

## MULTIPLE EPISODES OF CLAY ALTERATION AT THE PRECAMBRIAN/ PALEOZOIC UNCONFORMITY, APPALACHIAN BASIN: ISOTOPIC EVIDENCE FOR LONG-DISTANCE AND LOCAL FLUID MIGRATIONS

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**Abstract**—Chlorite and illite are commonly associated with ubiquitous secondary K-rich feldspar in the rocks located immediately above and below the Precambrian-Paleozoic unconformity in southwestern Ontario, and elsewhere in the mid-continent of North America. This alteration assemblage is attributed to long-distance migration of hot brines driven westward by orogenic processes originating along the eastern seaboard of North America. The  $\delta D$  and  $\delta^{18}O$  values of chlorite and illite, plus K-Ar dates for secondary K-rich feldspar and illite, were used to determine the nature, origin, and timing of the fluids that altered Precambrian granites and their overlying rocks in southwestern Ontario. The  $\delta^{18}O$  values of the chlorite-forming fluids are best explained by initial hot brines ( $\geq 150^\circ C$ ) evolved mostly from seawater. Secondary K-rich feldspar formation followed shortly thereafter, as the fluids cooled and perhaps mixed with meteoric water. Regional migration of the brines was induced by Taconic orogenic events to the east. The hydrogen and oxygen isotopic compositions for the secondary illite of the early to mid-Carboniferous indicate its crystallization from local meteoric water at low temperatures ( $40\text{--}55^\circ C$ ). Infiltration of local meteoric water into the Paleozoic and uppermost altered Precambrian rocks occurred during uplift, erosion, and subaerial exposure of local arches in southern Ontario. The local basement reactivation and associated secondary illite formation in this portion of the North American hinterland was likely a distal expression of east-coast Acadian and Alleghanian orogenic activity.

**Key Words**—Alteration, Brines, Chlorite, Illite, Isotopes, Meteoric Water, Precambrian Unconformity, Ontario.

### INTRODUCTION

The rocks immediately above and below the Precambrian-Paleozoic unconformity of many Paleozoic sedimentary basins in mid-continental North America contain secondary K-rich feldspar, and chlorite and illite from alteration. This paper examines the origin of such alteration in rocks from the uppermost Precambrian of southwestern (SW) Ontario. Thrusting of the Appalachian foreland during orogenic activity has been considered responsible for the migration of brines leading to the formation of this alteration assemblage (Oliver, 1986; Hearn *et al.*, 1987; Bethke and Marshak, 1990). The origin, migration, and geochemistry of these fluids are of special interest. These brines may be responsible for Mississippi Valley-type (MVT) mineral deposits and hydrocarbon accumulations throughout mid-continental North America. Dolomitization, paleomagnetic disturbances, and high paleotemperatures also have been attributed to these fluids (Bethke and Marshak, 1990).

The secondary K-rich feldspar within the Precambrian rocks has been studied extensively (*e.g.*, Mensing and Faure, 1983; Duffin, 1989; Hay and Liu, 1991; Harper *et al.*, 1995). Radiometric dates for such K-rich feldspar in uppermost Precambrian rocks of SW

Ontario (average age of 444 million years, Ma; Harper *et al.*, 1995) show that K-rich feldspar formation is not related to Precambrian subaerial weathering. Instead, secondary K-rich feldspar crystallization probably indicates rock/water interactions driven by Paleozoic tectonic processes (Harper *et al.*, 1995). Clay-mineral alteration in the Precambrian rocks has not received similar attention. In SW Ontario, plagioclase-replacing chlorite and albite are the initial alteration minerals, formed prior to K-rich feldspar, whereas illite is one of the last alteration products (Harper *et al.*, 1995). Such illite in the altered Precambrian rocks of New York, to the east of our study area, was dated at 355 Ma (Tiller and Selleck, 1992). Within southern Ontario, Ziegler and Longstaffe (2000) reported K-Ar illite dates of 365–321 Ma for Cambrian and Ordovician sedimentary rocks that immediately overlie the unconformity.

Stable and radiometric isotopic studies are prominent in the understanding of this intense alteration, which has affected a large portion of North America. Heyl *et al.* (1974), for example, reviewed isotopic evidence for the origin of the fluids responsible for MVT deposits in the Paleozoic rocks. They concluded that two, and sometimes three fluids were involved, with hot basinal brines and meteoric water as the main components and magmatic water as a minor component. The timing of the alteration has also been the subject

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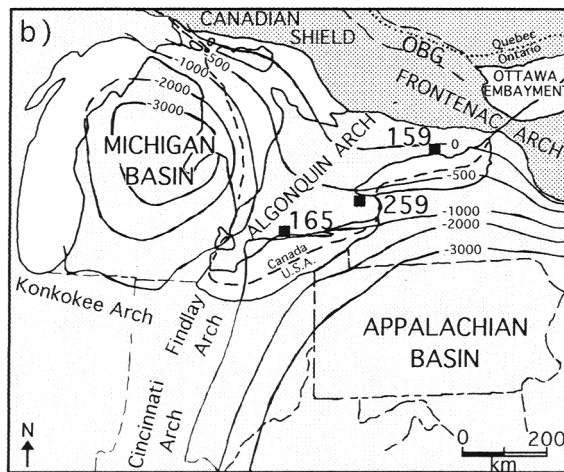
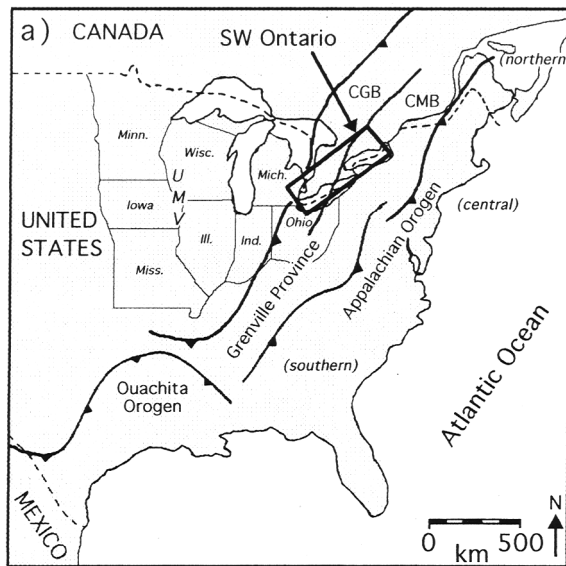


Figure 1. a) Location map for SW Ontario. CGB = Central Gneissic Belt; CMB = Central Metasedimentary Belt (after Carter and Easton, 1990); UMV = Upper Mississippi Valley district, including Minnesota (Minn.), Wisconsin (Wisc.), Iowa, and northern Illinois (Ill.), Miss. = Missouri, Mich. = Michigan, Ind. = Indiana. The foreland thrust-belt boundaries are taken from Aleinikoff *et al.* (1993). b) Study area, showing local arches, structure on top of the Precambrian basement (isopachs in m), and the location of boreholes (squares). OBG = Ottawa-Bonnechère Graben.

of much study. Many of the radiometric dates for the secondary K-rich feldspar cluster in broad yet overlapping ranges, whereas the illite dates generally are much younger but span a much larger interval (see summaries in Harper *et al.*, 1995, and Ziegler and Longstaffe, 2000). To explain these data, multiple episodes of fluid migration have been proposed. Most dates coincide with the succession of orogenic events along the Appalachian Belt (Bethke, 1986; Duffin *et*

*al.*, 1989; Hay *et al.*, 1988; Hearn and Sutter, 1985; Hearn *et al.*, 1987; Leach *et al.*, 1984; Rowan *et al.*, 1984). Thus, the fluids responsible for alteration migrated long distances, consistent with alteration that extends widely over space and time.

Compaction-driven flow and tectonic overpressuring of basal brines, and gravity-driven flow of meteoric water have been the principal mechanisms offered to explain such extensive fluid transport in the deep subsurface (Bethke, 1986; Bethke and Marshak, 1990; Jackson and Beales, 1967; Oliver, 1986). Harper *et al.* (1995) combined these mechanisms to explain the oxygen isotopic values of alteration minerals from the uppermost Precambrian rocks of SW Ontario. They proposed a substantial change in pore-water chemistry and temperature during the alteration, from hot brine (~150°C) originating from evolved Paleozoic seawater to much cooler meteoric water, which mixed with the earlier fluids. In the current study, we define more precisely the origin of the fluids that affected these rocks, using the hydrogen- and oxygen-isotope compositions of secondary chlorite and illite. Assuming that post-crystallization isotopic exchange was insignificant (Longstaffe and Ayalon, 1990), a difference should exist between the  $\delta D$  and  $\delta^{18}O$  values obtained for clays formed from seawater-dominated fluids *versus* those produced by interaction with fresh water.

## GEOLOGICAL BACKGROUND

The Precambrian rocks of SW Ontario (Figure 1a) form part of the Grenville Province, which is subdivided into the Central Metasedimentary Belt (CMB) in the southeast and the Central Gneissic Belt (CGB) in the northwest (Carter and Easton, 1990). Southwestern Ontario lies along the axis of the southwest-trending Findlay-Algonquin Arch, which separates the Appalachian Basin from the Michigan Basin (Figure 1b). During the Paleozoic, the arch acted as a hinge-line between the two basins, and periodically moved vertically in response to tectonism at the eastern margin of the craton (Quinlan and Beaumont, 1984). The Frontenac Arch, which is located to the northeast (Figure 1b), represents the pinchout margin of the sedimentary section in SW Ontario (Carter, 1990). The Appalachian foreland basin developed because of lithospheric flexure caused by crustal loading. The loading resulted from the emplacement of thrust sheets during Paleozoic orogenic activity along the eastern margin of the basin. The mostly clastic infill of the Appalachian Basin reaches a maximum thickness of 13 km. By comparison, the sedimentary succession of the intracratonic Michigan Basin consists mainly of carbonates, which attained thicknesses of 4.8 km at the depocentre (Quinlan and Beaumont, 1984; Johnson *et al.*, 1992).

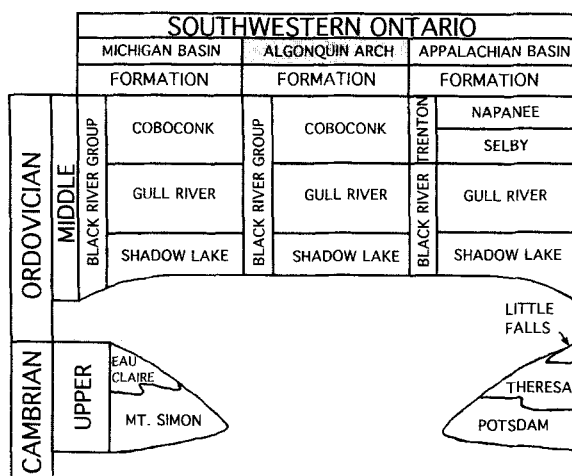


Figure 2. Cambrian and Ordovician stratigraphy of SW Ontario (Winder and Sanford, 1972).

