

**Analysis of white mica from the highly-weathered
Morton Gneiss near Redwood Falls, MN**

William Mitchell, Zack McGuire,
Michael Barrett and Jack Gibbons

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ABSTRACT

An ancient saprolite was developed on the Precambrian Morton Gneiss in the Minnesota River valley of southwestern Minnesota. This saprolite, containing the clay minerals kaolinite and sericite, X-ray diffractometry (XRD), scanning electron microscopy (SEM), electron dispersion spectroscopy (EDS), wavelength dispersion spectroscopy (WDS), electron microprobe, and Fourier-transform infrared spectroscopy (FTIR). SEM analysis indicates sericite within the saprolite is highly K-depleted, with a calculated range of 0.04 - 0.11 % K by weight compared to the accepted range of ~ 8-11 % by weight. We propose that the K-depletion of sericite resulted from an additional weathering event and/or previously unforeseen meteoric water conditions.

Keywords: Sericite, kaolinite, weathering, Morton Gneiss, saprolite

INTRODUCTION

The Morton Gneiss is among the oldest rock formations in North America, dating to 3.5 Ga (Bickford et al., 2006). In and around the town of Morton, Minnesota, outcrops of this ancient and still pristine gneiss can be found. However, in the town of Redwood Falls and other nearby locales, the Morton Gneiss has been severely weathered to a saprolite containing clay minerals such as kaolinite and sericite (Fig. 1 and 2; Goldich, 1938).

While there have been many studies on the age and metamorphic chronology of the Morton Gneiss, little attention has been paid to the saprolite remnants (Goldich, 1938; Goldich et al., 1980^{a,b}; Wooden et al., 1980). The abundant minerals found in the saprolite are kaolinite and quartz, while less abundant minerals include sericite and zircon. Analysis of these weathered clay products can be useful for determining the weathering history of the original rock (Islam et al., 2002).

Sericite, a fine grained micaceous mineral compositionally similar to muscovite and paragonite (Deer et al., 1992), is present exclusively as a weathering alteration mineral from K-feldspar. The oxide chemistry of sericite and kaolinite in this saprolite will be helpful in understanding the weathering history and conditions of the original Morton Gneiss. In this study we examined the bulk saprolite through X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Purified sericite was examined through electron dispersion spectroscopy (EDS), wavelength

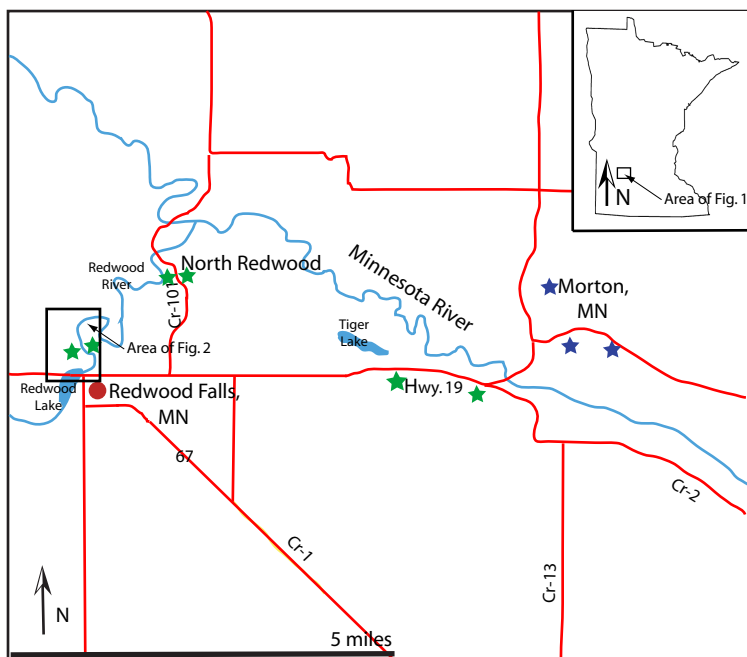


Figure 1. Location map of Redwood Falls and Morton, MN. The outlined area shows study area of Figure 2. Green stars indicate known outcrops of saprolite, while purple stars indicate known outcrops of Morton Gneiss (Goldich, 1938).

