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ILLITE/SMECTITE GEOTHERMOMETRY OF THE PROTEROZOIC ORONTO GROUP, MIDCONTINENT RIFT SYSTEM

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Abstract—Characterization of the Nonesuch Formation, middle unit of the Proterozoic Oronto Group, as a potential hydrocarbon source for the Lake Superior basin portion of the Midcontinent Rift system requires an understanding of the thermal maturity of the region and its relationship to the thermal history. Illite/smectite (I/S) expandability data were collected from the Nonesuch Formation and the overlying Freda Sandstone and compared with organic thermal maturity data; both data sets coupled with a thermal and burial history for the White Pine area of Michigan allow regional interpretation of maximum formation temperatures of the Nonesuch Formation and the Freda Sandstone with respect to time. Samples collected from drill holes in northeastern Wisconsin display nearly pure smectite within the lower Freda Sandstone trending abruptly to ordered I/S within the Nonesuch Formation. Regular trends of decreasing expandability with depth occur in four other drill holes to the northeast. Comparison of I/S expandability between similar stratigraphic intervals reveals a significant trend of increasing thermal maturity to the northeast, with the lowest thermal maturities observed in the Iron River Syncline area just west of White Pine, Michigan.

I/S geothermometry suggests maximum temperatures in the Nonesuch Formation of 140°C in Wisconsin, 115°C in the Iron River Syncline area, 160°C at White Pine, and 190°C near the southern portions of the Keweenaw Copper District. The geographic pattern of temperatures determined from I/S geothermometry is identical to that determined from organic thermal maturity indicators in the Nonesuch Formation (Imbus *et al.,* 1988, 1990; Hieshima and Pratt, 1991; Pratt *et al.,* 1991; Mauk and Hieshima, 1992).

Regular variations in I/S expandability with depth occur in the Freda Sandstone and the Nonesuch Formation near the southern limits of the Keweenaw Copper District. These variations suggest a fossil geothermal gradient of 55°C/km and limit the thickness of sediment above the Nonesuch Formation to approximately 3 km. In comparison, 3.6 km of Freda Sandstone are presently exposed near the Wisconsin border, and numerical modeling suggests a range of 4–6 km of sediment overlying the Nonesuch Formation. None of the data indicate the presence of the Bayfield Group sediments above the Nonesuch Formation at the time of clay diagenesis. Samples from White Pine suggest a two-stage burial history: 1) clay reaction, possible hydrocarbon maturation, and copper-sulfide mineralization at maximum temperatures above 100°C during the main rifting and burial event, followed by 2) fracturing, reverse faulting, and fluid circulation during a rift-terminating compressional event that may have allowed petroleum migration and native copper mineralization at temperatures below 100°C. Abrupt changes in I/S expandability with depth and the presence of poorly crystalline I/S (greater than 80% expandable) and kaolinite in the Freda Sandstone in Wisconsin appear to represent later overprinting of the diagenetic assemblage by fluids that were probably cooler and of differing composition than earlier diagenetic fluids. However, the authigenic assemblage from the vicinity of White Pine, Michigan, which includes up to 25% expandable I/S, appears to represent a diagenetic profile formed during the main rifting and burial event. Therefore, these expandable I/S-type clays are essentially 1.0 billion years old.

Key Words—Diagenesis, Illite/Smectite, Mineralization, Proterozoic, Retrograde, Thermal history.

INTRODUCTION

Hydrocarbon exploration in the Midcontinent Rift system of North America (Figure 1) has to date yielded no economic reserves of either oil or gas (Dickas, 1986). However, speculation regarding its potential as a frontier oil province continues. The Nonesuch Formation hosts the large stratiform copper-sulfide deposit at White Pine, Michigan. Mature oil seeps occur locally within the mine raising the possibility that the Nonesuch Formation may provide an economic hydrocarbon source within the Lake Superior region. Understanding the thermal evolution of the Nonesuch Formation is crucial to the evaluation of its potential as a hydrocarbon source rock.

The great age of the Nonesuch Formation and the other units of the Upper Keweenawan Oronto Group significantly reduces the availability and reliability of traditional methods of assessing the thermal maturity and thus the thermal history of sediments. To overcome this problem, illite/smectite (I/S) expandability (%Exp) data were used as a thermal maturity indicator (e.g., Waples, 1980; Pollastro and Barker, 1986; Pollastro, 1990) and compared with available organic thermal maturity data. These results were coupled with a calculated thermal and burial history model for White

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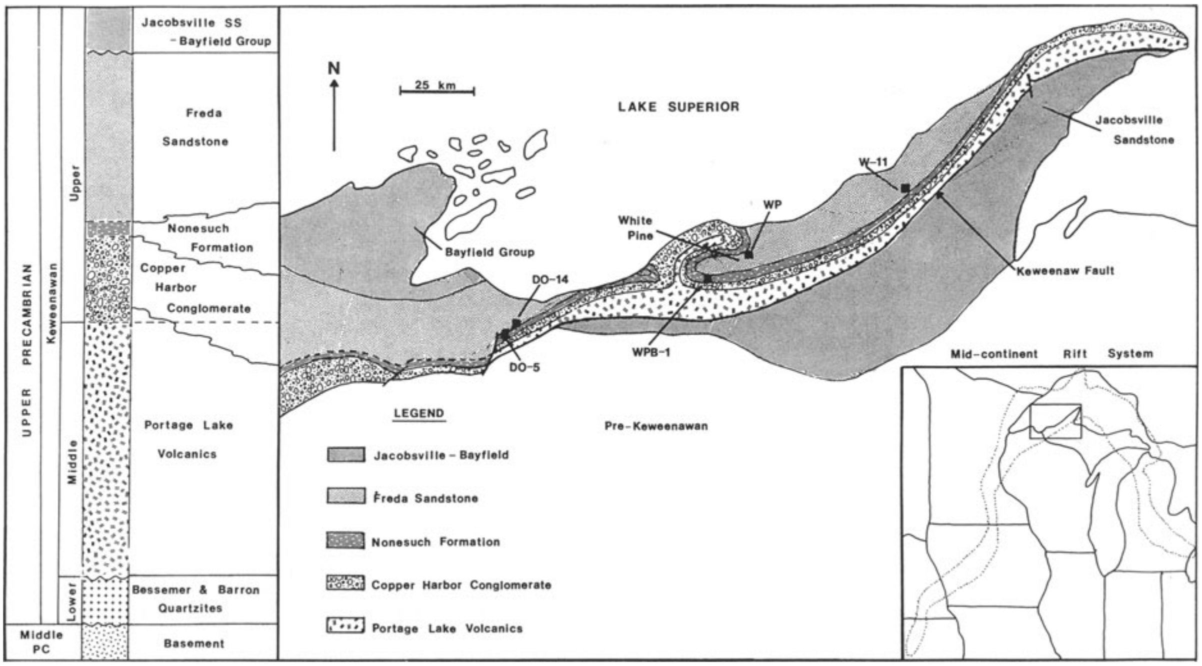

Figure 1. Geologic map of the Lake Superior region of the Midcontinent Rift system (inset) and the corresponding stratigraphy. DO-5, DO-14, WPB-1, WP, and W-11 refer to collar location of drill holes from which samples were taken for this study. The Presque Isle Syncline is located about 25 km west-southwest of White Pine, Michigan; drill hole WPB-1 is located on the southern limb of the Iron River Syncline. Modified from Daniels (1982), Green (1983) and Imbus *et al.* (1988).

