Fracture Wall Cements and Coatings from Two Clayey Till Aquitards

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Abstract

Secondary minerals occurring at the faces of fractures, the only reliable visual evidence of the presence of hydraulically conductive fractures in clayey un lithified aquitards, have been characterized for two uncontaminated field sites, Dalmeny, Saskatchewan, and Laidlaw, Ontario. Preliminary identification of secondary minerals and their variations with depth was made using a Munsell® Color Chart. Subsequent microscopic analyses (petrography, electron microprobe analysis, scanning electron microscopy, and X-ray diffraction) were used to identify iron-oxide mineralogy. Iron oxides were identified as goethite, ferrhydrite, and hematite at Dalmeny, where they occur to depths of 10 to 15 m, and goethite and ferrhydrite at Laidlaw, observed to depths of 7 m. In both cases, the identification of ferrhydrite was tentative due to the problems of small sample size and peak overlap in X-ray diffraction. The iron oxides do not form coatings on the surfaces of the fractures as had been previously thought; rather they form cements linking the matrix grains. Thus there is potential for decreased permeability and increased surface reactivity parallel to and inward from the fracture faces. The pattern of iron-oxide distribution suggests that the youngest depositions, and those with the greatest surface reactivity and potential for contaminant retardation, are found at greatest depths in the fractures. Manganese oxides form in isolated clusters in larger pores and indentations, although the exact manganese minerals could not be firmly identified.

Introduction

Much of the current research on clay-rich, un lithified aquitards has been on their increased permeability due to the presence of hydraulically conductive fractures and the implications for contaminant transport (McKay and Fredericia 1995; Keller et al. 1986; Grisak et al. 1976; Grisak and Cherry 1975; Jonge nsen and Fredericia 1992). In the field, fractures are difficult to detect visually except where their surfaces are coated with secondary minerals. These coatings, usually identified cursory as iron and manganese oxides (Fe and Mn-oxides), are pervasive in the weathered zones, which may be up to tens of meters deep, and frequently extend below the interface between the weathered and unweathered zones in clayey till aquitards.

The presence of minerals other than Fe- or Mn-oxides such as clays, calcite, and gypsum has also been reported on fracture faces in un lithified aquitards (Klint 1996; McKay and Fredericia 1995; Keller et al. 1991; Hendry et al. 1986). Secondary minerals occurring on fractures in tuffs, sandstones, and granites—referred to as fracture skins, coatings, or Liesegang bands—have been examined by Sharp et al. (1995), Fu et al. (1994), Wood et al. (1993), and Carlos et al. (1993). These studies indicate that the coatings reduce permeability at the fracture surface. Soll and Birdsell (1998) and Moench (1984) demonstrated, by use of numerical analyses, that the presence of coatings influenced flow and solute transport in fractures and the adjacent matrix.

Although they are the materials first encountered by fluids migrating in fractures in clayey till aquitards, little is known of coating mineralogy and distribution, or potential to impede contaminant movement. The mineralogy, surface area, and crystallinity of coatings will affect the fracture surface chemistry and, thus, may influence the transport of natural dissolved constituents and contaminants both along and into the fracture face. Secondary mineral coatings at fracture walls have the potential to alter the porosity and permeability of the matrix, thus knowledge of their distribution in relation to the matrix is essential for understanding ground water and solute movement across fracture surfaces. In addition, any geochemical modeling of water/rock interaction, including adsorption modeling, is based on identification of the stoichiometry and thermodynamic parameters of the minerals involved in the reaction. Incorrect assumptions regarding these minerals can lead to large errors in calculated water compositions.

In this study, we sought to characterize secondary minerals on fracture faces from two well-documented field sites, Dalmeny, Saskatchewan and Laidlaw, Ontario, both situated in clay-rich glacial sediments (Keller et al. 1988; Keller et al. 1991; Klint 1996; McKay and Fredericia 1995). The first of three goals was to develop a procedure, using a combination of macro- and microanalytical techniques, for analyzing secondary mineral coatings from samples where both the host matrix and the coating are clay-sized, and the volume of coating material, in comparison to the host matrix, is very small. The second goal was to use the procedure to identify the min-
eral salts and to describe the grain size, morphology, and distribution of coating minerals in relation to the matrix. The third goal was to test the hypothesis of the formation of Fe-oxide coatings.

The hypothesis for Fe-oxide coating formation is similar to that posed by Bermer (1969), to describe the formation of Fe-oxide rich layers in ocean sediments. We propose that Fe-oxides form at the interface between the relatively reducing conditions within the pore water of the matrix and relatively oxidizing conditions within the fracture. Reduced aqueous Fe diffuses toward the fracture face and dissolved oxygen from the fracture diffuses into the matrix. As Fe²⁺ reacts with O₂ near the interface, Fe-oxides are precipitated, as long as the activity product of dissolved oxygen and reduced aqueous Fe is large enough to enable the formation of particular Fe-oxide minerals at ambient conditions.

