Supplementary Information

for

Toward better timing of illitization by selective, tetraphenylborate-assisted extraction of K and Ar from micaceous clay minerals: Promising results from Illinois Basin paleosols

Arya Shabazi-Asi[1], J. M. Wampler[2], W. Crawford Elliott[2] Julia A. McIntosh[3]

1-Department of Chemistry, Georgia State University, Atlanta, GA 30302-3965, USA
2-Department of Geosciences, Georgia State University, Atlanta, GA 30302-3965, USA
3-U.S. Geological Survey, Denver, CO 80225-0046, USA

Email of corresponding author: wcelliott@gsu.edu

Contents

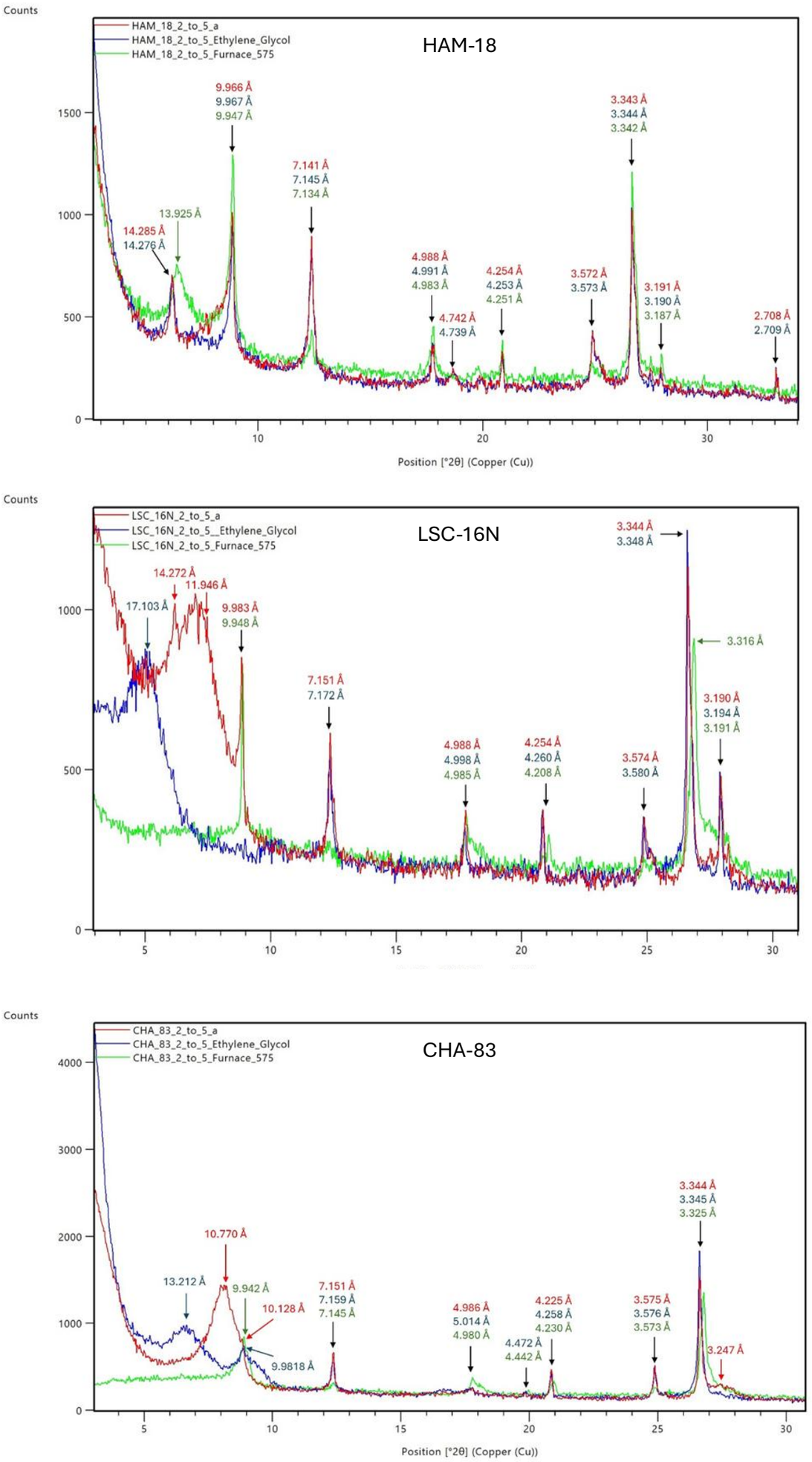

Figure S1a. X-ray diffraction patterns of the air-dried (red), glycol-solvated (blue), and heated (575°C; green) 2–5 μm fractions of HAM-18, LSC-16N, and CHA-83