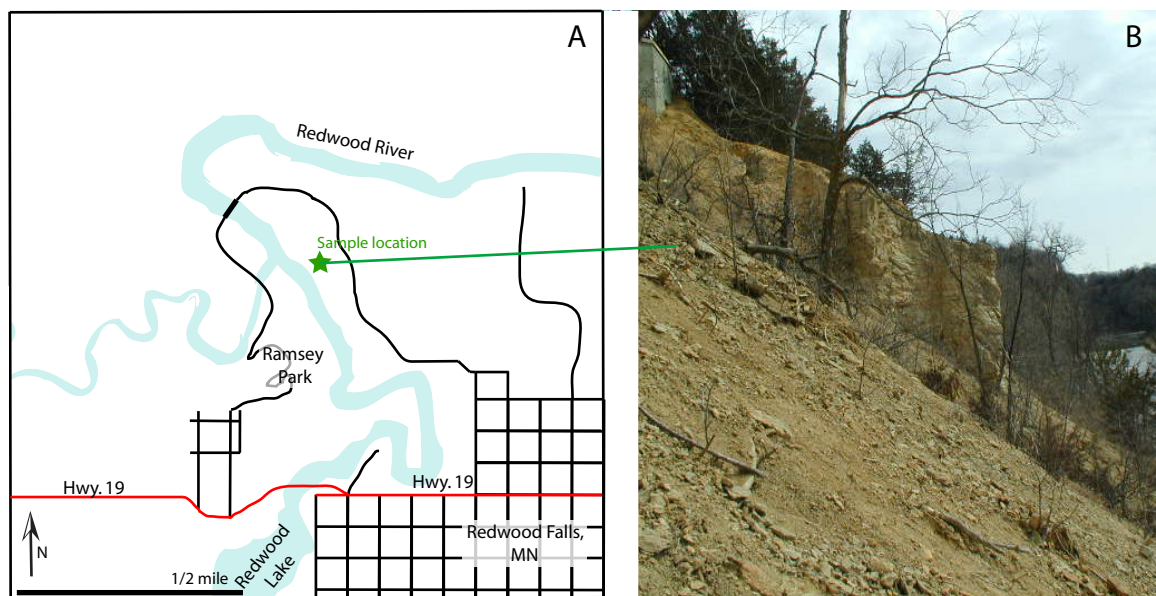


Figure 2. (A) For this study, a sample of weathered Morton Gneiss was taken from the east bank of the Redwood River just north of Redwood Falls, MN at $\sim 44^{\circ} 32' 53''$ N $95^{\circ} 07' 16''$ W; (B) Picture was taking facing south southeast along the Redwood River.

dispersion spectroscopy (WDS), electron microprobe, and Fourier-transform infrared spectroscopy (FTIR).

GEOLOGIC SETTING

The Redwood Falls study area is composed of a granitic intrusion that endured high-grade metamorphism during two periods in the Archean at 3.0 Ga and 2.6 Ga (Goldich, 1980), and is cross-cut by later quartz veins, pegmatites, and fine-grained granitic dikes of a reddish color (Goldich, 1938). It is described by three principal rock types: mafic inclusions (Wooden et al., 1980), gray tonalitic gneiss, and pink granitic gneiss (Goldich et al., 1980).

Amphibolite clasts occur within the tonalitic gneiss and fall into two distinct categories: a hornblende-rich, low-alumina amphibolite similar to basaltic komatiite, and a more common tholeiitic one (Wooden et al., 1980). Both amphibolite categories exhibit iron-rich chemical compositions and are considered to be of igneous origin (Wooden et al., 1980).

The mineral assemblage of the Morton Gneiss includes plagioclase feldspars, low calcium content oligoclase, orthoclase feldspars, quartz, biotite, and hornblende. In addition, accessory minerals are present in the form of magnetite, apatite, titanite, allanite, and zircon. Expected secondary minerals sericite, chlorite, epidote, calcite, leucoxene, and pyrite, are not abundant in the gneiss (Goldich, 1938).

METHODS

General Methods. Samples were collected from an outcrop of saprolite north of Redwood Falls (Fig. 1 and 2). Bulk rock samples were crushed and ground using a mortar and pestle, then sieved and sorted into three size fractions: 10, 35, and 100 microns. The 35 - 100 μm and 10-35 μm size fractions were then hand-picked to concentrate sericite grains. These grains were washed in deionized water, sonically cleaned, and baked to remove any excess water weight.

SEM, Electron Microprobe. Epoxy thin sections of the sericite and kaolinite-rich clay were made. Each slide was carbon coated and analyzed on the University of Minnesota's JEOL 8900 Superprobe, equipped with EDS and WDS for oxide chemistry, as well as the Carleton College Hitachi 3000N with attached Oxford Microanalysis EDS system running at 15kV.

