

Oxygen isotope analysis of sericite from a saprolite near Redwood Falls, Minnesota

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Abstract

Stable oxygen and hydrogen isotope ratios can be used to infer paleoclimatic and paleotemperature conditions for periods throughout Earth's history. Secondary minerals formed in igneous and metamorphic rocks during periods of weathering record isotope ratios of fluids at the time of weathering. Analyses of sericite grains collected from weathered Morton Gneiss saprolite near Redwood Falls, Minnesota yielded $\delta^{18}\text{O}$ values of 40-50 ‰, suggesting water-rock interaction with enriched ^{18}O waters. Recorded values are higher than those expected from natural processes, suggesting the need for further refinement of analysis methods in order to obtain accurate oxygen isotope ratios for micaceous minerals.

Key words: saprolite, sericite, the Morton Gneiss, Redwood Falls, Minnesota, oxygen isotope

Introduction

The Morton Gneiss (~3.4 Ga) is an amalgamation of granitic gneisses that have experienced multiple periods of deformation (Goldich, 1980; Schmitz et al., 2006). The Morton Gneiss is well exposed in the Minnesota River Valley region of southwestern Minnesota (Fig. 1A); fresh exposures can be seen in quarries near Morton, Minnesota and at other localities. Near Redwood Falls, Minnesota, a highly weathered saprolite sourced from the Morton Gneiss is exposed along the Redwood River (Fig. 1B, 1C). Sericite, a micaceous mineral formed as feldspars are weathered, is abundant at this locality.

As weathering progresses, oxygen from the surrounding environment becomes incorporated into the crystal structure of secondary minerals, preserving a record of isotope fractionation. Evaporation and precipitation of meteoric waters results in fractionation of oxygen and hydrogen stable isotopes through equilibrium processes (Drever, 1997). Oxygen isotope values can be used to infer sources of water (e.g. meteoric, hydrothermal, etc) as well as paleoenvironmental conditions such as ambient water temperature at the time of mineral formation. This study examines oxygen isotopes from sericite grains in the Morton Gneiss Saprolite at Redwood Falls in order to determine environmental conditions during the weathering events that triggered the saprolite formation.

Origin and History of the Morton Gneiss

The Morton Gneiss is a metamorphic complex composed of three principle rock types: mafic inclusions (amphibolites), tonalitic gneisses, and granitic gneisses of younger age (Goldich, 1980). Morton Gneiss units have been extensively mapped (Lund, 1968; Himmelberg, 1958; Grant et al., 1972; Bauer, 1980) and the oldest known

units have been geochronologically dated to at least 3400 Ma (Goldich, 1980; Schmitz et al., 2006). Using geochronological methods, Goldich (1980) identified three separate periods of metamorphism at ~3000 Ma, 2600 Ma, and 1,800 Ma that resulted in the heterogeneous gneiss existing today.

