

Geochemistry of Saprolite from Redwood Falls, MN

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ABSTRACT

A saprolite dominated by quartz, kaolinite, and sericite was formed from chemical weathering of Morton Gneiss in the Minnesota River Valley. Since sericite is a secondary mineral not found in the parent rock, its geochemistry is a useful tool for deciphering the weathering history of the saprolite. Electron microprobe analysis shows that the sericite is severely depleted in potassium, indicating cation exchange of both internal and surface cation sites. The total weight percent of interlayer cations is .08-.14%, compared to the expected ~11% in standard muscovite. The extent of potassium depletion suggests a more intensive and prolonged weathering process than required for mere surface cation exchange. Because the sericite has a low weight percent of common replacement cations such as Na and Ca, we propose that the K was replaced by hydrous species resulting from interaction with acidic waters.

Keywords: sericite, saprolite, weathering, Morton Gneiss

INTRODUCTION

The Morton Gneiss is an Archean aged rock suite found in the Minnesota River Valley (SW Minnesota). In an effort to better understand Precambrian igneous and metamorphic processes, previous studies have characterized the rock types, mineral and elemental composition, and metamorphic geochronology of this ancient gneiss (Goldich and Wooden, 1980a; Goldich et al., 1980; Schmitz, 2006). Post-metamorphic chemical weathering led to the alteration of gneiss to saprolite.

Glacial activity has eroded much of the Morton saprolite, leaving isolated outcrops of this weathering byproduct. Samples taken from outcrops in Redwood Falls, MN (Fig. 1 and 2) exhibit a kaolinite and quartz-rich composition, with sericite and zircon observed in lesser abundance. Beyond these observations, little has been done to understand the weathering conditions that resulted in the parent rock's alteration to saprolite. In other studies, analysis of geochemistry and mineralogy of saprolites has been used to reconstruct paleoclimate and weathering history (Islam et al., 2002a; Islam et al., 2002b); likewise, in our study, we aim to use geochemical analysis to better understand weathering processes that may have affected the Minnesota River Valley.

The objective of this study is to analyze the mineral and chemical characteristics of the saprolite in order to interpolate the weathering history of the Morton Gneiss. To this end, we use petrographic thin section analysis, X-ray diffraction, and X-ray fluorometry to determine the mineral composition and whole-rock chemistry of the saprolite. Composition of the saprolite is then compared to that of the parent rock. In addition, concentrated samples of sericite are examined through Fourier-Transform infrared spectroscopy and an electron microprobe for chemical analysis.

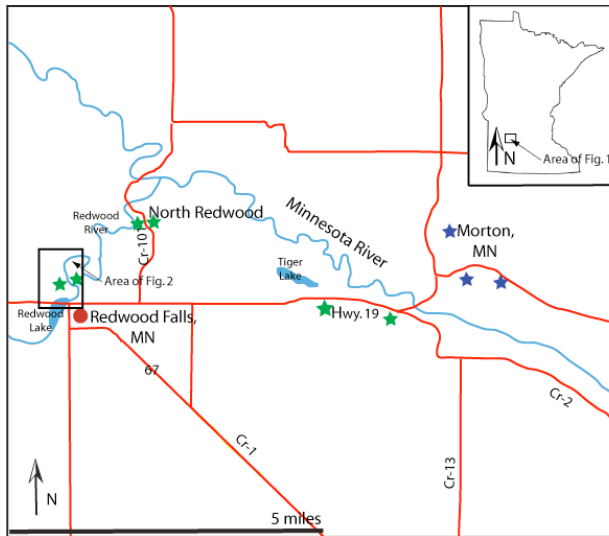


Figure 1. Location map of Redwood Falls and Morton, MN. The outlined area shows study area of Figure 2. Green stars indicate known outcrops of saprolite, while purple stars indicate known outcrops of Morton Gneiss (Goldich, 1938).

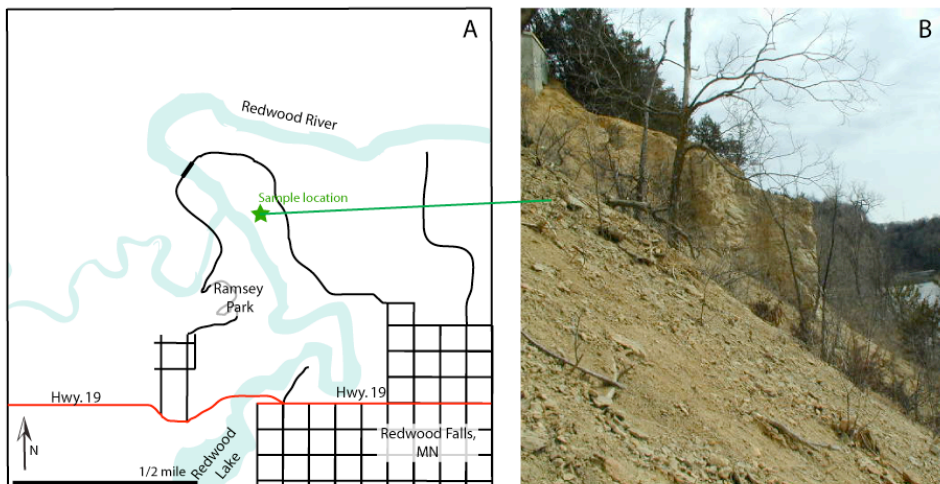


Figure 2. (A) For this study, a sample of weathered Morton Gneiss was taken from the east bank of the Redwood River just north of Redwood Falls, MN at $\sim 44^{\circ} 32' 53''$ N $95^{\circ} 07' 16''$ W; (B) Picture taken facing south southeast along the Redwood River. The saprolite in the foreground is unconsolidated, while the saprolite further away retains structure from the original Morton Gneiss.

Comparison of the sericite composition with standard muscovite can subsequently be used to determine the effects of weathering on the saprolite mica.

GEOLOGIC SETTING

Located in central and southern Minnesota, the Morton Gneiss is a metamorphic complex belonging to the Minnesota River Valley subprovince of the greater Superior Province (Schmitz, 2006). The unit is particularly well exposed in the town of Morton, Minnesota and nearby locales along a narrow corridor cleared of overlying Cretaceous and Mesoproterozoic sediment during the draining of glacial Lake Agassiz through the glacial River Warren (now the Minnesota River) during the Paleozoic (Schmitz, 2006). The Morton Gneiss has been described by three fundamental rock types: mafic inclusions, gray tonalitic gneiss, and pink granitic gneiss that range from quartz monzonite to leucogranite (Lund, 1956; Goldich et al., 1980). These distinct units have been amalgamated into a heterogeneous complex through multiple episodes of Archean metamorphism that Goldich and Wooden (1980b) attribute to three events occurring at ~3.0 Ga, 2.6 Ga and 1.8 Ga. Later quartz veins, pegmatites, and fine-grained granitic dikes cross-cut the complex (Goldich, 1938). Although the igneously-derived units dominate Morton, metasedimentary rocks have been reported at one site (Goldich and Wooden, 1980b).