XRD. Crushed bulk sample (10-35 μm) was washed with water and promptly decanted to eliminate quartz. The sample was vacuum filtered onto a sample disc, and analyzed with a Philips Analytical PW1800 XRD (40 kV, 55 mA, $2\theta = 0-80^\circ$).

FTIR. . A 1-mg sample of hand-picked sericite was used for infrared spectroscopy. The sample was crushed using a mortar and pestle, and 150 mg KBr was added and ground together. Once a fine powder mixture of the sericite and KBr was obtained, it was poured into a pellet press and placed under 20,000 lbs pressure. During pressing, the press was *not* under vacuum. The resulting pellet was analyzed using an Nicolet Infinity Series FTIR spectrometer from 350-4000 cm^{-1} under atmospheric conditions with an atmospheric spectrum subtracted.

RESULTS

SEM, Electron microprobe. The potassium content of the sericite ranges from 0.04-0.11 weight percent. There is no correlation between the potassium content of sericite and either the SiO₂ or Al₂O₃ content; however, as SiO₂ content increases, Al₂O₃ also increases (Table 1). Greater Al₂O₃ content occurs when less FeO is present. A list of all major oxides in the sericite grains were tabulated and ordered by weight percent (Table 1). Additionally, photographs of sericite grains were taken to show mica structure (Fig. 3).

XRD. XRD samples of the decanted clay correlated strongly with both a kaolinite standard and previous work on similar saprolites (Fig. 4; Islam et al., 2001, Islam et al., 2002). In XRD tests of both bulk sample and sericite concentrated samples, neither K-mica nor gibbsite peaks were identified.

FTIR. Infrared spectroscopy showed strong peaks at 350, 468, 537, 912, 1026, and 1096 cm⁻¹, and weaker peaks at 430, 699, 1656, 2345, 3621, and 3697 cm⁻¹. A broad, weak peak is present at 3100-3500 cm⁻¹(Fig. 5).

DISCUSSION

The clay minerals are characterized by their alternating hexagonal rings of SiO₄ tetrahedral layers (T-sheets) and Al₂O₆ octahedral layers (O-sheets). Gibbsite, composed of a single O-sheet, is the least complex member of this family. K-mica

Table 1. Weight % oxide chemistry of sericite from Redwood Falls, MN

Sample #	1	2	3	4	5	6	7	8	9	10	11
SiO2	51.11	50.59	50.77	50.93	50.85	51.02	49.47	50.52	49.63	50.98	50.90
TiO2	0.04	0.61	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.04
Al2O3	42.33	42.32	42.53	42.87	42.54	42.68	41.74	41.58	42.07	42.45	42.27
FeO	2.21	2.11	2.36	1.91	2.21	1.86	4.15	3.32	3.86	2.26	2.47
MnO	0.00	0.00	0.01	0.00	0.03	0.00	0.00	0.03	0.00	0.02	0.00
MgO	0.11	0.08	0.10	0.06	0.06	0.07	0.17	0.16	0.16	0.10	0.08
CaO	0.08	0.15	0.06	0.11	0.14	0.24	0.22	0.24	0.17	0.10	0.09
Na2O	0.09	0.08	0.12	0.06	0.08	0.05	0.13	0.12	0.05	0.05	0.09
K2O	0.04	0.07	0.06	0.05	0.10	0.07	0.11	0.04	0.05	0.04	0.07
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00

Table 1. cont.

Sample #	12	13	14	15	16	17	18	19	20	21	22
SiO2	50.72	51.29	50.94	50.75	51.26	51.28	51.31	50.44	51.37	51.57	50.68
TiO2	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.15
Al2O3	42.33	42.67	42.92	42.71	42.50	42.83	42.45	42.95	42.47	42.62	42.26
FeO	2.54	1.59	1.75	2.13	1.94	1.55	1.97	2.10	1.84	1.51	2.57
MnO	0.00	0.00	0.02	0.00	0.00	0.05	0.00	0.03	0.01	0.00	0.01
MgO	0.11	0.08	0.08	0.11	0.07	0.06	0.05	0.10	0.08	0.05	0.11
CaO	0.19	0.17	0.18	0.14	0.10	0.13	0.09	0.19	0.12	0.09	0.10
Na2O	0.06	0.08	0.06	0.08	0.08	0.04	0.09	0.12	0.06	0.09	0.08
K2O	0.05	0.10	0.05	0.08	0.06	0.05	0.05	0.05	0.05	0.07	0.04
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00

Table 1. cont.