In SW Ontario, the Precambrian basement is overlain unconformably by  $\leq 1500$  m of Paleozoic rocks (Sanford *et al.*, 1985). Upper Cambrian and Lower Ordovician rocks were completely eroded above the Findlay-Algonquin Arch (Figure 2). The Cambrian strata consist of conglomerates and arkosic sandstones, overlain by carbonates and clastic rocks. Middle Ordovician (Black River Group) limestones, and alternating silty and calcareous shales unconformably overly the Cambrian rocks. Silurian and Carboniferous units are composed of shales, sandstones, evaporites, and carbonates (Carter, 1990).

#### STUDY AREA AND SAMPLING

The uppermost several meters of Precambrian rocks in SW Ontario were sampled from boreholes penetrating the Precambrian-Paleozoic boundary. Three cores were sampled: #259 (Imperial #891, Wentworth Co., Saltfleet Twp., lot 11, conc. I), #165 (I.O.E.L. Atlas, Elgin Co., Dunwich Twp., lot 23, conc. IV), and #159 (Collins McIntyre, Peterborough Co., Otonabee Twp., lot 15, conc. X) (Figure 1b). The intensively altered core #165, originally of granitic composition, is located on the axis of the Findlay-Algonquin Arch. Cores #259 and #159, which consist mostly of tonalitic rocks, are located on the eastern flanks of the Arch; core #159 is situated much closer to the Frontenac Axis to the northeast. Core #259 shows intensive alteration; core #159 is less altered and penetrates deeply into the basement rocks. The Precambrian-Paleozoic unconformity occurs at different depths in the three cores: 184.1 m in core #159, 605.9 m in core #259, and 1102.5 m in core #165 (Figure 3). Samples of the Precambrian rocks were taken at intervals varying from a few centimeters to meters, with the interval generally decreasing with proximity to the unconformity.

#### METHODOLOGY

##### Analytical techniques

Following gentle crushing, the  $<2$ ,  $<1$ , and  $<0.2$ - $\mu\text{m}$  size fractions were separated by standard sedimentation and centrifugation techniques. Non-clay contamination in the  $<2$ - $\mu\text{m}$  size fraction consisted of minor quartz and feldspar. Both phases were eliminated using magnetic separation and/or by further separation to finer-size fractions. Concentrates very rich in chlorite or illite were obtained from the various fractions by liquid high-gradient magnetic separation (HGMS, Tellier *et al.*, 1988). Mineralogy and sample purity were determined by powder X-ray diffraction (XRD) of both oriented and randomly oriented mineral-aggregate samples (Rigaku rotating-anode diffractometer,  $\text{CoK}\alpha$  radiation). Treatments applied to the clay separates for the purposes of XRD included drying at 0 and 54% relative humidity, glycolation, and heating to 550°C. Clay polytypes were identified following the approach of Moore and Reynolds (1989). Compositional data were obtained by electron-microprobe analysis (JEOL JXA-8600), using a 5- $\mu\text{m}$  beam and 20-s counting periods.

Oxygen and hydrogen isotopic analyses are reported in the usual  $\delta$ -notation relative to the Vienna Standard Mean Ocean Water (VSMOW). Oxygen was extracted from the clay minerals using the  $\text{BrF}_5$  method of Clayton and Mayeda (1963) and converted quantitatively to  $\text{CO}_2$  over red-hot graphite. Dried samples were heated and pumped under vacuum at 150°C for 3 h prior to reaction with  $\text{BrF}_5$ . Hydrogen-isotope analyses were performed using a modified version of the uranium technique described by Bigeleisen *et al.* (1952), utilizing a torch as the heating device (Vennemann and O'Neil, 1993). Measurements of the D/H and  $^{18}\text{O}/^{16}\text{O}$  ratios were performed on VG Prism Series II and VG Optima mass spectrometers, respectively. Reproducibility was better than  $\pm 3\%$  for hydrogen isotopes ( $\pm 2\%$  on average) and  $\pm 0.3\%$  for oxygen isotopes ( $\pm 0.1\%$  on average). Laboratory standards calibrated to VSMOW and the Standard Light Antarctic Precipitation (SLAP) were accurate to within  $\pm 3\%$  for hydrogen isotopes and  $\pm 0.1\%$  for oxygen isotopes.

##### Hydrogen-isotope fractionation factors

Stable isotopic studies of clay mineral-water interactions depend upon the availability of fractionation factors that are appropriate for the chemistry and structure of the mineral, and the temperature of its formation. The hydrogen-isotope fractionations between illitic or chloritic minerals and water are not well known. Of the available studies for illite-water (ill-water), we assume that the equation (T in K) of Capuano (1992) is most suitable between 0–150°C:

$$10^3 \ln \alpha_{\text{ill-water}}^{\text{H}} = [45.3 \times 10^3 T^{-1}] + 94.7. \quad (1)$$

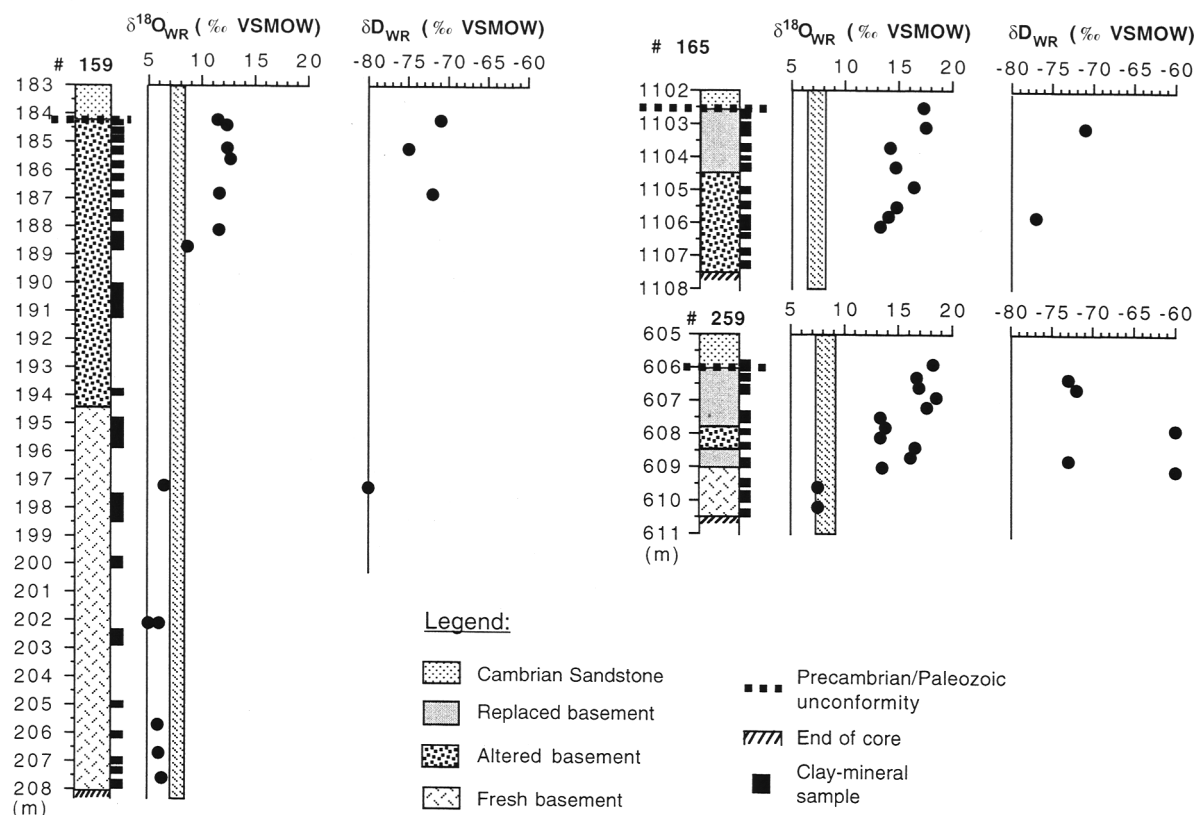


Figure 3. Alteration patterns, clay-sample locations, and whole-rock  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for Precambrian rocks from cores #165, #259, and #159. The range of  $\delta^{18}\text{O}$  values for unaltered, felsic Precambrian granitic rocks from southern Ontario is also shown (shaded) (Shieh and Schwarcz, 1974).

Chlorite-water hydrogen-isotope fractionations (chl-water) remain to be characterized fully. The hydrogen-isotope composition within chlorite is not homogeneous; hydroxyl groups associated with the brucite- or gibbsite-like interlayers normally concentrate H relative to the 2:1 layer. The effects of temperature, Fe/(Fe + Mg) ratio, and Fe(III) versus Fe(II) contents also have not been determined (Graham *et al.*, 1987). Suzuoki and Epstein (1976) proposed a systematic relationship between the value of  $\alpha^{\text{hy}}_{\text{phyllosilicate-water}}$  and the octahedral cation content (Mg, Al, Fe) of phyllosilicates. They suggested that the fractionation factor becomes larger as the abundance of Fe in octahedral sites increases, and that strong partitioning of Al into a gibbsite-like interlayer of chlorite should favor D enrichment of the associated hydroxyl groups. Suzuoki and Epstein (1976) also predicted that, at equilibrium, chlorite would be more depleted of D than chemically similar micas because of hydrogen bonding between the OH group of the interlayer and the Si-O tetrahedral sheet. Graham *et al.* (1980, 1987) and Satake and Matsuo (1984) suggested that long hydrogen bonds between brucite-like interlayers and 2:1 (talc-like) layers stabilize the chlorite structure, contributing to the interlayer bond energy. Graham *et al.* (1980, 1984) pro-

posed that shorter hydrogen bonds (*i.e.*, the O-H-O bridge) favor greater D depletion in chlorite.

Empirical estimates of  $\alpha^{\text{hy}}_{\text{chl-water}}$  were made by Taylor (1974), Kuroda *et al.* (1976), and Marumo *et al.* (1980). However, these values depend on assumptions of crystallization temperature, the isotopic composition of the water, and the absence of retrograde isotopic exchange (Graham, 1981). Over 130–250°C, Marumo *et al.* (1980, 1995) suggested that  $\alpha^{\text{hy}}_{\text{chl-water}}$  is more sensitive to Fe/(Fe + Mg) than to temperature, with  $\delta\text{D}$  values decreasing by >30‰ as the ratio increases. Studies of smectite suggest that Fe(III) content is most important in controlling this variation (Sheppard and Gilg, 1996). Similar behavior is expected for chlorite and 1:1 layer Fe-rich phases such as berthierine and odinite (Hornibrook and Longstaffe, 1996).

Experimental studies have also shown that temperature is no more than a subordinate control on the hydrogen-isotope composition of chlorite. Graham *et al.* (1987) found no temperature dependence between 700–500°C, with  $10^3 \ln \alpha^{\text{hy}}_{\text{chl-water}}$  remaining close to -28‰. Between 500–200°C, they observed only a slight dependence, with  $10^3 \ln \alpha^{\text{hy}}_{\text{chl-water}}$  changing from -30 to -40‰ with decreasing temperature. Graham

*et al.* (1987) used experimental data for epidote, boehmite, and serpentine (Graham *et al.*, 1980; Sakai and Tsutsumi, 1978) to infer a reversal of this trend below 200°C. However, measurements using molecular hydrogen as the exchange medium showed that the fractionation for epidote varies linearly with  $1/T^2$  between 150–400°C (Vennemann and O'Neil, 1996).

