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Structural variations in illite and chlorite in the Belt Supergroup western Montana and northern Idaho

Peter Ryan
The University of Montana

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University of Montana
STRUCTURAL VARIATIONS IN ILLITE AND CHLORITE IN THE BELT
SUPERGROUP, WESTERN MONTANA AND NORTHERN IDAHO

by

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A.B., Dartmouth College, 1988

Presented in partial fulfillment of the requirements for the degree of
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UNIVERSITY OF MONTANA
1991

Approved by

Chair, Board of Examiners

Dean, Graduate School

Date
Dec. 10, 1991

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Structural and compositional variations in coexisting illite and chlorite in the Proterozoic Belt Supergroup were examined over a wide range of low-grade burial metamorphic conditions. Samples were collected from the eastern portion of the Belt basin, where Belt sediments are thin and shallowly buried, from the western portion of the basin, where the thickness of the Belt is over 15,000 meters and burial depth was considerably greater, and from intermediate localities. The maximum temperature attained by eastern samples was 80°C, and that attained by western samples was approximately 380°C.

Chlorite from the low-temperature localities is predominantly the IIb polytype, with traces of the Ib polytype. Chlorite from all other localities is the IIb polytype. Chlorite from low-temperature localities is mixed-layered chlorite/smectite (C/S) with 6% smectite layers. Both the proportion of chlorite layers in C/S and chlorite crystallite thickness increase from east to west with increasing metamorphic grade. Chlorite from low-temperature localities is Mg-rich, whereas chlorites in higher temperature samples contain more iron. This compositional trend may be due to differences in bulk composition rather than increasing metamorphic grade.

Illite from low-temperature localities is mixed-layer illite/smectite (I/S) with 2% smectite layers, and both the proportion of illite layers in I/S and illite crystallite thickness increase with increasing metamorphic grade. The proportion of 2M₁ illite polytype increases from <10% to >95% with increasing burial depth and temperature.
ACKNOWLEDGEMENTS

Thanks to Gray Thompson for his advice and guidance during the course of this project. Gray encouraged me to ask and answer my own questions, and his timely advice and discussions were invaluable.

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Special thanks to Jeff Moe. His endless assistance with computer matters and infectious curiosity for clay mineralogy kept me afloat during frustrating periods.

Thanks to James Swierc for his friendship and great geology trips, and to Janet Riddell, whose sense of humor helped put things in perspective.

And finally, my deepest gratitude goes to Maggie Crowley, who was so patient, encouraging, and understanding during some very frantic moments; and to my family.

This study was supported by grants from the Clay Minerals Society, the U. of M. Geology Faculty, and the Belt Association.
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INTRODUCTION

Chlorite and illite commonly co-exist in low-grade metamorphic shales, mudstones, and similar fine-grained sedimentary rocks. However, few studies document simultaneous transformations of chlorite and co-existing illite during low-grade metamorphism (Walker and Thompson, 1990).

The purpose of this study is to investigate concurrent changes with increasing metamorphic grade in mixed-layering, polytypism, and sizes of coherent diffracting domains in co-existing illite and chlorite. The rocks studied are a low-grade metamorphic sequence of mudstone, argillite, and siltstone of the middle Proterozoic Belt Supergroup. Samples were taken from the lower part of the Belt Supergroup, ranging from the shallowly buried Big Snowy Mountains of central Montana to the deeply buried Clark Fork, Idaho section, and from sites of intermediate burial depth (Figures 1 and 2). Burial depth is considered to be proportional to intensity of low-grade metamorphism (Hyndman, 1985).

Systematic structural and compositional changes in illite in low-grade metamorphic sequences are described by Maxwell and Hower (1967), Frey (1970), Hower et al. (1976), Jennings and Thompson (1986), and Walker and Thompson (1990). Illite responds to progressive burial in three ways: 1) progressive disappearance of expandable (smectite) layers; 2) polytypic transformation from 1Md to (1Md + 1M) to (1M + 2M1) to 2M1.
(see Appendix for discussion of illite and chlorite polytypes); and 3) an increase in the number of unit cells comprising coherent X-ray scattering domains (Walker and Thompson, 1990). Reynolds (1963), Maxwell and Hower (1967) and Walker and Thompson (1990) report natural occurrences of 1M polytypes transforming to, and co-existing with, 2M$_1$ illite, and this reaction has been duplicated in the laboratory (Velde, 1965). 2M$_1$ illite appears at about 200°C during natural metamorphism (Eslinger and Savin, 1973), and at about 125°C in laboratory experiments (Velde, 1963).

A few studies suggest that chlorite may also exhibit systematic structural variations with increasing temperature in low-grade metamorphic environments (e.g. Brown and Bailey, 1963; Hayes, 1970; Walker, 1989; Walker and Thompson, 1990). Studies of chlorite transformations in low-grade metamorphic sequences are few (Karpova, 1969; Walker, 1989; and Walker and Thompson, 1990). Hayes (1970) showed that chlorite polytypes are temperature dependant, with the IIB polytype the stable structure above 200°C. The polytype sequence with increasing temperature described by Hayes (1970) is:

\[ \text{Ib}_d \rightarrow \text{Ib} (\beta = 97^\circ) \rightarrow \text{Ib} (\beta = 90^\circ) \rightarrow \text{IIB} \]