Pine, Michigan (Price *et al.*, in prep.) to estimate maximum formation temperatures for the Nonesuch Formation with respect to time. There are two primary objectives of this project: 1) assessment of the thermal maturity of the Oronto Group with respect to depth and geographic location using I/S geothermometry, and 2) comparison of I/S expandability values to organic thermal maturity indicators with respect to local and regional geologic events to assess the utility of I/S expandability as a thermal maturity indicator in ancient sedimentary basins.

Geologic setting

The Keweenawan stratigraphy (Figure 1) of the Lake Superior portion of the Midcontinent Rift system represents a classic rift sequence consisting of 3 to 5 km of Portage Lake Volcanics overlain by a minimum of 6 km of Oronto Group rift sediments. The Keweenawan section of the region also includes the Bayfield Group of northern Wisconsin and the Jacobsville Sandstone of Upper Michigan. The relationship between the Oronto Group, the Bayfield Group and the Jacobsville Sandstone remains unclear, although Bayfield Group equivalents may rest unconformably on the Oronto Group units offshore beneath Lake Superior (Cannon *et al.*, 1989). Exposures of the Portage Lake Volcanics and the Oronto Group occur along the Lake Superior shoreline from the Keweenaw Peninsula of Upper Michigan, southwest into Wisconsin (Figure 1). The oldest unit of the Oronto Group, the Copper Harbor Conglomerate, interfingers with the overlying Nonesuch Formation and includes lava flows known as the Lake Shore Traps. A high-precision U-Pb date of 1094.1 ± 3.6 Ma for the Lake Shore Traps provides the age of deposition for the middle Copper Harbor Conglomerate (Davis and Paces, 1990). The Nonesuch Formation and the Freda Sandstone exhibit a conformable and gradational contact frequently extending over several meters (Daniels, 1982).

To avoid complications resulting from comparison of different lithologies, the study excluded the Copper Harbor Conglomerate and focused on the Nonesuch Formation and the Freda Sandstone. The Nonesuch Formation consists primarily of gray to black micaceous siltstone and shale lithologies. Rock fragments and quartz dominate the detrital component. Lithic fragments include primarily mafic volcanic fragments, although silicic and intermediate volcanic fragments have also been identified (Hite, 1968). Twenty to 50 percent of the detrital component is composed of volcanic rock fragments, while undulatory quartz, plagioclase, potassium feldspars and opaque minerals comprise the remaining 50 to 80 percent. The most common cement is calcite, although silica, laumontite, and hematite also frequently occur (Hite, 1968). Matrix clays, primarily chlorite and illite (which probably includes I/S), average about 5.3% of the rock volume (Hite, 1968; Vogel *et al.*, 1976) and probably formed from

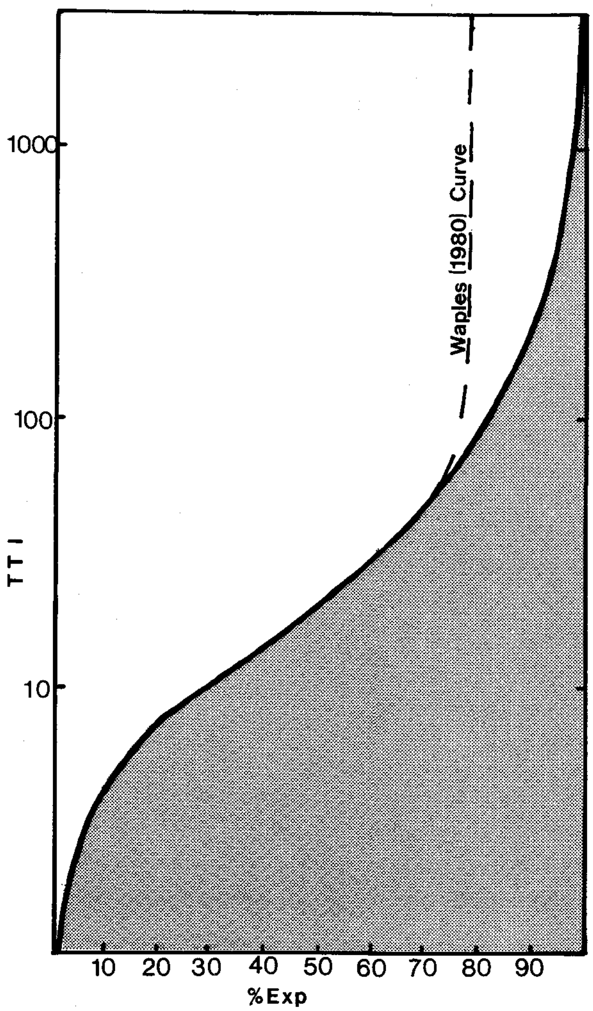

Figure 2. TTI vs. I/S expandability modified from Waples (1980). The solid line represents the log-normal curve-fit function which is allowed to approach 0%Exp. This curve-fit function was used to calculate %Exp from the time-temperature history generated by the computer model. Note that the curve form is actually the log of a log-normal function as TTI is itself a log function. The dashed line extension represents Waples' (1980) envelope based on Gulf Coast I/S expandability data. The shape of Waples' curve is attributed to widespread potassium deficiency in Gulf Coast sediments; thus, the smectite to illite reaction series did not proceed beyond 20%Exp values.

weathering of basaltic material (Vogel *et al.*, 1976; Autra, 1977), thus suggesting that early diagenesis likely resulted in smectite or highly expandable I/S-type clays.

The lithological transition from the Nonesuch Formation to the Freda Sandstone occurs as alternating bands of very fine-grained red and black siltstones and shales and is generally accompanied by increasing compositional maturity. The Freda Sandstone is composed of micaceous red-brown siltstones to very fine-grained sandstones. Like the Nonesuch Formation, lateral variations in compositional maturity are marked by fluctuations in the relative percentages of quartz and volcanic fragments (Hubbard, 1975). Silicic and intermediate volcanic fragments dominate mafic fragments, while other common framework minerals include potassium feldspars, plagioclase, and undifferentiated opaque minerals (Hite, 1968). As in the Nonesuch Formation, cements include calcite, quartz, laumontite, hematite, and occasionally chlorite (Hite, 1968). Clay minerals dominate the matrix, comprising about 7.8% of the rock volume (Hite, 1968). Preliminary XRD studies of the Freda Sandstone indicate that the clay composition, chlorite, illite, and I/S are very similar to that of the Nonesuch Formation (Price and McDowell, 1991).

Thermal history

A one-dimensional, transient, conductive heat-flow model (Furlong and Edman, 1989; Huntoon, 1990; Huntoon and Furlong, in press) was used to investigate the thermal history of the Nonesuch Formation at White Pine, Michigan, and its potential impact on oil generation (Price *et al.*, in prep.). The model uses the one-dimensional heat conduction equation,

$$\frac{\partial^2 T}{\partial z^2} - \frac{1}{a}\frac{\partial T}{\partial t} = \frac{-A}{k} \quad (1)$$

with variables temperature (T), depth (z), thermal diffusivity (a), time (t), heat production (A) and thermal conductivity (k) to calculate temperature distributions within a 30-km-thick section of the lithosphere over a specified period of time, in this case 1.2 billion years. The output file for this case study contains a time-temperature history for five stratigraphic horizons, which correspond to the lower Freda Sandstone (1), the top (2) and base (3) of the Nonesuch Formation, and the upper (4) and middle (5) Copper Harbor Conglomerate. The thermal history of the Oronto Group in terms of temperature (°C), vitrinite reflectance (%R_o), Time-Temperature Index (TTI) and I/S expandability (%Exp) is summarized in Figure 3. The modeling results represent the "best" case based on all available geologic data. Values for vitrinite reflectance (%R_o) are then calculated based on methods presented by Sweeney and Burnham (1991); the I/S expandability (%Exp) is calculated from Time-Temperature Index values (TTI) derived from the time-temperature history and based on Waples' (1980) empirical correlation between TTI and I/S expandability for Gulf Coast samples (Figure 2).