In addition to outcrops of Morton Gneiss, the rock assemblage of the Minnesota River Valley is also characterized by isolated areas of saprolite, the weathering byproduct of the gneiss. To date, very little has been written about this saprolite. Our field work and that of past Carleton students suggests that Morton Gneiss-derived saprolite is

relatively uncommon, found in only a few discontinuous pockets in southern Minnesota. Previous work suggests a much more expansive unit of ~30 m thick, chemically weathered Precambrian bedrock once covered a large portion of Minnesota, but was eroded by repeated glacial advances of the Des Moines lobe and other ice sheets (Patterson and Boerboom, 1999). It is thought that this process removed most of the weathered material, leaving only the localized pockets of saprolite. It is likely that glacial floods relating to the draining of Lake Agassiz that exposed the Archean bedrock near Morton also contributed to the localization of saprolite pockets by scouring the weathered material along the glacial River Warren.

Of the saprolite pockets that remain, one of the most extensive is a ~15 m by ~100 m exposure along the banks of the Minnesota River near Redwood Falls, where our samples were collected. Here, much of the saprolite has remnant structure from the original gneiss and is quite coherent; however, a significant portion of the saprolite is poorly consolidated and has undergone substantial erosion. The co-existence of structured and highly weathered saprolite suggests that chemical weathering occurred along a gradient at this site, and presumably elsewhere.

METHODS

Petrographic Thin Section Analysis

Three thin-sections of the Redwood Falls saprolite (UQW1, UQW2, UQW3) and the Morton Gneiss were examined with a petrographic microscope. Photomicrographs of the saprolite thin sections were captured with an attached camera.

X-Ray Diffraction.

Quartz and any other heavy mineral fraction were removed from crushed bulk sample of the saprolite by decanting it with water. The remaining clay was then vacuum-filtered onto a sample disk and analyzed for bulk chemistry on a Philips Analytical PW1800 XRD running at 45 kV and 55 mA, at angles of $2\theta = 0-80^\circ$.

X-Ray Fluorometry

Approximately 50 g of saprolite were rough-crushed in a jaw crusher and then pulverized in a Shatterbox using a tungsten carbide vessel. At high temperature, 0.4 g portions of the bulk sample were dissolved into lithium metaborate fusion disks. These disks were analyzed for major elements by X-ray fluorescence spectroscopy (XRF) at Carleton College. Two samples of saprolite, RFE1 and RFE2, were also analyzed for trace elements and rare earth elements by inductively coupled plasma mass spectrometry (ICP-MS) at Activation Laboratories Ltd., Ancaster, Ontario.

Fourier Transform Infrared Spectroscopy

A powder containing 1 mg of hand-picked sericite and 150 mg of potassium bromide was placed into a pellet press and subjected to 20,000 lbs of pressure. The resulting pellet was analyzed using a Nicolet Infinity Series FTIR spectrometer from 350-4000 cm^{-1} under atmospheric conditions (Chemistry Department, Carleton College). Since KBr does not generate an infrared spectrum, a pellet containing only KBr was used to obtain a spectrum that was subtracted to correct for the effects of the atmosphere.

Fourier Transform Infrared spectroscopy (FTIR) operates on the principle that the bonds of molecules vibrate at specific wavelengths. Since the wavelengths are characteristic to particular bonds, the infrared spectra can be used to identify molecules.

Electron Microprobe

Carbon-coated polished thin-sections were analyzed using the University of Minnesota's JEOL 8900 Superprobe, equipped with an energy-dispersive spectrometer (EDS) and five wavelength-dispersive spectrometers (WDS), for major and trace elements. The EDS gives a quantitative analysis of major elements in a sample based on the spectra of energies of the X-rays emitted by those elements. It quickly analyzes the entire spectrum but with relatively large error bars, so it is most useful when a rapid measurement of the major elements is desired. The WDS give a much more precise quantitative analysis of both major and trace elements in a sample based on the spectra of wavelengths of the same X-rays. The precision is achieved by analyzing only a small portion of the spectrum at a time.

RESULTS & DISCUSSION

Hand Sample Observations

In hand sample, the micaceous mineral specimens have the pearly luster and silver-white color characteristic of muscovite. It also exhibits cleavage planes that comprise “mica books” when viewed in thin section and electron microprobe photographs. Consequently, the appearance and morphology of the mica suggest it is a muscovite sericite.

Petrographic Thin Section Analysis

Kaolinite, quartz, biotite, zircon, and a white mica were observed in the thin sections of the saprolite (Fig. 3, Table 1). The white mica grains appear to be muscovite, but have slightly lower birefringence and a smaller 2V than is typical.

The mineral assemblage in the thin sections of the Morton Gneiss is dominated by K-feldspar and plagioclase, but also contains minor amounts of biotite. No muscovite or minerals resembling muscovite were observed in the Morton Gneiss.

X-ray Diffraction

A representative XRD analysis is shown in Figure 4. The XRD spectra of the decanted saprolite clay support the identification of kaolinite in hand sample and petrographic thin section. Kaolinite is typically identified by d-spacings of 7.17 ($2\theta = 11.14^\circ$) and 3.58 ($2\theta = 22.43^\circ$), both of which are confirmed in our XRD analysis. However, XRD analysis does not confirm the presence of sericite, which would be identified by d-spacings of 10.01 and 3.35.

X-Ray Fluorometry

X-ray fluorescence (XRF) results of two saprolite samples, RFE1 and RFE2, are reported in Table 2. Comparison of our saprolite bulk chemistry with that of the original Morton reported by Goldich and Wooded (1980) indicates significant enrichment in iron (III) and marked depletion in calcium, sodium, and potassium in the saprolite (Table 2).