Sample #	23	24	25	26	27	28	29	30
SiO2	51.23	50.71	51.56	51.32	50.75	50.09	50.83	51.72
TiO2	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.01
Al2O3	42.25	41.84	42.52	42.06	41.94	42.23	42.11	42.46
FeO	2.14	3.13	1.61	2.24	2.89	3.07	2.51	1.54
MnO	0.00	0.01	0.00	0.02	0.03	0.01	0.00	0.00
MgO	0.09	0.09	0.06	0.07	0.08	0.14	0.10	0.08
CaO	0.11	0.08	0.08	0.09	0.14	0.32	0.30	0.08
Na2O	0.10	0.09	0.08	0.10	0.11	0.09	0.09	0.04
K2O	0.06	0.05	0.08	0.08	0.05	0.05	0.05	0.07
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00

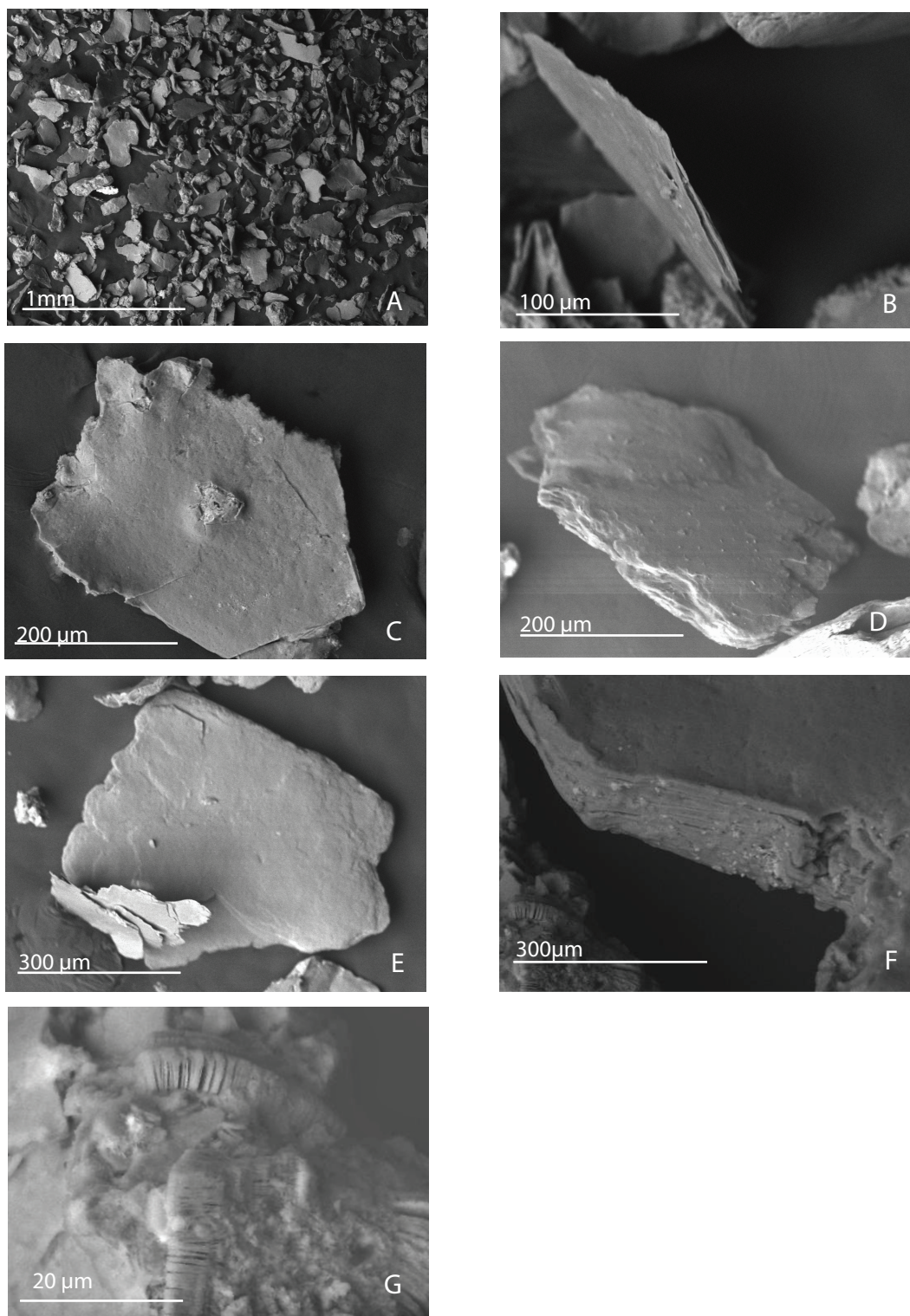


Figure 3. SEM photographs of sericite grains; (A) 40x view of sericite grains scattered onto carbon tape; (B) 500x view of a single sericite grain on its edge; (C) 300x view of sericite showing individual mica sheets; (D) 300x view of sericite grains at an angle again showing good mica sheets; (E) 200X 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.