The effect of potassium deficiency in Gulf Coast samples (Hower *et al.*, 1976) is accounted for by approximating the shape of the expandability "envelope" with a log-normal curve function and allowing the curve to approach zero expandability (Figure 3). Implicit in this method is the assumption that maximum expandabil-

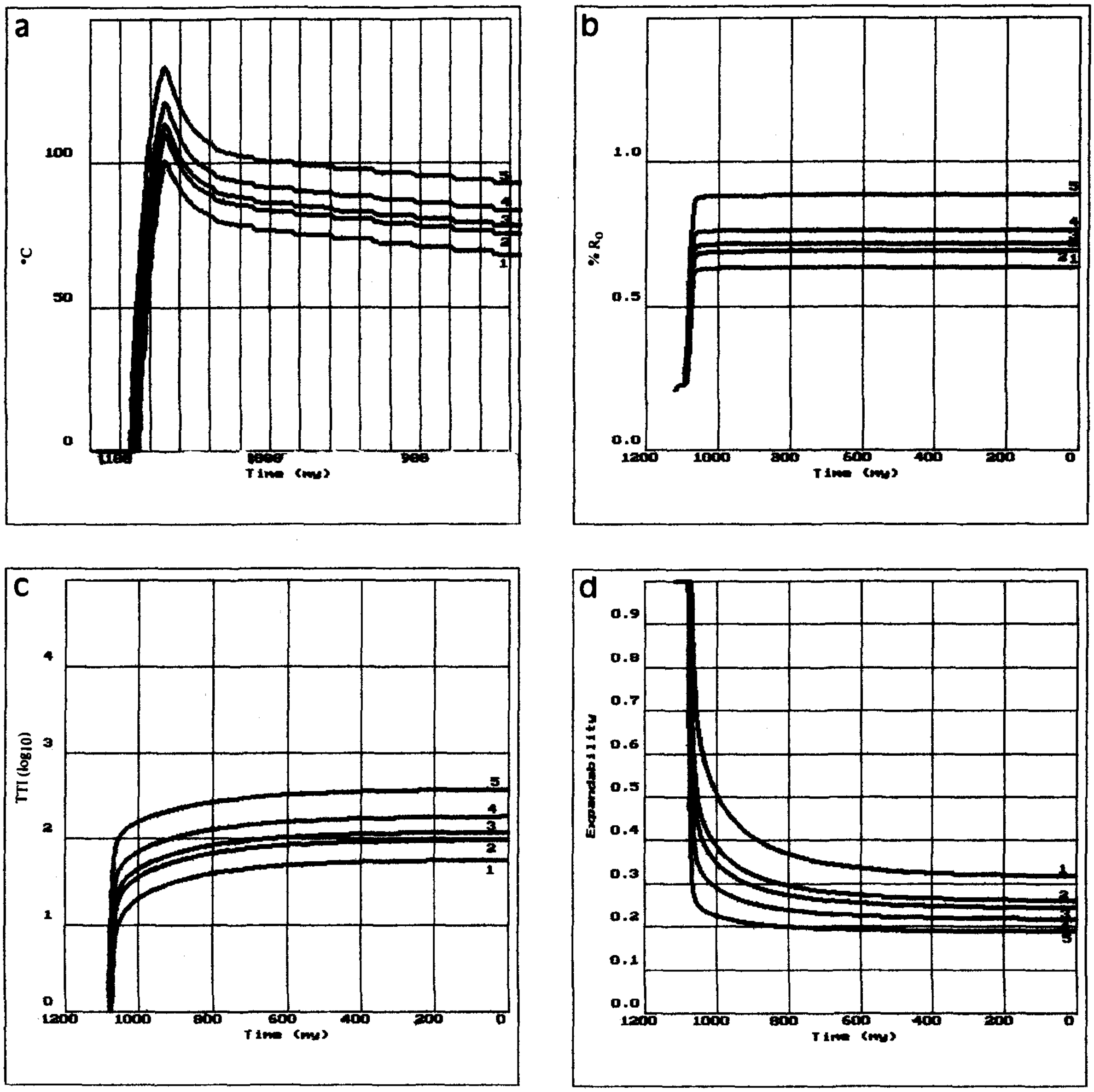

Figure 3. Temperature vs. Time (a), %R_o vs. Time (b), TTI vs. Time (c), %Exp vs. Time (d) for the preferred thermal history model, White Pine, Michigan (Price *et al.*, in prep.). Each numbered line represents a particular stratigraphic interval: the lower Freda Sandstone (1), the top (2) and base (3) of the Nonesuch Formation, and the upper (4) and middle (5) Copper Harbor Conglomerate.

ity for any particular value of TTI occurs when the initial %Exp is 100%; thus the scatter of points within Waples' (1980) "envelope" (Figure 2) could result from I/S particles whose initial expandability is less than 100%. Such scatter could also occur as a result either of detrital I/S particles or where multiple thermal episodes have impacted the stratigraphic column. In this particular case study, the thermal history is tracked beginning with deposition of the Oronto Group to eliminate the possibility of previous thermal episodes. Since the weathering of basaltic material likely produced much of the clay matrix (Vogel *et al.,* 1976; Autra, 1977), the assumption that the initial expandability approached 100%Exp seems reasonable. The possibility remains that detrital I/S has artificially reduced the observed %Exp values. However, preparation techniques were designed to minimize the presence of detrital material, and scanning electron microscopy techniques were used to verify the absence of significant amounts of very fine-grained detrital clay material, particularly illite or I/S type clays. Despite the potential drawbacks, use of this generalized correlation permits %Exp values to be tracked over time in a numerical simulation (Figure 3d).

In general, the thermal history of the White Pine area can be described as a pulse of elevated temperatures associated with rifting over a period of about 35 My (Figure 3a), followed immediately by cooling as a result of rapid uplift and erosion associated with compression (Price *et al.*, in prep.). Geochemical evidence reported by Mauk and Hieshima (1992) combined with thermal modeling results suggest that the observed thermal maturity, and by implication any hydrocarbon generation, occurred as a result of elevated heat flows and rapid burial during rifting. The thermal modeling also suggests that after experiencing initial temperatures of approximately 100° to 125°C at about 1070 Ma, the Nonesuch Formation likely remained at temperatures of less than 40°C for the ensuing 800 My (Figure 3a).

METHODS

Sampling

In excess of 150 Oronto Group samples were collected primarily from drill core but also from outcrop. The sample suite represents as much stratigraphic and geographic distance as possible (Figure 1). To eliminate potential complications due to surface weathering, the study focused on samples collected from drill core, although data from surface samples contributed to regional interpretations. The most fine-grained lithologies were preferentially sampled to minimize complications from regional fluid migration and to allow comparison with I/S geothermometry studies based on shales. The bulk of the drill core resulted from exploration programs targeting the lower Nonesuch Formation and were typically collared in the lower Freda Sandstone. As a result, complete sections of the Oronto Group were difficult to find. All sample depths have been converted to vertical meters above (+) or below (−) the Nonesuch Formation.

Sample preparation

Samples were first disaggregated manually in a mortar and pestle to "pea-size" particles, then ultrasonically with a Branson® ultrasonic cell disrupter (Moore and Reynolds, 1989). Stokes Law settling techniques were used to obtain 2–20 μm and <2 μm size fractions for each sample, then a <1 μm fraction from a selected suite of samples. Many samples contained little or no <1 μm fraction; samples for a <1 μm separation were selected to encompass the largest possible stratigraphic and spatial interval. Oriented samples from the two larger size fractions were mounted on glass slides using an eyedropper, whereas oriented samples from the <1 μm fraction were prepared on porous ceramic plates using a vacuum apparatus. Each of the <1 μm fraction samples was Sr saturated, then washed with distilled water to remove excess cations.