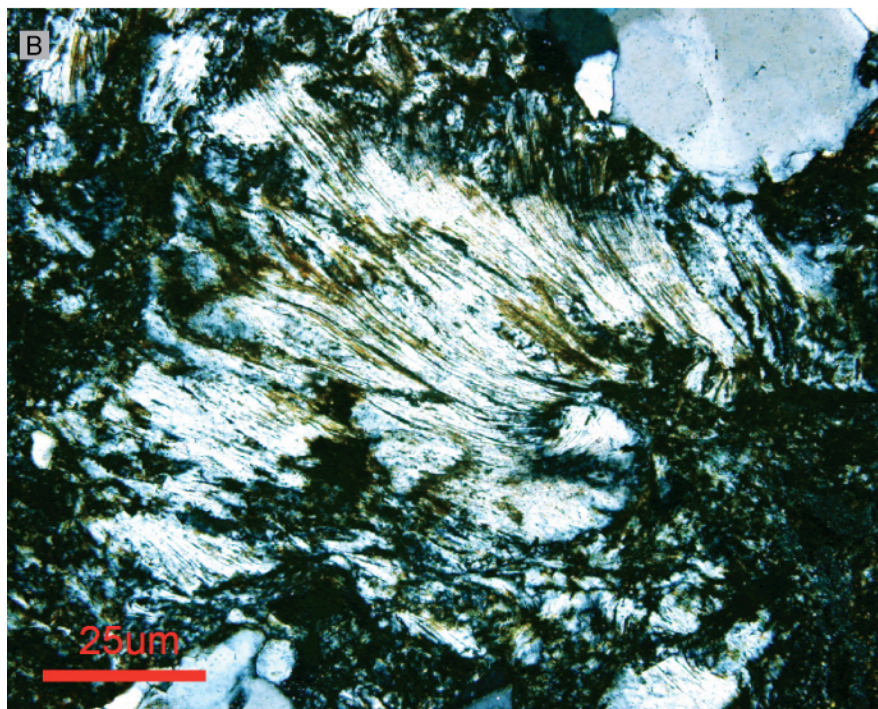
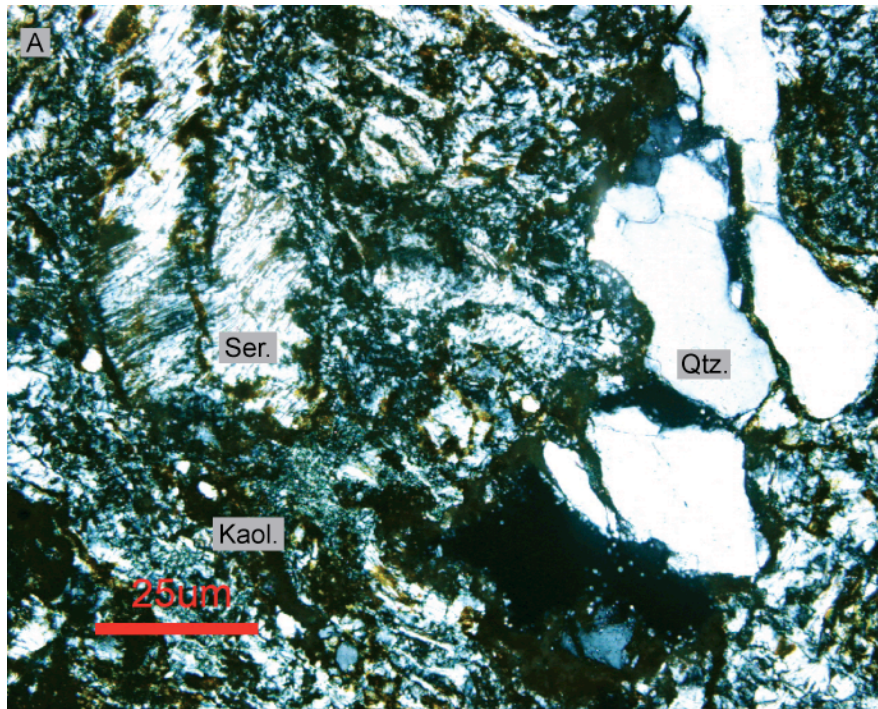


Figure 3. (A) Mineral assemblage of the saprolite, quartz, kaolinite, and sericite (4x magnification, xpl). (B) Sericite grain with kaolinite growth between mica cleavage planes (10x magnification, xpl).

Table 1. RELATIVE ABUNDANCE OF MINERALS IN THE SAPROLITE

Mineral	UQW1(%)	UQW2(%)	UQW3(%)
Quartz	27	35	30
Kaolinite	20	25	18
Sericite	50	35	50
Zircon	trace	trace	trace
Iron Oxides	3	5	2

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of the saprolite sericite (Fig. 5) shows strong peaks 350-1250 cm^{-1} . The peaks at 470 and 539 cm^{-1} relate to bending in Si-O_4 and Al-O_6 . Peaks at 1118 and 1036 cm^{-1} are associated with stretching of Si-O_4 and stretching of the tetrahedral-octahedral-tetrahedral (T-O-T) layers. Weaker peaks at 704, 716, and 802 cm^{-1} are attributed to Al-O stretching and bending of T-O-T layers. Detection of O-H bending is exhibited by the 916 cm^{-1} peak, and O-H stretching is shown by the absorbance peaks at 3623 and 3699 cm^{-1} .

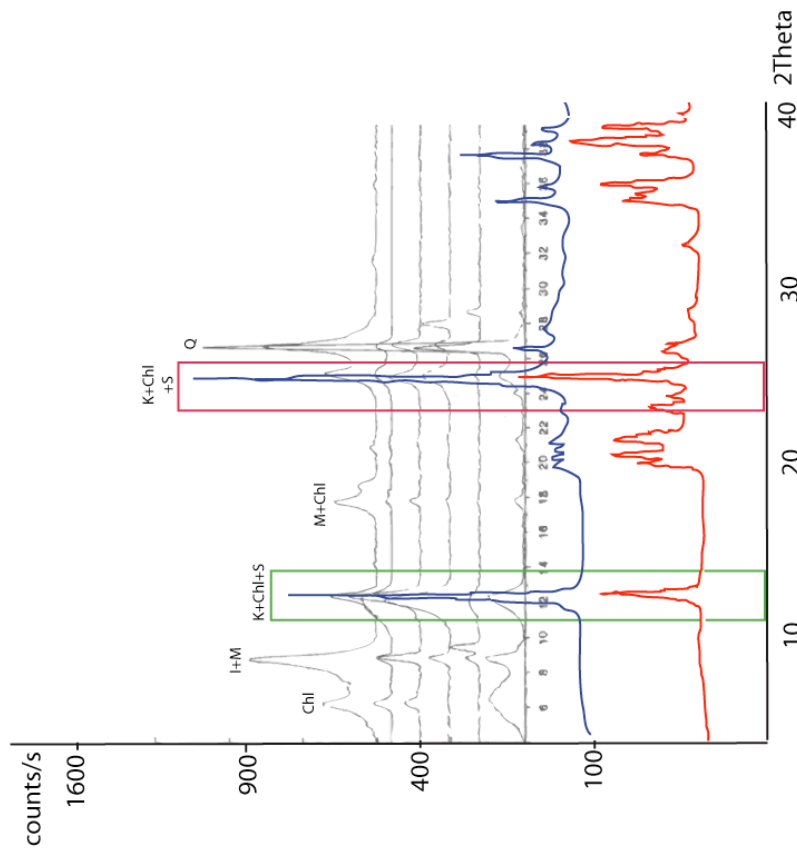


Figure 4. X-ray diffraction analysis of clay minerals. Blue line is sample taken from near Redwood Falls, MN, while grey line is a standard of kaolinite. Green and red boxes outline kaolinite peaks. Transparent graphs come from a saprolite in Bangladesh (Islam et al., 2002). Chl=chlorite, I = illite, M=muscovite, S=serpentine, K= kaolinite, G = gibbsite, Q= quartz. For this study, the absence of a quartz peak is due to removal of heavy non-clay minerals.