over a range of 20° to 200°C, with the transformation from Ib (\( \beta = 97^\circ \)) to IIB accompanied by a ±60° or 180° rotation of the hydroxide layer (Brown and Bailey, 1962). However, it is
important to note that (1) Hayes obtained his samples from a variety of geologic environments and rock types, including limestone, volcanic tuff, graywacke, and soil, but not from aluminous, clay-rich sedimentary rocks, and (2) type I chlorite has not been found in fine-grained mudrocks (Walker, 1989). Walker (1989) proposed that chlorite polytype transformations could be calibrated as a geothermometer, but chlorite polytype transformations have yet to be documented in a burial diagenetic sequence. Walker (1989) and Walker and Thompson (1990) found only IIb chlorite in diagenetic sequences, and suggest that it is stable at temperatures as low as 135°C. Mixed-layer serpentine/chlorite has been documented by TEM (Ahn and Peacor, 1985; Yau, et al., 1988), and by X-ray diffraction (Walker and Thompson, 1990). Walker and Thompson (1990) showed that mixed-layer serpentine/chlorite forms at low temperatures in Plio-Pleistocene Salton Sea sediments, and the proportion of serpentine layers decreases between 135°C and 195°C until no serpentine layers remain at 195°C. Chang et al. (1986), in their study of Brazilian Cretaceous offshore basins, reported progressive increase in the percentage of chlorite layers in chlorite/saponite (saponite is a trioctahedral smectite) with increasing burial depth. Moe (1990) reports a similar trend in the Williston basin.

The number of unit cells comprising coherent X-ray
scattering domains stacked in the C direction (crystallite thickness) influences the breadth of 001 diffracton peaks (e.g. Walker and Thompson, 1990). Kubler (1964) observed that illite 001 peaks progressively sharpen with increasing metamorphic grade and suggested that the breadth of the illite 001 peak at half-height be used as an indicator of metamorphic grade in diagenetic and low-grade metamorphic environments. Reynolds (1987, pers. comm.; in Walker and Thompson, 1990) later suggested that the illite 005 be used as an indicator of illite crystallinity. Comparison of the breadth of chlorite 001 peaks generated by NEWMOD (Reynolds, 1985) with chlorite 001 peaks from natural samples reveals that crystallite thickness in chlorite also increases with increasing temperature (Ishii, 1988; in Walker and Thompson, 1990).

Geologic Setting

The Proterozoic Belt Supergroup of western Montana and northern Idaho consists largely of clay-rich sedimentary and low-grade metamorphic mudstone, argillite, siltstone, quartzite, and carbonate. The sediment was deposited as smectite-rich mud (Eslinger and Sellars, 1982) in a subsiding basin and the sequence was metamorphosed in a normal geothermal gradient (Eslinger and Savin, 1973). The Belt Supergroup thickens from east to west, with a minimum thickness of about 300 m in the Big Snowy Mountains, and a maximum of about 16,000 m near Superior, Montana (Winston,
1986). Consequently, metamorphic grade increases from thermally unmetamorphosed sediment in the Big Snowy Mountains to greenschist facies in western Montana and northern Idaho (see below). Belt rocks were metamorphosed to amphibolite grade north of the Idaho batholith during the Cretaceous, but none of the rocks sampled for this study were affected by Cretaceous contact metamorphism.

Samples from the Newland Formation of the Big Snowy Mountains have been probably exposed to a maximum temperature of about 80°C. Patricia Weaver (pers. comm., 1991) reports that conodonts of the Cordylobus proavus zone in the Snowy Range Formation about 300 m above the Newland Formation have a color alteration index of 1 and fixed carbon range of 60%, which correlates to a maximum temperature of 50° to 80°C. Approximately 1900 m of post-Proterozoic sedimentary rocks overlie the Newland Formation in the Big Snowy Mountains (Warren Shepard, pers. comm., 1991), and erosion of the Belt Supergroup prior to deposition of the Cambrian Flathead Sandstone is probably no more than 1500 m (Don Winston, pers. comm., 1991; and D. Jay Johnson, pers. comm., 1991). This infers a maximum burial depth of no greater than 2,000 m for the Newland Formation. At a geothermal gradient of 30°C/km and estimated surface temperature of 20°C, I extrapolate a maximum temperature 80°C.

The Revett Formation and upper Burke Formation near Clark
Fork, Idaho have been metamorphosed to the chlorite zone of
greenschist facies (Harrison and Jobin, 1963), which
corresponds to a maximum temperature of 350° to 400°C
(Yardley, 1989).

Metamorphic grade of the Spokane Formation at Rogers Pass
and Wolf Creek is considered to be intermediate between the
Big Snowy Mountains and Clark Fork.

ANALYTICAL METHODS

Twenty-nine fine-grained rock samples from the Belt
Supergroup were collected from rocks exposed to a wide range
of low-grade metamorphic conditions, from the shallowly buried
Big Snowy Mountain section in central Montana to the deeply
buried Clark Fork section in northern Idaho. All samples were
washed in deionized water to remove weathering products,
gently crushed in an iron mortar and pestle, suspended in
deionized water, and ultrasonically disaggregated.
Polymetaphosphate was added to prevent flocculation, and clay
suspensions were Sr^{2+}-saturated to eliminate variations in
ethylene glycol complex thicknesses.

After all samples had been analyzed by a preliminary
X-ray diffraction study to determine relative amounts of
illite and chlorite (see below), subsamples from selected
localities were chosen for magnetic separation and detailed
X-ray analysis based on illite and chlorite content. Figure 1
shows sample localities and Figure 2 summarizes Belt Supergroup stratigraphy and sample horizons. Table 1 shows stratigraphic positions or units of the samples chosen for detailed analyses and the clay minerals analyzed from each sample.

