PETROLOGY, CHEMISTRY, AND CLAY MINERALOGY OF A K-BENTONITE IN THE PROTEROZOIC BELT SUPERGROUP OF WESTERN MONTANA

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ABSTRACT: **A K-bentonite in the Middle Carbonate Group of the Belt Supergroup is evidence for eruptive volcanic activity within or adjacent to the Belt basin during Middle Proterozoic deposition. The texture of this olive-green rock is dominated by a fine-grained groundmass similar to Paleozoic K-bentonites. Throughout this groundmass are a few randomly occurring angular, irregularly shaped clasts composed of quartz. The morphology of these clasts indicates the quartz grains have not been transported. Traces of small euhedral zircons are also present. The mineralogy and chemical composition of the groundmass in this K-bentonite is also similar to Paleozoic K-bentonites but appears to reflect a more evolved mineralogy as a result of its age and thermal history. Unlike Paleozoic K-bentonites, which are characteristically the 1M polytype, authigenic 1M and $2M_1$ illite/mica polytypes coexist in this Proterozoic K-bentonite and are separable by size fractionation. The K-Ar ages of the clay fractions range from 807 Ma in the coarser fraction to 606 Ma in the finer fraction. The 807 Ma K-Ar age of $2M_1$ mica indicates temperatures in excess of 250°C during this time. The 606 Ma K-Ar age of the fine-grained 1M polytype probably reflects later 1M crystallization at temperatures below 250°C. The reaction of 1M to $2M_1$ polytype in this K-bentonite did not require major changes in chemical composition, and the dominant controls on the 1M to $2M_1$ polytype transformation appear to have been temperature and time.**

INTRODUCTION

The middle Proterozoic Belt Supergroup in western Montana was deposited in a long-lived sedimentary basin with adjacent centers of contemporaneous felsic volcanism (Evans and Fischer 1986). Goldich et al. (1959) first studied a thin green bed in the Belt Supergroup at Glacier National Park and, from textural and mineralogical arguments, suggested that it might be a K-bentonite. Goldich et al. (1959) also reported Rb-Sr (780 Ma) and K-Ar (740 Ma) whole-rock ages of this bed. Obradovich et al. (1984) used the U-Pb method to obtain an age of 1345 Ma from a zircon crystal in the same bed, but the zircon was possibly zoned, and this age is suggested to be a maximum.

The purpose of this study is to re-sample and study the bed described by Goldich et al. (1959). A K-bentonite of this age would be far older than any previously reported. Thin-section petrography, XRD, chemical analyses, and K-Ar dating were used to establish the bentonitic nature of this bed, and K-Ar dating of the 1M to $2M_1$ polytypes allowed an interpretation of its diagenetic and thermal history.

GEOLOGIC SETTING

The middle Proterozoic Belt Supergroup is a sequence of argillite, quartzite, and carbonate rocks that unconformably overlie the Archean Wyoming province to the east and thicken southwestward to a maximum of 20 km in western Montana (Harrison et al. 1974; Winston 1986). It was deposited in either (1) a large intracratonic rift basin (Winston et al. 1984), or (2) a passive margin (McMechan 1981). Diabase sills intruded the Belt basin at 1430–1450 Ma (Zartman et al. 1982; Burwash and Wagner 1989), and the Purcell lava and Alderson Lake sill were emplaced at approximately 1307 Ma during or shortly after deposition of the upper Middle Belt Carbonate and lower Missoula Group (R.A. Burwash, oral communication 1993). Intrusive felsic rocks to the south and west of the basin could have produced air-fall ash deposits during deposition of the Belt Supergroup, and they may be contemporaneous with the 1307 Ma mafic rocks (Evans and Fischer 1986).

SAMPLE COLLECTION AND PREPARATION

In August 1992 we collected samples from a olive-green bed 20 cm thick in the uppermost Middle Belt Carbonate in a roadcut at Logan Pass in Glacier National Park, Montana (Fig. 1). The upper half of the bed is darker green than the lower, and faint planar laminae produced by alternating shades of green are present throughout the bed. The sampled bed exhibits axial planar cleavage inclined to bedding, but the surrounding carbonate beds exhibit no cleavage.