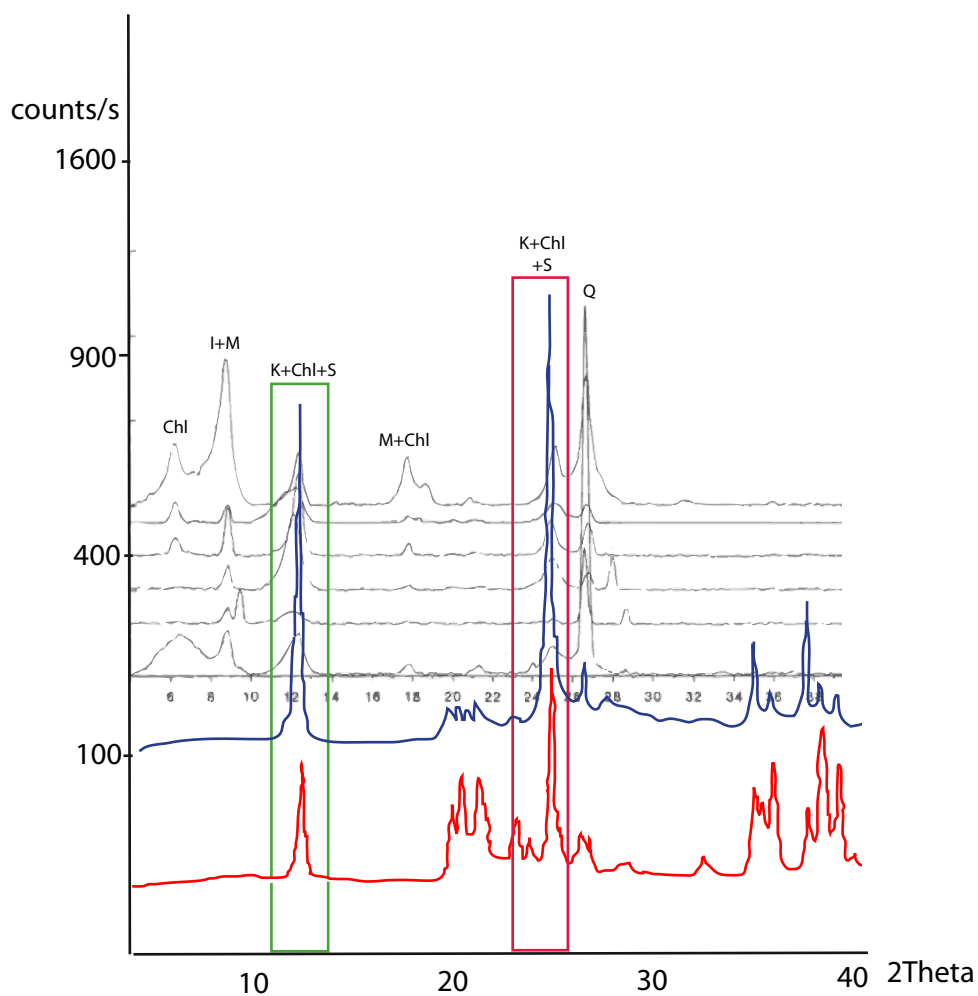


Figure 4. X-ray diffraction analysis of clay minerals. Blue line is sample taken from near Redwood Falls, MN, while grey line is a standard of kaolinite. Green and red boxes outline kaolinite peaks. Transparent graphs come from a saprolite in Bangladesh (Islam et al., 2002). Chl=chlorite, I = illite, 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 during concentration of sericite.