The conditions under which Mn-oxides form are poorly understood, thus we make no attempt at positing a hypothesis. Because of the complexities of this mineral group, and the extremely fine-grained nature of the Mn-oxides, our identification of Mn-oxide mineralogy is tentative and is reported elsewhere (Corrigall 1998).

Field Sites

Two field sites, one in southern Saskatchewan (Dalmeny) and one in southwestern Ontario (Laidlaw), were selected because their geology and hydrogeology have been characterized in numerous previous studies and because the ground water is uncontaminated (Figure 1). At both sites, vertical and horizontal fractures have been identified visually by the presence of secondary minerals on their faces. Secondary minerals on fracture surfaces can be observed to depths of about 10 to 15 m at Dalmeny and up to 7 m at Laidlaw. This is possible because the secondary minerals differ in color, both from each other and from the underlying matrix, which is relatively uniform in color. Below those depths the presence or absence of fractures can be determined only by detailed hydraulic testing.

The 18.5 m thick aquitard at Dalmeny comprises a single unit of clayey till, deposited about 38,000 years B.P., and overlies the sand and gravel Dalmeny Aquifer. The weathered zone (or oxidized zone) is 10 to 12 m deep, and is determined on the basis of color of the till matrix (Munsell® Color Chart [MCC] pale olive 5Y 6/3). Below, the unoxidized zone extends to the aquitard/aquifer boundary and is characterized by gray (5Y 5/1) till matrix. The results of hydraulic tests (Keller et al. 1986) have demonstrated that fractures occur throughout the deposit, although they are visible only where their faces are coated with secondary minerals. The fracture-enhanced, bulk hydraulic conductivity (Kᵥ) of the aquitard is about 5 × 10⁻⁶ m/s, whereas the matrix hydraulic conductivity (Kᵥ) is about 3 × 10⁻⁸ m/s.

The bulk mineralogy of the till consists of quartz, illite, dolomite, and plagioclase, with significant amounts of calcite and K-feldspar, and minor chlorite and mixed-layer clay (Keller et al. 1991). Because of the high mass of carbonates (1.5% dolomite, 4% calcite) available in the till, the oxidized zone, though weathered, still contains 2% by mass of calcite. The grain-size distribution is about 70% sand, 20% silt, and 10% clay (Christiansen 1968).

Although ground water flow is primarily downward at Dalmeny, subtle topographic depressions (5 to 50 cm) influence the position of the water table and the magnitude of the vertical gradients (iᵥ) (Keller et al. 1988). Under topographic highs, called unweathered settings, iᵥ = 0.02, and thus the vertical component of the Darcy flux (qᵥ) is 0.1 × 10⁻⁸ m/s. Under depressions, called weathered settings, iᵥ = 0.2 and qᵥ = 0.1 × 10⁻⁸ m/s. The hydraulic gradient is higher in the weathered settings because surface water pools in the depressions and infiltration is slow. In the unweathered settings, the weathered zone (as defined by the color of the bulk till matrix) is 10 to 12 m deep, the water table is found at 7 m depth, and gypsum crystals commonly occur on fracture surfaces. In the weathered setting, the weathered zone is approximately 8 m deep, the water table is approximately 4 m deep, and gypsum is not present. However, in both settings, oxides occur throughout the weathered zone and often persist up to a few meters into the unweathered zone (Keller et al. 1986).

At Laidlaw (Figure 1), 12 km south of Sarnia, Ontario, approximately 40 m of clay-rich, glaciolacustrine deposits overlie a 1 to 2 m gravel lens that overlies bedrock (Klint 1996; McKay and Frederica 1995). The sediments were deposited about 12,000 years B.P. (Klint 1996).

The mineralogy of the unweathered matrix is 40% quartz and feldspar, 35% carbonate, with the remaining amount consisting of clays including 2% smectite and vermiculite, 10% Fe-chlorite, and 14% illite (Rodvag 1987). The grain-size distribution is about 25% clay, 55% silt, and 20% sand and larger particles. The weathered zone extends to 3 m below surface, and secondary minerals typically occur to a depth of 4 m and occasionally to 7 m (Klint 1996). The deposit is highly fractured at surface (Kᵥ = 3 × 10⁻³ m/s), with fracture intensity decreasing with depth. Ruland et al. (1991) concluded that the depth of hydraulically conductive fractures varies from 7 to 13 m, below which Kᵥ is similar to Kᵥ, which is 4 × 10⁻⁸ m/s (McKay et al. 1993). The position of the water table varies from near surface to a depth of 2 m, and between the water table and the gravel interface ranges from 0.01 to 0.14 (McKay and Frederica 1995). Vertical components of qᵥ range from 4 × 10⁻⁸ m/s to 4 × 10⁻⁷ m/s, which implies that there is large component of horizontal flow within the active zone and that below the active zone transport is by diffusion.