The <2μ equivalent size diameter (e.s.d.) was separated by timed centrifugation, and oriented samples of the <2μ fraction were prepared on glass slides by the filter peel technique (Drever, 1973). To determine relative amounts of illite and chlorite in these samples, air-dried oriented samples were analyzed from 2° to 33° 26 with a Philips Norelco flat-specimen X-ray diffractometer using CuKα radiation at 30 kV and 30 mA with a graphite monochromater. Data were collected digitally using a databox stepper motor scanner (Radix Instruments, Inc) and plotted using NEWMOD software (Reynolds, 1985). Count times for the preliminary analyses were 10 seconds per 0.05° 26 step.

**Magnetic Separation**

The <2μ size fraction of selected samples was magnetically separated by high-gradient magnetic separation (HGMS) (Tellier et al., 1988; Walker and Thompson, 1990) into a chlorite-rich magnetic fraction and an illite-rich non-magnetic fraction. A flow rate of 300 ml/min was used for all samples, but it was necessary to alter the field strength according to the magnetic susceptibility of the minerals in
Figure 1. Location map of the Proterozoic Belt Supergroup showing sample localities (after Winston, 1986).

Figure 2. Cross-section of the Belt Supergroup showing sample localities (after Winston, pers. comm., 1991).

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Table 1. Samples studied from the Belt Supergroup, western Montana and northern Idaho.

<table>
<thead>
<tr>
<th>Sample Locality</th>
<th>Stratigraphic Group</th>
<th>Stratigraphic Formation</th>
<th>Mineral Used In Analysis</th>
</tr>
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<tbody>
<tr>
<td>Big Snowy Mts., MT</td>
<td>Lower Belt</td>
<td>Newland Fm</td>
<td>Chlorite</td>
</tr>
<tr>
<td>-sample BS-2</td>
<td>Lower Belt</td>
<td>Newland Fm</td>
<td>Illite ±nc.</td>
</tr>
<tr>
<td>-sample BS-3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rogers Pass, MT</td>
<td>Ravalli Gp</td>
<td>Spokane Fm</td>
<td>Chlorite</td>
</tr>
<tr>
<td>Wolf Creek, MT</td>
<td>Ravalli Gp</td>
<td>Spokane Fm</td>
<td>Illite ±nc.</td>
</tr>
<tr>
<td>Clark Fork, ID</td>
<td>Ravalli Gp</td>
<td>Burke Fm</td>
<td>Chlorite ±nc.</td>
</tr>
<tr>
<td>Little Spar Lk, MT</td>
<td>Ravalli Gp</td>
<td>Revett Fm</td>
<td>Illite ±nc.</td>
</tr>
</tbody>
</table>

-all rocks used in this study are argillites.

-Rogers Pass and Wolf Creek samples are at approximately equal burial depth.

-Clark Fork and Little Spar Lake samples are at approximately equal burial depth.

-the Spokane Formation is the eastern correlative of the Ravalli Group (Winston, 1986).

-argillite of the Spokane Formation from Wolf Creek was selected for illite analysis because of the ease with which illite could be separated from the <2μ fraction.

-argillite of the Spokane Formation from Rogers Pass was selected for chlorite analysis because of the ease with which chlorite could be separated from the <2μ fraction.

-argillite of the Revett Formation from Little Spar Lk was selected for illite analysis because of the ease with which illite could be separated from the <2μ fraction.

-argillite of the Burke Formation from Clark Fork, ID was selected for chlorite analysis because of the ease with which chlorite could be separated from the <2μ fraction.
each sample.

**Polytype Analyses of Illite and Chlorite**

Randomly oriented, infinitely thick samples of the <2μm magnetic and nonmagnetic fractions were prepared by mounting approximately 200 milligrams of powder into a backload sample holder. The samples were scanned from 2° to 65° 2θ with count times of 25 seconds per 0.025° 2θ step. Sample BS-3 from the Big Snowy Mountains was heated to 550°C for 1.5 hours to remove kaolinite interference for illite polytype determination. Chlorite and illite polytypes were identified from X-ray patterns using methods developed by Yoder and Eugster (1955), Velde and Hower (1963), Velde (1965), Maxwell and Hower (1967), Bailey (1980), and Moore and Reynolds (1989). The percentage of 2M₁ illite relative to total illite (1Md + 1M + 2M₁) was determined by dividing the intensity of the 3.74 Å peak by the intensity of the 2.58 Å peak (Maxwell and Hower, 1967), as well as the intensity of the 2.80 Å peak divided by the intensity of the 2.58 Å peak (Velde and Hower, 1963). The resultant ratios were then plotted on figure 3 after Velde and Hower (1963) and Maxwell and Hower (1967).

**Analyses of Mixed-layering**

In order to determine detailed structures of mixed-layered phases, oriented samples of the <2μm magnetic and nonmagnetic fractions were prepared by the filter peel
Figure 3. Curve for the determination of percent 2M₁ illite (after Velde and Hower, 1963; and Maxwell and Hower, 1967)
technique (Drever, 1973) and analyzed air-dried and after solvation in ethylene glycol for at least 24 hours at 40°C. X-ray diffraction scans were made from 2° to 33° 2θ using 0.025° 2θ steps and 25 second count times.

Comparisons of air-dried chlorite/smectite (C/S) and illite/smectite (I/S) NEWMOD patterns with ethylene glycol-solvated C/S and I/S NEWMOD patterns (Reynolds, 1985) show that peak positions, peak shapes and peak widths all change upon ethylene glycol-solvation. Peak width is a function of (1) machine parameters; (2) dispersion of incident radiation; (3) crystallite-size distribution; (4) nature and magnitude of lattice distortions (Klug and Alexander, 1974); and (5) the proportion of interstratified layers (Walker and Thompson, 1990).