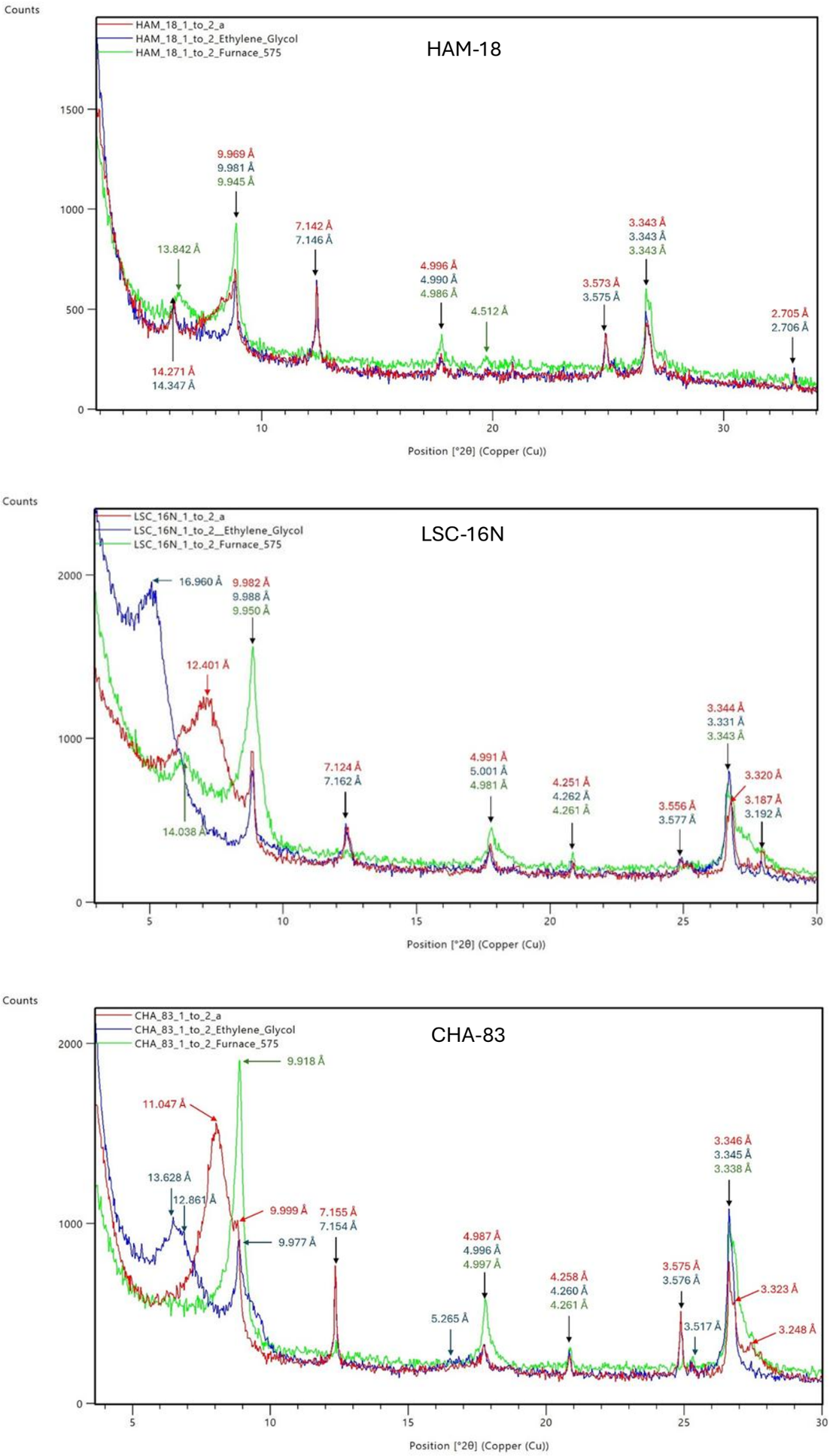

Figure S1b. X-ray diffraction patterns of the air-dried (red), glycol-solvated (blue), and heated (575°C; green) 1–2 μm fractions of HAM-18, LSC-16N, and CHA-83