TABLE 2. AVERAGE COMPOSITION OF MORTON GNEISS VS. MORTON SAPROLITE

	Morton Gneiss ¹				Morton Saprolite	
	Tonalitic Gneiss	Granodioritic Gneiss	Adamellitic Gneiss	Pegmatitic Gneiss	RFE1	RFE2
SiO ₂	68.70	70.00	74.80	72.70	57.97	56.99
Al ₂ O ₃	16.80	15.00	13.60	13.80	21.87	21.48
TiO ₂	0.36	0.37	0.08	0.08		
Fe ₂ O ₃	0.66	0.80	0.34	0.59	5.89	5.79
FeO	1.75	2.15	0.45	0.92		
MnO	0.04	0.05	0.01	0.02		
MgO	0.86	1.08	0.14	0.18	0.18	0.19
CaO	3.72	3.04	1.42	0.43	0.15	0.13
Na ₂ O	5.39	4.27	3.09	1.86	0.01	0.36
K ₂ O	1.52	2.73	5.36	8.90	0.16	0.37
P ₂ O ₅	0.09	0.13	0.03	0.03	0.03	0.03
H ₂ O ⁺	0.26	0.27	0.14	0.16		
H ₂ O ⁻	0.08	0.08	0.03	0.03		
CO ₂	0.00	0.07	0.09	0.06		
F	0.05	0.06	0.01	0.02		
LOI					9.89	9.66
Total	100.28	100.10	99.59		96.15	95.00

¹Goldich and Wooden, 1980

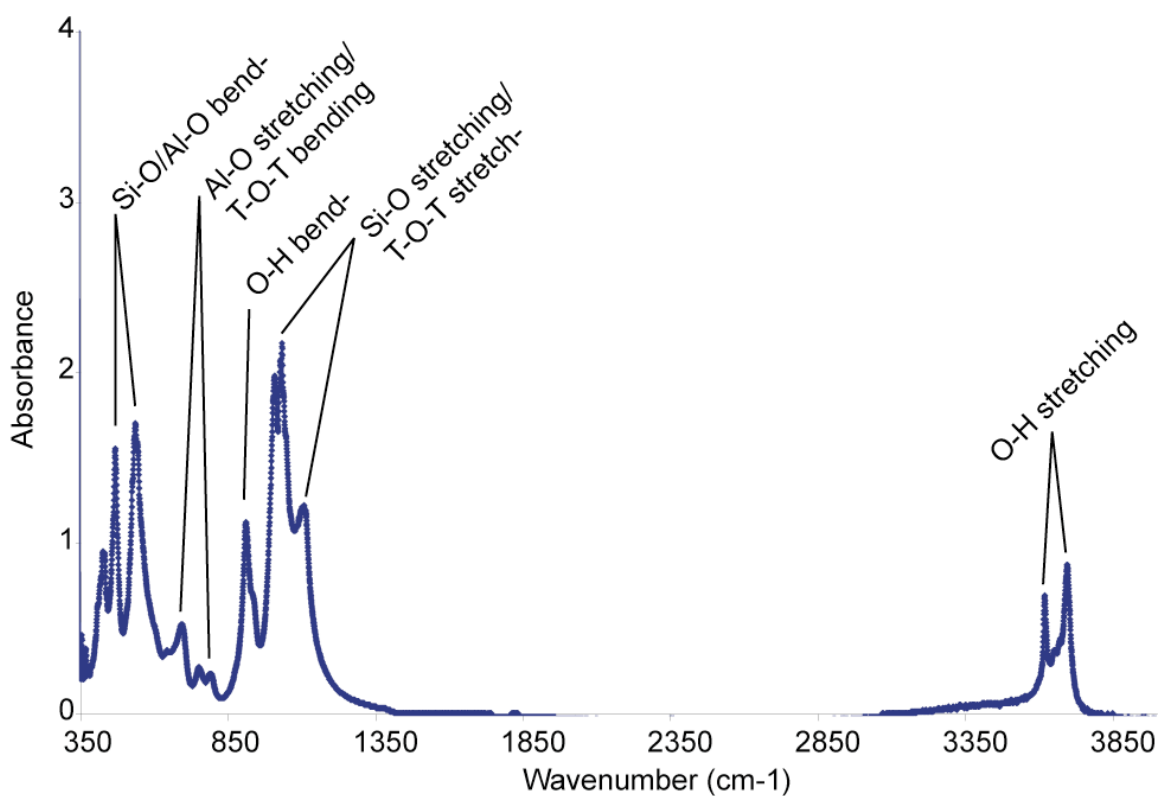


Figure 5. Fourier-Transform infrared spectroscopy analysis of the white mica for wavelengths between 350-4000 cm^{-1} . The peaks at 470 and 539 cm^{-1} relate to bending in Si-O4 and Al-O6, while Peaks at 1118 and 1036 cm^{-1} are associated with stretching of Si-O4 and the T-O-T layers. Weaker peaks at 704, 716, and 802 cm^{-1} are attributed to Al-O stretching and bending of T-O-T layers.

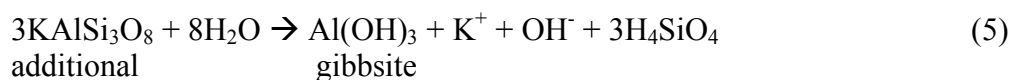
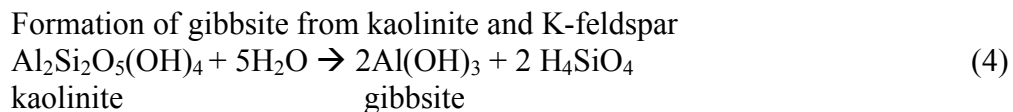
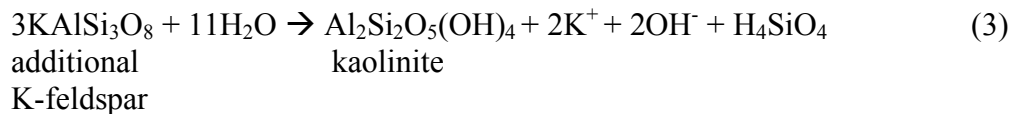
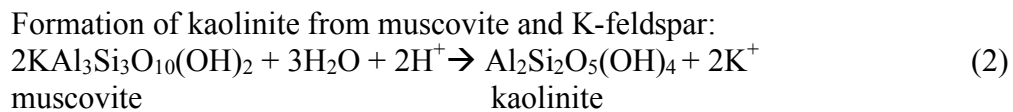
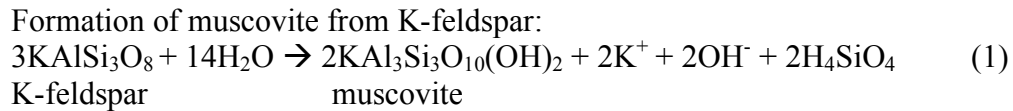
Potassium, the T-O-T interlayer cation, can also be identified using infrared spectroscopy. However, K-O vibrations typically result in peaks 90-200 cm^{-1} , a wavelength range in which we do not have usable IR data.