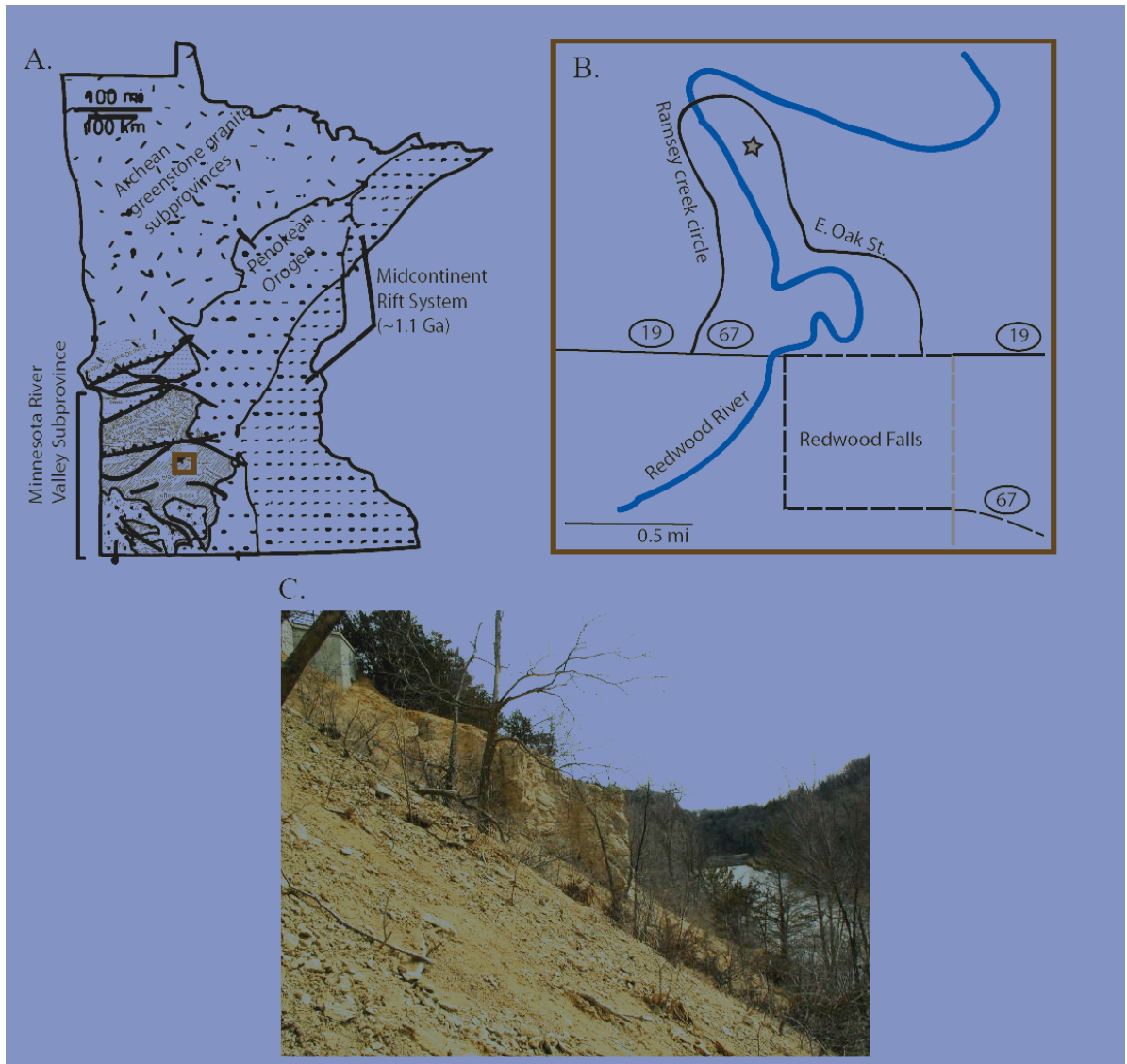


Figure 1. Study Location. A) Generalized geologic map of Minnesota with major geologic terranes. Box marks study area. Modified from Schmitz et al., 2006. B) Redwood Falls area. Star marks sample location, proximal to the Redwood River. C) Sample location in Redwood Falls. Vantage point is looking south with Redwood River in right-hand side of photograph. Outcrop height varies up to 5m.

Methods

Bulk samples were collected from the Morton Gneiss Saprolite on the east bank of the Redwood River in Redwood Falls, MN (Fig. 1B, 1C). The majority of the sampled material was unconsolidated regolith. Samples were crushed and sieved into 10, 35, and 100 micron size fractions, and clay size fraction was partially removed with distilled water. Using a Franz Magnetic Separator set at 20° side slope, 5 tilt, and 0.80 amp, well washed quartz material was removed.

Sample was disaggregated by ultrasonic cleaning, followed by a bromoform – acetone heavy liquid separation calibrated such that the micaceous material floated. The final purification step consisted of tweezer hand picking after which grains were placed on paper, slanted, and vibrated such that rounded quartz and feldspars would roll away and the {001} cleaved sericite grains would remain stationary. Selected sericite grains were mounted on thinsection and examined with a petrographic microscope (Fig. 2).

Samples were analyzed for $\delta^{18}\text{O}$ at the University of Wisconsin-Madison Geology Department on a dual-inlet five-collector Finnigan/MAT 251 mass spectrometer. After visual inspection for purity, samples were held in a drying oven prior to being loaded into the sample chamber and held for 48 hours at a vacuum. Using a rapid heating defocused beam technique, samples were reacted with gaseous bromine pentafluoride (BrF_5) with a 32 W Synrad CO_2 laser (Spicuzza, et al., 1998). The system was calibrated to Standard Mean Ocean Water (SMOW) using UWG-2, a garnet standard (Valley et al., 1995).