Driesner (1997) suggested that many conflicting experimental results for hydrogen-isotope fractionation in hydrous minerals could be reconciled by considering pressure effects. The largest changes in the mineral-water hydrogen-isotope fractionation ( $\leq 20\%$ ) were observed near the critical temperature for water (376°C) and at pressures below  $\sim 100$  MPa. However, below 200°C and  $\sim 20$  MPa (the situation in the present study), pressure effects on hydrogen-isotope fractionation are much smaller (Driesner, 1997).

Available data suggest that a temperature-insensitive value of  $10^3 \ln \alpha^{\text{hy}}_{\text{chl-water}}$  of  $-40\%$  is a useful approximation at  $\leq 200^\circ\text{C}$  (Kuroda *et al.*, 1976; Marumo *et al.*, 1980; Graham *et al.*, 1987). However, the apparent chemical dependence of the fractionation cannot be ignored. Accordingly, the data of Marumo *et al.*, (1980, 1995) are used to generate the following equation for use here:

$$10^3 \ln \alpha^{\text{hy}}_{\text{chl-water}} = 1.35 - \{93.17[\text{Fe}/(\text{Fe} + \text{Mg})]\}. \quad (2)$$

However, the conclusions of this study do not change significantly if the fixed value of  $-40\%$  is used instead of Equation (2).

#### Oxygen-isotope fractionation factors

The oxygen-isotope fractionations for ill-water and chl-water at low temperatures are better known than the hydrogen-isotope fractionations for these pairs. We use the ill-water fractionation equation (T in K) of Savin and Lee (1988) after Lee (1984):

$$10^3 \ln \alpha^{\text{ox}}_{\text{ill-water}} = -2.87 + [1.83 \times 10^6 T^{-2}] + [0.0614 \times (10^6 T^{-2})^2] - [0.0015 \times (10^6 T^{-2})^3]. \quad (3)$$

This relationship is based on high-temperature data and the assumption that illite and kaolinite fractionate oxygen isotopes similarly between 0–17°C. The equation of Sheppard and Gilg (1996) is less suitable for our study because it is derived from two low-temperature data points only. However, the use of this equation does not change the conclusions presented here.

For chlorite, we selected the equation (T in K) proposed by Cole *et al.* (1987):

$$10^3 \ln \alpha^{\text{ox}}_{\text{chl-water}} = [3.47 \times 10^6 T^{-2}] + [-5.79 \times 10^3 T^{-1}]. \quad (4)$$

Equation (4) was derived from regression of experimental results for chlorite formed by alteration of bi-

otite between 170–300°C (Cole, 1985), and from data for hydrous silicates condensed in meteorites at  $< 300^\circ\text{C}$  (Onuma *et al.*, 1972). This equation is preferred over that of Wenner and Taylor (1971), which was derived from coexisting minerals in metasedimentary rocks.

We also employed the bond-type method of Savin and Lee (1988) to obtain chl-water oxygen-isotope fractionation equations. The structural formulae of individual chlorite samples from SW Ontario were calculated following Foster (1962), and used to calculate the proportions of the different bond types. The  $\delta^{18}\text{O}_{\text{water}}$  values obtained using this approach are 1–2‰ more negative than those calculated using Equation (4), but this difference does not result in a different geological interpretation of our data. Equation (4) is used because it is based on chlorite crystallized at temperatures similar to those encountered in our study.

Cole and Ripley (1999) recently derived a new equation to describe oxygen-isotope fractionation between chlorite and water. Based on this equation, the  $\delta^{18}\text{O}_{\text{water}}$  values calculated for 150°C are  $\sim 1.4\%$  lower than those obtained using the relationship from Cole *et al.* (1987). This small change does not result in a different interpretation of our data. Accordingly, we have continued to use the expression of Cole *et al.* (1987) because this allows a direct comparison with earlier results for secondary chlorite from Lower Paleozoic rocks that immediately overlie the unconformity (Ziegler and Longstaffe, 2000).

## PREVIOUS WORK

### *Alteration zones and mode of occurrence of secondary clays*

Unaltered Precambrian granitoid rocks of the CGB are predominantly felsic to intermediate in composition. Gneissic banding varies from parallel to sub-parallel and weak to strong, and deformation is common. Medium- or coarse-grained bands, consisting mostly of quartz and feldspar, alternate with finer-grained, darker bands composed primarily of biotite, hornblende, and plagioclase. The altered uppermost Precambrian rocks were subdivided into three idealized zones by Harper *et al.* (1995). The first or 'fresh' zone consists of granitic to tonalitic gneisses exhibiting little observable alteration of primary quartz, feldspars, amphibole, and biotite. The second or 'altered' zone retains textures typical of the gneiss, but alteration of primary minerals is observable. The third or 'replaced' zone was intensely altered, and primary textures are rarely recognizable.

Secondary minerals are abundant within the 'altered' zone. Hornblende was converted to hydromuscovite and calcite, plagioclase was albitized and replaced by Fe-chlorite, and biotite was degraded to Fe-chlorite. The predominance of secondary albite is

characteristic of the 'altered' zone. In the more intensively modified 'replaced' zone, primary textures are obscured by masses of yellow to green clay minerals, several varieties of reddish secondary K-rich feldspar, and disseminated calcite. Many pre-existing grains were albitized, chloritized, or replaced by secondary K-rich feldspar. Veinlets of secondary quartz, calcite, and Fe-rich dolomite cross-cut these rocks, and illitic clay fills fractures and coats grains (Figure 4a and 4b). The earliest alteration minerals are albite and Fe-rich chlorite (replacing plagioclase), followed by chemically very pure secondary K-rich feldspar (Figure 4c–4e). Fracture- and vein-filling quartz and calcite crystallized still later. Illitic clay, which replaces secondary K-rich feldspar and fills fractures (Figure 4f), and fracture-filling Fe-rich dolomite are the latest alteration minerals.

The alteration zones are illustrated in Figure 3. Both 'altered' and 'replaced' zones are present in core #165, but fresh granitic rock was not observed. Core #259 contains the most intensively 'replaced' rocks, but also includes some fresh material. Core #159 consists of a relatively thick 'altered' zone, underlain by fresh granitic rocks; 'replaced' rocks were not observed. The intensity of alteration generally increases as the unconformity with Paleozoic rocks is approached. However, 'replaced' rocks can also occur at greater depths below the unconformity (e.g., core #259), within intervals where abundant secondary veinlets and fracture-fills provide evidence for enhanced fluid access.

Harper *et al.* (1995) reported that unaltered granitic rocks of the CGB underlying SW Ontario have average bulk  $\delta^{18}\text{O}$  values of about +7.5‰, and approach high-temperature oxygen-isotope equilibrium among the assemblages. Shieh and Schwarcz (1974) reported similar results for CGB samples from outcrops. Harper *et al.* (1995) showed that the Precambrian rocks from cores #259, #165, and #159 are significantly enriched in  $^{18}\text{O}$  towards the unconformity, a pattern that arises from the increasing abundance of  $^{18}\text{O}$ -rich secondary minerals formed at relatively low temperatures (<250°C; Beyth *et al.*, 1997; Wenner and Taylor, 1976). However, the  $\delta^{18}\text{O}$  value (+5.0‰) of the lowermost sample (202.1 m) from core #159 was depleted of  $^{18}\text{O}$  relative to most granitic rocks, which caused Harper *et al.* (1995) to suggest that it was altered at temperatures >250–300°C.

## RESULTS

### *Illite and chlorite compositions*

The abundance of illite and chlorite typically rises with increasing alteration, with illite generally being more common than chlorite (Table 1). For example, the amount of illite reaches ~21% and chlorite ~18% in the uppermost 3 m of 'replaced' and 'altered' rocks in core #259. Small amounts of other phyllosilicates

are also observed, particularly in 'fresh' samples. For example, smectite, illite-smectite, chlorite-smectite, and minor chlorite occur in 'fresh' samples of core #159, and are probably the initial alteration products of amphibole (Table 2). Illite is rare in such samples.

The illitic clay is generally a  $1M_d$  polytype with <10% smectite interstratification, although the two deepest samples from core #165 contain illitic clay with a higher percentage of smectite interstratification (20–30%). The average structural formula of the illitic clays is:  $\text{K}_{1.29}(\text{Al}_{2.92}\text{Fe}_{0.52}\text{Mg}_{0.88})(\text{Si}_{7.14}\text{Al}_{0.86})\text{O}_{20}(\text{OH})_4$  (Table 3). The high Fe and Mg contents probably are related to analytical problems owing to small-particle size, contamination by chlorite, and secondary porosity.

Chlorite is generally Mg-rich, ferroan clinocllore-*Ia*. Chlorite associated with authigenic, low-temperature illite- $1M_d$  or  $1M$  commonly occurs as an *Ia* form (Hurley *et al.*, 1962; Velde, 1965; Walker, 1993). The average structural formula of the chlorite is:  $(\text{Al}_{2.94}\text{Fe}_{4.01}\text{Mg}_{4.45})(\text{Si}_{6.26}\text{Al}_{1.74})\text{O}_{20}(\text{OH})_{16}$  (Table 3). Similar to illite, the fine-grained nature of the chlorite and its occurrence mostly within pore spaces is responsible for at least some of the compositional variation. However, there are systematic variations. For example, the average chlorite Fe/(Fe + Mg) ratio changes from 0.55 in core #259 to 0.33 in core #159 (Table 3), a variation that is probably inherited from the host rocks.

### *Sequence of clay alteration and comparison with other studies*

Knowledge of the timing of secondary chlorite and illite formation is required to understand the origin and evolution of fluids responsible for this clay formation. Most studies of this alteration elsewhere in North America make little mention of secondary chlorite, although Duffin *et al.* (1989) noted the occurrence of secondary chlorite with late illite in samples from Illinois. Scanning electron microscopy (SEM) and back-scattered electron imaging (BSE) are consistent with the suggestion of Harper *et al.* (1995) that chlorite predated most other alteration in SW Ontario, including secondary K-rich feldspar (Figure 4c and 4d), quartz, and illite (Figure 4a and 4b). Although chlorite and illite are closely associated physically (Figure 4f), illite formation postdated not only chlorite, but also secondary K-rich feldspar and quartz.