Chlorite/smectite Percent smectite in C/S was determined by comparing peak positions of analytical 001 and 002 reflections before and after ethylene glycol-solvation with peak positions of corresponding calculated NEWMOD reflections (Reynolds, 1985) for water and ethylene glycol-solvated modeled clay structures. I attempted to correlate peak width at half-height (β) with percent expandability (smectite) in C/S. β was measured for the 002, 003, and 004 C/S reflections from analytical patterns in both the air-dried and ethylene glycol-solvated states and compared with C/S 002, 003, and 004 β values measured from calculated NEWMOD patterns (Reynolds,
1985) for water and ethylene glycol-solvated modeled structures. However, because I was unable to correlate simultaneously each of the three analytical $B$ values with all three calculated $B$ values, $B$ values and variations in peak shapes were used only as qualitative indicators of interstratified smectite in C/S and I/S.

**Serpentine/chlorite** To test for the presence of interstratified serpentine layers in chlorite, $B$ values for the chlorite 002, 003, and 004 peaks from oriented experimental patterns were compared with calculated NEWMOD patterns (Reynolds, 1985). The presence of serpentine layers in chlorite broadens odd-order chlorite peaks, but not even-order peaks. The broadening is due to superimposed 7 Å serpentine reflections on the even-order chlorite reflections (Reynolds, 1988; Walker and Thompson, 1990).

In determining analytical $B$ values, X-ray patterns were scanned over the angular range of the respective peaks with 0.01° 20 steps and 25 second counts.

**Illite/smectite** Peak positions, peak widths at half-height ($B$), and peak shapes of I/S patterns change upon ethylene glycol-solvation. $B$ values and peak shapes were used as qualitative indicators of interstratified smectite in I/S. To determine percent smectite in I/S, peak positions of the illite 001 and 002 reflections before and after ethylene glycol-solvation were compared with corresponding NEWMOD
reflections (Reynolds, 1985) for water and ethylene glycol-solvated clay structures.

**Sizes of Coherent Scattering Domains**

Analytical $\beta$ values were compared with NEWMOD calculated $\beta$ values to determine mean thicknesses of coherent scattering domains (crystallite thicknesses) in C/S. However, $\beta$ is a function of both crystallite thickness and exandability in C/S. Thus, in order to determine thicknesses of scattering domains, it is necessary to isolate the effects of expandability on $\beta$. This was accomplished by plotting NEWMOD calculated $\beta$ (002) values against percent smectite in C/S for varying N values (Figure 4), where N is the NEWMOD input parameter for crystallite thickness in the Z direction (Reynolds, 1985). The percent smectite in C/S of natural samples was plotted on the graph to determine N values. The N values were then used as input parameters in NEWMOD C/S calculations. The process was repeated until the calculated and analytical X-ray diffraction patterns converged, and further calculations failed to improve their correlation.

Relative thicknesses of coherent scattering domains in illite were determined in a similar manner.

**Chemical Composition**

Chemical compositions of both illite and chlorite were estimated by comparing peak intensities of analytical patterns with peak intensities of calculated NEWMOD patterns (Reynolds,
Figure 4. Curve for the determination of N values of chlorite and chlorite/smectite (C/S). X-axis is percent smectite in C/S and Y-axis is $\beta$ (002). Values used in the graph were generated by NEWMOD (Reynolds, 1985) computer modelling.
1985).

RESULTS

X-ray diffraction patterns of oriented mounts of the magnetic and nonmagnetic fractions separated by the HGMS procedure (Tellier, et al., 1988) are shown in Figure 5. Complications with magnetic separation are discussed in the following section.

Chlorite

Polytypes Except for the Big Snowy Mountains, all chlorite is the IIb polytype (Figure 6). In the Big Snowy Mountains, the 2.49, 2.28, 2.20, and 1.78 Å peaks suggest additional traces of the Ib chlorite polytype.

Mixed-layering The proportion of chlorite layers in mixed-layer C/S increases with increasing burial depth and metamorphic grade (Figures 7 and 8). Chlorite from the Big Snowy Mountains and Rogers Pass is mixed-layer chlorite/smectite. Upon ethylene glycol-solvation, C/S from both sites exhibits (1) an increase in peak asymmetry, (2) an increase in peak width at half-height (B), and (3) peak migration.

Chlorite in the Big Snowy Mountains is C/S with 6% expandable (smectite) layers. The chlorite 001 peak shifts from 14.34 to 14.49 Å, and the 002 shifts from 7.145 to 7.166
BIG SNOWY MTS

- Magnetic separation was not possible. BS-2 was used for chlorite analysis, and BS-3 was used for illite analysis.

ROGER'S PASS

unseparated

WOLF CREEK

unseparated

magnetic fraction

magnetic fraction

non-magnetic fraction

non-magnetic fraction

Figure 5. X-ray powder diffraction patterns of oriented samples, Belt Supergroup, separated using high-gradient magnetic separation (Tellier, et al., 1988). M = machine artifact, C = chlorite, I = illite, Q = quartz.

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Figure 5 (continued). Results of magnetic separation
Figure 6. Randomly oriented X-ray powder diffraction patterns of chlorite, Belt Supergroup. M = machine artifact, Q = quartz, I = illite.
Figure 7. Ethylene glycol-solvated X-ray powder diffraction patterns from the Belt Supergroup compared with chlorite and C/S NEWMOD (Reynolds, 1985) patterns. M = machine artifact, I = illite, Q = quartz, CC = calcite, A = albite, K = Kspar.
Figure 8. Mixed-layered variations in chlorite/smectite (C/S) with increasing burial depth in the Belt Supergroup. Burial depth increases from east to west.
Å upon ethylene glycol-solvation. β (002) increases from 0.371 to 0.427° 2θ upon ethylene glycol-solvation. Peak positions for both the air-dried and ethylene glycol-solvated states closely match those of calculated NEWMOD (Reynolds, 1985) patterns (Figure 7).