In the weathered zone, the carbonate has been leached away and much of the chloride has been altered to smectite (Quigley and Ogunbadejo 1973). In the unweathered zone, this clay alteration has been observed at some fracture faces (McKay 1991). McKay (1991) noted the presence of streaks of calcite along intersections of vertical fractures in a zone from 0.8 to 1.5 m below ground surface. Light-gray material was also noted on fracture surfaces, and McKay and Frederica (1995) suggested that it is reduced Fe minerals.
Each of the two sites exhibits a different flow regime. At Dalmeny, the primary flow regime is vertical, although the magnitude of the downward flux varies spatially. Infiltrating water is carried primarily through vertical fractures, which enables recharge to the underlying aquifer. At Laidlaw, most of the flow is confined to the shallow zone, where a network of horizontal and vertical fractures carry infiltrating water laterally. Infiltrating water penetrates some vertical fractures, but probably not all. Below the zone of active ground water circulation the vertical flux is very small.

Field Methods

At Dalmeny, samples were obtained by augering to the desired depth, reaming out the borehole, and pushing a 0.08 m diameter, 0.6 m long Shelby tube into the till to retrieve a core sample. Till samples from both leached settings (Boreholes D45, D50, and D51, depths ranging from 1.5 to 16 m) and unleached settings (Boreholes D46 and D48, depths ranging from 3 to 17.2 m) were obtained. The core was then extruded on site, cleaned, and air-dried.

At Laidlaw, samples were obtained from a trench excavated by a backhoe to three benches (depths of 1.1, 1.8, and 4.3 m below surface). Smearing was removed from the walls of the trench, and 16 intact samples, varying in size from 0.3 m (longest dimension) to 0.1 m were cut from the trench walls and allowed to air dry. A careful photographic record of air drying was made, with MCC as reference. No changes in color were observed, confirming that no new minerals formed as a result of drying.

Analytical Procedures

Hand samples were selected for detailed analysis on the basis of depth, hydrogeological position, and the presence of secondary minerals on fracture faces. Color was compared to an MCC for soils and was reported according to hue, value, chroma notation, and descriptions (e.g., 10YR 6/6, dark yellowish-orange). Where possible, Fe-oxides were differentiated on the basis of color. Mn-oxides were distinguished from Fe-oxides on the basis of their gray to black color. Petrographic examination and electron microprobe analysis confirmed that these were indeed Fe- and Mn-oxides.

Bulk analytical methods were not applicable in this study due to the extremely small amount of sample available. The use of bulk analytical methods, such as chemical extraction, was precluded by the extremely small amount of sample available as the coatings are less than 1 mm thick, and less than 40 mg of material could be scraped from core sample segments for analyses such as X-ray diffraction. In addition, these extraction techniques are most useful for separating Fe-oxides into crystalline and amorphous phases and are not as helpful in distinguishing goethite, hematite, and ferricyanide.

Microanalytical Methods

Petrography. Thin sections made from till and coatings from Dalmeny were cold-impregnated, ground in oil, and cold-mounted with kerosene to guard against phase changes or losses. For samples from Laidlaw, the difficulty in preparing thin sections necessitated the use of handmade 7 mm diameter polished sections. These enabled petrographic observations in reflected, though not transmitted light, and were used for electron microprobe analysis and back-scattered electron (BSE) imaging.

Electron Microprobe Analysis with Quantitative Energy Dispersive Spectrometry (EDS). Mineral analyses and BSE images were performed with an ARL-SEMQ electron microprobe operating at an accelerating voltage of 15 kV and a beam current of 40 nanocamps (Corrigan 1998).

Scanning Electron Microscopy (SEM) and Qualitative EDS. Samples of till including both coating and matrix were carbon-coated and analyzed with a JEOL JSM-840 SEM run using an accelerating voltage of 20 kV. Images were acquired at magnifications ranging from 750 to 10,000 times, and qualitative EDS analyses were performed on the imaged areas.

X-Ray Diffraction (XRD). Gandolfi and Debye-Scherrer cameras were used, rather than powder diffractometry, owing to the difficulty in obtaining the necessary volumes of pure coating material. The diffraction pattern was collected over a period of approximately 24 hours, using Co radiation with an Fe filter.