Secondary K-rich feldspar (Harper *et al.*, 1995) and clay-mineral (this study) separates from the altered Precambrian rocks of SW Ontario have been dated using K-Ar or Rb-Sr methods (Table 4). The K-rich feldspar is substantially older (K-Ar: 453–412 Ma, average 444 Ma; Rb-Sr model ages: 482–394 Ma; Rb-Sr errorchron date: 440 Ma) than the illite. A clay separate containing 64% chlorite has the oldest clay K-Ar date (358 Ma). Younger K-Ar dates were obtained for

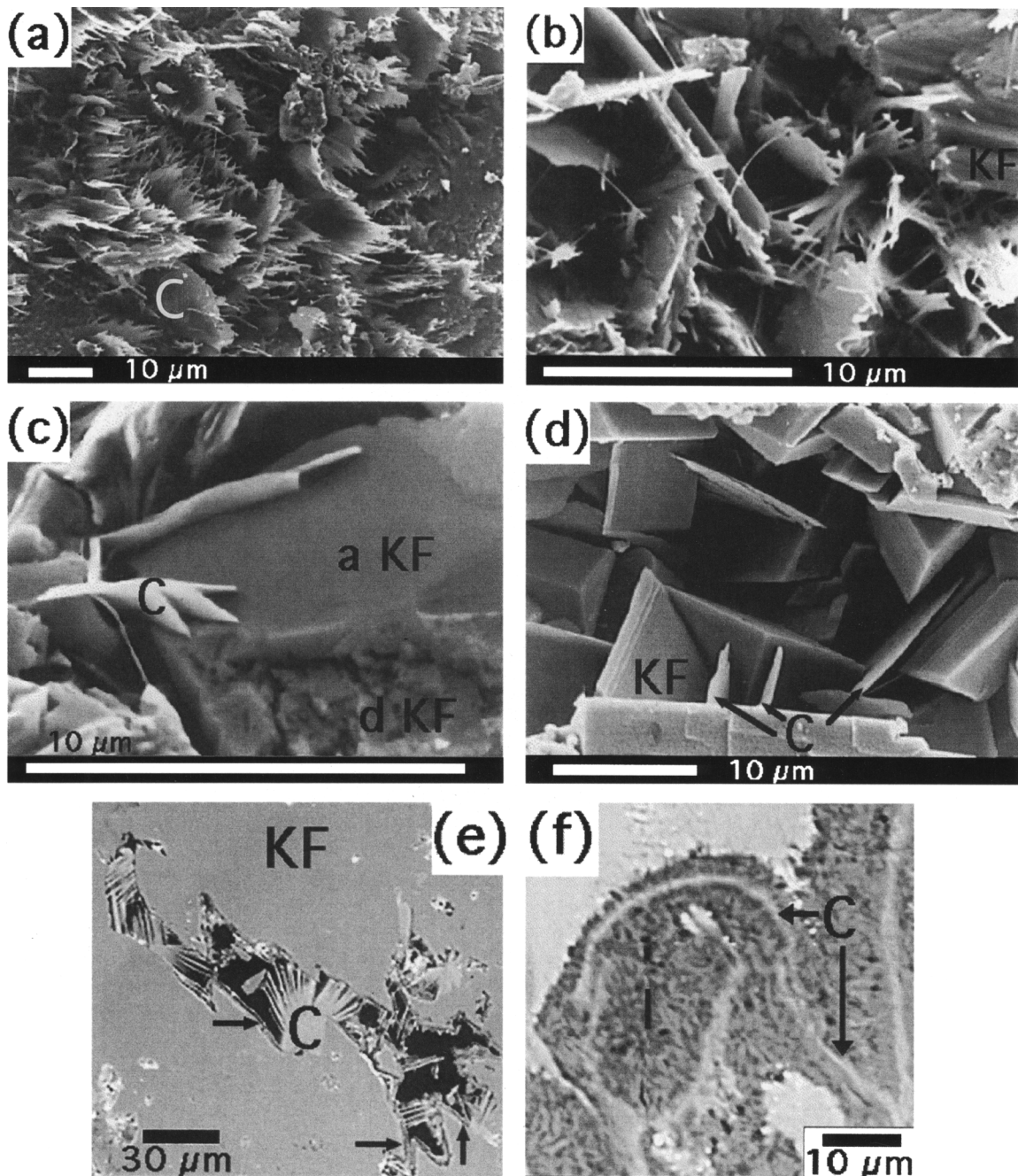


Figure 4. (a) SEM photomicrograph, core #259 (605.9 m): secondary illite with fibrous (“hairy”) and lath-like morphologies; secondary chlorite plates (C) are overgrown by illite; (b) SEM photomicrograph, core #259 (605.9 m): platy chlorite overgrown by lath-like and fibrous (“hairy”) illite; authigenic K-rich feldspar (KF) is also present; (c) SEM photomicrograph, core #259 (605.9 m): detrital K-rich feldspar (d KF) with an authigenic (a KF) overgrowth that has partially enveloped earlier chlorite (C); (d) SEM photomicrograph, core #259 (605.9 m): rhombic secondary K-rich feldspar (KF) that has partially enclosed earlier chlorite (C); (e) BSE photomicrograph, core #165 (1106.1 m): fracture in detrital K-rich feldspar grain (KF) filled with platy chlorite (C). The thin lining on the fracture (arrows) consists of Cu-Pb sulfides, typical of high-temperature MVT mineralizing fluids; (f) SEM photomicrograph, core #165 (1106.1 m): secondary chlorite (C) linings on detrital K-rich feldspar; subsequently the K-rich feldspar was altered to illite (I).

Table 1. Whole-rock clay content, and  $\delta D$  and  $\delta^{18}O$  values.

Depth (m)	Alteration zone	<sup>1</sup> I(M) : C : A <sup>2</sup> (% in WR)	$\delta D$ (‰ VSMOW)	$\delta^{18}O$
<b>Core #259</b>				
605.9	replaced	05 : 04 : 00		18.2 <sup>3</sup>
606.3	replaced	15 : 13 : 00	-73	16.7 <sup>3</sup>
606.6	replaced	21 : 18 : 00	-72	16.9 <sup>3</sup>
606.9	replaced	12 : 03 : 00		18.5 <sup>3</sup>
607.2	replaced	02 : 01 : 00		17.6 <sup>3</sup>
607.5	replaced	03 : 02 : 00		13.3 <sup>3</sup>
607.8	altered	11 : 10 : 00	-60	13.8 <sup>3</sup>
608.1	altered	05 : 09 : 00		13.3 <sup>3</sup>
608.4	altered	05 : 08 : 00		16.5 <sup>3</sup>
608.7	altered	03 : 06 : 00	-73	16.1 <sup>3</sup>
609.0	altered/fresh	19 : 07 : 00	-60	13.5 <sup>3</sup>
609.6	fresh	03 : 00 : 32		7.5 <sup>3</sup>
610.2	fresh	?		7.5 <sup>3</sup>
<b>Core #165</b>				
1102.5	replaced	03 : 03 : 00		17.3 <sup>3</sup>
1103.1	replaced	15 : 00 : 00	-71	17.5 <sup>3</sup>
1103.7	replaced	04 : 03 : 00		14.2 <sup>3</sup>
1104.3	replaced	22 : 04 : 00		14.7 <sup>3</sup>
1104.9	altered	06 : 02 : 00		16.4 <sup>3</sup>
1105.5	altered	05 : 04 : 00		14.8 <sup>3</sup>
1105.8	altered	10 : 02 : 00	-77	14.1
1106.1	altered	02 : 00 : 00		13.3 <sup>3</sup>
<b>Core #159</b>				
184.1–184.3	altered	03 : 01 : 00	-71	11.5 <sup>3</sup>
184.4	altered	02 : 01 : 00		12.3 <sup>3</sup>
185.1–185.3	altered	01 : 01 : 00	-75	12.4 <sup>3</sup>
185.6	altered	02 : 01 : 00		12.7 <sup>3</sup>
186.8	altered	01 : 00 : 00	-72	11.6 <sup>3</sup>
188.1	altered	01 : 00 : 00		11.6 <sup>3</sup>
188.7	altered	03 : 00 : 00	-84	8.6 <sup>3</sup>
197.2	fresh	23(+B) : 00 : 00	-80	6.5 <sup>3</sup>
202.1	fresh	24(+B) : 00 : 05		6.0
202.1	fresh	24(+B) : 00 : 05		5.0 <sup>3</sup>
205.7	fresh	20(+B) : 01 : 09		5.9
206.7	fresh	13(+B) : 00 : 08		5.9
207.6	fresh	11(+B) : 00 : 08		6.2

<sup>1</sup> I = illite; M = mica; C = chlorite; A = amphibole; WR = whole rock; B = biotite.

<sup>2</sup> Estimated using XRD peak height ratios.

<sup>3</sup> From Harper *et al.*, 1995.

samples containing 17–32% chlorite (342–329 Ma). The youngest K-Ar dates (311–299 Ma) were obtained for the purest (~93%) illite samples. The K-Ar dates for the secondary K-rich feldspar coincide with the middle to late stages of the Taconic orogeny in eastern North America (480–420 Ma; Drake *et al.*, 1989), and serve as a minimum age for the chlorite. The dates for the secondary illite postdate the Acadian orogeny (410–360 Ma; Osberg *et al.*, 1989), but match the earlier stage of the Alleghanian/Quachita orogeny (327–266 Ma; Secor *et al.*, 1986).

Such a significant difference between the age of secondary K-rich feldspar and illitic clays has been documented for many other areas affected by this alteration, as have multiple episodes of illitic clay formation (Lee and Aronson, 1991; Harper *et al.*, 1995; Liu *et al.*, 1996). Duffin *et al.* (1989) obtained dates of 395 Ma for secondary K-rich feldspar *versus* 271–214

Ma for illitic clay from altered Cambrian sandstones in Illinois; Doe *et al.* (1983) inferred a hydrothermal episode at ~400 Ma in this area. Secondary K-rich feldspar from altered Precambrian rocks in Wisconsin has average dates of 430–397 Ma; samples from Missouri were older (454–444 Ma) (Hay *et al.*, 1992). Liu *et al.* (1996) reported much younger dates (383–315 Ma) for illite-smectite from altered Precambrian rocks in the same regions. K-Ar dates of 432–400 and 436–377 Ma were summarized by Krueger and Woodward (1972) and Marshall *et al.* (1986) for secondary K-rich feldspar from Ordovician sandstones in Wisconsin. Hay *et al.* (1988) obtained similar K-rich feldspar K-Ar and Rb-Sr dates (406–368 Ma) for Ordovician tuffs and sandstones from the Upper Mississippi Valley area in Iowa, Minnesota, and Wisconsin; illite-smectite was younger (375–351 Ma). Illite K-Ar dates of ~360, 340, 310–300, and 230–215 Ma were re-



Table 2. Mineralogy and stable-isotope geochemistry of clay minerals.