Thin sections were cut parallel and normal to both bedding and cleavage. Slabs in the same orientations were cut and ground to a flat surface with emery cloth for X-ray diffraction (XRD) analysis. Freeze-dry preparation minimizes reaggregation during drying, thus enhancing random orientation of clay crystals in powders loaded into side-load sample holders (Reynolds 1992). Random powders were analyzed in the air-dried, ethylene-glycol-solvated, and heated (250°C) states. X-ray diffraction scans of the random mounts were made from 16 to 44° 2θ using 20 second counts and 0.05° steps. The relative proportions of mica polytypes in a given size fraction were estimated using NEWMOD and WILDFIRE software (Reynolds 1985; 1993).

Small amounts of the freeze-dried powders were resuspended and evaporated onto glass slides to produce oriented mounts. These preparations were analyzed to determine percent expandability (percent smectite) in illite using the methods of Srodon (1980) and Moore and Reynolds (1989). The oriented mounts were scanned from 2° to 48° 2θ using 5 second counts and 0.05° steps. All XRD data were collected at Dartmouth College on a Siemens D500 X-ray diffractometer with Ni-filtered Cu radiation and a Databox stepper motor scanner. After all powders had been examined by XRD, the 1–2 mm, 0.2–1 mm, and < 0.2 mm fractions were split and analyzed for major elements, K-Ar dating, and oxygen isotopes.

Major element oxide analysis of whole rock and all size cuts were obtained from X-ral Laboratories (Ontario, Canada) using ICP techniques.

The methods of K-Ar measurements are described in Elliott and Aronson (1987). Approximately 50–100 mg of illite from the whole rock and the three size fractions were analyzed for argon and potassium. The argon isotopic compositions were measured on-line with an MS-10 mass spectrometer with computerized measurement capabilities. K-Ar ages were calculated using the ^{40}K decay and abundance constants described in Steiger and Jäger (1977).

Oxygen isotope extraction was performed at Dartmouth College following the methods of Clayton and Mayeda (1963). Illite from the fine clay and coarse clay fractions was reacted with BrF_5 at 550°C and then passed over hot graphite to produce CO_2 gas for analysis. Analyses were performed on a Finnigan Delta E mass spectrometer at Dartmouth College, and d^{18} values are reported relative to SMOW. The accuracy of these analyses is ± 0.3‰.

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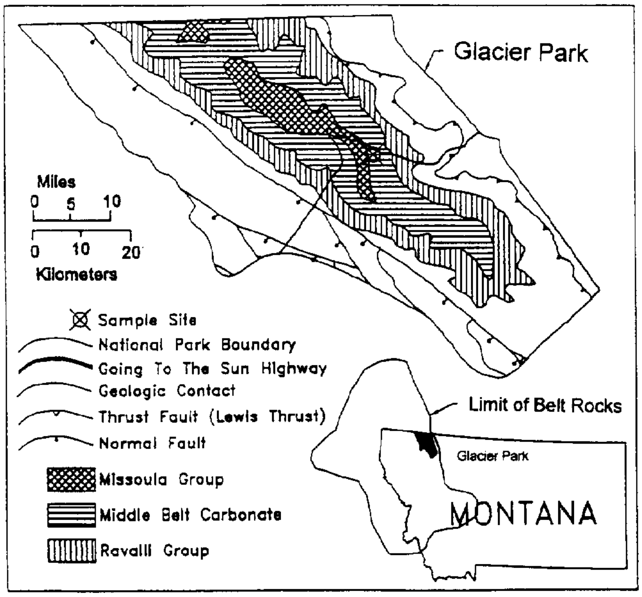

FIG. 1.—Sample location and generalized geology of Glacier Park in Western Montana (after Whipple 1992).

RESULTS

Optical Microscopy

Thin sections are dominated by sericitic groundmass that is colorless under plain light and birefringent under crossed polarizers. The ground mass exhibits little preferred orientation or layering. Clasts are minor ($<$ 2%) but persistent. The most common and largest clasts are angular shard-like quartz grains up to 1 mm long. The angular and irregular shapes of the quartz grains indicates that these are probably relict quartz deposited with the ash and/or authigenic grains that have not been transported as detrital grains. Euhedral zircon crystals up to 0.3 mm long are also scattered throughout the groundmass with no discernible preferred orientation. The zircons appear fresh and unaltered under plain light and are extremely birefringent under crossed polarizers.

X-ray Diffraction

XRD patterns of the whole-rock powder (Fig. 2A) and rock slabs (Fig. 2B) are nearly identical and contain peaks from mica and/or illite, quartz, and a small amount of kaolin and/or chlorite. Comparison of the relative intensities of quartz 101 and mica 00*l* peaks indicate that mica constitutes $> 95\%$ of the whole rock. By the presence of the 060 reflection at 1.51 Å (Fig. 2C), the micas are dioctahedral. The dominant mica peaks between 16° and 44° 2θ have spacings and intensities consistent with the $2M_1$ mica polytype. These patterns also exhibit a group of weak, broad peaks between 20° and 34° 2θ, which are ascribed to the 1M illite polytype.