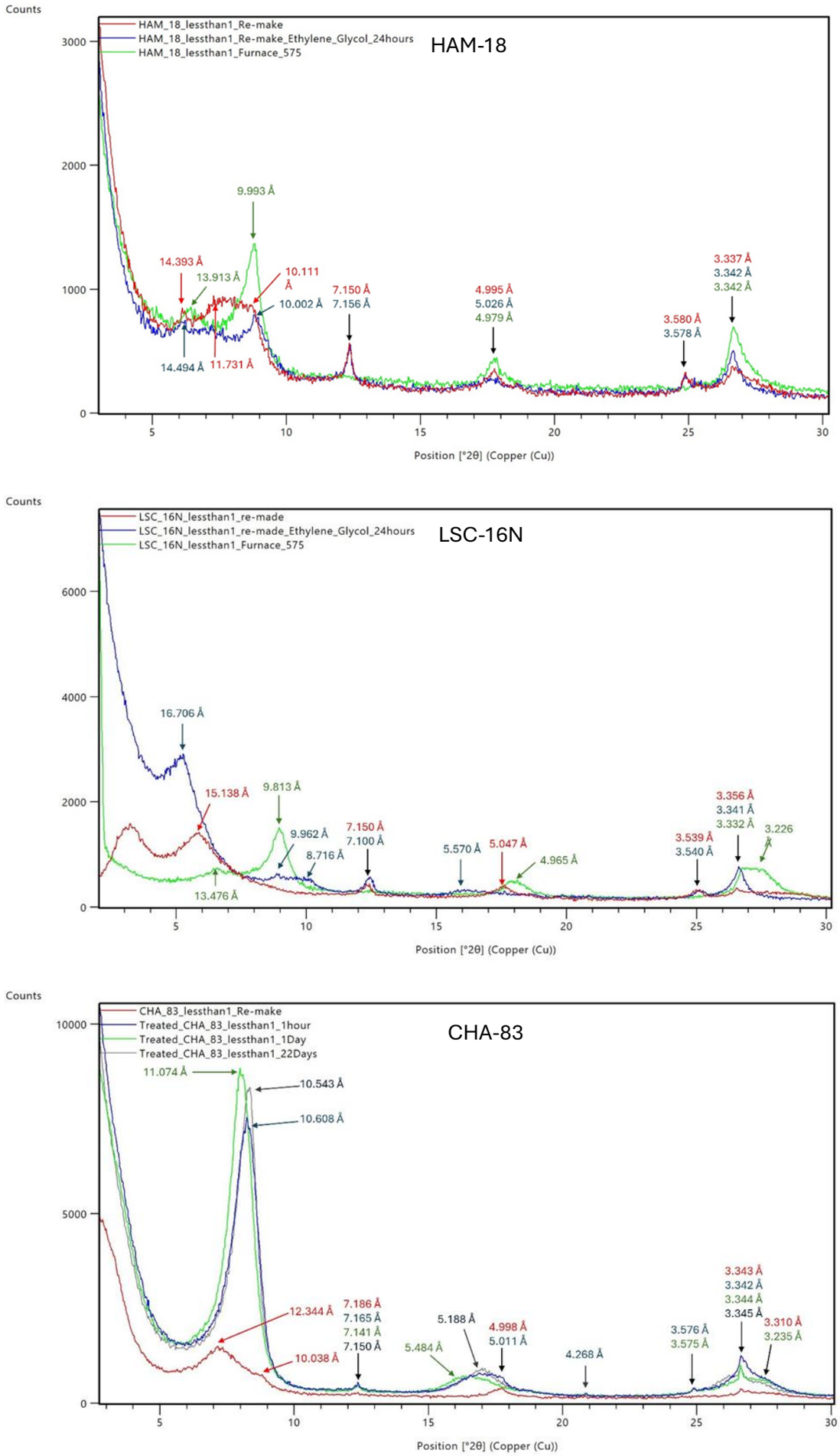

Figure S1c. X-ray diffraction patterns of the air-dried (red), glycol-solvated (blue), and heated (575°C; green) < 1 μm fractions of HAM-18, LSC-16N, and CHA-83