Core #	Depth (m)	Distance from u/c (m)	Alteration zone	Size ( $\mu\text{m}$ )	I : C (%)	Illite		Chlorite		
						$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	
						( $\text{‰}$ VSMOW)				
259	605.9	0.0	replaced	<0.2	70 : 30		16.3 <sup>3</sup>			
				0.2–1	36 : 64				16.7 <sup>3</sup>	
				<1	88 : 12	-65	19.2			
				<1	36 : 64			-64	17.5	
				<1	calc illite	-66	19.6			
				<1	calc chlorite			-64	16.4	
259	606.2	0.3	replaced	1–2	27 : 73				-59 <sup>2</sup>	
				<2	53 : 47					
				<1	29 : 71			-65	15.6	
				<1	52 : 48	-60	16.8			
				<1	calc illite	-50	19.4			
				<1	calc chlorite			-71	14.0	
259	606.3	0.4	replaced	<2	26 : 74					
				<1	85 : 15		18.9 <sup>3</sup>			
				1–2	?				14.5 <sup>3</sup>	
259	606.6–606.7	0.7–0.8	replaced	<2	48 : 52				15.9 <sup>3</sup>	
				<1	97 : 03	-54				
				<1	69 : 31	-71				
				<1	calc illite	-54				
259	606.9	1.0	replaced	<2	64 : 36					
				<2	83 : 17		17.7 <sup>3</sup>			
259	607.4–607.5	1.5–1.6	replaced	<1	71 : 29		18.6			
				<1	83 : 17		18.8 <sup>3</sup>			
				<1	calc illite		19.2			
				1–2	?		14.4 <sup>3</sup>			
				<2	52 : 48					
				<2	75 : 25		16.8 <sup>3</sup>			
259	607.8	1.9	altered	<2	60 : 40		16.0 <sup>3</sup>			
				<2	31 : 69					
259	608.4	2.5	altered	<0.2	43 : 57				16.9 <sup>3</sup>	
				0.2–1	40 : 60				15.4 <sup>3</sup>	
				1–2	??		15.1			
259	608.8	2.9	altered	<2	57 : 43 <sup>3</sup>					
				<2	47 : 53					
259	609.0	3.1	altered/fresh	<0.2	59 : 41		11.8 <sup>3</sup>			
				0.2–1	68 : 32		13.8 <sup>3</sup>			
259	609.1	3.2	fresh	<1	85 : 15	-63				
				<1	68 : 32	-66	16.6			
				<1	calc illite	-61				
259	609.5	3.6	fresh	1–2	0 : 100 (1.4 nm)			-89	9.3	
				0.2–1	48 : 52				17.3 <sup>3</sup>	
165	1102.5–1102.8	0.0–0.3	replaced	<1	22 : 78				-71	15.2 <sup>2</sup>
				<1	86 : 14	-50 <sup>2</sup>	19.5			
				<1	calc illite	-46	20.5			
				<1	calc chlorite				-78	13.7
				<2	44 : 56					
				<0.2	88 : 12		18.8 <sup>3</sup>			
165	1103.1–1103.4	0.6–0.9	replaced	0.2–1	45 : 55				16.8	
				<1	91 : 09	-54	19.5			
				<1	25 : 75				-68	15.7
				<1	50 : 50	-65	17.1			
				<1	calc illite	-52	20.1			
				<1	calc chlorite				-73	14.2
165	1103.7	1.2	replaced	<2	56 : 44					
				<2	52 : 48					
165	1104.1	1.6	replaced	<2	67 : 33					
				<2	93 : 07		17.3 <sup>3</sup>			
165	1104.3–1104.6	1.8–2.1	replaced	<0.2	83 : 17		17.8 <sup>3</sup>			
				0.2–1	82 : 18		17.9 <sup>2</sup>			
				<1	78 : 22	53 <sup>2</sup>				
				<2	93 : 07		18.2 <sup>3</sup>			
165	1104.9	2.4	altered	<0.2	78 : 22		18.3 <sup>3</sup>			
				0.2–1	93 : 07					

Table 2. Continued.

Core #	Depth (m)	Distance from u/c (m)	Alteration zone	Size ( $\mu\text{m}$ )	I : C (%)	Illite		Chlorite	
						$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$
						(%o VSMOW)			
165	1105.1	2.6	altered	<2	76 : 24				
165	1105.5	3.0	altered	<1	89 : 11	-55 <sup>2</sup>	19.7		
				0.2-1	83 : 17		18.2 <sup>3</sup>		
				<2	66 : 34 <sup>3</sup>				
165	1105.8-1106.0	3.3-3.5	altered	<1	78 : 22	-54 <sup>2</sup>	18.2		
				<2	71 : 29				
165	1106.4	3.9	altered	<2	45 : 55				
165	1106.9	4.4	altered	<1	90 : 10	-58			
				<1	calc illite	-58			
				<2	51 : 49 (Sm)				
165	1107.0	4.5	altered	<2	57 : 43 (Sm)				
165	>1107.0	>4.5	altered	<1	85 : 15	-56	18.0		
				<2	56 : 44				
159	184.1-184.3	0.0-0.2	altered	<2	81 : 19	-63	14.8		
159	184.4-184.56	0.3-0.46	altered	<1	79 : 21	-57	16.8		
				<2	78 : 20				
159	184.7-184.9	0.6-0.8	altered	<1	84 : 16	-67 <sup>2</sup>	17.0		
				<2	80 : 20				
159	185.1-185.32	1.0-1.22	altered	<2	75 : 25	-71	15.1		
159	185.6	1.5	altered	<2	82 : 18	-68 <sup>2</sup>	16.9 <sup>2</sup>		
159	186.08-186.23	1.98-2.13	altered	<1	76 : 24	-59	16.4		
				<2	69 : 31				
159	186.72-186.84	2.62-2.74	altered	<2	68 : 32	-60	16.0		
159	187.5-187.8	3.4-3.7	altered	<2	79 : 21	-59 <sup>2</sup>	17.1		
159	188.06-188.82	3.96-4.72	altered	<1	84 : 16	-60	16.8		
				<2	70 : 30				
159	189.9-191.1	5.8-7.0	altered	<1	64 : 36	-53	17.0		
				<2	62 : 38				
159	190.8	6.7	altered	<1	51 : 49	-56	16.5		
				<2	44 : 56				
159	192.02-192.33	7.92-8.21	altered	<2	40 : 60 (Sm)				
159	193.6-193.7	9.5-9.6	altered	<2	35 : 65			-58	14.0
				<2	65 : 35		17.0		
				<2	calc illite		20.5		
				<2	calc chlorite				10.4
159	194.8-195.7	10.7-11.6	fresh	<1	C > S				
				1-2	C $\gg$ S				
				<2	0 : 100 (Sm)				
159	197.2-198.1	13.1-14.0	fresh	1-2	C > I > S				
				<2	30 : 70 (Sm)				
159	199.6	15.5	fresh	1-2	C $\gg$ I-S + C-S				
				<2	50 : 50 (Sm)				
159	202.1-202.4	18.0-18.3	fresh	<1	C + S				
				1-2	S $\gg$ C				
				<2	0 : 100 (Sm)				
159	204.5	20.4	fresh	<1	C > C-S > S				
				1-2	C > S				
				<2	13 : 87 (Sm)				
159	205.7	21.6	fresh	<1	C > S > C-S				
				1-2	C $\gg$ C-S + S				
				<2	tr : 100 (Sm)				
159	206.7	22.6	fresh	<1	C > C-S > I-S				
				1-2	C $\gg$ S				
				<2	tr : 100 (Sm)				
159	207.0	22.9	fresh	<1	C + C-S + I-S				
				1-2	C $\gg$ I-S + C-S				
				<2	tr : 100 (Sm)				
159	207.6	23.5	fresh	<1	C + C-S + ?				
				1-2	C > S				
				<2	tr : 100 (Sm)				

u/c = Precambrian/Paleozoic unconformity.

<sup>1</sup> Estimated using XRD peak height ratios; calc = calculated end-member.

<sup>2</sup> Average of duplicate measurements.

<sup>3</sup> From Harper *et al.*, 1995.

I = illite; C = chlorite; S = smectite; C-S = chlorite-smectite; I-S = illite-smectite; Sm = presence of unidentified smectitic component; tr = trace.

Table 3. Average structural formulae of illite and chlorite.

Illite <sup>1,2</sup>	K	<sup>VI</sup> Al	Fe	Mg	Si	<sup>IV</sup> Al
core #259	1.25	2.67	0.76	1.00	7.22	0.78
core #159	1.06	3.46	0.29	0.53	6.93	1.07
core #165	1.45	2.91	0.39	0.94	7.16	0.84
Chlorite <sup>1,3</sup>	<sup>VI</sup> Al	Fe	Mg	Si	<sup>IV</sup> Al	Fe/(Fe + Mg)
core #259	2.84	4.75	3.85	6.27	1.73	0.55
core #159	3.03	2.65	5.47	6.65	1.35	0.33
core #165	3.02	3.79	4.68	6.00	2.00	0.45

<sup>1</sup> 5–10 analyses per sample.

<sup>2</sup> Normalized to O<sub>20</sub>(OH)<sub>4</sub>.

<sup>3</sup> Normalized to O<sub>20</sub>(OH)<sub>16</sub>.

ported by Lee and Aronson (1991) for Cambro-Ordovician rocks from the same general area. K-rich feldspar from similar rocks in Missouri was dated at 390–368 Ma; much younger dates were obtained for illite-smectite from K-bentonites (318–316 Ma) and tuffs (279–254 Ma) in this area (Hay *et al.*, 1988). Illite-smectite from Ordovician sandstones of Michigan was dated at 367–322 Ma (Barnes *et al.*, 1992; Girard and Barnes, 1995).

#### Whole-rock stable-isotope results

Whole-rock oxygen-isotope data from Harper *et al.* (1995) plus new oxygen- and hydrogen-isotope data for cores #259, #165, and #159 are listed in Table 1 and illustrated in Figure 3. The amount of <sup>18</sup>O enrichment is consistent with the degree of alteration. 'Replaced' rocks have  $\delta^{18}\text{O}$  values as high as +18.5‰ (core #259), whereas 'altered' rocks from the least affected core (#159) have maximum values of +12.7‰. 'Fresh' samples from cores #159 and #259 have  $\delta^{18}\text{O}$

values of +6 to +8‰, within the low end of the normal range for unaltered granitic rocks. In particular, reanalysis of the +5‰ sample (202.1 m; Harper *et al.*, 1995) from core #159 produced a higher result (+6‰), and the values for samples from greater depths remain constant at 5.9–6.2‰ (Figure 3; Table 1). Thus, the possibility of higher temperature alteration (>300°C) with greater depth proposed by Harper *et al.* (1995) seems unlikely. Relatively low whole-rock  $\delta^{18}\text{O}$  values (~7‰) have also been reported for unaltered, more felsic Precambrian granitic rocks sampled from drill cores in Illinois, and attributed to differentiation from magmas formed in the lower crust or upper mantle (Kombrink and Clayton, 1983; Shieh, 1983; Kyser, 1986).

The whole-rock  $\delta\text{D}$  values vary from –84 to –60‰ (Table 1), depending on the relative abundances of primary and altered biotite, secondary chlorite, and secondary illite. No hydrogen-isotope data are available for amphibole from unweathered samples, but biotite in these rocks has  $\delta\text{D}$  values of  $-80 \pm 4\%$  (Ziegler and Longstaffe, unpub.), which may be a signature of the igneous and metamorphic processes that originally produced these rocks. As the unconformity is approached, amphibole is neither present in the 'altered' nor 'replaced' rocks, and biotite becomes rare (Table 1). Altered biotite that has persisted is ragged, intergrown with chlorite, enriched in <sup>18</sup>O relative to fresh biotite, and has a higher average  $\delta\text{D}$  value of  $-72 \pm 3\%$  (Ziegler and Longstaffe, unpub.). Identical values (–74 to –71‰) were obtained for biotite from altered granitic rocks intersected by the Illinois Deep Hole near the unconformity, and these values are interpreted to reflect exchange of the biotite with hydrothermal fluids (Kyser, 1986). The  $\delta\text{D}$  values of the altered bi-

Table 4. Dates for secondary illite and K-rich feldspar.