XRD analysis

Preliminary XRD analyses of the <2 μm and 2–20 μm size fractions were carried out on a Philips X-ray diffractometer using CuKα radiation and a 1° slit size. Samples were scanned from 2° to 50°2θ at a 0.05°2θ step increment for 2 seconds per step. From these preliminary diffraction patterns, a subset of oriented <1 μm size fraction samples was chosen representing as large a stratigraphic and geographic spread as possible.

Analysis of all <1 μm samples was carried out on a Siemens D-500 diffractometer with a graphite monochonometer using CuKα radiation and a 0.3° slit size. All <1 μm samples were scanned from 2° to 20°2θ at a 0.05°2θ step for 5 seconds per step. After collecting diffraction patterns for air dried samples, all samples were ethylene glycol solvated in a glass desiccator for 24 hr at room temperature. Testing determined that solvation in excess of 24 hr did not measurably increase expandability. Identification of I/S and determination of %Exp were carried out using combinations of techniques described by Srodon (1984) and Moore and Reynolds (1989). Calculated patterns from NEWMOD© 2.0 (Reynolds, 1985) were also generated for comparison. Verification of the authigenic mineral assemblage was carried out using Scanning Electron Microscopy (SEM) techniques, including Energy Dispersive System (EDS) analysis.

RESULTS

Kaolinite-chlorite

X-ray diffraction patterns show the transition from kaolinite to chlorite in the Wisconsin drill holes. At +229 m and deeper, minor amounts of very poorly crystalline kaolinite are present; indications of trace amounts of chlorite occur in the +229 m to +335 m range. Abundant, well-crystallized kaolinite, free of chlorite, occurs at +159 m in drill hole DO-5, but all deeper samples are free of kaolinite and contain well-crystallized chlorite. The kaolinite to chlorite transition directly overlaps the abrupt transition from disordered to ordered I/S. All drill hole samples from Michigan contain chlorite, but no kaolinite was observed.

The chlorite present in most samples (Figure 4) contains a roughly equal distribution of Fe between silicate and hydroxide octahedral sheets [I(003)/I(001) = 0.5–1.4] (Brown and Brindley, 1980). The most asymmetrical Fe distribution occurs in the single sample taken from the White Pine Mine, where D = +1 on a 20 oxygen formula basis; most D values range from +0.5 to −0.6 (Brown and Brindley, 1980). Drill hole W-11 displays a clear trend of decreasing silicate and increasing hydroxide sheet Fe content with increasing depth (Figure 4); similar trends occur in drill holes WP and

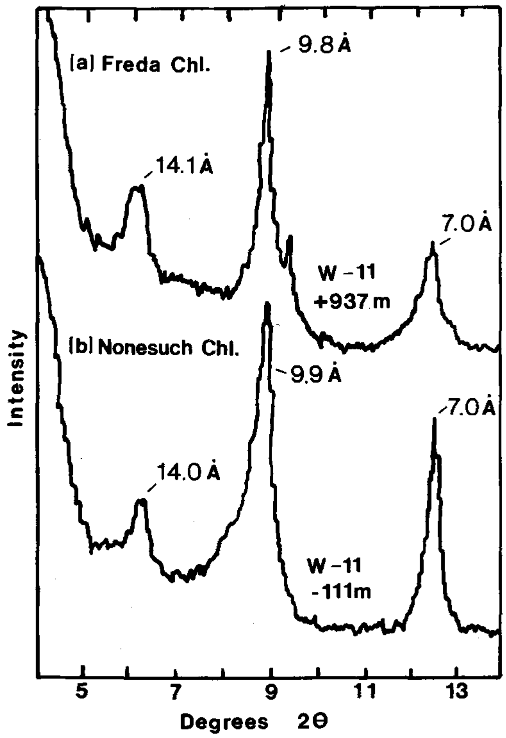

Figure 4. (a) XRD pattern representing a typical Mg-rich chlorite, [I(003)/I(001)] = 0.7, from the Freda Sandstone. The ethylene glycol solvated, <2 μm sample is taken from drill hole W-11 at +937 m. Note traces of laumontite (9.3 Å peak). (b) XRD pattern representing a more Fe-rich chlorite, [I(003)/I(001)] = 1.6, from the Nonesuch Formation. The air dried <2 μm sample is taken from drill hole W-11 at −111 m.

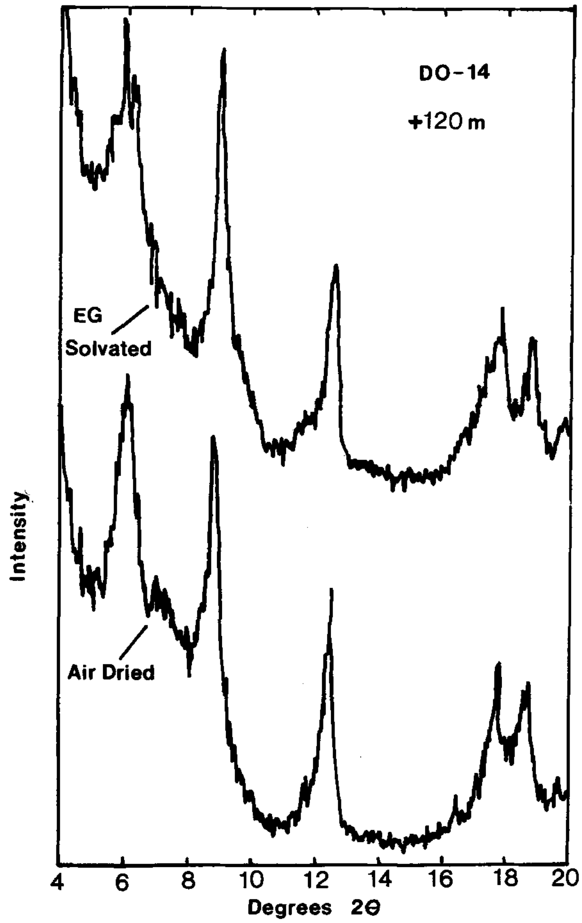

Figure 5. XRD pattern showing expandable chlorite phase represented by a peak shift to 14.5 Å and 15.0 Å upon glycolation. Also note peak shift broad peak between 6° and 8°2θ, which shifts upon glycolation to form a shoulder near 9.5°2θ, indicating an expandable I/S phase.

A-5 (located 14 km northeast of W-11). The trend is more apparent in the <2 μm samples than in the <1 μm samples, but is observed in both. Comparison of even/odd basal reflection intensity ratios indicates generally homogeneous chlorite compositions within both the Freda Sandstone and the Nonesuch Formation, but chlorites within the Nonesuch Formation are distinctly more Fe-rich (3–5 Fe/20 oxygens) than those within the Freda Sandstone (<1 Fe/20 oxygens).

In the Wisconsin drill holes, both chlorite and expandable chlorite (15.0–15.2 Å, EG) are present in the +120 m to +70 m range at the base of the Freda Sandstone where chlorite first appears (Figure 5). Similar expandable chlorite (possibly interstratified chlorite/smectite) appears sporadically in drill holes W-11 and W-7 (located 15 km southwest of W-11). While peak overlaps prevent determination of the rationality of basal peak spacings, mixtures of corrensite and chlorite commonly occur within the native copper deposits of the Keweenaw Copper District in both Oronto Group sediments and the underlying Portage Lake Volcanics (Hong and McDowell, unpublished data).