Electron Microprobe

Images and mineral composition obtained from electron microprobe analysis are shown in Figure 6 and Table 3. Most notably, the white mica is depleted in sodium and potassium compared to a standard muscovite sample. Specifically, potassium content is only .01-.02 weight percent in the sericite compared to 11.23 weight percent of standard muscovite.

Mineral Weathering Processes

Theoretically, the gneiss-water interaction would result in a sequence of chemical reactions that weather K-feldspar to muscovite and kaolinite, and subsequently gibbsite (Islam et al., 2002a; Islam et al., 2002b) by means of the following processes:



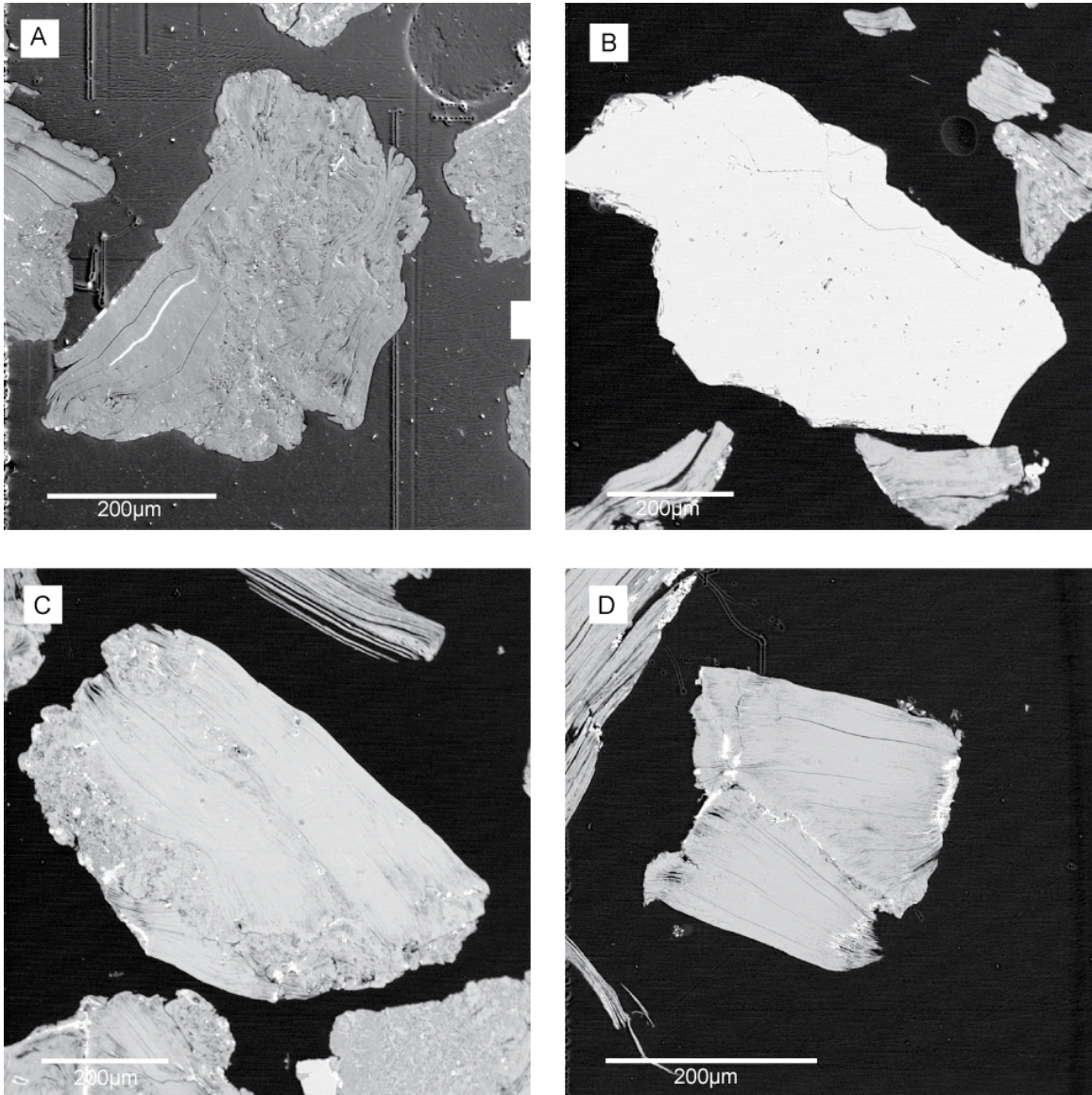


Figure 6. (A-L) Sericite grains exhibiting micaceous cleavage. Highly reflective mineral is zircon.