Core #	Depth (m)	Mineral	Illite		K <sub>2</sub> O (%)	K-Ar (Ma)	Error ±	Rb-Sr (Ma)
			(%)	Size (µm)				
165	1104.2	I	93	0.2–1	7.48	310.5 <sup>1</sup>	7.3	
165	1104.2	I	93	<0.2	7.46	299.2 <sup>1</sup>	7.1	
165	1105.5	I	83	0.2–1	7.72	336.5 <sup>1</sup>	8.1	
165	1102.4	KF	—	—	16.39	447.9 <sup>1</sup>	10.5	442 <sup>2</sup>
165	1102.7	KF	—	—	16.34	452.8 <sup>1</sup>	11.1	482 <sup>2</sup>
165	1103.0	KF	—	—	—	—	—	431 <sup>2</sup>
165	1103.3	KF	—	—	16.50	450.4 <sup>1</sup>	10.6	434 <sup>2</sup>
165	1103.6	KF	—	—	13.26	450.3 <sup>1</sup>	10.6	437 <sup>2</sup>
259	605.9	C > I	36	0.2–1	5.84	357.7 <sup>1</sup>	8.4	
259	605.9	I	70	<0.2	6.44	341.5 <sup>1</sup>	8.0	
259	609.0	I	68	0.2–1	6.09	329.1 <sup>1</sup>	7.8	
259	605.9	KF	—	—	16.52	443.1 <sup>1</sup>	10.4	
259	607.4	KF	—	—	—	—	—	394 <sup>2</sup>
259	608.7	KF	—	—	—	—	—	433 <sup>2</sup>
259	608.7	KF	—	veinlet	—	412 <sup>2</sup>	8.0	454 <sup>2</sup>
259	608.9	KF	—	veinlet	—	453 <sup>2</sup>	9.0	

<sup>1</sup> Analyzed by J. Aronson.

<sup>2</sup> From Harper *et al.*, 1995.

I = illite; KF = K-rich feldspar; C = chlorite.

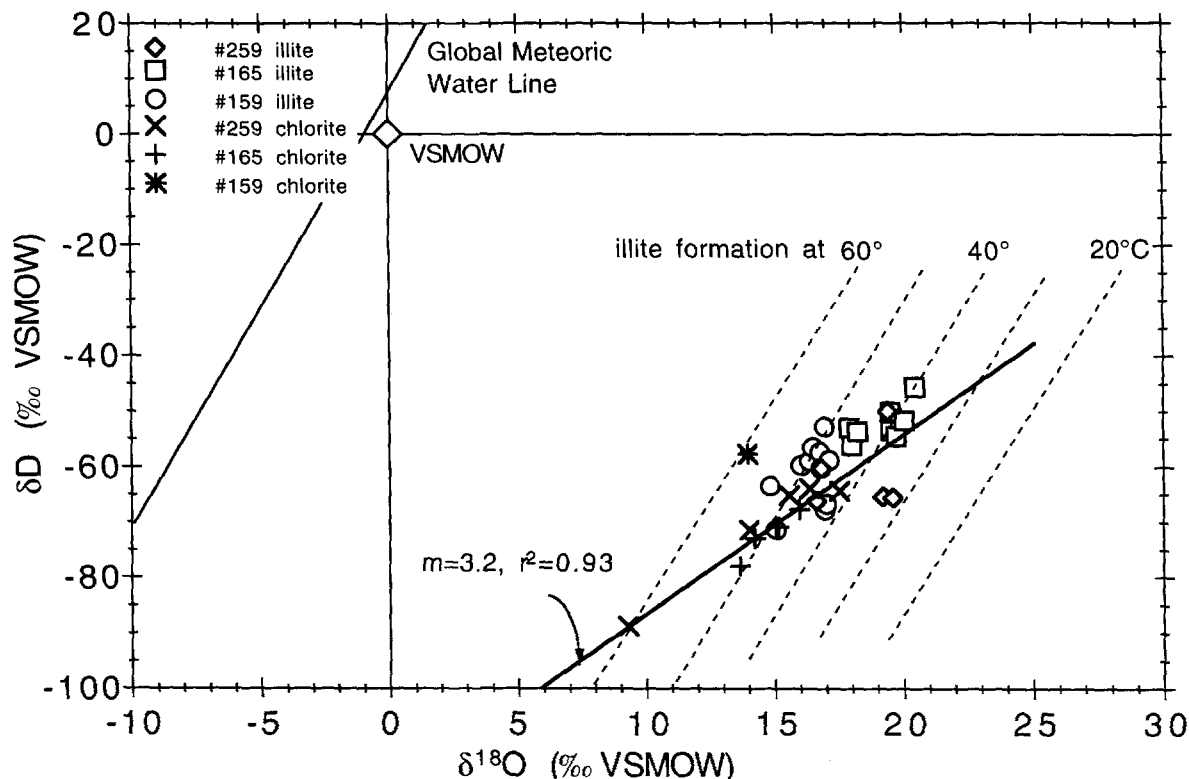


Figure 5. The  $\delta D$  and  $\delta^{18}O$  values for illite- and chlorite-dominated (>70%) clay-size fractions and calculated end-members (Table 2). Lines for illite formation at 20–60°C were calculated using Equations (1) and (3) (see text). The regression line describes the trend obtained for secondary chlorite. The position of the Global Meteoric Water Line is taken from Craig (1961).

otite and associated secondary chlorite are similar (Table 2), and probably reflect interaction with the same fluid. However, the  $\delta D$  values of illite are substantially higher (Table 2). Because the most intensively altered samples tend to have greater amounts of illitic clay, lesser amounts of chlorite, and no biotite, they generally have the highest whole-rock  $\delta D$  values (Figure 3).

#### Stable-isotope results for illite and chlorite

The  $\delta D$  and  $\delta^{18}O$  values for clays separated from cores #159, #165, and #259 are listed in Table 2. These samples are composed predominantly (70–90%) of illite and chlorite, and are nearly free of contamination by non-clay minerals. Aliquots of the same size-fraction with different illite to chlorite ratios were obtained for some samples, and this allowed the extrapolation (see “calc”, Table 2) of isotopic compositions to pure end-members. For other samples, corrections for contamination were not possible. Nevertheless, assuming that the XRD determinations of illite to chlorite ratios are accurate, the maximum error in isotopic composition for the major phase is <2‰ for oxygen and <5‰ for hydrogen for a sample purity of >70%. Such

analytical variations do not affect the following discussion. For the calculated end-member results, the clays display a wide range of  $\delta^{18}O$  (19.2 to 20.5‰ for illite, 10.4 to 16.4‰ for chlorite) and  $\delta D$  (–66 to –46‰ for illite, –78 to –64‰ for chlorite) values over distances of a few meters.

Table 2 also summarizes previously reported  $\delta^{18}O$  values for various clay-size fractions from the same cores (Harper *et al.*, 1995). These values are consistent with data obtained in this study, and show that illite-rich samples (commonly the finer fractions) generally have higher  $\delta^{18}O$  values. No systematic trends in isotopic composition were detected for different size fractions of the same sample that contained similar quantities of chlorite and illite.

On a  $\delta D$  versus  $\delta^{18}O$  diagram (Figure 5), the clay minerals cluster to the left of the region commonly associated with clay formation in terrestrial weathering environments (*i.e.*, to the left of the dashed line labeled 20°C). Regression of the chlorite-isotopic data produces a trend with a slope ( $m = 3.2$ ,  $r^2 = 0.93$ ) that is different from that expected for clays formed from meteoric water, but similar to that expected for basinal brines. The scatter of the illite-isotopic data on Figure

5 is much larger than for chlorite, and does not yield a statistically significant regression line. Most results plot between the lines for illite formation at 35–55°C, which suggests that illite formation occurred over a range of temperatures and water compositions.

## DISCUSSION

### *Chlorite formation*

The crystallization temperature of the chlorite-*Ia* in SW Ontario can be assessed in several ways. According to Hayes (1970), chlorite-*I* forms at lower temperature and pressure than chlorite-*II*, which is common in igneous and metamorphic environments or high-temperature sulphide mineralization. Hayes (1970) proposed that conversion from chlorite-*I* to chlorite-*II* requires minimum conditions of low-grade metamorphism. Weaver *et al.* (1984) suggested that chlorite-*Ia* forms at  $\leq 250^\circ\text{C}$ , but it remains stable to  $300^\circ\text{C}$ . Walker (1989, 1993) proposed a range of  $150\text{--}200^\circ\text{C}$  for the transition from chlorite-*I* to chlorite-*II*, but Walker and Thompson (1990) noted that chlorite-*II* can occur at temperatures as low as  $135^\circ\text{C}$ .

Several chlorite geothermometers are based on chemical composition. From studies of diagenetic chlorite in sandstones of the North Sea Basin (Aagaard *et al.*, 1988) and uranium deposits of the Salt-Wash Basin, Colorado (Meunier, 1984), it is inferred that  $^{IV}\text{Al}$  contents of 0.4–0.7 (atoms per half unit cell, apfu) correlate to crystallization temperatures of  $100\text{--}140^\circ\text{C}$ . de Caritat *et al.* (1993) concluded that higher  $^{IV}\text{Al}$  contents (0.6–1.6 apfu) reflect hydrothermal-metamorphic temperatures. The  $^{IV}\text{Al}$  contents of chlorite sampled in this study vary between 0.4–1.2 apfu, and average 0.87 apfu (Table 3). Cathelineau (1988) also argued that the  $^{IV}\text{Al}$  content of chlorite formed in geothermal systems is related to crystallization temperature. By applying this geothermometer (Cathelineau, 1988) to the data in Table 3, the following average apparent crystallization temperatures were obtained: core #165,  $260^\circ\text{C}$ ; core #259,  $200^\circ\text{C}$  ( $215^\circ\text{C}$  if an apparently high value for  $^{IV}\text{Al}$  is included), and core #159,  $100^\circ\text{C}$  ( $150^\circ\text{C}$  if an isolated high value for  $^{IV}\text{Al}$  is included). Secondary chlorite from overlying Cambro-Ordovician rocks of the Ottawa Embayment to the east (Figure 1b) has an apparent temperature of  $155\text{--}185^\circ\text{C}$  (Ziegler and Longstaffe, 2000; their Table 2).

The validity of chlorite geothermometry based upon the proportion of apparent octahedral vacancies or  $^{IV}\text{Al}$  content has been challenged by many investigators (Shau *et al.*, 1990; de Caritat *et al.*, 1993; Jiang *et al.*, 1994). However, Jiang *et al.* (1994) do not rule out successful chlorite geothermometry, and de Caritat *et al.* (1993) suggested that the method of Cathelineau (1988) produced satisfactory results for environments similar to the environment used in the calibration. The calibration environment was hydrothermal alteration

of andesite and rhyolite; such parental materials are similar in chemical composition to the basement rocks of SW Ontario.

The combined results of  $^{IV}\text{Al}$  geothermometry and chlorite polytypism indicate relatively high temperatures ( $100\text{--}260^\circ\text{C}$ ) for chlorite crystallization in the altered Precambrian rocks of SW Ontario. Elsewhere in the mid-continent, a homogenization temperature of fluid-inclusions of  $140^\circ\text{C}$  was reported for later-formed secondary K-rich feldspar (Hearn *et al.*, 1987), and a minimum average homogenization temperature of  $101^\circ\text{C}$  was obtained for still later secondary quartz from SW Ontario (Harper *et al.*, 1995). Harper *et al.* (1995) concluded from these data, phase equilibria, and oxygen-isotope results that secondary chlorite crystallized during the warmest stage of alteration, with K-rich feldspar and then quartz forming as the fluids cooled and changed in composition. Accordingly, we suggest that chlorite is an early, high-temperature phase. To calculate the stable-isotope composition of the chlorite-forming fluid (Figure 6), we used the minimum temperature of  $150^\circ\text{C}$  proposed by Harper *et al.* (1995). If higher temperatures are used, the following discussion is strengthened.

