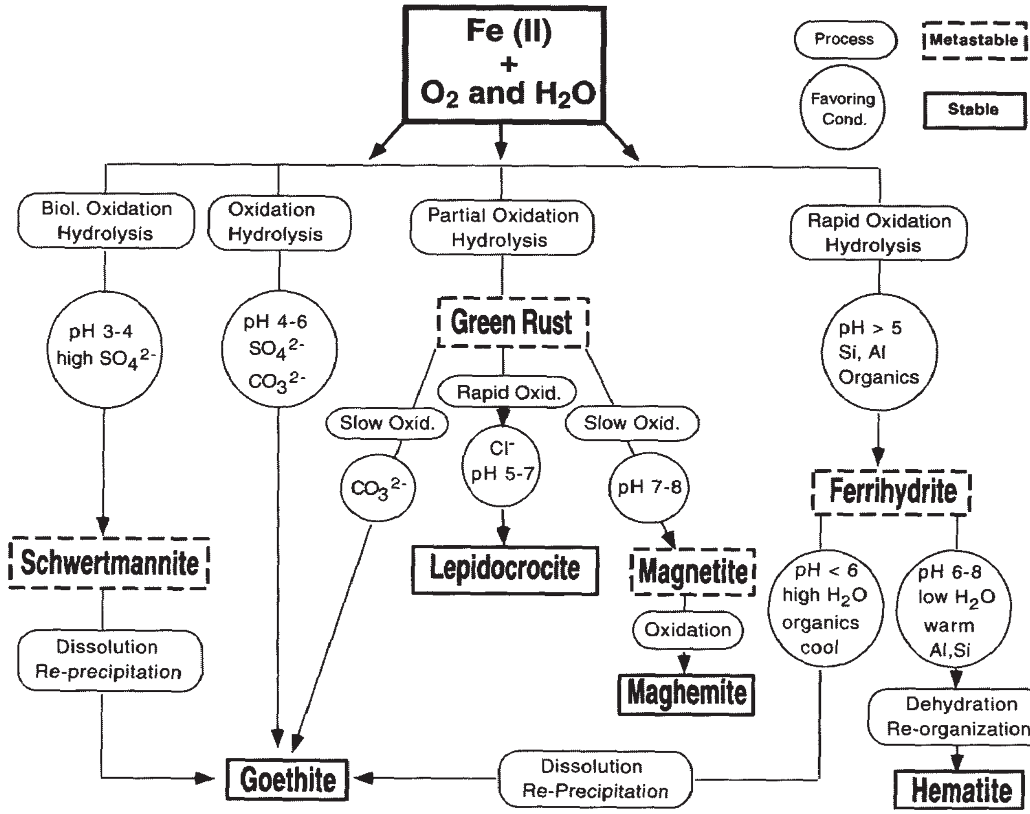

FIGURE 3. Pathways of Fe oxide formation and transformation for the Fe (II) system. Reprinted from Bigham and others (2002) with permission of the Soil Science Society of America.

photograph of the sample (Fig. 2). Note the dark coloration along the edges of the varved laminations. Here, the "green rust" in the lacustrine materials was slowly oxidized to magnetite (Fig. 3). Core samples from this unit preserved in sealed glass jars at the CECOS site were virtually black in color, demonstrating the completion of the oxidization process to magnetite.

All modern-aged water and oxygen move along the horizontal and vertical fractures in the lacustrine unit at the site, so the matrix simply was never part of the flow process. This same situation occurred in the till cut at Backbone Creek. Even though the sand and gravel deposit that makes up the deeply weathered pre-Illinoian-age paleosol may be 300,000 to 500,000 years old, during all that time, water moving through the unit went around the matrix of the clay balls and not through them, creating a rind of yellowish-brown goethite color (Schwertmann 1993) surrounding the preserved "green rust" interior.

This is incredibly significant. The matrix material can be measured for hydraulic conductivity. It is permeable, albeit, very slowly. However, if the matrix hydraulic conductivity value is entered into a ground-water flow calculation or computer model, the answer derived would not represent the conditions found at this site. All significant flow is fracture flow, and all meaningful measurements must be for the fractured flow system, not for the matrix materials.