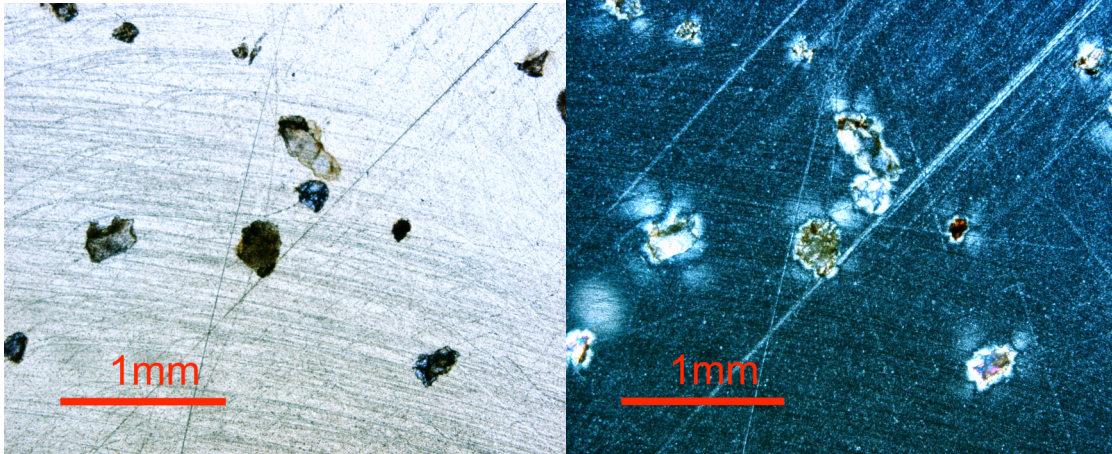


Figure 2. Sericite grains mounted in epoxy on a thin section under plane polarized light and cross polarized light.

Results

$\delta^{18}\text{O}$ isotope values ranged from 40.49-50.18 parts per mil relative to SMOW, and percent yields for each sample ranged from 29-37% (Table 1). Isotope values were plotted versus sample weight (mg), percent yield, and $\mu\text{moles CO}_2/\text{mg}$ sample (Figs. 3-5). Low R-squared values on all plots indicate a lack of correlation.

Table 1. MASS SPECTROMETRY RESULTS FOR $\delta^{18}\text{O}$ VALUES FOR ALL SAMPLES

Sample #	Sample Weight (mg)	$\mu\text{moles CO}_2$	$\mu\text{moles CO}_2/\text{mg}$ sample	$\delta^{18}\text{O}$	% yield *
UWG2	3.22	37.20	11.55	5.42	69.39
UWG2	2.64	34.30	12.99	5.92	78.03
UWG2	2.79	32.00	11.47	5.96	68.89
UWG2	2.15	27.50	12.79	6.05	76.82
RWFE #1	3.34	19.40	5.81	44.65	34.89
RWFE #1	2.38	13.20	5.55	48.22	33.31
RWFE #2	2.47	15.20	6.15	43.43	36.96
RWFE #2	2.27	12.50	5.51	44.00	33.07
RWFE #3	2.12	11.20	5.28	49.91	31.73
RWFE #3	1.49	7.60	5.10	42.60	30.63
RWFE #4	1.30	7.80	6.00	40.49	36.04
RWFE #4	2.00	9.70	4.85	50.18	29.13
RWFE #5	2.30	12.30	5.35	45.86	32.12
RWFE #5	2.03	11.70	5.76	45.65	34.62

* % yields were calculated based in 16.65 $\mu\text{mol}/\text{mg}$ expected yield for standards and 33.4 $\mu\text{mol}/\text{mg}$ for samples.