Laumontite is observed as a trace constituent on the Freda Formation from drill holes WP and WPB-1 (Figure 5). In W-11, laumontite represents a significant constituent in almost all samples of the <2 μm fraction from the Freda Sandstone, but occurs in the <1 μm fraction in only one sample.

Illite-smectite

Representative XRD patterns (Figure 6) illustrate the variability of I/S expandability, which ranges from up to 80% decreasing to essentially 0%. Two trends occur with respect to I/S expandability. First, each drill hole displays a consistent trend of decreasing expandability with increasing depth (Figure 7). Second, expandability generally decreases along strike moving away from the Iron River Syncline area (WPB-1) within equivalent stratigraphic horizons (Figures 7 and 8). At shallower depths within the Freda Sandstone, expandabilities increase to the southwest toward Wisconsin. These general trends are also present in the <2 μm data set.

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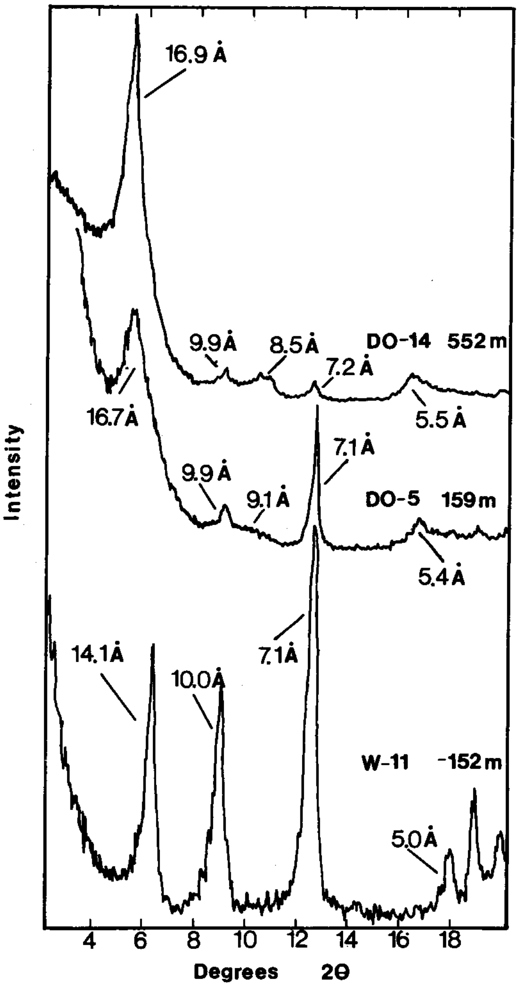


Figure 6. Representative XRD patterns illustrating decreasing expandability and increasing "crystallinity" with depth. Note the presence of two I/S phases in the uppermost pattern.

The transition from R0 (disordered) smectite-rich I/S to R1 (ordered) illite-rich I/S appears only in drill holes from the Wisconsin section (DO-14 and DO-5). The most expandable I/S phase, in excess of 80%Exp, occurs in the Freda Sandstone in Wisconsin at +200 m above the Nonesuch datum. It is characterized by a sharp, slightly asymmetrical 16.8–16.9 Å (001, EG) reflection, but very broad, low-intensity higher order reflections. To emphasize the width of the higher order reflections, %Exp estimates utilize both the peak centroids (filled circles, Figure 7) and the shoulders of the peaks (limits of the range bars, Figure 7). The ranges indicated may be due to real variations in the I/S ratio of the <1 μm fraction clays, although grain size and crystallinity clearly have an effect. The same procedure for estimating the mean and range of %Exp was followed for all samples to assess the potential sample variability. The samples in the +229 m to +412 m range in DO-14 have the same general characteristics as the shallower samples except that upon glycolation, the expanded peak occurs at 16.2–16.4 Å.

The transition from 85%Exp to less than 20%Exp occurs over a depth interval of less than 125 meters, between +229 m and +105 m in the Wisconsin section (Figures 7 and 8). Patterns at +159 m in drill hole DO-5 suggest an average of 47%Exp, a large range of %Exp, and the presence of *both* R0 and R1 ordering. Samples at +120 m and +105 m indicate R1 ordering, while at +70 m and below, the presence of R > 1 ordering is indicated. At +120 m, a distinct illite (001) peak in the 9.9–9.98 Å range appears and persists with increasing depth in both the remaining Freda Sandstone and the entire Nonesuch Formation. This phenomenon is entirely consistent with the growth of discrete illite patches or grains within regions as observed in TEM by Ahn and Peacor (1986) and Yau and others (1987), suggesting a direct simultaneous reaction of smectite-rich I/S to both illite and illite-rich I/S.

In all drill holes sampled in Michigan, the most expandable clays observed were R1 ordered with about 30%Exp. Within the Freda Sandstone, less expandable I/S occurs progressively higher in the section, toward the northeast (Figures 7 and 8). The transition from 20%Exp to only a trace expandable I/S occurs over a 400 m vertical interval in drill hole W-11 and over a 200 m interval in drill hole WP; in both cases, the transition occurs entirely within the Freda Sandstone. The least expandable I/S occurs near the base of drill hole W-11. The R0/R1 transition occurs at approximately +600 m to +700 m in W-11, but near the Freda-Nonesuch contact at White Pine. No R3 long-range ordering was observed within the Nonesuch Formation in WPB-1.

Despite the obvious variation in the rate of change in expandability with depth in the Freda Sandstone, I/S expandability within the Nonesuch Formation itself is typically 10%Exp or less. The only exception occurs in drill hole WPB-1, located west-southwest of the White Pine ore body near the axis of the Iron River Syncline; here, expandabilities within the Nonesuch Formation vary from 25 to 30%Exp (Figure 7). Thus, expandabilities in the Nonesuch Formation decrease away from WPB-1 to less than 15%Exp in Wisconsin, less than 5% at White Pine (only 20 km away), and to only a trace expandable 70 km to the northeast.

SEM

SEM analysis of several samples from the Wisconsin DO drill holes suggests an overall trend of increasing crystal size and more euhedral morphology with depth in addition to significant changes in the overall authigenic mineral assemblage. An anhedral smectite-kaolinite(+microcline-quartz) authigenic assemblage dominates the <1 μm size fraction in the shallower portions of drill hole DO-5 (above the abrupt reduction in %Exp) and occurs primarily as a cement. Discrete