Coatings were examined and scraped under a binocular microscope to obtain samples as mono-mineralic as possible for XRD. Because the coatings could not be completely isolated from the matrix minerals, comparison with analyses of adjacent matrix samples was necessary for delineating coating phases. Mineral identification was accomplished by considering only the main peaks as was suggested by Schwertmann and Taylor (1989) and Childs (1992). Analyses were performed on the light greenish-gray material and adjacent matrix material from Laidlaw using powder diffractometry in addition to the Gandolfi and Debye-Scherrer cameras.

Results

Definition of Coating Horizons from Hand Sample

Examination of fracture coating samples from leached and unleached settings at Dalmeny showed almost no color variation laterally between boreholes and consistent color variations with depth. At Laidlaw, our examination of hand samples indicated that, in addition to the previously documented color variations with depth (Klint 1996), variations in coating thickness and degree of development also existed with depth.

Although pure Fe-oxide minerals may have a diagnostic MCC color (Schwertmann and Cornell 1991), our early identifications were tentative because color may be affected by cation substitution, grain size, and grain distribution. The strong pigmenting effect of Mn-oxides and the Fe-oxide hematite can also mask the appearance of other minerals (Dixon and Skinner 1992; Schwertmann and Cornell 1991).

Four horizons were identified at each site: D1 to D4 at Dalmeny, and L1 to L4 at Laidlaw (Tables 1 and 2). In this paper, the term horizon is used to describe a vertical zone that has a diagnostic Fe-oxide or non-oxide MCC color, and spatial distribution of Mn-oxides associated with the fracture surface.

D1 occurs from ground surface to a depth of 2 or 3 m. It is characterized by a highly weathered till matrix and the presence of calcite and, if in the unleached setting, gypsum. Fe-oxides are predominantly pale, rusty-brown (7.5YR 6-7/8) with the occasional bright reddish-yellow spots (5YR 5-6/8). D2, (from 3 to 5 m) is characterized by light yellowish-brown Fe-oxides (10YR 6-7/4-6), intermittent bright reddish-yellow spots (5YR 5-6/8), and very dark gray Mn-oxide (10YR 3/1) mottles. In D3 (Figure 2) the Fe-oxides are darker and more yellowish-red than in the first horizon, but vary slightly in brightness and color saturation (5YR 5/8 3-4/4-6). Mn-oxides are a minor component and are present as small black dots. This horizon occurs to the bottom of the weathered zone. D4 is
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<tr>
<td>D1 3 m</td>
<td>Fe-oxides: pale rusty brown (7.5YR 6/7-8) calcite; bright reddish spots (5YR 5/6-8)</td>
<td>Fe-oxides: yellow internal reflections</td>
<td></td>
<td>Fe-oxides: goethite, hematite spots</td>
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<tr>
<td>D2 4 m (weathered)</td>
<td>Fe-oxides: yellowish brown (10 YR 7/4-6), local bright reddish spots (5YR 5/6-8) Mn-oxides: dark brown mottles (10 YR 5/1)</td>
<td>Fe-oxides: yellow internal reflections</td>
<td></td>
<td>Fe-oxides: goethite, hematite Mn-oxides: nd</td>
<td></td>
</tr>
<tr>
<td>D3 7 m (unweathered)</td>
<td>Fe-oxides: dark rusty brown (5 YR 5/4, 3.5/4-6) Mn-oxides: minor black spots</td>
<td>Fe-oxides: yellow internal reflections</td>
<td></td>
<td>Fe-oxides: goethite Mn-oxides: nd</td>
<td></td>
</tr>
<tr>
<td>D4 5.5-6.5 m below surface</td>
<td>Bright rusty brown Fe-oxides: (7.5YR 5-6/8) no Mn-oxides</td>
<td></td>
<td>Fe-oxides: goethite Mn-oxides: nd</td>
<td>Fe-oxides: goethite Mn-oxides: ferrihydrite</td>
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Table 1. Dalmeny: Summary of Observed Features and Conclusions

D3. Yellowish red to dark reddish brown Mn-oxides and black Mn-oxide spots 5.5-6.5 m below surface

Figure 2. Samples from D3 displaying typical coatings of that horizon.

defined by its bright reddish-yellow Fe-oxides (7.5Y 5-6/8), the absence of Mn-oxides, and gray (5Y 5/1) unweathered till matrix. D4 can extend up to a few meters below the weathered/unweathered interface.

The overall light yellowish-brown colour of D2 suggests that goethite is the dominant mineral, with little influence from the brighter minerals such as ferrihydrite and hematite. The yellowish hue suggests the presence of needle-like, μm-sized grains (Schwertmann and Cornell 1991), and the pale color of D2 suggests that the minerals are mixed with other minerals. The occasional brighter spots indicate that hematite and/or ferrihydrite are restricted to only these small areas.