Chlorite from Rogers Pass is mixed-layer C/S with 2% expandable (smectite) layers. The chlorite 001 shifts from 14.05 to 14.18 Å, and the 002 shifts from 7.081 to 7.092 Å with ethylene glycol-solvation. β (002) increases from 0.236 to 0.253° 2θ upon ethylene glycol-solvation. Again, peak positions and migrations very closely match calculated NEWMOD (Reynolds, 1985) patterns (Figure 7).

Chlorite samples from Clark Fork exhibit no change in peak position, peak width, or peak shape upon ethylene glycol-solvation, indicating no expandable layers in chlorite from the highest grade argillites (Figure 7).

Odd-order chlorite reflections are no broader than even-order reflections in any samples, suggesting the absence of interstratified serpentine layers.

β Values β values are shown in Table 2. In general, β decreases from east to west with increasing burial depth. Ethylene glycol-solvation alters β values of chlorite peaks from the Big Snowy Mountains and Rogers Pass, but not Clark Fork, indicating the presence of expandable (smectite) layers in low and medium-grade samples, but not in high-grade
Table 2. β values (in °2θ) for chlorite and illite in the Belt Supergroup, western Montana and northern Idaho.

**CHLORITE**

<table>
<thead>
<tr>
<th>Locality</th>
<th>(002) AD</th>
<th>(002) EG</th>
<th>(003) AD</th>
<th>(003) EG</th>
<th>(004) AD</th>
<th>(004) EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Snowy Mts</td>
<td>0.371</td>
<td>0.427</td>
<td>0.343</td>
<td>0.365</td>
<td>0.393</td>
<td>0.340</td>
</tr>
<tr>
<td>Rogers Pass</td>
<td>0.236</td>
<td>0.253</td>
<td>0.242</td>
<td>0.249</td>
<td>0.244</td>
<td>0.249</td>
</tr>
<tr>
<td>Clark Fork</td>
<td>0.214</td>
<td>0.216</td>
<td>0.207</td>
<td>0.207</td>
<td>0.205</td>
<td>0.208</td>
</tr>
</tbody>
</table>

**ILLITE**

<table>
<thead>
<tr>
<th>Locality</th>
<th>(005) AD</th>
<th>(005) EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Snowy Mts</td>
<td>0.493</td>
<td>0.513</td>
</tr>
<tr>
<td>Wolf Creek</td>
<td>0.480</td>
<td>0.499</td>
</tr>
<tr>
<td>Little Spar Lk</td>
<td>0.474</td>
<td>0.470</td>
</tr>
</tbody>
</table>

AD = Air-dried  
EG = Ethylene glycol-solvated
samples.

**Chemical Composition** Comparison of analytical peak intensities with calculated NEWMOD peak intensities (Reynolds, 1985) reveals that all chlorite and intercalated smectite is trioctahedral. C/S from the Big Snowy Mountains is Mg-rich and contains 0.6 Fe atoms per 3 octahedral sites in both chlorite and smectite (saponite) layers. C/S from Rogers Pass contains 1.2 Fe atoms per 3 octahedral sites in both chlorite and saponite, and Clark Fork chlorite contains 1.0 Fe atoms per 3 octahedral sites.

**Illite**

**Polytypes** Illite polytype data are summarized in Figures 9 and 10. 1Md and 1M illite occur at lower metamorphic grades, and the proportion of 2M$_1$ illite increases with increasing metamorphic grade.

Low-grade illite in the Big Snowy Mountains contains strong 1Md reflections and no 1M reflections. Weak 2M$_1$ reflections suggest the presence of minor amounts of 2M$_1$ illite. The average ratio of the intensities of the 3.74/2.58 Å and 2.80/2.58 Å reflections (Velde and Hower, 1963; Maxwell and Hower, 1967) is 0.021. Figure 3 shows this value to indicate >90% 1Md and <10% 2M$_1$ illite in the Big Snowy Mountains.
ILLITE POLYTYPISM

<table>
<thead>
<tr>
<th>Locality</th>
<th>Peaks</th>
<th>Polytype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Snowy Mts.</td>
<td>1Md</td>
<td>&gt;90% 1Md</td>
</tr>
<tr>
<td></td>
<td>1Md</td>
<td>&lt;10% 2M1</td>
</tr>
<tr>
<td>Wolf Creek</td>
<td>1M</td>
<td>65% 1M</td>
</tr>
<tr>
<td></td>
<td>1M</td>
<td>35% 2M1</td>
</tr>
<tr>
<td>Little Spar Lake</td>
<td>2M1</td>
<td>&gt;95% 2M1</td>
</tr>
</tbody>
</table>

Figure 9a. Schematic diagram of randomly oriented X-ray powder diffraction pattern showing illite $\delta$$\alpha$$\delta$ reflections between 1.9 and 4.3 Å in the Belt Supergroup (CuKα radiation).

Figure 9b. Variations in percent 2M1 illite polytype with increasing burial depth in the Belt Supergroup. Burial depth increases westward. The vertical axis is percent 2M1 illite relative to total illite ($2M_1 + 1M + 1Md$), and the horizontal axis represents geographic location.
Figure 10. Randomly oriented X-ray powder diffraction patterns of illite, Belt Supergroup. M = machine artifact, Q = quartz, Ch = chlorite, CC = calcite.
Wolf Creek illite shows no 1Md reflections. However, both 1M and 2M\textsubscript{1} reflections are strong. The average ratio of the intensities of the 3.74/2.58 \AA\ and 2.80/2.58 \AA\ peaks is 0.079, correlating to 65% 1M and 35% 2M\textsubscript{1} illite at Wolf Creek.