The two mica polytypes were segregated using size fractionation (Fig.

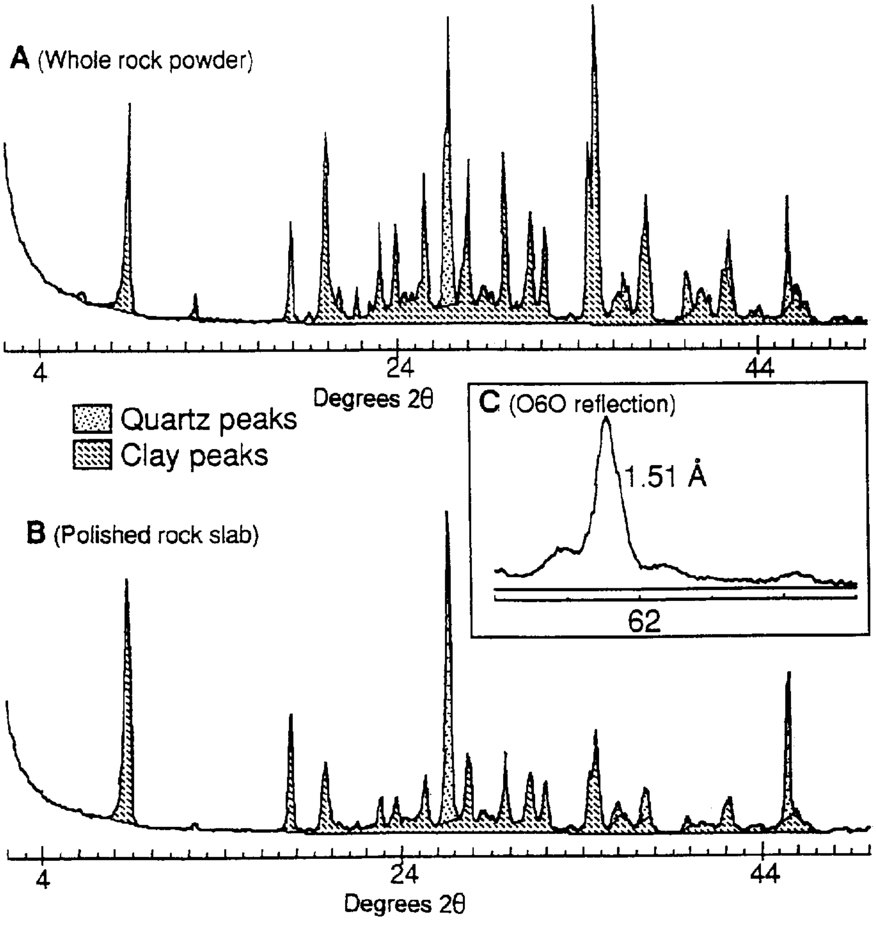

FIG. 2.—X-ray diffraction patterns of **A**) pulverized whole rock and **B**) polished rock slab with **C**) typical 060 reflection.