The reddish-yellow hue of the other horizons suggests an influence from one of the other more pigmented minerals, either hematite and/or ferrihydrite, or possibly a mixture of different Fe-oxides. The change in brightness over depth in the lower two horizons indicates a change in Fe-oxide grain size, with D4 character- ized by the smallest grains, and D3 by the largest.

L1 is characterized by highly weathered till with pinkish-white calcite streaks (2.5YR 8/2) and a light bluish-gray material (2.5 Y 8/5B). L2 is characterized by fine-grained, light greenish-gray material (1 gley, 8-7N-10Y) haloed by brownish-yellow (10 YR 7-6/8) Fe-oxides. In L2, the secondary minerals appear to penetrate up to 0.005 m into the matrix. Within some fractures, L3 is a thin (0.01 to 0.02 m) zone between L2 and L4 (Figure 3), characterized by Mn-oxide mottles. In other fractures, it is a thicker zone of up to 1 m and consisting of mottles and dendrites of Mn-oxides, dark gray to black in color, with the light greenish-gray material as background. L4 is defined by dark reddish-brown to reddish-yellow Mn-oxides.

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<tbody>
<tr>
<td>L1</td>
<td>Bright, pinkish (2.5YR 8/2) streaks (calcite) whitish-gray (2.5Y 8/2B) material</td>
<td>Alumino-silicates, carbonates, Fine-grained, uniform surface</td>
<td></td>
<td></td>
<td>Calcite</td>
</tr>
<tr>
<td>L2</td>
<td>Silvery-gray (10YR 7/10Y), banded by brownish-yellow Fe-oxides (10YR 7-6/8)</td>
<td>Fe-oxides</td>
<td>Higher amount of carbonate</td>
<td>Fe-oxides</td>
<td>Carbonate clay minerals</td>
</tr>
<tr>
<td>L3</td>
<td>Dark gray to black Mn-oxides, mottles dendirite on background of silvery-gray</td>
<td>Mn-oxides</td>
<td>Mn-oxides</td>
<td></td>
<td>Mn-oxides</td>
</tr>
<tr>
<td>L4</td>
<td>Bright rusty Fe-oxides (7.5YR 5/6) black Mn-oxides mottles</td>
<td>Fe-oxides yellow internal reflections</td>
<td>Mn-oxides</td>
<td>Mn-oxides</td>
<td>Mn-oxides</td>
</tr>
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- = mineral identification tentative
\$ = unidentified
nd = not detected
\$ = position of water table
\$ = depth to which horizon occurs if observable

When observed in hand sample, appear to be limited to the fracture surface. At Laidlaw there is both variation with depth, and variation inward from the fracture face. At Laidlaw it is not possible to define horizons as occurring over specific depth intervals because at some depths all horizons may be present, though in different fractures. For example, in the major fractures, which are typically the deepest, L1 may persist to much greater depths than in minor fractures. In small, discontinuous fractures, L4 is the only horizon present. Conversely, at Dalmeny, the four horizons appear to be consistent with depth, i.e., D1 occurs to a depth of 2 or 3 m throughout the site. Because K3 at Dalmeny, is more uniform with depth, it is reasonable to assume that the fracture network is more uniform, and therefore the coating horizons vary more systematically with depth.

**Microanalytical Methods**

Isolation of secondary minerals for microanalysis is difficult because almost all matrix grains and secondary minerals are clay-sized and because their volume is small compared to the volume of matrix. Separation techniques developed for Fe- and Mn-oxides formed in other geologic environments, such as separation on the basis of grain size (Koljonen et al. 1976), differential extraction, or selective dissolution combined with Mossbauer or infrared spec-troscopy (Dixon and Skinner 1992; Schwertmann et al. 1982; Schulze 1981) were not possible for these samples.
Petrography. In transmitted light, coatings from Dalmeny appeared as a dark, semipaque, rust material covering matrix minerals or surrounding larger grains and large pores or cracks. The only distinctly visible grains were those of the matrix. Under reflected light, the coating material glowed with the diagnostic bright yellow of goethite internal reflections (Figure 4). In some places the material was darker, semipaque, and formed indistinct grains; it also showed bright yellow internal reflections. Thus, goethite was identified as the dominant coating mineral in D2 and D3.

Goethite was identified in L4 on the basis of bright yellow internal reflections on Laidlaw samples. As observed in the Dalmeny samples, distinct goethite grains were not visible but the overall matrix glowed a bright yellow.