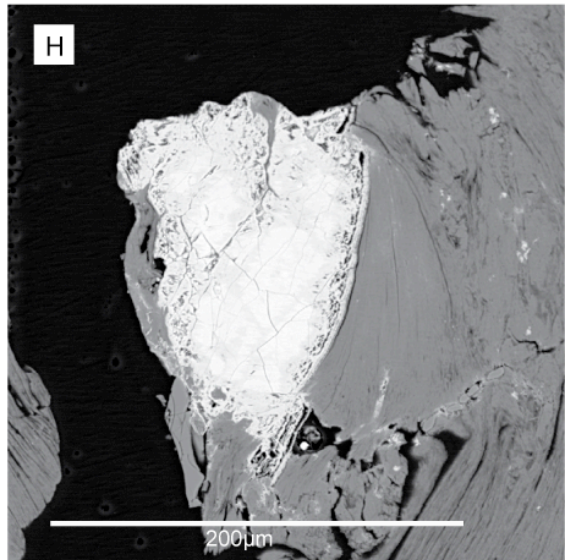
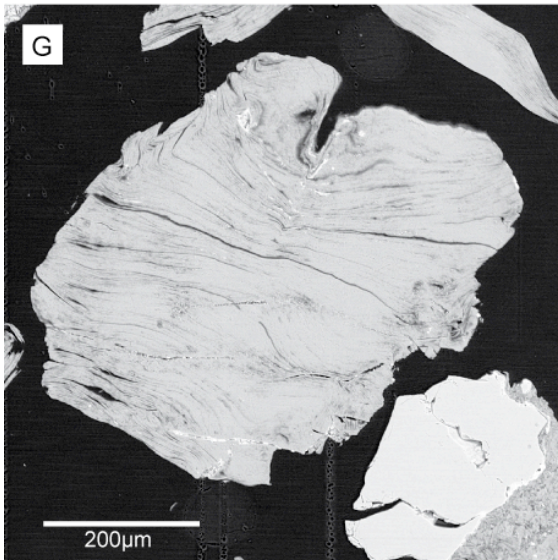
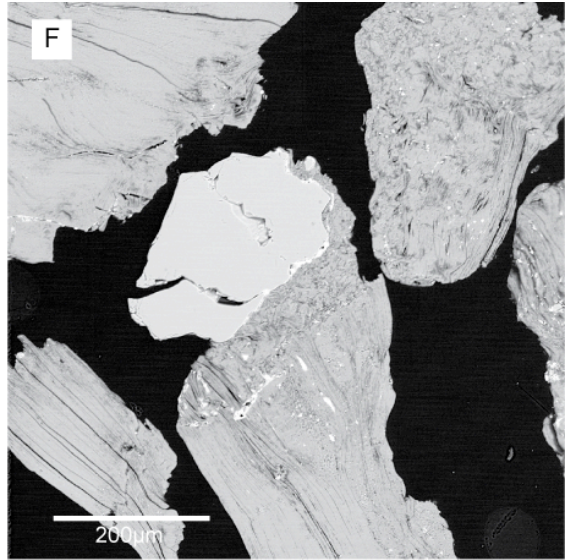
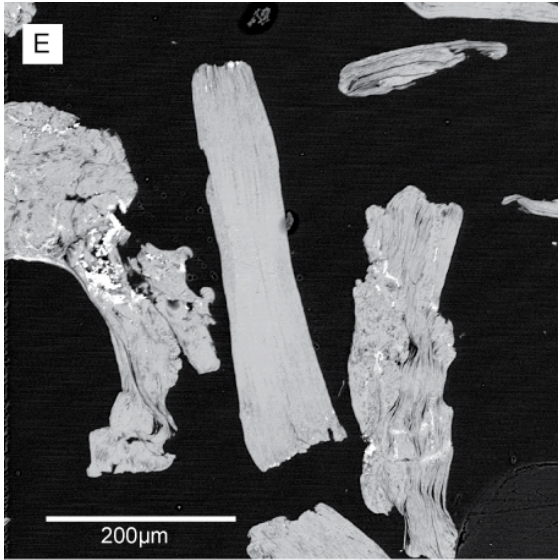


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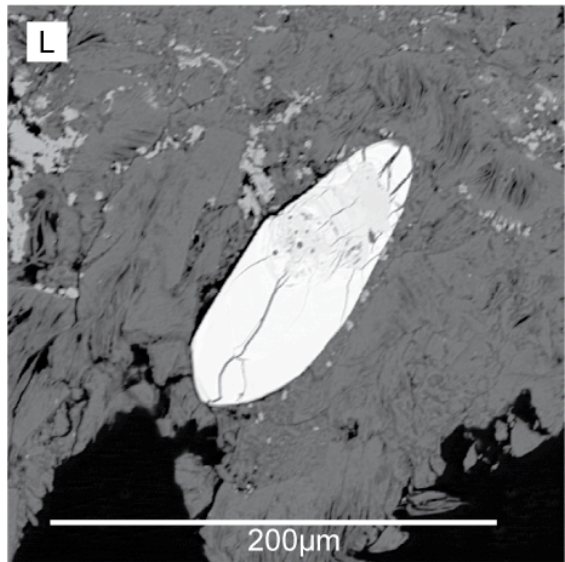
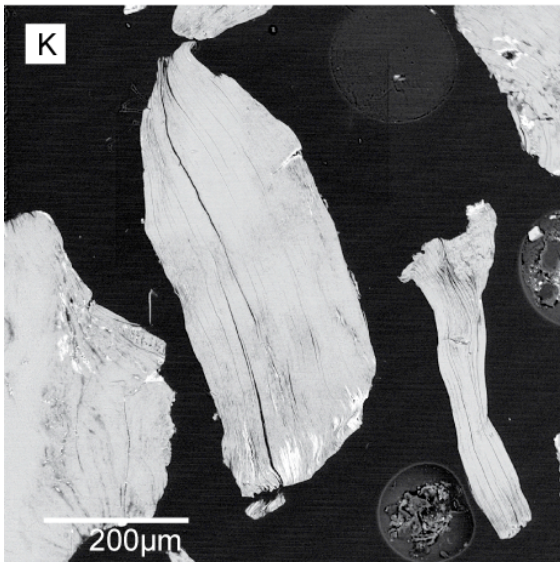
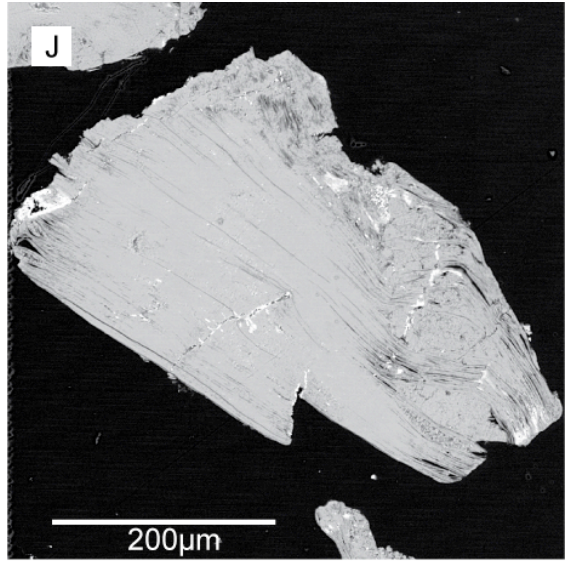
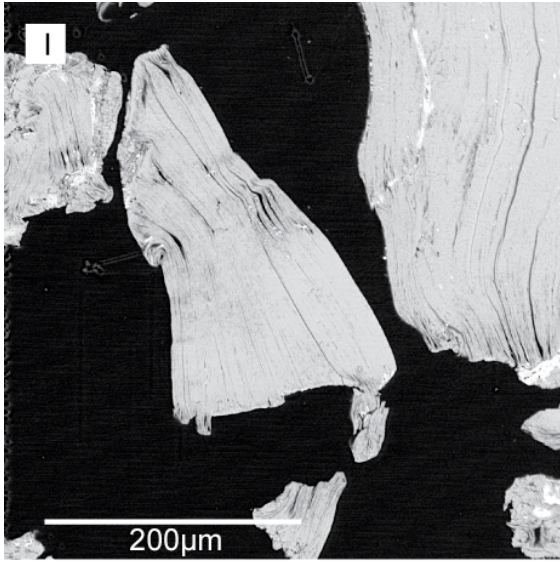


Figure 6 cont.