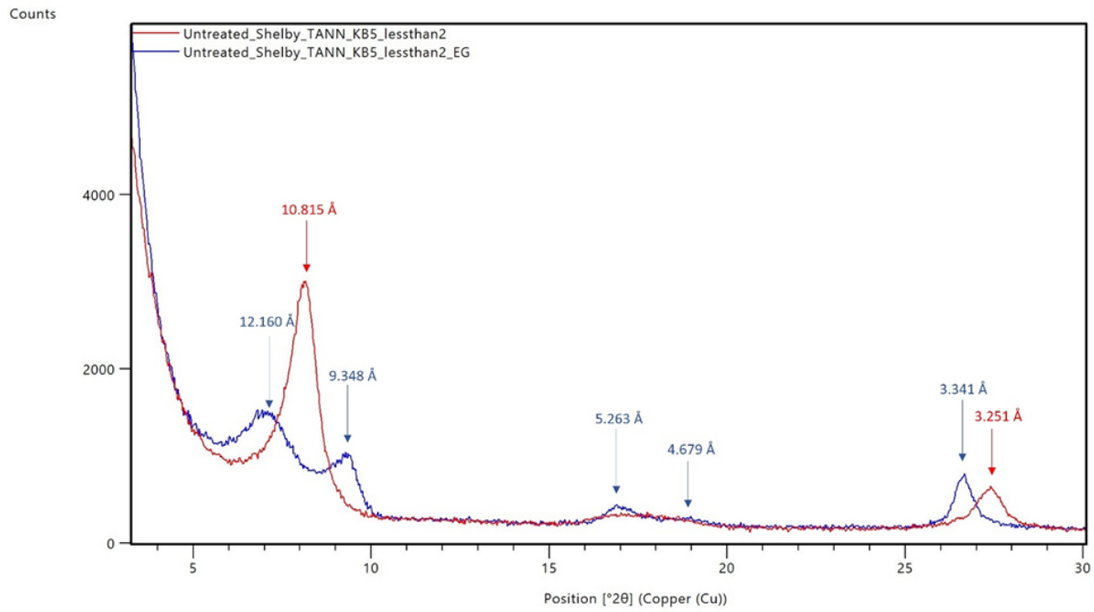

Figure S1d. X-ray diffraction patterns of the air-dried (red) and glycol-solvated (blue) < 2 μm fraction of the potassium bentonite

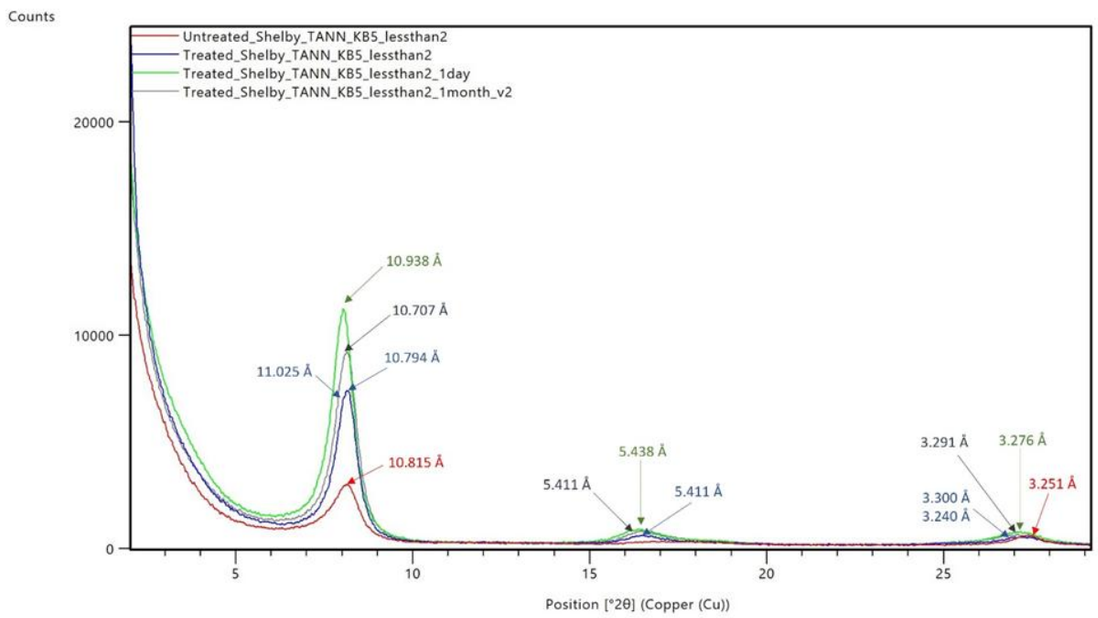

Figure S2. X-ray diffraction patterns of the air-dried < 2 μm fraction of the potassium bentonite before treatment and after TPB treatment for 1 hour, 1 day, and 27 days