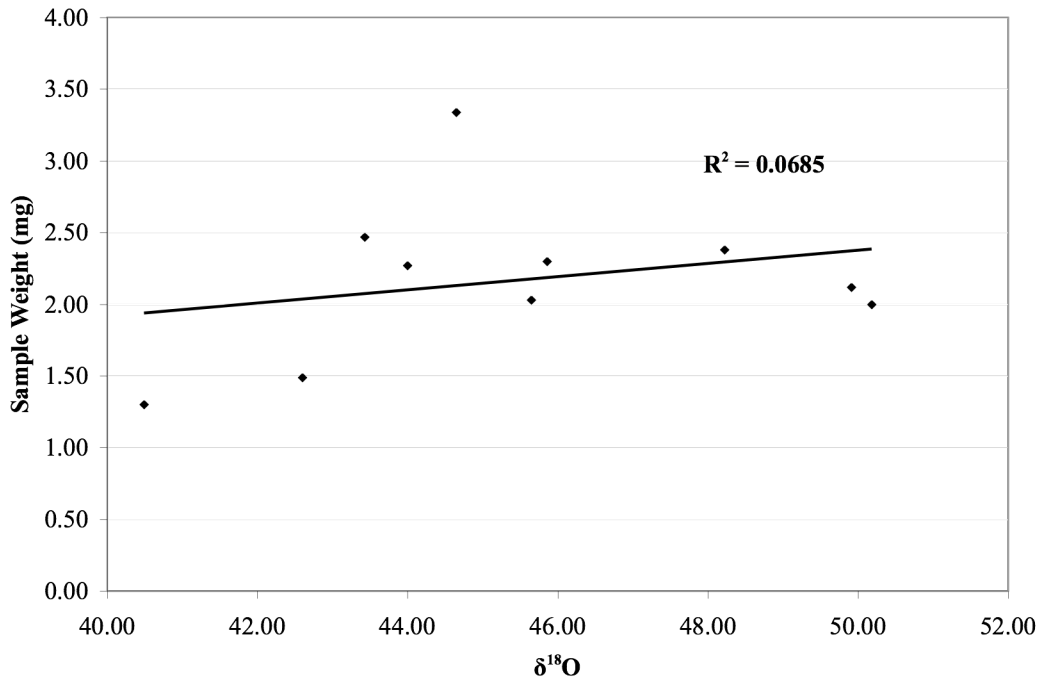


Figure 3. Sample weight vs. measured $\delta^{18}\text{O}$ values for each sample.

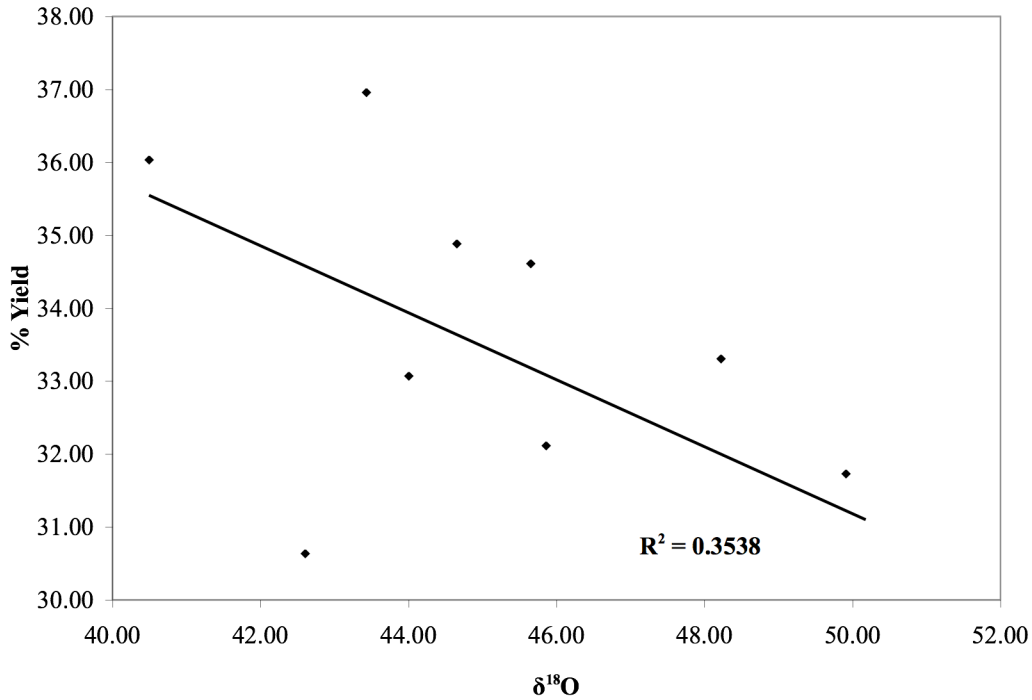


Figure 4. Percent yield versus measured $\delta^{18}\text{O}$ values for each sample. The expected yield values for the samples were based on a molecular weight of 359.21 g/mol, the weight of potassium-depleted sericite. Ion microprobe analysis of the sericite samples confirms that they are depleted in potassium.