Electron Microprobe Analysis. Fe-oxide-rich areas appeared as brighter regions in BSE images due to the higher average atomic number relative to other minerals present. Quantitative analysis of Fe-oxides was difficult due to the absence of discrete grains. EDS analysis of the bright regions yielded a spectrum typical of that expected for matrix minerals but with a high Fe peak, demonstrating the presence of Fe-oxides.

Both reflected light and BSE images demonstrated that at both sites, Fe-oxides form as coatings around pre-existing matrix grains (Figure 4). They do not form a distinct layer on the fracture surface. Thus the Fe-oxides, regardless of the horizon in which they are found, are more precisely described as intergranular cement rather than a fracture surface coating.

SEM and EDS. SEM provided information on grain size and morphology of coating minerals, and provided better resolution of the relationship of coating minerals to matrix minerals than the electron microscope. Qualitative EDS analyses from the SEM provided information on the elements present and their relative proportions. This method was most useful for viewing Mn-oxide morphology.

The Mn-minerals in D2 are delicate and occur in clusters of fibers or laths, and/or irregularly shaped platelets. The grains are about 1 μm in length and orders of magnitude smaller in width. EDS analyses verified that the clusters consist of essentially a single mineral. Mn-oxides from D3 are laths or fibers mixed with cloud-like masses. Composition is constant throughout. The fibers from D3 are longer than those in D2.

Under the binocular microscope, Fe-oxides from D3 appeared uniform and continuous; however, examination with SEM did not allow for resolution of individual Fe minerals. Fe-rich zones with the appearance of desiccated crusts were visible in some locations (Figure 5), but EDS analyses of these areas yielded high Si peaks (higher than Fe), with Ca, Al, K, and Mg also present in significant proportions, indicating the contribution of admixed silicates.

EDS analysis of a region of light greenish-gray material from Laidlaw (L2) yielded a spectrum with large Si, Ca, and Mg peaks, significant Al, lesser K, and minor Fe, typical of aluminosilicates and carbonates. This material appears as a fine-grained, uniform surface, suggesting that it consists of allochthonous aluminosilicates and carbonates that may be authigenic. The small Fe peak clearly indicates that this material is not re-deposited Fe, as had been suggested previously.

Mn-oxides from L3 are irregularly shaped platelets less than 1 μm in diameter. They appear curled and folded. As with Dalmeny, the Mn-oxides deposits are chemically uniform, with only minor admixed phases.

Mn-oxides from L4 differ significantly in appearance from those in L3. The larger grains are platy, but the morphology of the

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smaller grains is not clear. Grain size varies from approximately 1 \( \mu m \) to at least an order of magnitude less.

Figure 6 illustrates the differences, typical of both sites, between Fe- and Mn-oxides. The Mn-oxides are finer-grained and compositionally more uniform than the Fe-oxides. EDS analyses showed that in even in the Fe-rich areas, the Si content generated from admixed silicates is approximately equal to the Fe, and there are also significant amounts of Mn, Al, Ca, and K. In Mn-rich areas, Mn is the most abundant element in the spectra, and only minor amounts of other cations were detected. Mn-oxides are well-developed and form distinct grains. In contrast, no distinct morphology can be attributed to the Fe-oxides, and they occur as an admixed phase. This indicates, as did the petrographic and electron microscope work, that Fe-oxides form a cement and not a coating at the fracture face.

**XRD.** The coatings could not be isolated from the matrix minerals thus comparison with analyses of adjacent matrix samples was necessary. In addition, definitive identification of coating minerals was impeded by peak overprinting by matrix minerals and by weak, broad peaks due to small grain size, poor crystallinity, and cation substitution. Thus, mineral identification was accomplished by considering only the main peaks, a technique suggested by Schwertmann and Taylor (1989) and Childs (1992). Because of the high degree of peak overprinting, the identification of ferrhydrite was tentative.

At Dalmeny, goethite was identified by XRD in all horizons, confirming the petrographic observations. In two samples from D2, hematite was identified. In these samples, hematite occurred as bright inclusions in large pores. In hand specimen and under the binocular microscope, the pore fillings appeared much redder and coarser grained, and upon scraping the outermost grains, the underlying material appeared yellow. In one sample, consisting of red material, the 0.27 nm line (the most intense hematite line) was distinct and was the second most intense line on the film (the most intense being the strongest quartz line), which identifies hematite. In another more yellowish sample, goethite was present but the strength of the 0.27 nm line (the third most intense line for goethite) compared to the goethite 0.418 nm line (the most intense goethite line) indicates that it is admixed with hematite.

Samples of the dominant, yellowish-brown coating of D2 produced few d-spacings, and some samples yielded no data for Fe-oxide minerals. The yellow color of the coatings suggests larger (jumbo) goethite grains (Schwertmann and Cornell 1991) than those from D3 and D4.