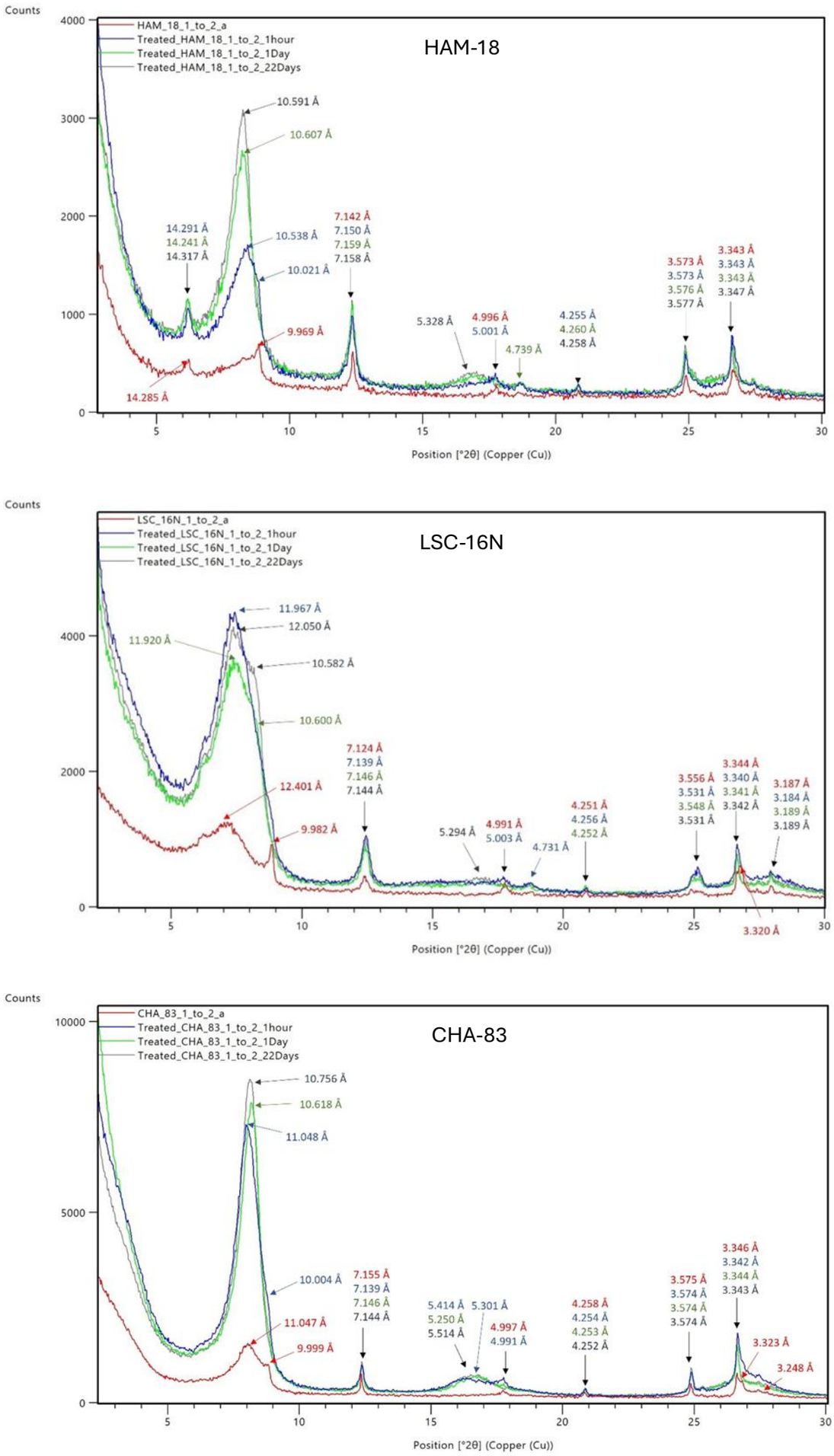

Figure S3. X-ray diffraction patterns of the air-dried 1-2 μm fractions of HAM-18, LSC-16N, and CHA-83 before treatment and after TPB treatment for 1 hour, 1 day, and 22 days