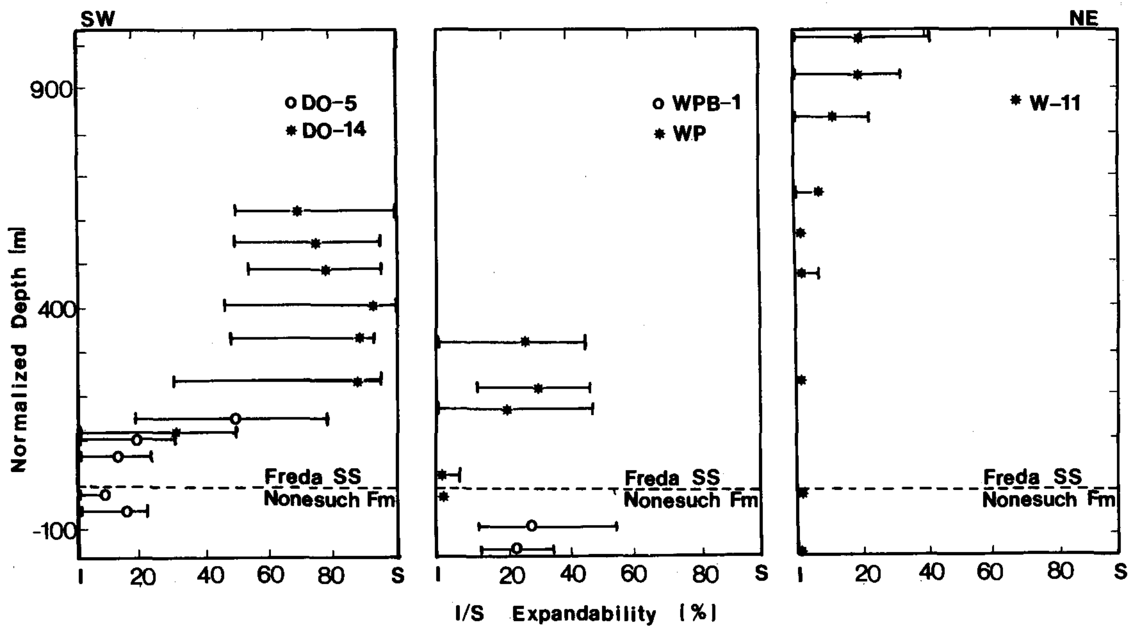


Figure 7. I/S expandability relative to the top of the Nonesuch Formation for drill holes DO-5, DO-14, WPB-1, WP, and W-11. See text for discussion of averages and range bars. Drill holes WP and W-11 (and to some extent drill hole WPB-1) clearly show the trend of decreasing expandability with depth. Drill holes DO-5 and DO-14 show a similar trend within the Nonesuch Formation and the lower portions of the Freda Sandstone. However, the upper portions of drill hole DO-14 do not conform to this trend and, in fact, appear to contradict the trend above the +400 m horizon.

flakes of authigenic illite and chlorite also occur, but infrequently. With increasing depth, authigenic illite and chlorite flakes become more common. According to XRD analyses of the <1 μm fraction, kaolinite and chlorite occur together as authigenic phases in some samples, assuming that this finest size fraction successfully eliminated detrital contamination. Although no individual kaolinite packets were observed in SEM, chlorite pseudomorphs after kaolinite occur in the deepest part of drill hole DO-14 (Figure 9a). In the most thermally mature samples, intergrown "cabbage leaves" of illite and chlorite dominate although chlorite and illite occasionally occur as laths and illite also occurs as ribbon-like pore filling (Figure 9b). The pattern

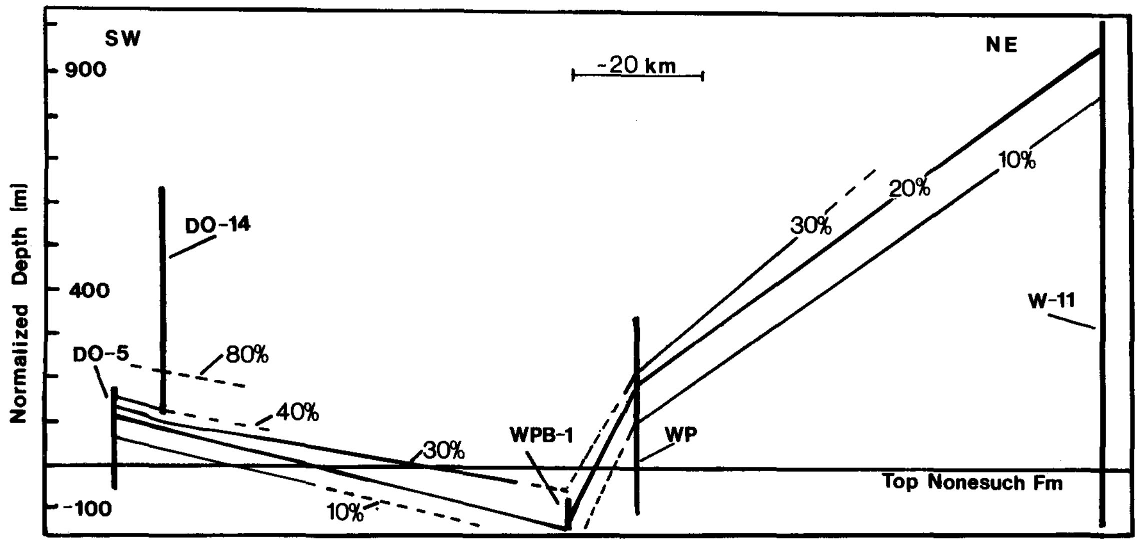
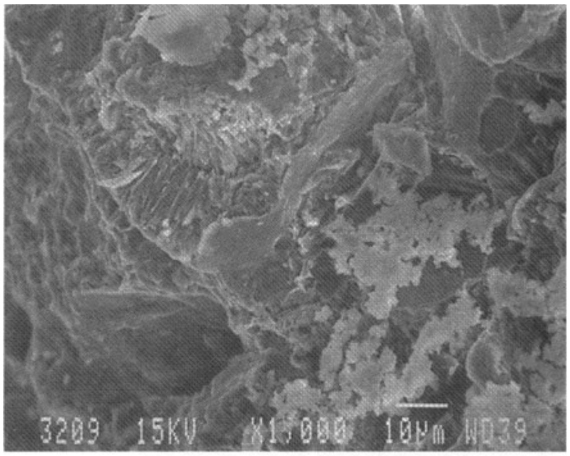


Figure 8. Schematic cross-section showing horizontal and vertical trends in I/S expandability. Note that the Iron River Syncline area (drill hole WPB-1) represents a thermal maturity low; the data show an increase in thermal maturity to the southwest within the Nonesuch Formation, but the most significant increase occurs to the northeast.



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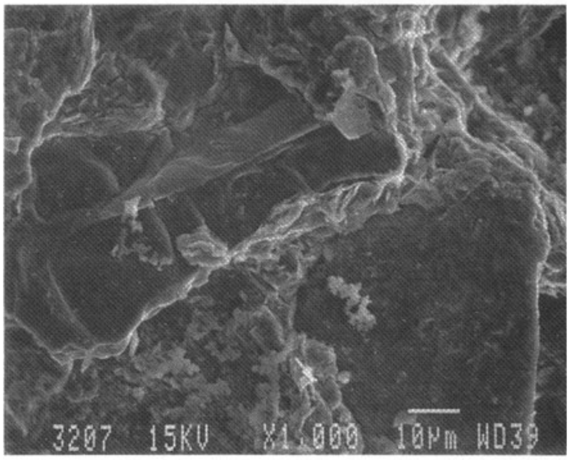

B

Figure 9. (A) SEM photomicrograph of chlorite after kaolinite, and (B) SEM photomicrograph of ribbon-like illite pore filling.

of increasingly euhedral crystal morphology observed in SEM directly parallels the trend of increasing crystallinity of the clay minerals observed by XRD methods.

I/S geothermometry

Pollastro (1990) has summarized the relationship between maximum burial temperatures and I/S expandability. Only systems exposed to elevated temperatures for more than 2 million years are considered in this data base. Using the data sources cited in Pollastro (1990) to produce an approximate geothermometer generally conforming to the model proposed for shales by Hoffman and Hower (1979), we have correlated temperatures to particular values of %Exp. Application of this geothermometer to the Nonesuch Formation yields maximum temperature estimates of about 140°C for the Wisconsin section, 115°C for WPB-1, 160°C for WP, and up to 190°C for W-11. The R0/R1 transition near +159 m in drill hole DO-14 indicates a temperature of 105°C. Thus, temperatures well above 100°C are required for all sampled portions of both the Freda Sandstone and the Nonesuch Formation in Michigan, and for the Nonesuch Formation in Wisconsin, according to the "traditional" use of the I/S geothermometer. Note that despite being referred to as "sandstone," the Freda Sandstone contains significant siltstone lithologies with high clay content, and the grain-size contrast between the Nonesuch and the Freda is, in fact, very small. Thus, we have assumed that the shale-based I/S geothermometer applies to both the Nonesuch Formation and the Freda Sandstone.