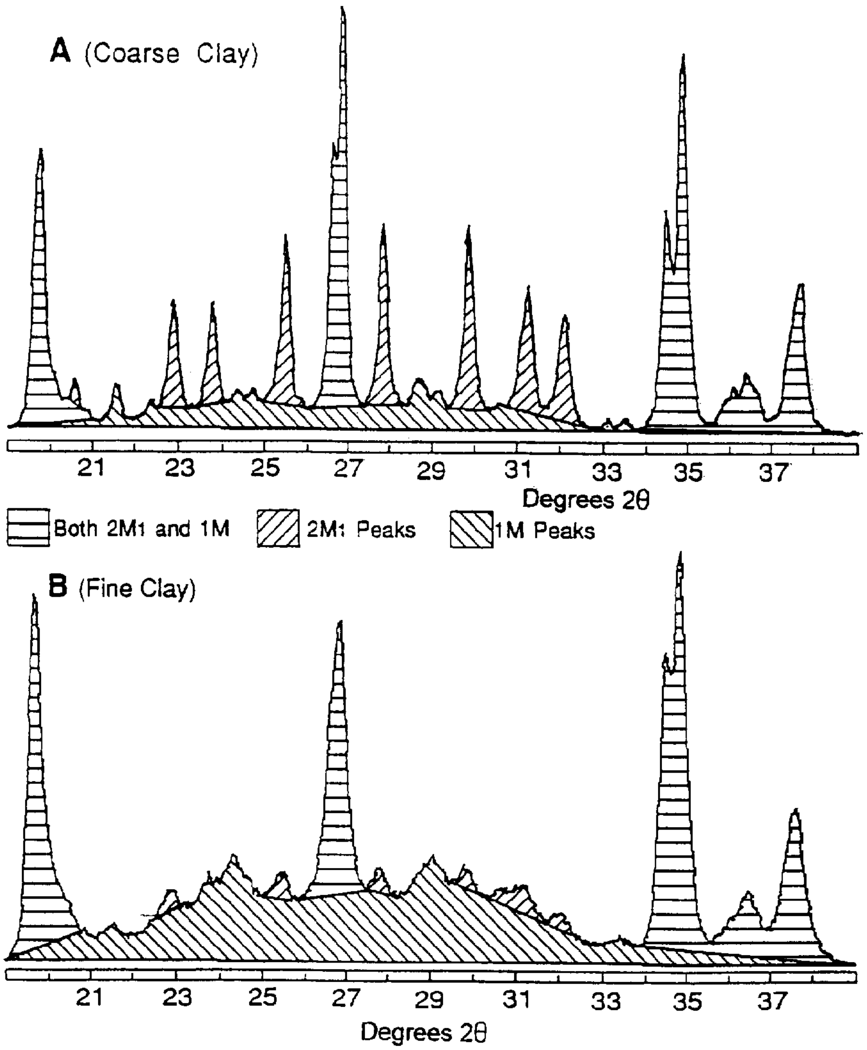

FIG. 3.—X-ray diffraction patterns from random powder mounts of **A**) 1–2 μm clay fraction and **B**) < 0.2 μm clay fraction identifying the different polytype peaks.

3A, B). The 1–2 mm (coarse clay) size fraction is dominated by the $2M_1$ polytype but does contain 5% of the 1M polytype, whereas the < 0.2 mm (fine clay) size fraction is dominated by the 1M polytype and contains 15% $2M_1$ (Fig. 3A, B). Ethylene glycol solvation of oriented mounts produces little change in the oriented patterns and indicates an expandability of < 2% in all size fractions (Fig. 4). Peak width of the illite 005 in the coarse clay fraction is 0.23° 2θ, whereas peak width of the illite 005 in the fine clay fraction is 0.37° 2θ. The difference in peak width reflects smaller crystallite size in the finer size fraction (Srodon and Eberl 1984). No other peaks are evident in the 1–2 mm, 0.2–1 mm, and < 0.2 mm size fractions, suggesting the absence of nonclay minerals such as quartz or K-feldspar in the clay fraction of this K-bentonite.

Chemistry

All three size fractions and whole rock were analyzed for major elements. These data were calculated to a standard dioctahedral mica stoichiometry (Table 1) excluding titanium and phosphorus. The potassium value for the < 0.2 mm (commercial analysis) is significantly lower than the potassium content measured by flame photometry for K-Ar dating (Table 2). The stoichiometry in Table 1 was calculated using the potassium values from K-Ar dating; this produces a better charge balance for all of the formulae.

The chemical compositions of all size fractions are nearly identical. The structural formula of $2M_1$ mica in the coarse clay fraction is virtually identical to the whole rock, and this chemical composition is consistent with that of phengite (Bailey 1984). The chemistry of the 1M polytype in the fine clay fraction is similar to the coarse clay fraction and whole-rock powder, but the slightly lower K and Al content of this phase is consistent with illite (Brindley and Brown 1980).

Isotope Analyses

K-Ar ages are as follows: < 0.2 mm size fraction, 606 ± 8 Ma; 0.2–1 mm fraction, 675 ± 9 Ma; 1–2 mm fraction, 807 ± 11 Ma; whole-rock age, 775 ± 11 Ma (Table 1).

The oxygen isotope composition of 1M illite in the fine clay fraction is 17.4 ± 0.3‰ (SMOW), and the oxygen isotope composition of $2M_1$ illite in the coarse clay fraction is 17.5 ± 0.3‰ (SMOW).