TABLE 3. AVERAGE WEIGHT PERCENT OF STANDARD MUSCOVITE VS. SERICITE IN THE MORTON SAPROLITE

	Standard Muscovite ¹	UVQ1	UVQ2
SiO ₂	48.42	66.41	41.75
Al ₂ O ₃	27.16	19.98	34.72
TiO ₂	0.87	0.03	0.18
Fe ₂ O ₃	6.57	x	x
FeO	0.81	1.57	2.34
MnO		0.00	0.00
MgO	trace	0.07	0.11
CaO	trace	0.06	0.10
Na ₂ O	0.35	0.01	0.02
K ₂ O	11.23	0.01	0.02
F		0.00	0.00
H ₂ O	4.50	x	x
Total	99.91	88.14	79.23

¹Lambert, 1959

We believe the lack of K-feldspar and abundance of clay minerals in the saprolite is the result of complete dissolution of the feldspars to muscovite and kaolinite by the reactions listed above. The weathering of K-feldspar to kaolinite in the saprolite indicates at least one prolonged weathering event or a shorter but more severe event, as the water-rock interactions needed to be intense or prolonged enough for K-feldspar to undergo two mineral alterations (to muscovite, then to kaolinite). The lack of gibbsite, however, indicates that weathering did not go all the way to completion, which suggests a change in conditions at some point in the weathering process.

K-Depletion of the Mica

Microprobe analysis of the two mica samples shows that the mineral is highly depleted in potassium, with only 0.01-0.02 weight percent K₂O as opposed to a standard composition of ~11 weight percent. The sericite is also depleted in Ca and Na, which often act as exchange cations. To explain these discrepancies, we explore the possibility that the mica mineral is the remnant of a sericite (that was once K-rich) that has since been depleted in K and other interlayer cations.

Scientific opinions vary regarding the exchangeability of muscovite's interlayer cations after the mineral has been formed. Some view cation exchange as a surficial process that only affects the outermost sheets of a mica book (Osman et al., 1998). The exchangeable ions are generally alkali and alkaline earth metals (Osman and Suter, 2000), mainly Na, Ca, Ba, Rb, or Cs (Drever, 1997). These studies provide a possible explanation for the depletion of K⁺ cations at mica surfaces, but fail to account for the nearly 11-weight percent potassium difference between the saprolite's sericite and the standard, as interlayer depletion is necessary to account for such a difference.

Experimental research has also proven the possibility of ion-exchange along internal cleavage planes (Gaines, 1957). However, the study maintains that most of the ion exchange is taken up at the surface, as suggested by the previously mentioned studies. Internal cation exchange is slight in the interaction of muscovite with neutral aqueous solutions at room temperature. Clearly, this does not fully explain the severe potassium depletion of the saprolite sericites, except to demonstrate that minimal exchange is possible.

The most likely explanation for K-depletion of the sericite is hydrolysis. Studies have shown that the hydrolysis of muscovite can cause the mineral to split along cleavage planes as a result of the increase in volume (Chen, 1997) due to the larger size of water molecules. This process results in the release of part or all of the mineral's K to the external solution, along with excess SiO_2 . Previously taken SEM images of the sericite provide evidence of this process, as splitting along cleavage planes is visible in Figure 7. Kaolinite can also become depleted in K by the same process, which explains why our XRF data shows K-depletion of the entire saprolite.

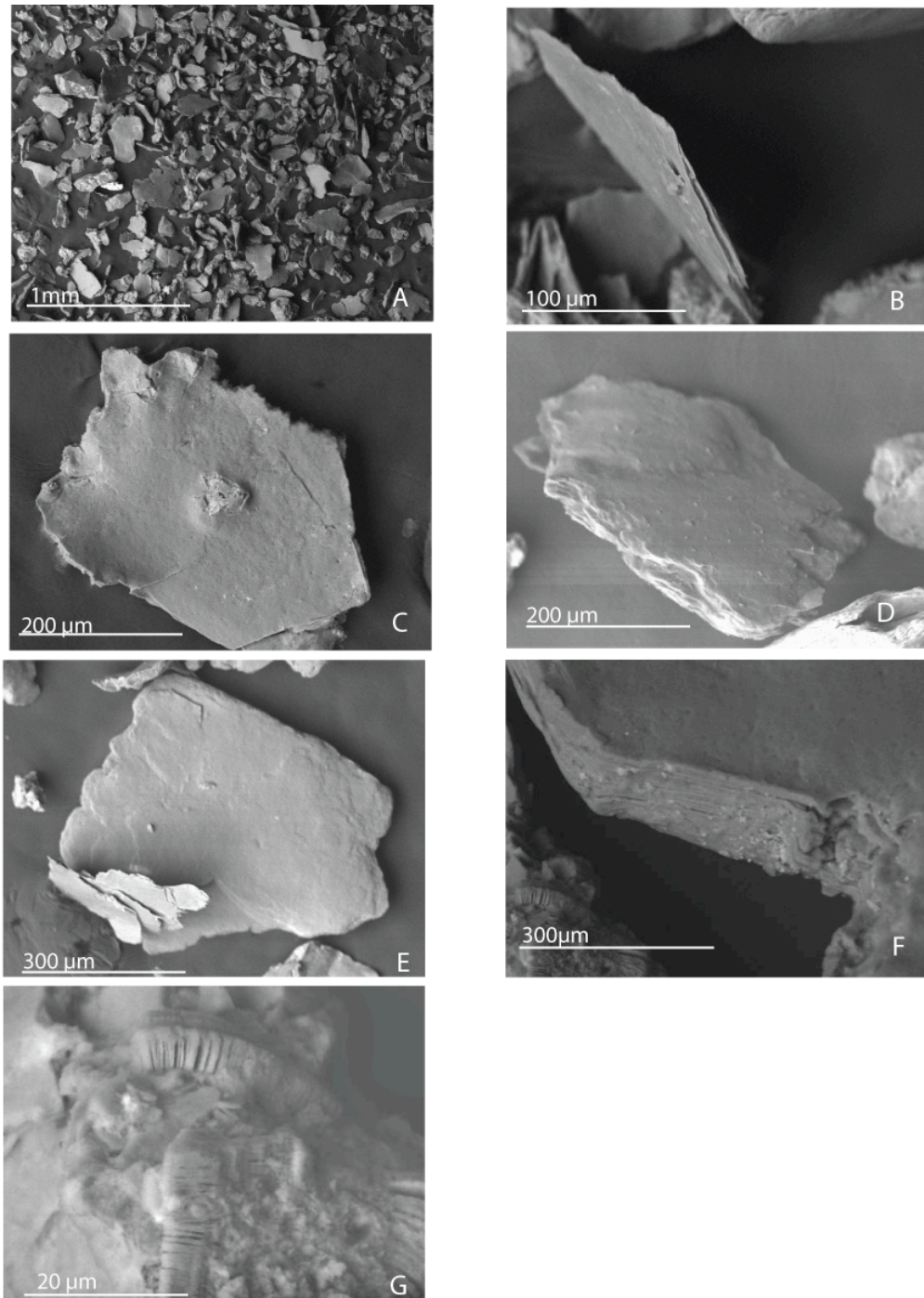


Figure 7. SEM images of sericite grains from 2007; (A) 40x view of sericite grains scattered onto carbon tape; (B) 500x view of a single sericite grain on its edge; (C) 300x view of sericite showing individual mica sheets; (D) 300x view of sericite grains at an angle again showing good mica sheets; (E) 200X Sericite grain that has had one edge folded (bottom left) showing very clearly mica sheets and their interlayer spaces; (F) 200x view of sericite book of layers; (G) 1000X view of sericite book showing separation between its layers.