DISCUSSION

The Nonesuch Formation appears thermally mature everywhere with respect to I/S data; the lowest inferred paleotemperatures occur just southwest of White Pine in the vicinity of drill hole WPB-1 (Figures 7 and 8). Organic thermal maturity indicators within the Nonesuch Formation (Table 1), particularly biomarker indices reported by Pratt and others (1991), suggest relatively low thermal maturities at White Pine, increasing to the southwest. Their data appear consistent with the lower to middle range of the "oil window" (Heroux *et al.*, 1979; Waples and Machihara, 1991). I/S expandability values corroborate the increasing thermal maturity to the southwest, although the highest inferred paleotemperatures (from %Exp values) within the Nonesuch Formation occur toward the northeast, as only trace expandabilities persist in drill hole WP as compared to WPB-1. Even farther to the northeast, in drill hole W-11, the illite-chlorite assemblage seems more reminiscent of lower greenschist facies rocks. Thus, a very clear pattern emerges when maximum paleotemperatures are inferred from the observed I/S expandability trends. The agreement in the geographic pattern of thermal maturity using clay expandabilities coupled with organic indicators suggests that, at least in the Nonesuch Formation, the clay expandabilities are controlled primarily by burial diagenesis during the main rifting and thermal event.

The highest inferred paleotemperatures (drill hole W-11) coincide with that part of the sampling area closest to the most productive native copper deposits in the underlying Portage Lake Volcanics. I/S data from drill hole W-11 indicates a maximum paleogeothermal gradient of approximately 55°C/km, which falls well within the range expected in a rift setting. This estimated gradient is identical to that of the background gradient of the currently active Salton Trough of California and adjacent Mexico (Lachenbruch *et al.*, 1985).

Table 1. Organic thermal maturity indicators for the Nonesuch Formation.

Data type	Range of values	Reference
Rock Eval® (T_{max})	421°C–437°C	Hieshima and Pratt (1991)
	435°C–440°C	Pratt and others (1991)
	435°C–447°C	Imbus and others (1990)
TOC (total organic carbon)	0.05%–2.66%	Hieshima and Pratt (1991)
	0.1%–3.0%	Imbus and others (1990)
CPI (carbon preference)	0.90–1.07	Imbus and others (1988)
Biomarker index		
Hopane ratio	0.58–0.61	Pratt and others (1991)
Sterane ratio	0.34–0.57	Pratt and others (1991)

Extrapolation of this gradient to reasonable surface temperatures suggests approximately 3 km of section above the Nonesuch Formation at this location; in comparison, a maximum of 3.6 km of Freda Sandstone are presently exposed near the Michigan-Wisconsin border.

While thermal effects could have controlled the observed vertical trends in expandability in the Freda Sandstone to the northeast, a simple thermal interpretation is not reasonable in the Wisconsin DO drill holes. Here the abrupt transition from >80%Exp to <20%Exp requires implausibly high geothermal gradients. A variety of factors including a complex temperature history, fluid circulation, fluid composition, or combinations of these could be responsible for the observed expandabilities. While the highly expandable, poorly crystalline I/S and kaolinite within the shallower parts of the Wisconsin drill holes may represent unmodified low temperature clay, it is unlikely that this clay material was produced during initial burial diagenesis. Any explanation of the observed expandability distribution must take into account the following geological constraints:

1) The lithology, stratigraphy, and physical properties of both the Freda Sandstone and Nonesuch Formation are very similar across the sampled area.

2) There is abundant evidence for extensive fluid circulation during emplacement of the native copper deposits in the Portage Lake Volcanics from the general vicinity of drill hole W-11 and on to the northeast. The evidence for significant fluid movement dies out to the southwest approaching Wisconsin. Thus, elevated geothermal gradients near W-11 are quite plausible, but it is difficult to appeal to fluid circulation (or changes in fluid chemistry) in the deeper parts of the Wisconsin DO drill holes as sole cause of the abrupt decrease in expandabilities down section. In addition, if the deeper fluids were hotter, clay reaction kinetics during decay of the thermal anomaly should have allowed the abrupt variation in clay expandabilities to be smoothed out.

3) The Freda Sandstone northwest of the DO drill holes may be overlain by a younger basin of Precambrian Bayfield Group sediments, now exposed on Wisconsin's Bayfield Peninsula (Cannon *et al.*, 1989).

In light of the above, we suggest that the abrupt upward increase in clay expandabilities near the base of the Freda Sandstone was due to later fluid circulation in the shallower parts of the section, possibly during formation of the Bayfield Group sedimentary basin. This fluid was most likely both cooler and of significantly different composition than fluids associated with clay diagenesis during the original depositional/thermal cycle. This type of overprinting by a much cooler hydrothermal event should result in two phases of I/S, the second much more expandable than the first. The presence of a 9.9 Å peak in the <1 μm samples from the Wisconsin section (Figure 6) provides further evidence that cooler fluids may have overprinted earlier diagenetic trends. Because the later event occurred at lower temperatures, clay reaction kinetics would allow the discontinuity in expandabilities with depth to be preserved. Lower temperature alteration may have been limited to the shallower portions of the Freda Sandstone because of a slight porosity and permeability decrease down section as the rocks fined slightly and became more clay-rich toward the Nonesuch Formation. It should be emphasized, however, that the lithologic and petrophysical differences between the two formations are very slight, and both units are relatively fine-grained. No overprinting occurred to the northeast in Michigan, thus suggesting that the younger basin either did not exist there, or was located well offshore to the northwest along the axis of Lake Superior.

Maximum formation temperature estimates for the Nonesuch Formation from I/S geothermometry range from 115° to 190°C, depending on geographic location. Thermal modeling (Price *et al.*, in prep.) suggests that the Nonesuch Formation reached maximum temperatures of 110° to 125°C in the vicinity of White Pine, Michigan. Since the thermal model is based on conductive heat flow only, it clearly does not apply to the northeast in Michigan where abundant evidence of presumably advective fluid flow exists in the Portage Lake Volcanics associated with native copper deposition. I/S geothermometry in the area from White Pine, Michigan, to Wisconsin yields temperatures in the 115°–160°C range, slightly higher than but still overlapping estimates from thermal modeling. Organic biomarker indices (Hieshima and Pratt, 1991; Pratt *et al.,* 1991) from this area suggest temperatures in the low to middle range of the "oil window." Since oil generation spans the range from roughly 50° to 200°C (Hunt, 1979; Ammosov, 1981), with maximum oil generation in the 100° to 150°C range (Quigley and Mackenzie, 1988), organic thermal maturity data and I/S geothermometry indicate a thermal history consistent with oil generation.

The 160°C estimate from I/S geothermometry for the Nonesuch Formation in the White Pine mine (drill hole WP) is significantly higher than the best available temperature estimates from calcite veins within the mine, which are consistently below 100°C (Kelly and Nishioka, 1985; Nishioka *et al.,* 1985). Most of these veins are probably associated with late or second-stage native copper mineralization contemporaneous with the post-rift compressional event. The veins contain inclusions of liquid petroleum and solid pyrobitumen whose chemistry indicates an origin from the Nonesuch Formation (Mauk and Hieshima, 1992). The copper-sulfide bearing rocks in the mine containing the clays sampled for this investigation may have been subjected to an earlier, higher temperature heating event, followed by faulting, vein-filling, petroleum migration, and native copper mineralization as outlined by Mauk and others (1992). These authors also suggest that the second-stage mineralization at White Pine may be contemporaneous with and genetically related to massive native copper mineralization hosted by the Portage Lake Volcanics within the Keweenaw District.