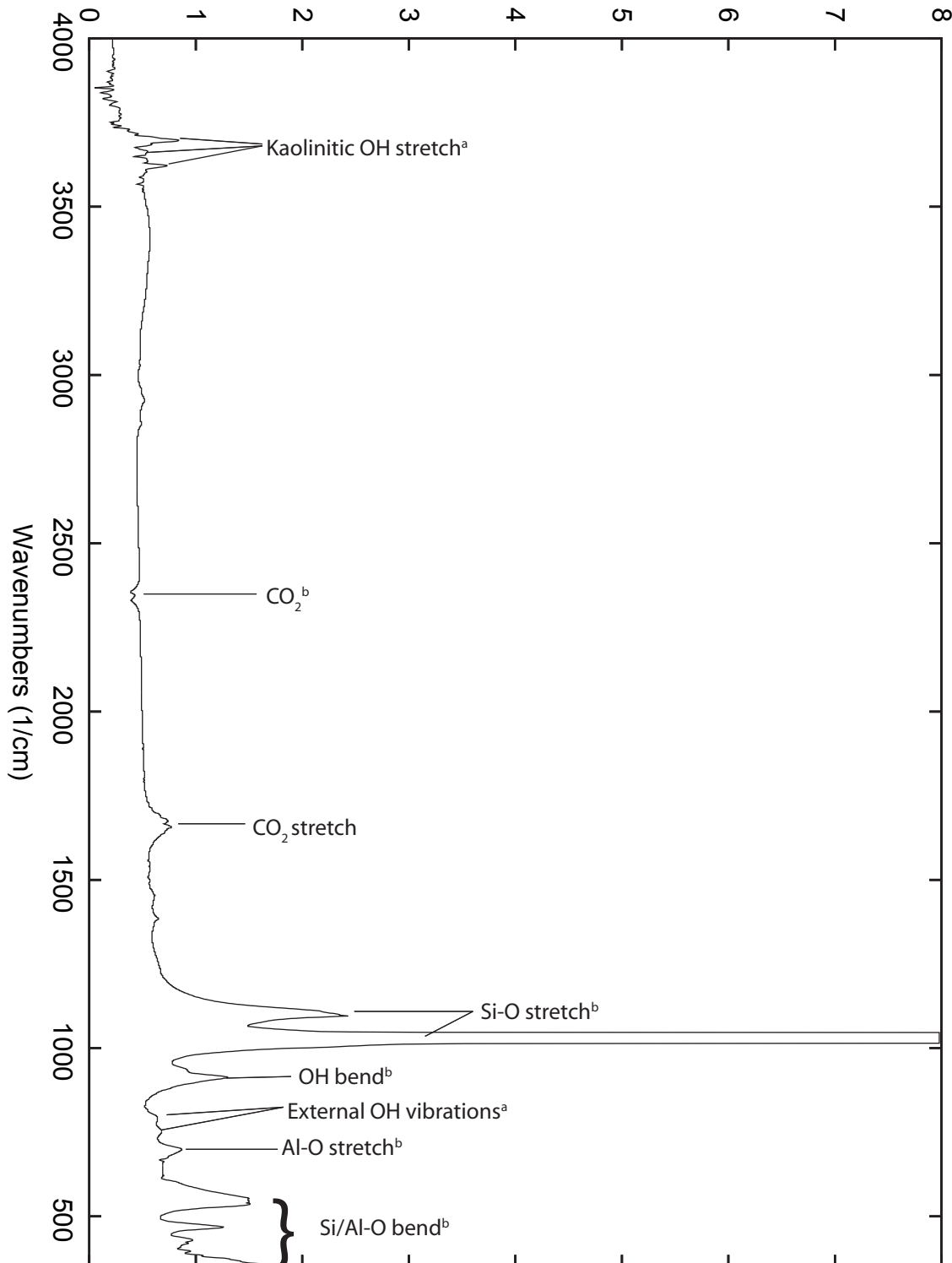


Figure 5. Fourier-transform infrared spectroscopy results. Peaks are labeled according to guidelines established by Zhang et al. (2005) and Cuadros et al. (2006). Peaks correspond to the stretching regions of certain bonds within the T-O-T structure of sericite.