For this high-temperature model, the oxygen isotopic values obtained for the chlorite-forming fluid are markedly positive (Figure 6), and consistent with an assumed composition of Paleozoic seawater that had evaporated partially (Knauth and Beeunas, 1986). However, most hydrogen-isotope values calculated for the fluid ( $-55$  to  $+5\text{‰}$ ) are more negative than expected for such an origin ( $-10$  to  $+10\text{‰}$ ), even for brines that were more highly evaporated (Figure 6). Similar compositions were obtained for chlorite-forming fluids that had interacted with overlying Cambro-Ordovician sedimentary rocks (Ziegler and Longstaffe, 2000). These low  $\delta\text{D}_{\text{fluid}}$  values may be primary. Ziegler and Longstaffe (2000) proposed that the chlorite-forming fluid was a mixture of Appalachian and Michigan basin brines, because the Michigan Basin brines are reported to have lower  $\delta\text{D}$  values for a given oxygen-isotope composition. However, Kesler *et al.* (1997) also obtained low  $\delta\text{D}$  values ( $-119$  to  $-51\text{‰}$ ) for fluid inclusions from MVT ore and gangue minerals from the southern Appalachians. They proposed that the  $\delta\text{D}_{\text{fluid}}$  values were lowered by interaction between the brines derived from seawater and organic material, including gaseous hydrocarbons, and/or by mixing with shale-derived pore waters.

Chlorite hydrogen-isotope compositions possibly were modified by post-crystallization exchange (Ziegler and Longstaffe, 1997). Based on the alteration pattern, fluid-rock interactions were extensive at the Precambrian-Paleozoic unconformity in SW Ontario and this would potentially favor isotopic exchange between chlorite and post-formational fluids (Longstaffe and Ayalon, 1990). The significant overlap between

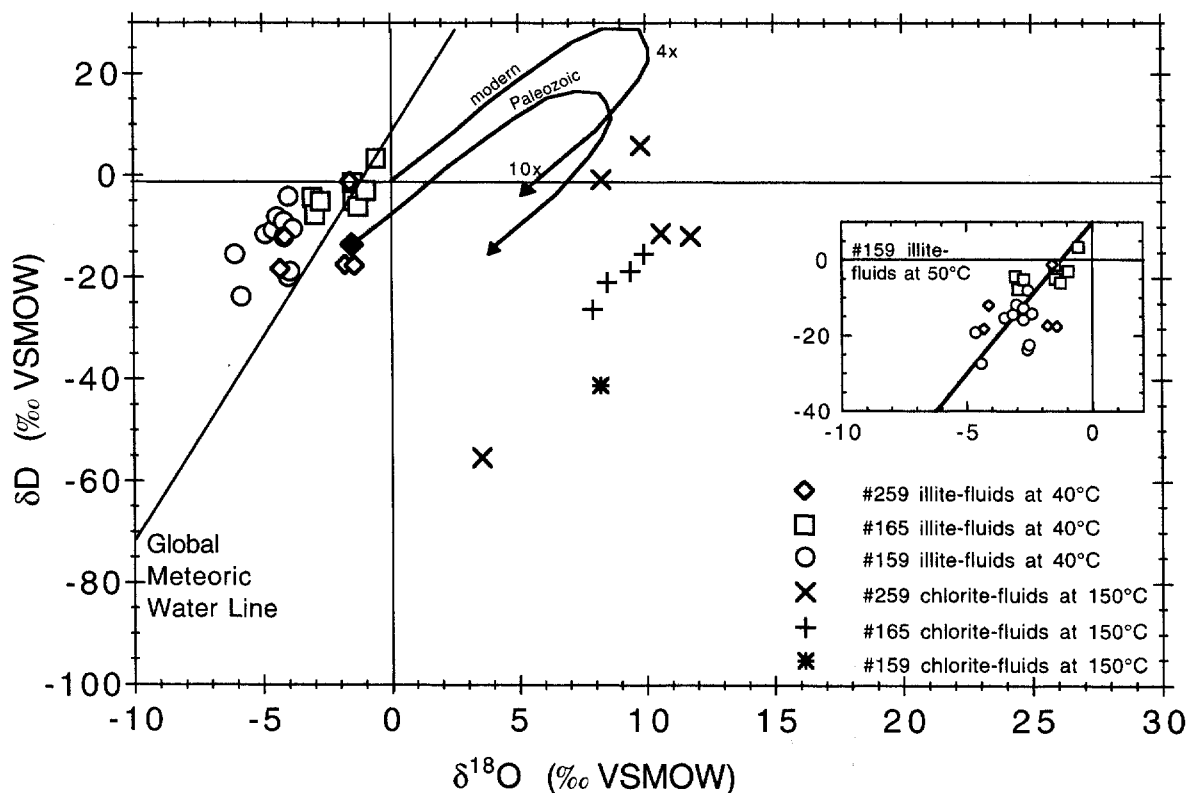


Figure 6. The  $\delta D$  and  $\delta^{18}O$  values of fluids responsible for secondary clay formation, calculated at  $150^{\circ}C$  for chlorite and  $40^{\circ}C$  for illite using Equations (1) to (4) (see text). The trajectories for evaporation of modern and Paleozoic seawater are modified from Holser (1979) and Knauth and Beeunas (1986). The ends of these curves (arrow) correspond to halite saturation. The solid diamond is the estimate from Knauth and Beeunas (1986) for Paleozoic seawater. Inset: the stable isotopic compositions of fluids responsible for secondary illite formation, as modified by calculation for core #159 at a temperature of  $50^{\circ}C$ .

the  $\delta D$  values of the early chlorite- and late illite-forming fluids, and the wide range of  $\delta D$  values compared to  $\delta^{18}O$  values for the chlorite-forming fluid are consistent also with isotope exchange (Figure 6). However, if such exchange did occur, the conclusion remains that the chlorite-forming fluids were derived largely from evaporated Paleozoic seawater.

The presence of hot, chlorite-forming fluids evolved primarily from Early Paleozoic seawater is consistent with regional geology. Marine waters transgressed the Precambrian basement during the Cambrian, and these depositional fluids would occur in most Paleozoic strata throughout mid-continental North America. The high fluid temperature was probably a consequence of deep burial in many parts of the Appalachian Basin. Moreover, the minimum age of fluid migration, inferred from the dates of secondary K-rich feldspar, correlates well with the latter portion of the Taconic orogeny, which probably induced this stage of fluid migration. The long and deep westward migration of the Appalachian brines also probably produced rock-

water interactions, which may explain the high  $\delta^{18}O$  values of the chlorite-forming fluids.

Oliver (1986) suggested that tectonic overpressuring created by the closure of the proto-Atlantic Ocean produced large-scale movement of connate brines in adjacent sedimentary basins. Bethke and Marshak (1990) suggested instead that topographic relief along the eastern margin of North America caused the migration of meteoric water through the basins at a sufficient rate to transport heated fluids. Harper *et al.* (1995) invoked tectonic overpressuring to obtain hot, evolved seawater during the early alteration responsible for secondary albite and chlorite. The stable-isotope data reported here for chlorite support such a model (Figure 7). However, Harper *et al.* (1995) also proposed that secondary K-rich feldspar crystallization, which followed chlorite formation, was initiated by mixing between the connate basinal brine and limited amounts of meteoric water. The source of this meteoric water probably was the Appalachian orogen to the east.

Westward expulsion of brines from the Appalachian foreland basin, as a consequence of the Taconic orog-

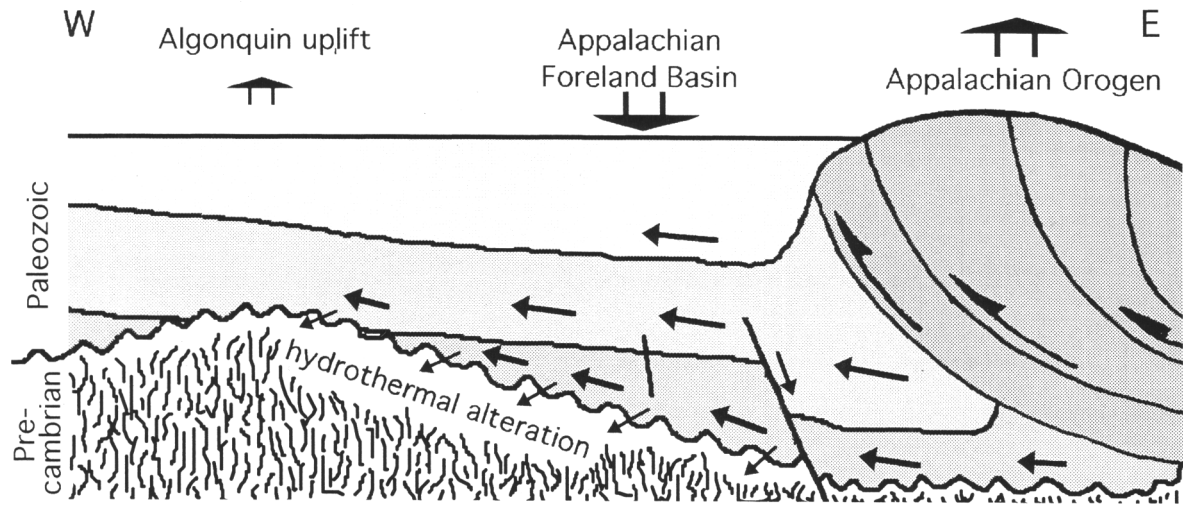


Figure 7. Schematic illustrating the proposed origin and migration of hot brines responsible for secondary chlorite and K-rich feldspar formation in SW Ontario, beginning in the Late Ordovician. Taconic thrusting along the eastern seaboard of North America caused the formation and deep burial of the Appalachian foreland basin. The connate waters trapped in the Paleozoic section were mostly of marine origin. Burial-related heating, a thrust-induced driving-mechanism (Oliver, 1986), and creation of a hydraulic pressure head in the rising orogen (Bethke and Marshak, 1990) combined to cause westward migration of brines towards the basin margins. Faults within the Paleozoic section facilitated brine movement towards the unconformity. Westward flow was focused along the unconformity, and resulted in hydrothermal alteration of the uppermost Precambrian rocks and immediately overlying Paleozoic sedimentary rocks.

eny, should have imparted a common alteration signature on the mid-continental rocks where fluid interactions were concentrated, such as at the Paleozoic-Precambrian unconformity. Thus, the age of formation of secondary chlorite and K-rich feldspar should correlate with the timing of the orogeny and distance from the orogen. The Taconic orogeny is thought to have been strongly diachronous, occurring earlier in the southern and northern Appalachians, and later in the central Appalachians (Drake *et al.*, 1989; Hatcher, 1987) with the latter most proximal to SW Ontario (Figure 1a). The timing of secondary K-rich feldspar formation in SW Ontario (453–412 Ma; average 444 Ma) closely matches the late Ordovician start of the central Taconic orogeny. The age of secondary K-rich feldspar in Wisconsin, Illinois, Minnesota, and Iowa, which are located west along the flow path (Figure 1a), is younger (Precambrian host rocks, 430–397 Ma; Cambrian host rocks, 395 Ma; Ordovician host rocks, 436–368 Ma), as expected.