Haefner (2000) also cautions against using laboratory hydraulic conductivity measurements of the matrix materials when trying to determine the rate of flow through fine-grained, unlithified glacial materials. While researchers have intuitively recognized the importance of fracture flow systems, most have assumed that matrix materials must also play a part in the water and contaminant storage and transport, as reflected in the double-block porosity (dual porosity, Huyakorn and others 1983) model. Apparently here in Clermont County, in this setting of buried valley lacustrine materials, with this set of grain-size analyses, and this set of clay mineralogies, the dual porosity model shuts down and the transport is through the fractures only.

Other Important Correlations

The gray-green color of gleyed soils, as they are commonly identified in Ohio's wetland settings (hydric and hydric included soils), can be attributed to the absence of iron oxides, not the presence of Fe (II)-bearing minerals like "green rust." Once the iron oxides are removed by chemical reduction, dissolution, and leaching, the gray colors of the matrix silicates and carbonates are stable and will remain so when exposed to air. Iron would have to be reintroduced to cause pigmentation. When "green rust" is present, the Fe (II) is retained in a mineral form with distinct spectral qualities. This condition implies *NO* movement of Fe(II)-rich pore waters, and persistent low redox conditions over time. The black magnetite rinds surrounding the fracture faces demonstrate

FIGURE 4. Ripped up “Clay Ball” clasts of Clermont lacustrine materials found at the Backbone Creek till cut, exhibiting the characteristic “green rust” colorations discovered in the borings around the CECOS site, next buried valley north. The unstable color of the matrix of the material was preserved in place from the time of deposition until they were discovered during a field investigation, Fall 1999. A characteristic yellowish-brown goethite color weathering rind forms around each section of the clay (Schwertmann 1993). Upon opening, the lacustrine matrix quickly oxidizes to the typical goethite colors. Photos by Julie Weatherington-Rice.

Fig. 4-A: Photo of an *in situ* “Clay Ball” after the yellowish-brown goethite color rind is removed (Schwertmann 1993). The deep rust colored portion of the ball is 10R (Red Yellow-Red) 3/6, dark red (Munsell 1954), less oxidized portions are 5PB (Purple Blue) 4/10, royal blue (Munsell 1942). Photo width is approximately 1.0 m. (See next page for Fig. 4-B.)

a slow oxidization process (Fig. 2), and the matrix materials, including “green rust,” are preserved.

The “green rust” structure requires an anion (CO_3^{2-}, SO_4^{2-}, Cl^-, or OH^-) to balance the positive layer charge arising from partial oxidation of Fe(II) to Fe(III). The carbonate ion would seem a good possibility, but the Clermont County lacustrine deposits are leached of calcium carbonate and therefore do not react when sprayed with dilute hydrochloric acid. Two attempts were made to analyze the “green rust” samples in the Soil Characterization Laboratory at The Ohio State University, one simply in open air and one in an argon-filled chamber. In each case, the oxidation process was too rapid to allow for full characterization. At this point in time the authors have not confirmed the anion involved at these sites.

One very interesting correlation can be made between the presence and/or absence of gleyed colors in the deposits in the CECOS area. Only two of the parent materials exhibit gleyed colors, the Clermont lacustrine materials and the pre-Illinoian-age Backbone Creek Till. Since the broader Clermont classification takes into consideration regolith paleosols and the various peat deposits formed in the shallowing lakes, there are several groups of yellow-red colors demonstrating various stages of oxidation of the iron pigmentation as well. The “green rust” conditions of the Clermont lacustrine materials can ONLY be preserved if no water moves through them. Therefore, in this setting, the only pathway for groundwater movement is through the fractures. The matrix materials are not involved in water and/or contaminant transport at the site.