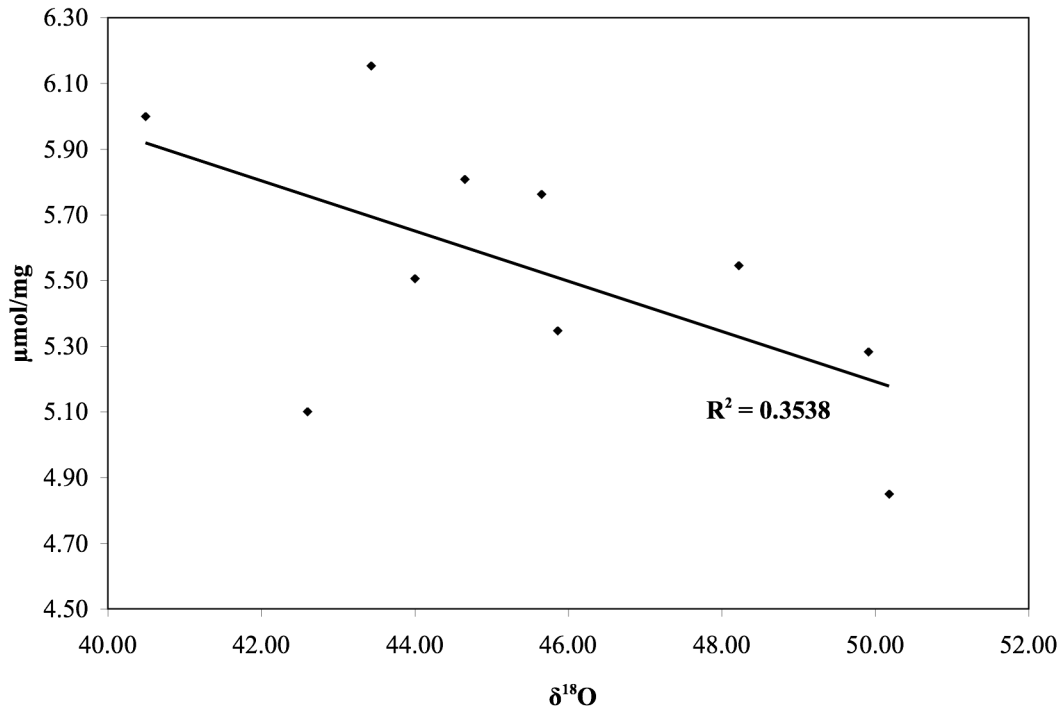


Figure 5. Micromoles of CO_2 / sample mass(mg) versus $\delta^{18}\text{O}$ values for each sample.

Discussion

Previous empirical observations give a $\delta^{18}\text{O}$ value of 27 ‰ as the maximum observed value for kaolinite formed from interaction with meteoric or groundwaters (Sheppard and Gilg, 1971). Sericite isotope values of 40-50 ‰ cannot be explained by any known natural fractionation processes. Therefore, the $\delta^{18}\text{O}$ isotope results for the Redwood Falls sericite are not comparable to the meteoric water line or kaolinite line (Fig. 6). However, the absence of observed structural and mineralogical evidence of hydrothermal activity at the sample site suggests that meteoric waters were responsible for sericite formation in the Morton Gneiss.

We present several possible explanations for the low yields and high $\delta^{18}\text{O}$ values. One explanation could be an external leak in the system. The garnet standards, however,

produced acceptable yields, excluding the possibility of a leak. Alternatively, samples may have been pre-fluorinated. The chemical formula for sericite, $\text{KA}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, contains OH groups which are highly reactive. There is the potential for contamination by residual fluoride gas, F_2 , created from the breakdown of bromine pentafluoride, within the vacuum chamber. If the samples reacted with F_2 before the O_2 extraction, additional fractionation is possible. Thus there would be an increased level of $\delta^{18}\text{O}$ recorded in the analysis relative to the actual composition of the sericite samples.