High-grade illite from Little Spar Lake consists of greater than 95% 2M\textsubscript{1} polytype, indicated by an average intensity ratio of 0.23.

**Mixed-layering** Small proportions of expandable (smectite) layers occur in the Big Snowy Mountain and Wolf Creek samples. No expandable layers were detected in the highest grade samples from Little Spar Lake (Figures 11 and 12).

I/S in the Big Snowy Mountains contains 1-2% expandable (smectite) layers. The 001 reflection migrates from 10.10 \AA\ to 10.04 \AA\ and becomes slightly less asymmetrical towards the low-angle side upon ethylene glycol-solvation. \(\beta\) (005) increases from 0.493 to 0.513° 2\theta upon ethylene glycol-solvation.

I/S from Wolf Creek contains 1-2% expandable (smectite) layers, and like Big Snowy Mountains illite, the 001 reflection migrates from 10.10 \AA\ to 10.04 \AA\ and becomes slightly less asymmetrical towards the low-angle side upon ethylene glycol-solvation. \(\beta\) (005) changes from 0.480 to 0.499° 2\theta upon ethylene glycol-solvation.
Figure 11. Ethylene glycol-solvated X-ray powder diffraction patterns from the Belt Supergroup compared with illite and I/S NEWMOD (Reynolds, 1985) patterns. M = machine artifact, K = kaolin, Q = quartz.

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Figure 12. Mixed-layered variations in illite/smectite (I/S) with increasing burial depth in the Belt Supergroup. Burial depth increases from east to west.
Peak positions, peak shapes, and peak widths for illite from Little Spar Lake do not change upon ethylene glycol-solvation, indicating no expandable (smectite) layers in the highest-grade illite samples.

**Values**  
Values are shown in Table 2. B diminishes slightly from east to west. Ethylene glycol-solvation alters B values of illite peaks from the Big Snowy Mountains and Wolf Creek, but not Little Spar Lake, indicating the presence of expandable (smectite) layers in low and medium-grade samples, but not in high-grade samples.

**Chemical Composition**  
I/S from the Big Snowy Mountains contains no iron. I/S from Wolf Creek and Little Spar Lake each contain about 0.1 Fe atoms per 2.0 possible dioctahedral sites.

**DISCUSSION**

**Magnetic Separation**  
I was unable to separate chlorite and illite in low-grade samples from the Big Snowy Mountains. Comparison of analytical patterns with calculated NEWMOD patterns (Reynolds, 1985) reveals that chlorite from the Big Snowy Mountains is Mg-rich. The separation difficulties may have been caused by the low magnetic susceptibility of magnesian chlorite. Chlorite and illite separate easily in higher-grade, more Fe-rich, samples. Walker (1989) and Walker and Thompson (1990) document a similar relationship. The

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separation difficulties may also have been caused by intimate intergrowth of illite and chlorite in low-grade samples.

**Chlorite**

**Polytypes** Traces of Ib chlorite in the Big Snowy Mountain section may represent the final stage of a Ib -> IIb chlorite polytype transformation. Previous estimates of the minimum temperature of formation for IIb chlorite vary from 135°C (Walker and Thompson, 1990) to 200°C (Hayes, 1970). However, the occurrence of IIb chlorite in low-grade argillite of the Big Snowy Mountains indicates that the minimum temperature of formation of IIb chlorite can be as low as 80°C. If chlorite polytype transformations are temperature dependant, the transformation from type-I to type-II chlorite may occur at temperatures lower than 80°C.

**Mixed-layering** C/S and chlorite in Belt Supergroup argillite may have formed (1) as magnesium and iron were lost by illite/smectite during illitization of smectite (Hower, et al., 1976), or (2) by progressive increase in the proportion of chlorite layers in chlorite/smectite (saponite) with increasing temperature until nearly pure chlorite developed (Chang, et al., 1986; Moe, 1990). The progressive loss of expandable layers from C/S with increasing grade may indicate that chlorite with 6% expandable (smectite) layers is unstable at temperatures higher than 80°C. Alternatively, the presence of C/S with 6% expandable layers may reflect the slow rate at
which Fe-rich mixed-layer phases convert to homogeneous phases during diagenesis (Anjos, 1986).

**β Values** Two factors affect β: (1) proportion of expandable layers in mixed-layer phases, and (2) sizes of coherent scattering domains (crystallite thickness, N).

Changes in analytical β values upon ethylene glycol-solvation were approximately three times greater for C/S with 6% smectite from the Big Snowy Mountains than for C/S with 2% smectite from Rogers Pass, suggesting a systematic inverse relationship between β and percent smectite in C/S.

Plotting experimental β values against percent smectite (expandability) in C/S isolates the effect of expandability on β in C/S, and reveals that N (crystallite thickness) increases from low N=17/ high N=21 in the Big Snowy Mountains, to low N=27/ high N=30 at Rogers Pass, to low N=28/ high N=31 at Clark Fork (Figure 13). The increasing N indicates progressive increase in the size of coherent scattering domains with increasing metamorphic grade.