In summary, the XRD results from Dalmeny indicate that goethite is present in D2, D3, and D4. In D2, hematite and goethite are both present in discrete pore infillings. Ferrhydrite could be only tentatively identified in any horizon. The difficulty in isolating Fe-oxides coatings from the matrix provides additional support that they form cements.

Analyses were performed on the light greenish-gray material and adjacent matrix material from Laidlaw (L2) using the powder diffractometer in addition to the Gandolfi and Debye-Scherrer cameras. The light greenish-gray material has an increased proportion of carbonate minerals (especially calcite) to quartz, relative to the matrix, suggesting precipitation of carbonate minerals in this horizon. This confirms the findings of SEM work and observations of Rodväng (1987).

Goethite was identified in L4 and L2. The evidence for ferrhydrite in L4, though still not definitive, was stronger than for Dalmeny samples.

None of the Mn-oxides scraped from the Dalmeny and Laidlaw samples diffracted X-rays, probably because of poor crystallinity.

**Discussion**

At the macroscopic scale, the initial observations in hand sample of Fe-oxide color (yellowish-brown to reddish), especially for goethite and hematite, were remarkably diagnostic indicators of mineralogy. No single microanalytical method identified the Fe-oxides in every sample but a combination of methods provided unambiguous results in most cases.

**Mode of Occurrence of Fe-Oxides**

Fe-oxides are very fine-grained, dispersed, and intimately associated with matrix minerals. In hand samples, Fe-oxides appear to occur on the surface of fracture faces. However, our findings indicate that they occur as coatings around larger grains, admixed with smaller matrix grains, and occasionally form local crusts overlapping the fracture face. Thus we conclude that the Fe-oxides are a cement linking matrix grains rather than a coating on the fracture face.

The formation of Fe-oxide minerals around matrix grains and at fracture surfaces is expected to decrease both porosity and permeability adjacent to the fracture. The porosity decrease is probably small. However, because the Fe-oxides form around grains and the perimeter of pores and may fill very fine pores, it is the connectivity of the pore space or permeability (and thus K) that is decreased.

**Distribution and Relative Age of Fe-Oxides**

Field evidence and experimental data from other studies (references cited later) suggest that the distribution of ferrhydrite, fine-grained goethite, coarse-grained goethite, and hematite, at Dalmeny and Laidlaw, may indicate the relative age of fracture coatings. At both sites, ferrhydrite is found only at the deepest horizons (D3, D4, and L4). Goethite is found at all depths at both sites, although fine-grained goethite occurs in deeper horizons and coarse-grained goethite occurs in shallow horizons. Hematite is found only in the shallowest horizons, D1 and D2, at Dalmeny.

Ferrhydrite forms under conditions of rapid oxidation. It eventually recrystallizes to hematite or is converted to goethite through dissolution and reprecipitation (Schwertmann and Taylor 1989). Thus the presence of ferrhydrite at the greatest depth at each site suggests that those Fe-oxides are the most recently deposited. The relatively fine-grained goethite found in the deeper horizons at Dalmeny, itself a product of either direct precipitation or transformation from ferrhydrite (Schwertmann and Taylor 1989), may be the precursor of the coarser-grained goethite found in more shallow horizons.

Hematite does not form directly from aqueous solution but from ferrhydrite (Schwertmann and Taylor 1989) or from goethite through a dissolution/reprecipitation reaction in which goethite dissolved, ferrhydrite is precipitated, with ferrhydrite ultimately being converted to hematite (Fischer and Schwertmann 1975). In most natural environments, goethite, which is usually fine-grained, is less stable than the coarser-grained hematite (Murray 1979). Thus the hematite observed in the shallow horizons at Dalmeny (D2) probably represents the oldest secondary Fe-oxides, likely formed from pre-existing ferrhydrite and/or goethite at that location. No hematite was observed at Laidlaw. A possible explanation may be that the till is only 12,000 years old, considerably younger than the till at Dalmeny, which is approximately 38,000 years old.
Implications of Age and Variation of Fe-Oxides with Depth

The presence of very fine-grained Fe-oxides suggests that there is the potential for high surface reactivity along and inward from the fracture face. The term surface reactivity refers to the range of chemical reactions that occur at the surface of the Fe-oxides which may affect solute transport; these include primarily surface adsorption, but also chemisorption (specific adsorption) and coprecipitation. Surface reactivity, then, is dependent on surface area, and is therefore inversely proportional to grain size. Coatings consisting of fine-grained goethite are thus more reactive than coatings of coarse-grained goethite. Furthermore, ferrihydrite is more reactive than goethite or hematite due to its typical spherical morphology and poor crystal structure (Schwertmann and Taylor 1989). Consequently, the surface reactivity may vary with depth owing to changes in both Fe-oxide mineralogy and grain size. Surface reactivity probably increases with depth at both Laidlaw and Dalmeny.