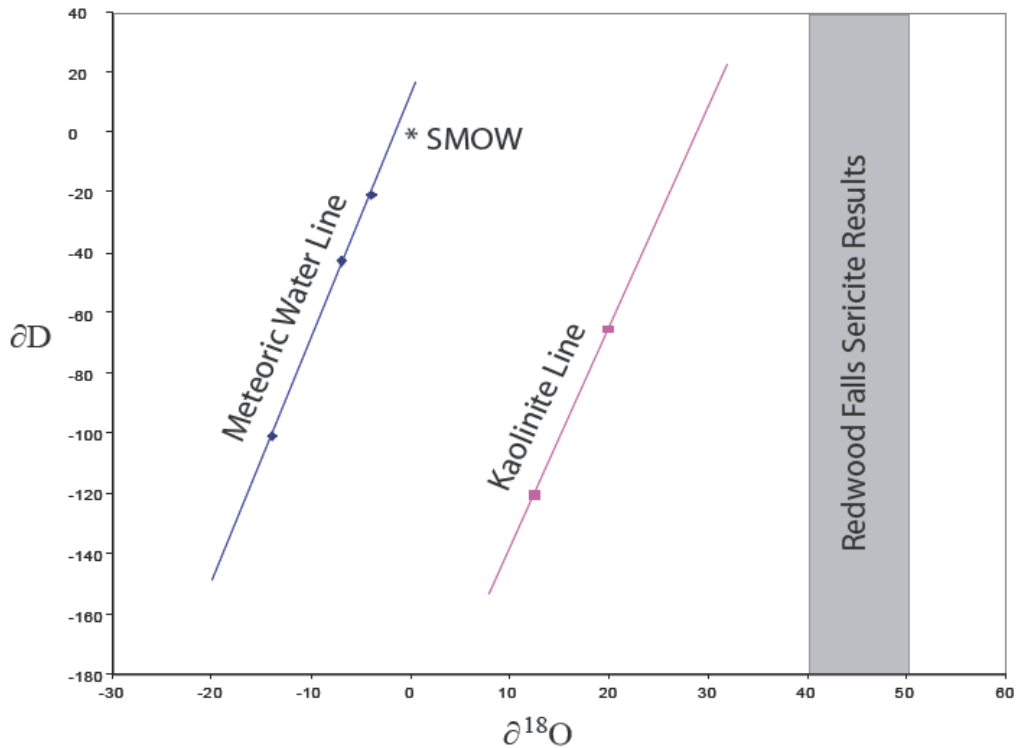


Figure 6. Expected δD vs $\delta^{18}\text{O}$ values for samples formed by meteoric weathering and the expected ratios δD vs $\delta^{18}\text{O}$ for Kaolinite (adapted from Sheppard & Gilg 1971.) Deuterium isotopic values for sericite samples were not measured, thus Redwood Falls sericite results are presented as a range of experimental $\delta^{18}\text{O}$ values.

Conclusions

Sericite from the Morton Gneiss Saprolite near Redwood Falls, MN yield oxygen isotope ratios higher than those empirically calculated from meteoric water weathering. These high $\delta^{18}\text{O}$ values are likely attributed to pre-fluorination of samples; however, further studies are needed to support these conclusions. Had isotopic data correlated with previous data from studies of weathering and secondary mineral systems, inferences could have been made about local paleotemperature and paleoclimate conditions at the time of sericite formation.

Future Work

We suggest doing stable isotope $\delta^{18}\text{O}$ and δD analysis on sericite such that there is no opportunity for fractionation in the sample chamber. It is possible that older methods, which utilize a single container per analysis, could eliminate the problem (Clayton, 1962). Assuming that sericite fractionates comparably to kaolinite, high δD values would be expected.

Further studies should sample a core of the complete saprolite weathering profile. Additional stable isotope $\delta^{18}\text{O}$ analysis on more stable minerals found in the saprolite, would provide more insight into the relationship between isotopic fractionation and weathering.

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