These observations suggest a two-stage alteration model for both the Oronto Group sediments and the underlying rocks: 1) The thermal event associated with rifting provided the driving energy for most of the clay diagenesis in the sediments investigated here, and much of the zeolite-grade burial metamorphism of the deeper sediments and volcanics. Relatively little fluid circulation occurred within the Nonesuch Formation and the overlying units; heat was transferred mainly by conduction. Deeper in the section, fluid movement may have taken place, but it was probably relatively minor and confined to up-dip movement along permeable flow tops and interflow sediments. And 2) the rift-terminating compressional event caused uplift and accelerated cooling; upward penetration of compression-driven fluids occurred locally, as at White Pine. Compression also led, in the deeper rocks, to a period of extensive fluid transport that utilized channels created along the faults and fractures generated during compression. The magnitude of fluid movement generally increased to the northeast as reflected by the volume distribution of native copper deposits, which effectively begin near Mass City, Michigan, roughly midway between drill holes WP and W-11 on Figure 1, and increased substantially in size toward the northeast. Within the Keweenaw Copper District, it is entirely possible that temperatures remained high, despite uplift, because of the great volume of hot fluids that moved upward into these rocks. Thus, the 55°C/km geothermal gradient estimated for drill hole W-11 could have been affected by deeper advective heat transfer during compression and uplift. However, the relative lack of extensive veining and copper deposition in the deeper volcanics to the southwest of White Pine suggests that, in this region, later fluid circulation was minor and probably had little thermal effect on the Nonesuch Formation and the overlying units.

It should be emphasized that we regard the temperatures produced by I/S geothermometry to be maximum values. The relationship between temperature and I/S expandability is based mainly on data from rocks in currently active basins for which the maximum temperature is the temperature now observed. It is clear, for kinetic reasons, that the reaction continues on the cooling limb of a basin thermal/burial cycle. The cumulative %Exp attained in a currently subsiding basin can be duplicated by rocks that reached lower peak temperatures in a fossil system that has *completed* a heating and cooling cycle. Thus, the I/S geothermometer will tend to overestimate maximum formation temperatures in proportion to the length of the cooling limb of the thermal history curve. For this particular basin, thermal modeling suggests that the actual maximum temperature of a full thermal cycle is approximately 85% of the temperature estimated from I/S geothermometry (Price *et al.,* in prep.). Adjustment of the I/S-derived temperatures improves the agreement with organic thermal maturity indicators slightly, but the geographic pattern of estimated temperatures is unchanged. Despite these adjustments, the results of both I/S geothermometry and heat transfer modeling indicate somewhat higher temperatures within the Nonesuch Formation than results reported from fluid inclusion studies of veins hosted by the Nonesuch Formation at White Pine.

CONCLUSIONS

Perhaps the most important result of this study is the documentation of expandable I/S-type clays in rocks nearly 1.0 billion years of age. In addition, regular trends of decreasing expandability with depth have been preserved suggesting that at least in the vicinity of White Pine, Michigan, the I/S expandability values reflect a thermal profile produced during burial diagenesis. The preservation of expandable I/S-type clays can be directly attributed to the cooling effect of rift termination and uplift associated with the compressional event dated at approximately 1060 Ma (Cannon *et al.,* 1990) and the absence of significant tectonic activity later in the basin's history.

Temperatures estimated from I/S geothermometry (e.g., Hoffman and Hower, 1979; Pollastro, 1990) for clay from the Nonesuch Formation range from 115° to 190°C. Where independent information is available on organic thermal maturity indicators from the Nonesuch Formation, there is general agreement between the low to moderate thermal maturities estimated from the hydrocarbons and I/S geothermometry. In addition, the geographic distribution of temperatures estimated from the clay minerals is in excellent agreement with the pattern of thermal maturity estimated from organic material in the Nonesuch Formation. Both organic thermal maturity and I/S %Exp values for the Nonesuch Formation are lowest in the Iron Mountain Syncline area (115°C, drill hole WPB-1) and increase southwest toward Wisconsin (140°C, DO-5, DO-14) and northeast toward White Pine (160°C, WP).

I/S geothermometry indicates a significant temperature increase toward the northeast within the Nonesuch Formation, which parallels an increase in the amount of uplift along the Keweenaw Fault, as well as progressively more pervasive alteration and native copper mineralization in the Portage Lake Volcanics. The estimated temperature gradient of 55°C/km from drill hole W-11, near the southwestern limit of the copper district, is a reasonable gradient for a rift setting, and implies that no more than 3 km of sediment existed above the Nonesuch Formation at the time the gradient was formed. The maximum thickness of the overlying Freda Sandstone, measured near the Michigan-Wisconsin border, is 3.6 km, implying that no younger sediments, such as those of the Bayfield Group, existed above the Oronto Group at this location. Intuitively, the presence of 3.6 km of Freda Sandstone near the Michigan-Wisconsin border (as opposed to less than 1.0 km near White Pine) should correlate to increased thermal maturity within both the Nonesuch Formation and the Freda Sandstone. However, I/S expandability data from the Freda Sandstone suggest anomalously low thermal maturities.

The very abrupt transition from highly expandable I/S to well-crystallized, much less expandable I/S near the base of the Freda Sandstone in the Wisconsin DO-series drill holes is most reasonably interpreted to be the result of alteration during later circulation of fluids that were both cooler and of different chemistry than the original diagenetic fluids. The timing of this later alteration is unknown, but may have occurred during deposition of younger Bayfield Group sediments which may overlie the Freda Sandstone to the northwest. Note that overprinting of diagenetic assemblages by younger groundwater systems after uplift, or from later, superimposed sedimentation and basin formation, is to be expected in many geologic settings, and is, in our opinion, a process whose presence is very easy to underestimate.

At White Pine, I/S geothermometry suggests maximum temperatures near 160°C; here, shale from the Nonesuch Formation contains both copper-sulfides and solid pyrobitumens. However, cross-cutting veins that contain native copper and liquid petroleum inclusions were apparently emplaced at temperatures less than 100°C (Mauk and Hieshima, 1992). The chemistry of both liquid and solid hydrocarbon phases indicates that the liquid petroleum had its origin from the Nonesuch Formation; the later veins are apparently associated with late compression and reverse faulting (Mauk and Hieshima, 1992). Thus, petroleum generation probably occurred within the Nonesuch Formation at maximum temperatures well above 100°C during the main thermal event, while fluid driven petroleum migration occurred later, and at lower temperatures through faults and fractures created during the rift-terminating compressional event.

A comparison of peak temperatures produced during a complete burial thermal cycle, and temperatures estimated directly by I/S geothermometry, shows that the I/S-derived temperatures should be reduced by roughly 15% for this particular basin. The amount of temperature overestimation depends on the thermal history of each basin and, in particular, on how much reaction occurred on the cooling limb of that basin's thermal history curve. It is clear that temperatures based on I/S geothermometry are maximum values. In the case of this Proterozoic basin, adjustment of the I/S-based temperatures downward does not affect the general conclusions, although it does appear to improve the agreement between these temperature estimates and the very general temperature estimates available from organic thermal maturity data. Because the traditional use of I/S expandability as a true geothermometer inherently overestimates maximum formation temperatures, such techniques should be utilized in the context of a thermal and burial history model that can calculate temperature-time paths for various units, and make kinetically based estimates of cumulative organic maturation and clay expandabilities.

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