If variations in surface reactivity and permeability are related to changes in the dominant Fe-oxide with depth along the fracture, then it follows that, as Fu et al. (1994) suggested, the heterogeneity of secondary mineral deposits causes heterogeneity of permeability along the length of fractures. The combination of high surface reactivity and decreased permeability may decrease the effective diffusivity of a naturally occurring or contaminant solute, thereby decreasing the potential for mass loss across the fracture face.

Hypothesis Testing

The mode of occurrence of the secondary minerals and their relative ages support our initial hypothesis. At both sites the conditions within fractures are generally more oxidizing and the conditions within the matrix are comparatively reducing. That Fe-oxides form within the matrix pore spaces and not exclusively at the fracture surface suggests that the redox interface, where reduced aqueous Fe meets dissolved oxygen and subsequently precipitates as Fe-oxide, moves inward from the fracture face. Thus it appears that there is diffusion of both dissolved oxygen and aqueous Fe$^{2+}$, dissolved oxygen from the fracture to the matrix owing to the concentration gradient between the two, and Fe$^{3+}$ from the matrix toward the fracture owing to the concentration gradient between the matrix and the fracture. As long as water in the fracture is more oxidizing than water in the matrix, this process continues until the concentration gradient in Fe$^{2+}$ no longer exists. This notion is supported by our observation that within the first meter or so at Dalmeny (and at other similar field sites in southern Saskatchewan), there is little or no color distinction between fracture faces and matrix.

It follows then that at early times, much of the oxygen is consumed at shallow depths, depending on the rate of advection in a particular fracture. Later, the oxidizing front proceeds further down the fracture. An implication of the hypothesis is that secondary minerals found in deep horizons are more recent, whereas secondary minerals in shallow horizons are older. This is consistent with the distribution of the three Fe-oxide minerals. The presence of fine-grained ferrihydrite at depth, which is formed in conditions of rapid precipitation, suggests that the redox gradient between the matrix and fracture is very pronounced.

Further support for this hypothesis is that at Laidlaw, where vertical fractures penetrate to varying depths and are not uniformly conductive, not all of the vertical fractures exhibit the four horizons. In large, deep, hydraulically active fractures, the upper horizons persist to greater depths than in the smaller, less hydraulically active fractures. Thus the oxygen supply has been limited in the less hydraulically active fractures. That we do not see this at Dalmeny may be an artifact of the method of sampling or may be because the fracture network extends throughout the thickness of the deposit.

Mn-Oxide Coating Distribution

The Mn-oxides differ significantly in character from the Fe-oxides. They form localized, uniform deposits in large pores or indentations at surface. This may be because Mn-oxides tend to form where other Mn-oxides already exist. The surface of a Mn-oxide grain may become the site for autocatalytic oxidation in solution and subsequent precipitation of further Mn-oxides, or may enhance the formation of Fe-oxides by providing an oxidizing agent for Fe$^{2+}$, so the oxidation leads to the dissolution of Mn-oxides (Dixon and Skinner 1992). This may explain why Mn-oxides are not as extensive as the Fe-oxides. Alternatively, the Eh of the solution may have been high enough to induce the precipitation of Fe oxides but not sufficiently high to stabilize Mn-oxides.

Aluminosilicate-Carbonate Coatings

The light greenish-gray material from L2 consists of carbonates and aluminosilicates that form a smooth, thin blanket overlying the matrix. The effect of these coatings is unclear because they are actually creating new surfaces with unknown porosity and surface reactivity on the fracture faces.

Conclusions

Field observations of Fe-oxide color using an MCC provide a good estimation of mineralogy and, thus, physical and chemical effects. A combination of microanalytical techniques, including petrography, electron microprobe analyses, SEM, EDS, and XRD is recommended for Fe-oxide identification. Mn-oxide mineralogy is more problematic, and only tentative identifications were made in this study.

The mode of occurrence and distribution of Fe-oxides indicates that they form a cement that has the potential to decrease permeability and increase surface reactivity inward from the fracture face. Since coating mineralogy suggests that the most recently deposited and most reactive Fe-oxides occur at depth, the potential for retardation of contaminants is expected to increase with depth.

In contrast to Fe-oxides, the mode of occurrence and distribution of Mn-oxides indicates that they do not form a cement, but rather in discrete locations where surface reactivity may locally be increased. Unless the coatings are continuous, they are unlikely to have a significant effect on solute transport.

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