The Backbone Creek Till was formed from local materials that were incorporated as the ice moved over the Pre-Illinoian-age landscape in Clermont County. Since the tills were deposited before much of the parent materials could be exposed to oxygen or leached of iron, it appears that they were deposited in their original gleyed condition. Common color references to the Backbone Creek till in boring logs are “olive,” “olive green,” or “olive brown.” Unlike the Clermont lacustrine unit, however, these materials were not leached and react to

Fig. 4-B: Close up of interior "Clay Ball" shown. Matrix of large section to the right is 5B (Blue) 5/6, sky blue (Munsell 1942). The small sections on the left side of the photo are 5PB (Purple-Blue) 4/10, royal blue, and 5RP (Red-Purple) 3/8, magenta (Munsell 1942). Note halo of oxidized materials around the excavated "Clay Ball." Width of photo is approximately 0.5 m.

dilute hydrochloric acid. While they do not exhibit the vibrant colors of the Clermont lakebeds, these deposits also exhibit zones and fractures with oxidized colors and the surfaces of samples also oxidize, although more slowly than the Clermont lakebeds, when exposed to air.

Possible Correlations to Late-Wisconsinan-Age Deposits in Northwest Ohio

There are other places in the state where the same pattern can be seen. In northwest Ohio, the fine-grained lacustrine deposits of glacial-stage Lake Erie, from the Lake Maumee shorelines to current sediment being deposited in Lake Erie, are often described as gleyed. Additionally, where these fine-grained parent materials were incorporated into the tills of the Wabash, Fort Wayne, and Defiance end moraines and the intervening ground moraines, they are also often described with gleyed colors. Where the soils formed on these materials have remained in a hydric redoximorphic condition, the gleyed coloration remains but the iron is removed. The parent materials, however, maintain their iron. Does this maintenance of the gleyed states of iron pigmentation mean that the matrix of these saturated parent materials, originally deposited in water, have never completely dried out? If the matrix materials have never had their connate waters removed by desiccation and/or the historical lowering of water tables in the region, does this mean that all regional dewatering has been along fractures and matrix borders only? Have the internal matrix portions of the materials never been exposed to oxygen since deposition? Does it mean that here, too, the movement of water and contaminants is not one of dual-porosity but rather one of fracture flow only?

On the other hand, the color descriptors for the Illinoian-age Rainsboro and Batavia tills, which are not gleyed, are very typical of colors seen in Late-Wisconsinan-age tills in southern and central Ohio, south of the lacustrine dominated fine-grained tills of the post-Erie Interstadial (Flint 1971). When these tills are viewed fresh cut in the field, they look very much like the younger Late-Wisconsinan-age tills, being distinguished only by their location south of the mapped Late-Wisconsinan-age advances, the depth of leaching, the thickness of the soil horizons, and the covering of wind-blown loess. Quinn and Goldthwait (1985), when viewing both the Illinoian-age Rainsboro and the Late-Wisconsinan-age Caesar tills in Ross County, discussed the great similarity that existed between these two tills. One of the compelling similarities was the color of the tills, even though there was a significant difference between the overlying soils. The tills also represented depositional events perhaps 100,000 years separated in time. Does the absence of gleyed coloration in these materials mean that they have drained since deposition?

Correlation with Other Naturally Occurring "Green Rust" Deposits

There has been limited research conducted on naturally occurring "green rust" deposits because they oxidize so quickly that, if encountered in the field, they are generally lost before they can be studied in the laboratory. One notable exception however is the paper by Genin and others (1998), which discusses, at length, samples taken from three sites in Brittany, France, at Fougeres, Quintin, and Naizin. None of these sites had anything in common with the glacially buried valley sites in Clermont County.

In all cases, the French samples were extracted from waterlogged soils less than 2.0 m in depth. The Fougeres site is a residual soil formed from a granitic saprolite. The Quintin site is also a granitic saprolite. At the Naizin site, the soil was formed in a colluvial-alluvial system on top of a schistose saprolite. While the samples that were left to oxidize in the air underwent the typical shifting in color, even the most vivid coloration of the Fougeres site only began as greenish-gray (5BG 6/1), a much paler color with a lower chroma than the "green rust" seen in Clermont County. The Quintin site began slightly darker as 5BG 5/1 and the Naizin samples as a slightly more yellow greenish-gray (5GY 6/1). In addition, none of the French sites had associated ferrous minerals, such as siderite or vivianite.