C/S percent expandability drops sharply from 6% to 2% and N increases sharply from 19-23 to 27-30 between the Big Snowy Mountains and Rogers Pass. In the same interval, β drops from 0.427 to 0.253° 2θ. Similarly, a small decrease in percent expandability between Rogers Pass and Clark Fork (2% --> 0%) and a small increase in N (27-30 --> 28-31) correlate to a
Figure 13. Curve for the determination of N values of chlorite and chlorite/smectite (C/S). X-axis is percent smectite in C/S, and Y-axis is $\beta$ (002). Samples are plotted with $\beta$ values and percent smectite as determined by comparing analytical X-ray patterns with NEWNOD (Reynolds, 1985) calculated patterns.

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small drop in B (0.253 -> 0.216° 2θ). Decrease in percent expandability and increase in crystallite thickness in C/S appear to reflect a single process, and seem to be consistent with a progressive increase in the size of fundamental particles (Nadeau, et al., 1984; Eberl, et al., 1990).

Chemical Composition Although Fe content in chlorite varies between the Big Snowy Mountains and Clark Fork, the variations may be due to differences in system composition rather than diagenesis. The Newland Formation is a reduced, dolomitic argillite, and much of the Fe may be incorporated in dolomite or pyrite. All other samples used in this study lack dolomite, so more Fe was possibly available to go into the structure of clay minerals (Winston, pers. comm., 1991).

Illite

Polytypes 1Md and 1M illite coexist with small amounts of 2M₃ illite in low-grade samples. The proportion of 2M₃ illite increases with increasing burial depth as 1Md and 1M convert to the 2M₃ polytype (1Md -> 1M -> 2M₃). Occurrence of the 1Md polytype in illite of low expandability (1-2%) corresponds with results of Brindley (1984), Srodon and Eberl (1984), and Walker and Thompson (1990), who suggest that the 1Md polytype exists only in illite of measurable expandability.

The persistence of 1Md illite in the Newland Fm of the
Big Snowy Mountains is consistent with interpretations of shallow burial depth of the Belt Supergroup in the Big Snowy Mountains.

Many workers (Yoder and Eugster, 1955; Velde, 1965; Maxwell and Hower, 1967; Walker and Thompson, 1990) have documented the $1\text{Md} \rightarrow 1\text{M} \rightarrow 2\text{M}_1$ illite polytype conversion with increasing metamorphic grade. It is well established that kinetic factors control the smectite to illite conversion during low-grade metamorphism (e.g. Hower, et al, 1976; Jennings and Thompson, 1986). In this reaction, nearly pure illite forms at low temperatures in old mudrocks, but younger mudrocks at comparable temperatures consist of I/S with substantial proportions of smectite layers. However, the persistence of the $1\text{Md}$ polytype in the 1.4 billion year old Newland Formation suggests that similar kinetic factors do not control the conversion of the $1\text{Md}$ polytype to the $1\text{M}$ and $2\text{M}_1$ polytypes. These data suggest that the $1\text{Md}$ polytype is stable or persists for a very long time at $\leq 80^\circ\text{C}$. The persistence of $1\text{Md}$ illite in rocks of the Big Snowy Mountains interpreted to have experienced temperatures no hotter than $80^\circ\text{C}$ supports the conclusion that the $1\text{Md}$ polytype is stable at temperatures lower than $300^\circ\text{C}$ in laboratory experiments (Yoder and Eugster, 1955), and $200^\circ\text{C}$ in natural samples (Walker and Thompson, 1990).

Eslinger and Savin (1973), in their study of Belt
argillites in Glacier National Park, recognized a correlation between quartz-illite isotopic temperatures and percent $2M_1$ illite relative to total illite. Data from this study were plotted on Figure 14 (Eslinger and Savin, 1973) to determine maximum temperatures to which selected Belt argillites were heated. 35% $2M_1$ illite at Wolf Creek indicates that the Spokane Formation at Wolf Creek has been exposed to a maximum temperature of about 250°C. >95% $2M_1$ illite at Little Spar Lake indicates that argillite from the lower Revett Formation at Little Spar Lake was exposed to a maximum temperature of about 380°C.

**Mixed-layering** I/S with <2% smectite layers formed from initially smectite-rich mud (Eslinger and Sellars, 1981) at temperatures ≤80°C in Proterozoic mudrocks from the Big Snowy Mountains. Mudrock samples from Wolf Creek indicate that I/S with <2% smectite layers may be stable at temperatures as high as 250°C. However, no smectite layers remain in I/S from Little Spar Lake argillite, suggesting that illite of measurable expandability is not stable at temperatures ≥380°C.

**$\beta$ Values** Changes in $\beta$ upon ethylene glycol-solvation are similar for I/S from the Big Snowy Mountains and Wolf Creek, and both samples contain 1–2% smectite layers. This similarity suggests that $\beta$ and percent smectite in I/S are related. $\beta$ does not change upon ethylene glycol-solvation of
Figure 14. Correlation between quartz-illite isotopic temperatures and percent 2M1 illite relative to total illite (after Eslinger and Savin, 1973).
illite from Little Spar Lake, reflecting no smectite layers in the highest-grade illite.

Comparing analytical β values of ethylene glycol-solvated samples with corresponding NEWMOD (Reynolds, 1985) β values indicates that N increases slightly between the Big Snowy Mountains and Little Spar Lake. Percent expandability in I/S diminishes slightly over the same interval, suggesting that β and N vary systematically and inversely with increasing grade.

**Chemical Composition** Illites examined in this study are Fe-poor. Minor variations in Fe content are likely due to differences in system composition.

**Coexisting Illite and Chlorite**

Coexisting illite and chlorite in the Belt Supergroup undergo systematic structural variations with increasing burial depth as low-grade phases progressively convert to higher-grade phases. However, the diagenetic trends of illite and chlorite differ.