#### Illite formation

Harper *et al.* (1995) suggested that late illite formed at temperatures of 40–50°C from pore waters containing a sizable fraction of meteoric water. A test of this conclusion at 40°C using the hydrogen- and oxygen-isotope results for secondary illite produces fluid compositions close to the Global Meteoric Water Line (GMWL) (Figure 6). Data for cores #165 and #259 scatter about the GMWL, whereas results for core #159 plot to its left. By increasing the illite crystalli-

zation temperature to ~50°C for core #159, a better distribution about the GMWL is obtained (Figure 6, inset). However, these low temperatures and such a pattern of hydrogen- and oxygen-isotope compositions for the illite-forming fluids probably would not be preserved if these fluids had migrated long distances at high temperatures during westward movement through the Appalachian Basin. Water-rock interaction and mixing with pre-existing connate waters would have produced a fluid with a stable-isotope composition much different from the GMWL.

We suggest that the meteoric water was derived locally (Figure 8). The calculated fluid compositions for the illite are consistent with this suggestion, matching expected values for Paleozoic meteoric water in this area during middle to late Paleozoic time ( $\delta D = -25$  to  $0\text{‰}$ ,  $\delta^{18}O = -6$  to  $0\text{‰}$ ) (Anderson and Arthur, 1983; Miller and Kent, 1988). However, this scenario also requires an appropriate timing and a low temperature of formation for the secondary illite.

**Secondary illite crystallization.** The K-Ar dates obtained for the purest fractions of secondary illite (>90% illite, 311–299 Ma; Table 4) from the Precambrian rocks lie very close to the boundary between the Early and Late Carboniferous. There are no known Carboniferous strata in SW Ontario, but clastic sediments of that age probably were deposited. However, this detritus derived from the Appalachian orogen was emplaced in two stages, first during the Early Carboniferous and then during the Late Carboniferous. These

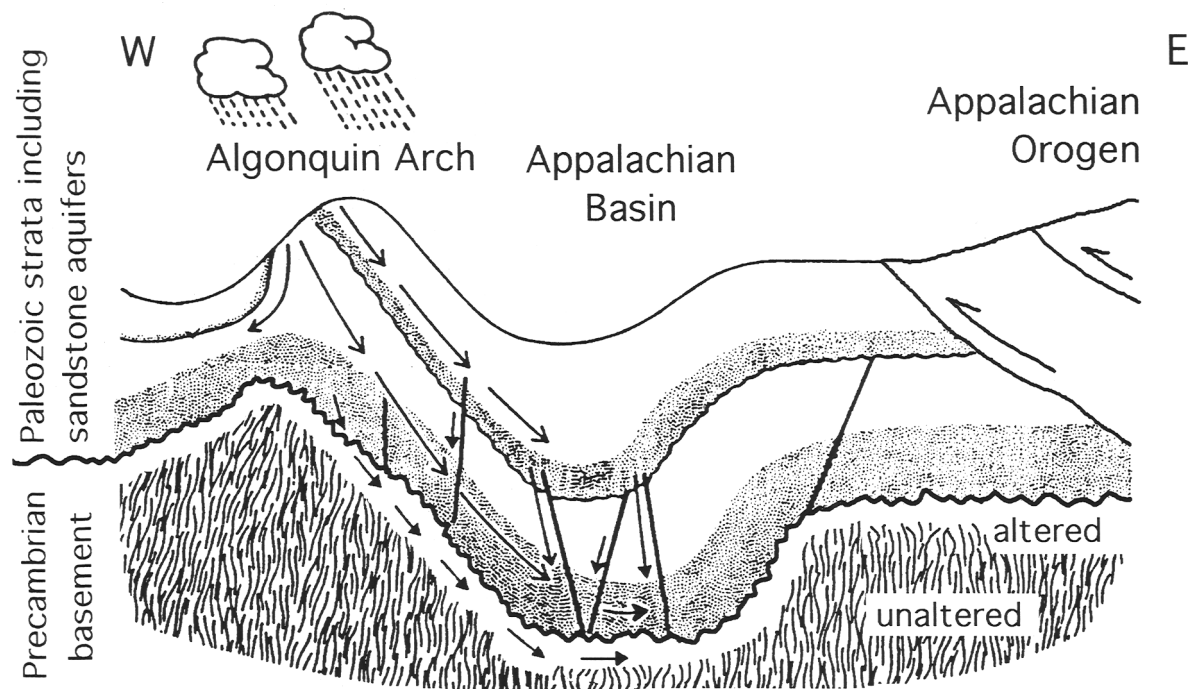


Figure 8. Schematic illustrating the proposed paleohydrogeological conditions for mid-Carboniferous illite formation in the altered Precambrian rocks of SW Ontario. Uplift of the Findlay-Algonquin Arch (and the Frontenac Arch further to the northeast) was a local response to Alleghanian (and Acadian) orogenic activity along the eastern seaboard of North America. The ensuing subaerial erosion of the Paleozoic section over the arch allowed meteoric water to enter and percolate along sandstone aquifers (stippled pattern), including those adjacent to the unconformity with the Precambrian basement. Downward infiltration of fresh water to the unconformity was further facilitated by reactivation of numerous faults during these periods of local basement tectonic activity. The tepid, fresh waters reacted with the pre-existing K-rich alteration assemblage near the unconformity, resulting in the crystallization of secondary illite.

periods of deposition were separated by an interval of erosion (Fisher *et al.*, 1988; Johnson *et al.*, 1992; Quinlan and Beaumont, 1984). This deposition and erosion cycle is one in a series relating to late Devonian to mid-Carboniferous intracratonic movements, which produced intermittent uplift and subaerial exposure of the Findlay-Algonquin and Frontenac arches in southern Ontario. Subaerial exposure allowed local meteoric water to enter the subsurface. Concurrent tectonic reactivation of vertical fractures, which are characteristic of this area, further facilitated downward movement of fresh water to the Precambrian/Paleozoic unconformity (Figure 8; Sanford *et al.*, 1985; Hay *et al.*, 1988; Duffin *et al.*, 1989; Coniglio and Williams-Jones, 1992). This local tectonism was the basement response to the Acadian (410–360 Ma; Osberg *et al.*, 1989) and Alleghanian (327–266 Ma; Secor *et al.*, 1986) orogenies to the east. Similar movement of other arches occurred throughout the mid-continent. The exact timing in each locality probably depended on local crustal stability and sedimentary loading, as well as distance from and intensity of the orogenic activity.

The wide range and multiple episodes of secondary illite formation indicated by the K-Ar dates from various locations within the Upper Mississippi Valley

area (Figure 1a) also suggest local variability. Ziegler and Longstaffe (2000) concluded that secondary illite in Cambrian and Ordovician sedimentary rocks from both SW Ontario and the Ottawa Embayment (Figure 1b) crystallized from local meteoric water following the Acadian Orogeny. In the Ottawa Embayment, K-Ar illite dates for the purest samples ( $\geq 93\%$  illite) range from  $364.5 \pm 6.8$  to  $326.7 \pm 6.2$  Ma (average 343 Ma; Ziegler and Longstaffe, 2000). However, the data reported here suggest a trend where the illite K-Ar dates become younger from the Ottawa Embayment towards SW Ontario. Secondary illite in Precambrian host rocks from core #259 in SW Ontario has dates of  $341.5 \pm 8.0$  to  $329.1 \pm 7.8$  Ma. The dates are even younger further to the southwest, from or near core #165 (Figure 1b) ( $336.5 \pm 8.1$  to  $299.2 \pm 7.1$  Ma; see Table 4, and Ziegler and Longstaffe, 2000). These latter dates coincide with the onset of the Alleghanian orogeny in the east. Such similarity in timing may imply a rapid tectonic response of the hinterland to distant orogenic activity. Such behavior was proposed previously to relate stratigraphic features of Middle Ordovician sedimentary rocks in the Ottawa Embayment to the distal Taconic orogeny (Dix and Molgat, 1998). To summarize, tectonic remobilization



of the Findlay-Algonquin and Frontenac arches, probably in response to distal orogenic activity, allowed local meteoric water to migrate into the rocks of southwestern and southeastern Ontario at different times in different locations.

The K-Ar dates for the purest samples ( $\geq 93\%$  illite) from (or near) core #165 decrease with depth:  $330.8 \pm 6.3$  Ma in Ordovician strata,  $325.2 \pm 6.2$  Ma in Cambro-Ordovician strata,  $320.5 \pm 6.1$  Ma in Cambrian strata, and  $310.5 \pm 7.3$  to  $299.2 \pm 7.1$  Ma in altered Precambrian rocks (Table 4, and Ziegler and Longstaffe, 2000). These results are consistent with downward infiltration of local meteoric water towards the impermeable, unaltered Precambrian rocks at the base of the sedimentary section. The slow rate of flow is consistent with development of modest relief on the Findlay-Algonquin Arch during episodes of uplift and subaerial erosion.

*Secondary illite crystallization at low temperatures.* Reports of illite authigenesis at low temperatures are not at all uncommon (e.g., Kirsimäe *et al.*, 1999). In the case of SW Ontario, the arguments of Ziegler and Longstaffe (2000) for low-temperature illite formation in systems with high  $K^+$  to  $H^+$  ratios are not repeated. We discuss instead the thermal data available for the region. Present bottom-hole temperatures near the Precambrian-Paleozoic boundary are  $\sim 30^\circ\text{C}$  in SW Ontario, below  $\sim 1000$  m of sedimentary cover (Harper *et al.*, 1995). Conodont and acritarch color-alteration studies suggest that maximum burial temperatures in SW Ontario did not exceed  $60^\circ\text{C}$  in the Middle Ordovician Trenton Group (Figure 2), and these temperatures were never higher than  $60\text{--}90^\circ\text{C}$  in Lower Ordovician rocks located further east (Legall *et al.*, 1981). Maximum burial temperatures were not reached until post-Carboniferous time ( $\leq 286$  Ma) (Legall *et al.*, 1981), well after secondary illite formation was completed in both the Precambrian and Paleozoic rocks. The temperature range ( $40\text{--}50^\circ\text{C}$ ) proposed here for secondary illite formation is consistent with such a thermal history.

Legall *et al.* (1981) reported increasing thermal alteration from SW Ontario towards eastern Ontario, and noted that the trend of increasing temperature to the east is detected within discrete stratigraphic units. This increase in heat flow towards and east of the Frontenac Arch, including the Ottawa Embayment, may have been an early harbinger of the Cretaceous-Tertiary rifting in the vicinity of the Ottawa-Bonnechère Graben (Figure 1b) (Legall *et al.*, 1981). The isotopic temperature range inferred for secondary illite formation in the Precambrian host rocks is consistent with this pattern, increasing northeastward from  $40^\circ\text{C}$  for core #165 to  $50^\circ\text{C}$  for core #159 (Figure 1b). Likewise, in the overlying Paleozoic host rocks, temperatures of secondary illite crystallization increased from  $40^\circ\text{C}$  in

the vicinity of core #165 to  $55^\circ\text{C}$  further to the northeast, in the Ottawa Embayment (Figure 1b) (Ziegler and Longstaffe, 2000).

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