DISCUSSION

The texture, mineralogy, and chemical composition of this bed are similar to known Paleozoic K-bentonites except for coexisting authigenic 1M

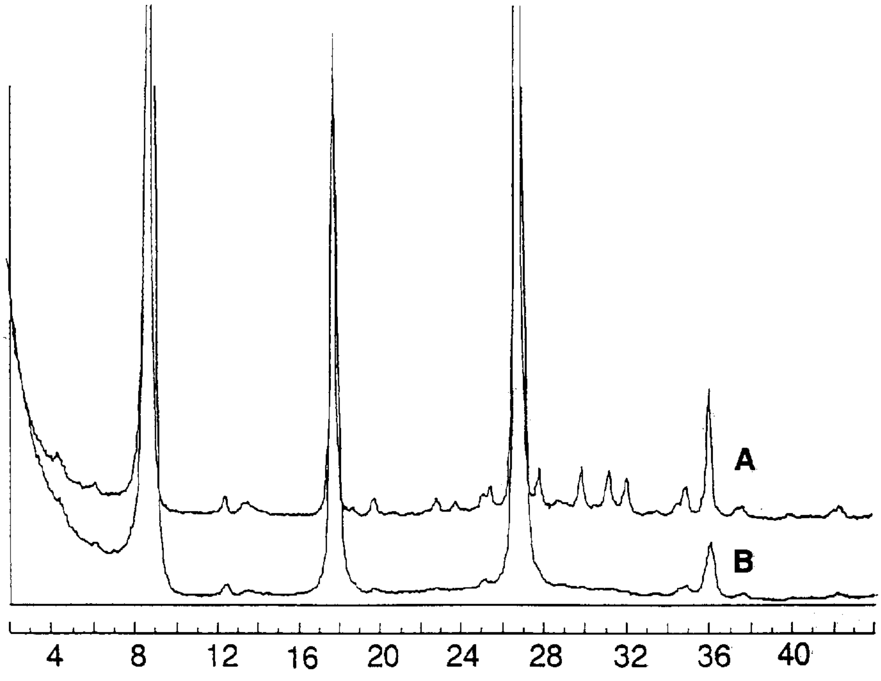

FIG. 4.—X-ray diffraction patterns from oriented aggregate mounts of **A**) 1–2 μm clay fraction (small peaks are three-dimensional bands resulting from poor orientation of this mount) and **B**) < 0.2 μm clay fraction.

illite and $2M_1$ phengite (e.g., McCarty 1993). The uniform groundmass and the presence of quartz shards and euhedral zircon crystals suggests that this rock originated as an airfall deposit of volcanic ash (Person 1982). This appears to be the only documented K-bentonite in the Belt Supergroup or any other Precambrian rock. It is evidence of eruptive volcanic activity proximal to the Belt basin during deposition of the Middle Belt carbonate. Presumably, this bed was initially composed of volcanic glass that devitrified to smectite soon after deposition. During diagenesis, the smectite reacted to form mixed-layer illite/smectite and eventually 1M illite with very little expandability (Eslinger and Sellars 1981). The presence of a coexisting $2M_1$ mica phase could represent short-lived heating above normal diagenetic temperatures, or it may be the end product of diagenesis if given enough time. This Precambrian K-bentonite is evidence that eruptive volcanism, marine deposition of ash, and diagenesis of the resulting sediments followed the same reaction path in Proterozoic time as it has during Phanerozoic time. The presence of two coexisting, nondetrital polytypes in this K-bentonite provides an opportunity to date a thermal history of this bed.

Obradovich and Peterman (1968) dated 1M glauconites from strata both above and below this K-bentonite bed and obtained concordant K-Ar and Rb-Sr ages of 1049 to 1130 Ma. Glauconites appear to neoform at the sediment-seawater interface, so glauconite dates are thought to represent minimum depositional ages. Glauconite is known to exist only as the 1M polytype. Therefore, 1M glauconite, unlike 1M illite, apparently does not transform to the $2M_1$ polytype (Odom 1984), although it may transform into biotite and/or chlorite. Thus, the reported K-Ar ages of Obradovich and Peterman (1968) for 1M glauconite provide a minimum depositional age of Belt rocks, whereas the $2M_1$ mica reflects recrystallization of diagenetic 1M illite and the onset of low-grade metamorphism of the Belt Supergroup (Maxwell and Hower 1967) at around 807 Ma.

The 807 Ma K-Ar age of $2M_1$ mica implies that preexisting diagenetic 1M illite transformed to $2M_1$ mica during low-grade metamorphism in late Proterozoic time. The presence of this polytype ($2M_1$) indicates temperatures in excess of 250°C during the transformation. The 807 Ma age of the $2M_1$ mica correlates with the onset of magmatism, block faulting, and deposition of the Windermere Supergroup, postulated to represent a Late Proterozoic rifting event (Stewart 1972; Young 1984; Bond et al. 1984; Eisbacher 1985; Roots and Parrish 1988; Hoffman 1989; Oldow et al. 1989). Heat flow associated with this event probably induced the $2M_1$ mica crystallization in this K-bentonite. However, it is impossible to rule out the possibility that the $2M_1$ mica formed in response to deep burial diagenesis.