By visual identification, vivianite crystals may have been found in a number of the core samples that have intersected the Clermont lacustrine materials in the buried valley. Siderite ($FeCO_3$), or "clay ironstone," is one of the most common sources of iron ore found in Ohio. The Ordovician of Clermont County is strongly basic in nature, consisting mainly of limestones, dolomites, and carbonate rich marine shales, all of which can contribute carbonate anions to iron. However, the materials that exhibited the most brilliant "green rust" coloration were, in fact, leached, and did not react to dilute hydrochloric acid so, in at least these cases, the carbonate anion is not the completing anion.

SUMMARY AND CONCLUSIONS

Typically, when soil scientists study soil profiles, an identification of gleyed colors includes both a redoximorphic depletion of iron and an accumulation of that same iron in other portions of the soil matrix. These are leached conditions where the iron mineral is actually removed from (portions of) the soil horizon and the resulting gleyed color remains stable. Since there is no remaining iron to oxidize in the gleyed portions of the profile, the color will not revert unless iron-rich water and/or materials are reintroduced into that portion of the soil matrix, replacing the leached iron. This condition has been long recognized and recorded in soils literature. An informed discussion can be found in Bigham and others (2002).

That is NOT what has happened at the locations in Clermont County. In the Clermont lacustrine materials, the materials are carbonate free, but the iron in the material matrix has remained suspended in a combination of both Fe (II) and Fe (III) states for approximately 700,000 years. This abundance of "green rust" is simply not documented on a regular basis in the soils literature although Bigham has observed the actual colors in both laboratory settings and in ore processing sludges, where the materials oxidize rapidly as soon as they are exposed to oxygen. Clearly, in the buried Clermont lacustrine unit at CECOS and in the Backbone Creek paleosol "till balls," the pathway for water and contaminant migration is through fractures, between the varves, and around the "till balls." While it is possible to measure the hydraulic conductivity of the matrix materials in the laboratory, this measurement is not relevant to a prediction of how rapidly water and contaminants would move through these materials. This setting is not a "double-block porosity" setting; it is a "fracture only" setting.

The conclusions that can be drawn from the gleyed Backbone Creek Pre-Illinoian-age tills are less clear. Here again, the iron has not been removed. These materials, when exposed to air, do oxidize to more traditional colors. However, these materials are also not leached of their calcium carbonate composition. Like lime tills of younger ages in Ohio, these materials will react to dilute hydrochloric acid. There is a significant soil profile found on these materials (Weatherington-Rice and others 2000a,b, 2006) and oxidized iron along the fractures in the underlying materials. Given that set of conditions, it appears that from the period of time since their deposition until now, any water and/or contaminants moving through this unit moves through fractures and other shortcuts. If acidic rainwater had been moving through the matrix materials for all of that time, then the materials would be leached and the iron removed as in the paleosols above them. That is not the case here. If carbonate-rich water had been moving down from the Illinoian-age surface, then the paleosols would have recalcified. That also did not happen and the thick leached "A" and "B" horizons are preserved on top of the Backbone Creek Till.

The Backbone Creek Till materials bear a striking resemblance in color and mineralogy to the unleached, gleyed colored lacustrine and lacustrine-based fine-grained till parent materials found in northwest Ohio. In northwest Ohio, like the Backbone Creek setting, these materials are unleached and they also react with oxygen, unlike the gleyed hydric soils that cap them. It is this characteristic, to oxidize when exposed to air, that triggered the original interest in the Ohio Fracture Flow Working Group (Weatherington-Rice and others 1993, 1994). Many questions remain. Is it possible to take the information discovered at the Clermont County sites and project the same conditions to the fine-grained northwest Ohio deposits? Do they also actually exhibit a condition without matrix interaction where all movement of water and contaminants is through the fractures, between the varves, through the sand stringers, and along the paleosol unconformities? Clearly, this topic needs additional research to determine the actual contribution of the parent material matrix to storage and flow. In the meantime, we recommend assuming that flow is predominately through the fractures, varves, sand stringers, and paleosols in these settings unless proven otherwise.

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