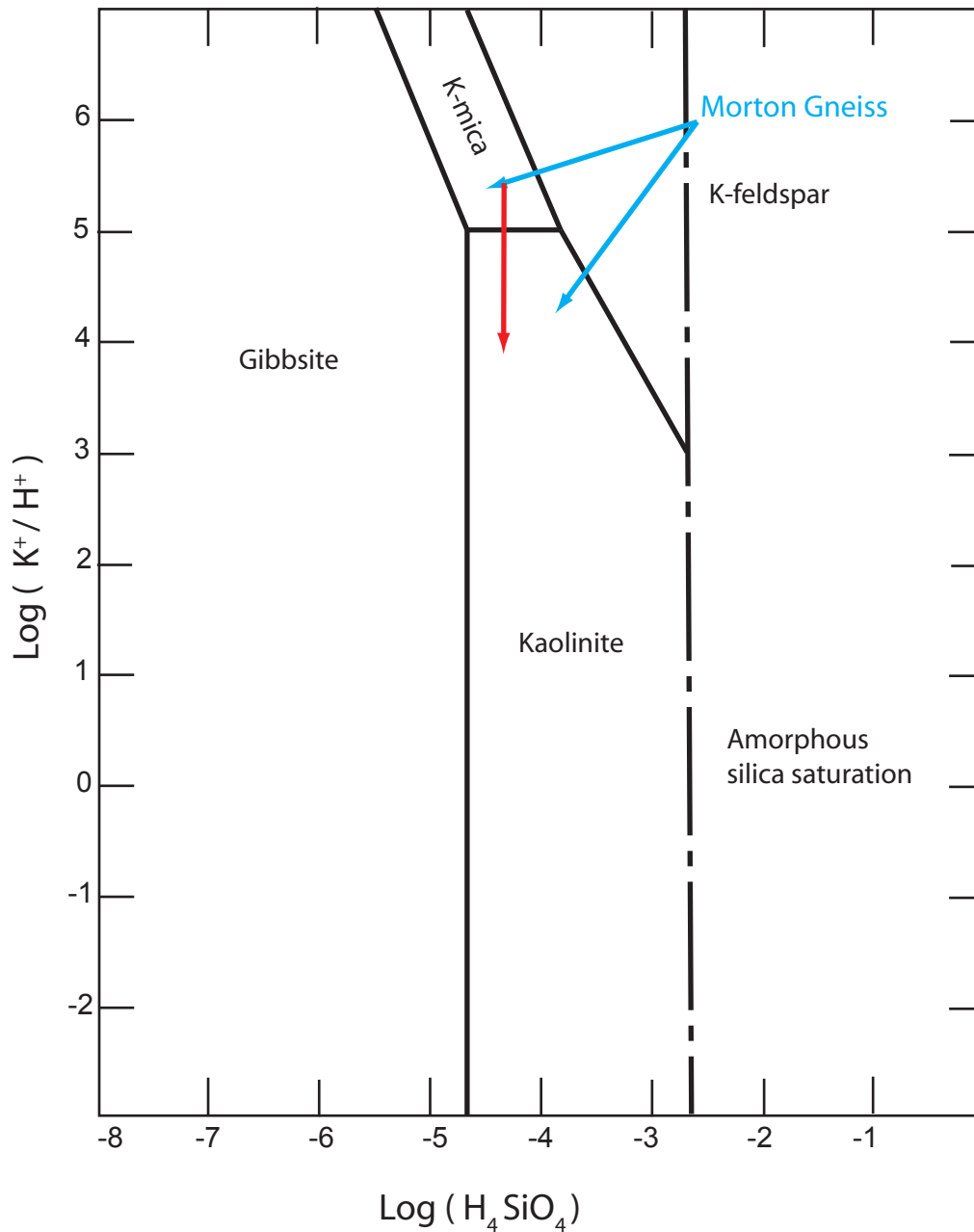


Figure 6. Phase diagram for the system $K_2O-Al_2O_3-SiO_2-H_2O$ at 25 degrees C, unit activity of water, and 1 atm. Modified from Hegelson et al. (1969). Initial weathering of K-feldspar within the Morton Gneiss are shown by the two blue arrows leading to both kaolinite and K-mica; secondary weathering of the K-mica to kaolinite is shown by the red arrow.

different than those that depleted the interlayer cations. Second, the later weathering conditions lead sericite to have a oxide chemistry that is very similar to that of kaolinite, suggesting that the sericite are trending compositionally towards kaolinite (Tables 1 and 2).

Aside from SiO_2 and Al_2O_3 , FeO is the only significant oxide present in the sericite. FeO concentration, which varies between 1.5% and 4.2% by weight, increases with decreasing Al_2O_3 . This implies that Fe exists in the sericite as a replacement mineral for aluminum (Table 1; Deer et al., 1996).

Infrared spectra were primarily assigned by comparison with previous literature (Zhang, et al., 2005, Cuadros et al., 2006). The OH stretching region from 3500-3750 cm^{-1} exhibits peaks in areas consistent with OH stretching in kaolinite (Cuadros et al., 2006). Surprisingly, the broad OH peak that Zhang et al. reported is not apparent in this spectrum. A peak from water is observed as the very broad peak at 3100-3500 cm^{-1} . The water present in the sample is attributed to slightly hydrated potassium bromide, which was stored without active desiccant.