Evidence for Excess Water

The accepted chemical formula for sericite is $K_2Al_4(Si_6Al_2O_2)(OH)_4$, although replacement of the K_2 , Al_2 tetrahedral, (Si_2Al_2) octahedral, and $(OH)_4$ subcomponents is possible. As noted previously, replacement of interlayer cations is minimal, and K^+ typically remains the major component along the mica cleavage planes. Table 4 shows the number of ions of each relevant element from chemical analysis of UVQ1 and UVQ2 (electron microprobe).

However, note that the measured oxides of UVQ1 and UVQ2 only make up 88.14 and 79.23 weight percent, respectively, of the total sericite sample. We have recalculated the number of ions in the formula (Table 5), and have made the assumption that the remaining 11.86 and 20.77 weight percent of each sample represents the loss of volatile substances; furthermore, we assume that 100% of the volatile substances lost are water.

Analysis shows that there are 9.07 and 15.34 OH-based cations (per molecule) for UVQ1 and UVQ2, respectively, based on our assumption that the volatile substances lost on ignition are water. These values are far higher than the expected 4 OH ions for each muscovite molecule which allows sufficient water for to fill the interlayer sites.

Furthermore, it appears the interlayer cation sites experience only minimal exchange with typical Ca and Na replacements. Consequently K, Ca, and Na make up 0.01-0.02 of the 2 interlayer ion sites per muscovite molecule. Overall, the depletion of interlayer cations and the excess water content in the sericite support our initial interpretation that hydrolysis is the catalyst for cation exchange; additionally, the excess water is likely the major component of the interlayer sites.

TABLE 4. ELEMENTAL ANALYSIS OF SERICITE IN MORTON SAPROLIT
(NOT ASSUMING WATER CONTENT)

	Number of anions based on 24O	
	UVQ1	UVQ2
Si	9.15	6.80
Al (III)	3.64	6.67
Al(III)		
Ti	0.00	0.02
Fe (II)	0.21	0.21
Mn	0.00	0.00
Mg	0.02	0.03
Ca	0.01	0.02
Na	0.00	0.01
K	0.00	0.00
F	0.00	0.00
OH	x	x
Total	13.03	13.86

TABLE 5. ELEMENTAL ANALYSIS OF SERICITE IN MORTON SAPROLITE
(ASSUMING WATER CONTENT)

	Number of cations based on 24O			
	UVQ1	Number of Ions	UVQ2	Number of Ions
Si	7.62	8.00	4.62	8.00
Al (III)	0.38		3.38	
Al(III)	2.32	2.48	1.16	1.40
Ti	0.00		0.01	
Fe (II)	0.15		0.22	
Mn	0.00		0.00	
Mg	0.01		0.02	
Ca	0.01	0.01	0.01	0.02
Na	0.00		0.00	
K	0.00		0.00	
F	0.00	9.07	0.00	15.35
OH	9.07		15.35	
Total	19.57		24.77	

Hydrolysis

During the weathering event, saprolite-water interaction resulted in an equilibrium reaction, involving the exchange of the sericite's K ions with ions in the surrounding solution (Wilson, 2004). The removal of K from the sericite creates negative charges in the interlayers that must be filled by some cation or combination of cations. We believe hydrous elements are most likely filling these interlayer sites.

Possible replacement for the cleavage-plane cations are H_3O^+ and H^+ , as their charge would neutralize the negative charge created by the T-O-T layers. Experimentally, studies have been able to perform $\text{H}_3\text{O}^+/\text{K}^+$ exchanges and reduce potassium content from 7.38 to 1.4 weight percent (White and Burns, 1963), a significant depletion (although not to the extent observed in our study). The H^+/K^+ exchange has also been proven experimentally, although only for the surface ions of micas. While Osman et al. (1998) concluded that H^+/K^+ exchange is relatively slow, they also presented the possibility that the exchange rate could increase with increasing H^+ in solution. Thus, it is likely that the cations entered the sericite's structure through interaction with acidic waters. This may imply that precipitation was more acidic when weathering occurred. A comparison of current literature on paleoclimate with the age of the sericite would help confirm this interpretation.

One inconsistency with this interpretation is presented by the FTIR data. In infrared spectroscopy, vibrations of H_3O^+ are shown by a band between 3450 to 3470 cm^{-1} . No such band is recorded by the FTIR spectra of the sericite. However, the intensity of this band is generally very low (White and Burns, 1963), which may explain why it is not present in our analysis.

As we cannot definitively conclude that the sericite's interlayer cation spaces are being replaced by charged hydrous species, we must also consider the possibility of K-replacement by the non-charged species, H₂O. In this case, ion-dipole moment would likely neutralize the negative charges of the T-O-T layers. Previous studies suggest that the alteration of muscovite to kaolinite takes the following path:

Muscovite → muscovite/montmorillonite → montmorillonite → kaolinite
(Stoch and Sikora, 1976)

In the intermediate phases, muscovite alters to a montmorillonite. Montmorillonite is structurally similar to muscovite, but contains water in interlayer spaces. As the above reactions progress, muscovite and kaolinite become intergrown along cleavage planes.

CONCLUSIONS

Despite the morphology and hand sample appearance of the mica, thin section analysis and microprobe elemental analysis indicate that the chemical structure of the presumed muscovite sericite is atypical of standard samples. In thin section (xpl), the mica exhibits first-order birefringence, whereas typical muscovite shows vivid second- or third-order colors. Microprobe analysis of the two mica samples shows that the mineral is highly depleted in potassium, with only 0.01-0.02 weight percent K₂O as opposed to a standard composition of ~11 weight percent. Based on our high calculated water content, we present the possibility of hydrous T-O-T interlayers. We were unable to determine the precise exchange species, although possibilities include H₃O⁺, H⁺, and H₂O.

Overall, K-depletion indicates intense weathering of the Morton Gneiss and subsequent alteration products. Acidic precipitation, which breaks down the interlayer structure, was likely the cause of near complete K removal in the sericites.

Unfortunately, geochemical analysis of the saprolite and sericite do not allow us to infer a timeframe for this weathering event.

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