Illite polytypes vary systematically (from 1Md --> 1M --> 2M₁) with increasing diagenetic grade, but chlorite polytypes do not. Traces of Ib chlorite in the Big Snowy Mountains may indicate that (1) a large proportion of Ib once existed and has converted to IIb at temperatures less than 80°C, or (2) IIb chlorite neoforms at temperatures less than 80°C. Chlorite may reach an end-member polytype at a lower temperature than illite.
The percentage of I in I/S is known to increase from 0% to 100% with increasing temperature (e.g. Jennings and Thompson, 1986), but few studies document similar changes in C/S (Chang, et al., 1986; Moe, 1990). In Belt Supergroup argillites, both I/S and C/S appear to convert progressively to pure end-members with increasing metamorphic grade. However, low-grade illite from the Big Snowy Mountains contains a smaller proportion of smectite layers and lesser variations in crystallite thickness than chlorite. Mixed-layer I/S varies from 1-2% smectite in low-grade samples to pure illite in higher-grade samples, and illite crystallite thickness increases slightly from 17-20 to 18-21 over the same interval. In contrast, C/S varies from 6% smectite in low-grade samples to pure chlorite in higher-grade samples, and crystallite thickness increases from 19-23 to 28-31 over the same interval.

SUMMARY AND CONCLUSIONS
1. Between the shallowly buried, low temperature Big Snowy Mountain section (<80°C) and the deeply buried, higher temperature Clark Fork section:
   a. Illite polytypes transform progressively from 1Md (with <10% 2M₁) to 1M (with 35% 2M₁) to 2M₁ (with <5% 1M)
   b. I/S changes from I/S with 1-2% smectite layers to
pure illite.
c. Illite $\beta$ (005) decreases from 0.513 to 0.474.
d. Mixed-layer C/S varies systematically from C/S with
   6$\%$ smectite layers to pure chlorite.
e. Chlorite $\beta$ (002) decreases from 0.427 to 0.216.

2- I/S with 1-2$\%$ smectite layers formed from smectite or
initially smectite-rich I/S at temperatures less than $80^\circ$C in
the Big Snowy Mountains.

3- The persistence of the 1Md illite polytype at
   temperatures $\leq 80^\circ$C suggests that that 1Md polytype is stable
   or very persistent at temperatures as high as $80^\circ$C.

4- IIb chlorite formed at $\leq 80^\circ$C in the Big Snowy
   Mountains.

5- The Spokane Fm at Wolf Creek has been exposed to a
   maximum temperature of about $250^\circ$C.

6- The lower Revett Fm at Little Spar Lake has been
   exposed to a maximum temperature of about $380^\circ$C.
REFERENCES


Harrison, J.E., and Jobin, D.A. (1963) Geology of the Clark Fork...


Reynolds, R.C., Jr. (1985) NEWMOD-A computer program for the calculation of one-dimensional diffraction profiles of clays: published by the author, 8 Brook Road, Hanover, New Hampshire.


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**Chlorite Polytypes**

Increase in relative structural stabilities based on cation-cation repulsion

(Ibd is not shown above)

After Bailey (1988)

Tetrahedral Sheet

Octahedral Sheet

* Cations
The three most common chlorite polytypes are illustrated on the previous page. Hayes (1970) proposed that chlorite polytypes are temperature dependant, and the proposed sequence of transformations with increasing temperature is:

\[ \text{Ibd} \rightarrow \text{Ib} (\beta = 97^\circ) \rightarrow \text{Ib} (\beta = 90^\circ) \rightarrow \text{IIb} \]

over a range of 20° to 200°C.

- the lowest temperature chlorite polytype is Ibd (not shown), which is characterized by disordered stacking (Bailey, 1988).

- the transformation from Ib (\(\beta = 97^\circ\)) to Ib (\(\beta = 90^\circ\)) is accompanied by a \(\pm \frac{b}{3}\) shift (Bailey, 1988).

- the transformation from Ib (\(\beta = 90^\circ\)) to IIb is accompanied by a rotation of the interlayer metal-hydroxyl complex by 60° or 180° (Brown and Bailey, 1962).

- two primary factors explain chlorite polytype stabilities
  1. cation-cation repulsion between silicate layer cations and metal-hydroxyl layer cations (illustrated on previous page).
  2. lengths of hydrogen bonds between basal tetrahedral oxygens and hydroxyls of the metal-hydroxyl layer (Bailey, 1988).

- IIb chlorite has minimal cation-cation repulsion and strong hydrogen bonds, and is considered the most stable chlorite polytype. Less favorable cation-cation repulsion and weaker hydrogen bonds make type-I chlorites less stable than type-II. Ib (\(\beta = 90^\circ\)) is more stable than Ib (\(\beta = 90^\circ\)) due to greater spacing of superimposed cations i.e. less cation-cation repulsion (Brown and Bailey, 1962).
Chlorite and Mixed-layer Chlorite/Smectite

On the left is pure chlorite with a 14 Å d-spacing.

On the right is mixed-layer chlorite/smectite, with a 17 Å smectite layer surrounded by 14 Å chlorite layers.

(After Moore and Reynolds, 1989)
- 1Md illite (not shown) is characterized by a stacking arrangement in which rotations from one 10 Å 2:1 layer to another is n·60°, where n is a random integer.
- n = 0 in 1M illite.
- the transformation from 1M to 2M₁ is accompanied by a 180° rotation between two adjacent 2:1 layers

(After Moore and Reynolds, 1989)
Illite and Mixed-layer Illite/Smectite

On the left is pure illite with a 10 Å d-spacing
On the right is illite/smectite with a 17 Å smectite layer surrounded by 10 Å illite layers.

(After Moore and Reynolds, 1989)

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