Two peaks are attributed to CO_2 , both 2345 and 1656 cm^{-1} . Carbon dioxide may have been introduced to the sample by pressing the pellet without evacuating the pellet press. Strangely, Zhang et al. report a peak at a similar frequency, but it is not observed except with temperatures ranging from 500-700 °C.

The peaks at 1095 and 1026 cm^{-1} are assigned to Si-O stretching motions, and the peak at 913 cm^{-1} is believed to arise from an Al-OH-Al bend (Cuadros et al., 2006).

The bands at 790 and 750 cm^{-1} are difficult to assign. Very similar bands are reported by Zhang et al. and Cuadros et al., though their spectra were of sericite and kaolinite respectively. Zhang assigns the peaks to distortions in the bonds between the tetrahedral and octahedral layers, while Cuadros assigns them to external OH vibrations from kaolinite. Either of these assignments is plausible, and neither has features that conclusively identify which of these assignments (if either) is correct.

The peak at 699 cm^{-1} is likely the result of Al-O stretching (Zhang et al., 2005). The peaks from 537-350 cm^{-1} are attributed to Si-O and Al-O bending (Zhang et al., 2005).

These data confirm the identification of the mineral as sericite, but the OH region is more complicated than Zhang et al. reported, and seems to show peaks at the correct frequencies for kaolinite. It is quite possible that the kaolinite is a trace contaminant. The lack of the sericite OH stretches at 3700-3600 cm^{-1} reported by Zhang et al. is very surprising—only kaolinite OH stretches are seen (Fig. 5).

It is quite plausible that the two unassigned bands at 790 and 750 cm^{-1} are indeed from the same vibrations as in kaolinite. This would imply that the sericite is weathering to kaolinite in certain T-O-T layers within the sericite, but has not reached the point where the macro-scale structure of the crystal is changed. These results indicate that certain T-O-T layers of sericite have weathered to T-O layers of kaolinite (Fig. 5).

CONCLUSIONS

The saprolite was clearly created as a result of intense weathering. Two extremes of weathering conditions exist. The first involves undersaturation of the soil water with respect to gibbsite caused by weathering of the feldspar in a high-rainfall, water-dominated, open soil system. The other extreme involves saturation of the water with respect to K-feldspar caused by a rock-dominated, low-rainfall, relatively closed, deep soil system in which K-feldspar persists fresh and unweathered (Langmuir, 1997).

There was no evidence of any preserved K-feldspar within the weathered gneiss, thus our saprolite was probably subjected to a high rainfall environment. The present day climatic regime of southwestern Minnesota is transitional between the prairie grasslands of the Great Plains and the temperate hardwood forest of south-central Minnesota. Since mean annual precipitation, the primary mechanism of saprolite weathering, is only ~ 35", it is inferred that the saprolite is ancient, having formed in a much wetter climate.

While the weathering conditions were almost certainly defined by a wet environment, outcrops of saprolite are extremely localized. Weathered saprolite crops out only a few miles from exposed, unweathered Morton Gneiss (Fig. 2). The initial conclusion from these observations is that weathering was a localized event that affected some rocks and left others untouched. Instead, it is inferred that wide scale climate change caused weathering of Morton Gneiss over a much broader area. Only recent glaciation has eroded away most of the weathered gneiss, leaving isolated saprolite pockets. Analysis of glacial till from Wisconsin Period glaciation shows that clay deposits rich in kaolinite have been transported from southwestern Minnesota (Grimley, 1999).

FUTURE WORK

Analysis of the bulk rock composition (XRF) of both weathered Redwood Falls rock as well as the original Morton Gneiss could be useful in further constraining the climatic and environmental conditions present for the weathering of the Morton Gneiss. There appears to be no published research giving the bulk composition of the weathered saprolite, however there are documented results of compositional analysis of the original Gneiss (Goldich, 1980). Comparison between these two compositions would tell precisely how much of each oxide has been lost to weathering and may further constrain pH or rainfall rates during weathering events.

In addition, we were only able to analyze the kaolinite in the Redwood Falls saprolite using an SEM, which gives relatively low-resolution values for the oxide concentrations. We suggest microprobe analysis of the kaolinite, which would yield more precise results.

Also, a collection of vertical and horizontal core samples at Redwood Falls could lead to a study about the gradient of weathering. Our samples were collected entirely from the surface of weathered rock outcrops and One would expect the SiO_2 and Al_2O_3 concentrations to trend negatively the further from the surface one samples, based on the similar work done by Islam et al. (2002).