The younger age of the 1M illite (606 Ma) suggests that this phase formed after crystallization of the 807 Ma $2M_1$ mica. If this is the source of the 1M illite, the 606 Ma age is the average age of formation of all 1M after the 807 Ma event. The 1M illite phase could also be the product of continued dissolution and reprecipitation of remnant I/S still present after the low-grade metamorphic event (Eberl 1993) that did not react to $2M_1$ during low-grade metamorphism, possibly because of kinetic factors. If this is true, the 606 Ma age of the 1M illite in the finest fraction reflects argon loss that occurred during continuous dissolution and reprecipitation reset-

TABLE 1.—*Summary of mica polytypes, chemical formulas, and K-Ar ages*

Size (μm) Fraction	Polytype	Age (Ma)	Composition
< 0.2	15% $2M_1$	606	$(Ca_{.031},Na_{.005},K_{.829})(Fe_{.072},Mg_{.421},Al_{1.516})(Si_{3.496},Al_{.504})O_{10}(OH)_2$
0.2–1	55% $2M_1$	675	$(Ca_{.020},Na_{.005},K_{.864})(Fe_{.072},Mg_{.425},Al_{1.513})(Si_{3.484},Al_{.516})O_{10}(OH)_2$
1–2	95% $2M_1$	807	$(Ca_{.037},Na_{.008},K_{.862})(Fe_{.072},Mg_{.421},Al_{1.506})(Si_{3.477},Al_{.523})O_{10}(OH)_2$
Whole rock	80% $2M_1$	775	$(Ca_{.036},Na_{.015},K_{.882})(Fe_{.082},Mg_{.443},Al_{1.482})(Si_{3.452},Al_{.548})O_{10}(OH)_2$

TABLE 2.—*K-Ar data*

Size Fraction (μm)	K_2O wt%	%^{40}Ar* radiogenic	^{40}Ar* mole/ g × 10^{-9}	K-Ar age (Ma)
< 0.2	9.404	98.95	9.744	606 ± 8
0.2–1	9.911	99.16	11.682	675 ± 9
1–2	9.887	99.45	14.479	807 ± 11
Whole rock	10.16	99.55	14.160	775 ± 12
LP6 standard	10.03*	95.94	1.917**	128 ± 2

* Assumed (Odin 1982).

** 1.930 = Accepted value (Odin 1982).

ting the K-Ar system. It is likely that both mechanisms are responsible for the younger age of the 1M illite. Regardless of the mechanism, the age of the 1M illite indicates a post–807 Ma cooling of the Belt rocks below 250°C.

The extremely fine-grained nature of K-bentonites leads to a low water-to-rock ratio and low permeability, producing a stable, long-lived chemical environment. For example, Altaner et al. (1984) studied Cretaceous bentonites and showed that the only major chemical change involved metasomatism of potassium into the bentonite during burial diagenesis in response to thrusting. In the Belt K-bentonite, the nearly identical chemical compositions and oxygen isotope compositions of the coarse and fine clay fractions indicate that the $2M_1$ and 1M polytypes formed in nearly identical chemical environments. With the exception of minor differences in potassium and aluminum content, no major changes in chemical composition were required for the transformation of 1M to $2M_1$. Thus, temperature and time controlled the 1M to $2M_1$ polytype transformation in this Proterozoic K-bentonite.

SUMMARY

The texture, mineralogy, and chemical composition of an olive-green bed in the Belt Supergroup of western Montana indicate that the bed is a K-bentonite. The existence of this bentonite reflects eruptive volcanic activity within or adjacent to the Belt basin during middle Belt carbonate deposition. The 807 Ma $2M_1$ polytype formed from heat flow ($> 250°C$) associated with late Proterozoic low-grade metamorphism related to either rifting or burial, and the younger 606 Ma 1M age reflects later illite crystallization at lower temperatures. The existence of $2M_1$ mica as young as 807 Ma indicates that heat flow in this part of the basin was greatest during Late Proterozoic time. The transformation of 1M to $2M_1$ did not require major changes in chemical composition. Therefore, temperature and time apparently controlled the polytype conversion of 1M to $2M_1$.

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