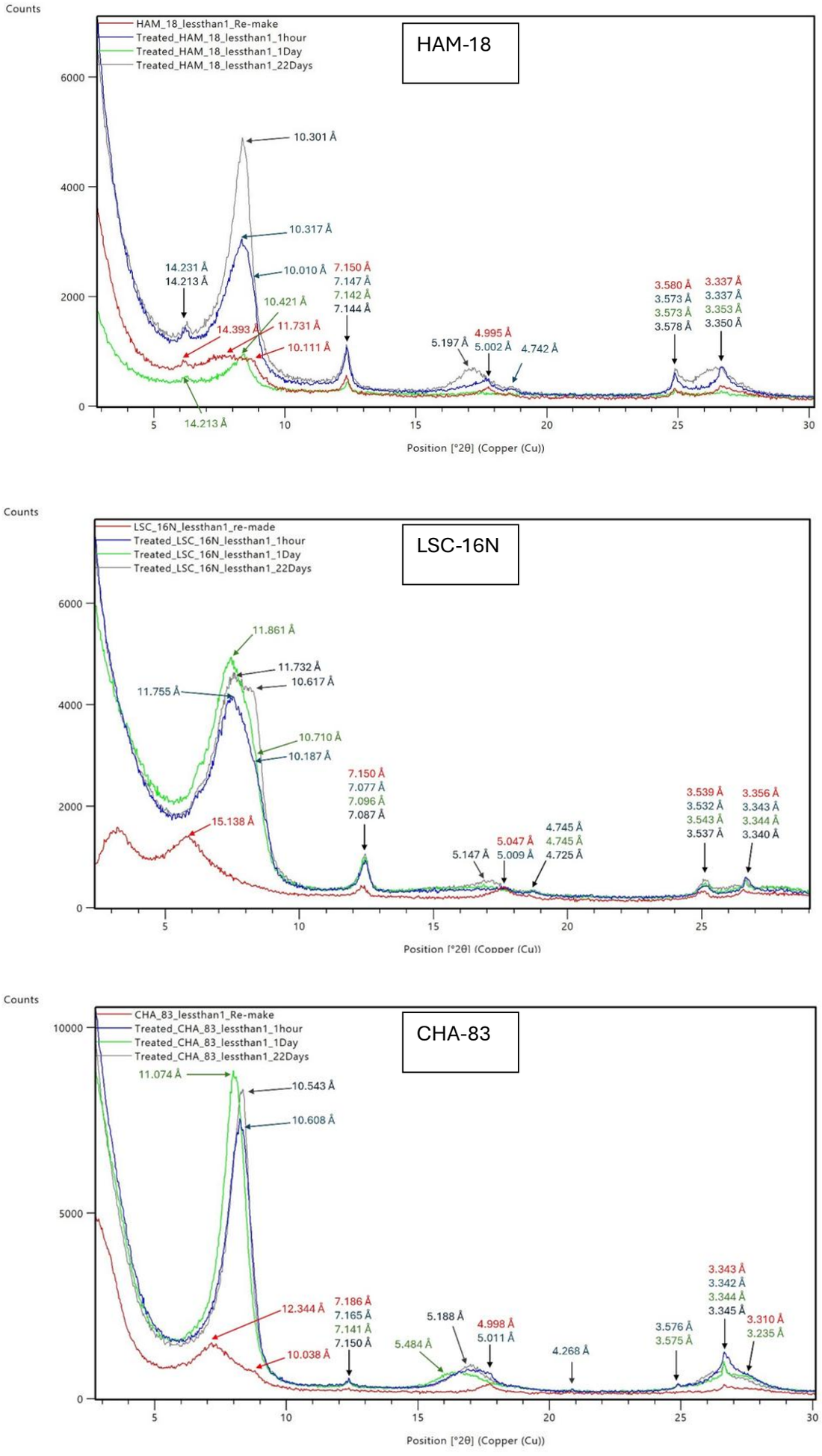

Figure S4. X-ray diffraction patterns of the air-dried < 1 μm fractions of HAM-18, LSC-16N, and CHA-83 before treatment and after TPB treatment for 1 hour, 1 day, and 27 days

Mass change of clay during TPB treatment

The K contents and K-Ar ages of two size fractions of the illite-smectite (Ilt-Sme) rich LSC-16N paleosol show that the portions of these fractions that were TPB treated for one hour were substantially less massive after the treatment than before. The changes in mass of the clay may be attributed to changes in interlayer materials during the K extraction and during the subsequent processes of quenching with NH_4Cl in acetone-water solution, rinsing, and air drying. Disregarding minor species, the original interlayer materials were K ions in contracted interlayers and Na and/or Ca ions and water in expanded interlayers. Because replacement of interlayer K^+ with Na^+ is the essence of the $NaBPh_4$ method, because NH_4^+ replaced Na^+ and any Ca^{2+} more or less completely during quenching, and because Na^+ and Ca^{2+} hold water of hydration more strongly than the two other cations, the interlayer material of each treated clay fraction was different from that of the untreated clay. That the interlayer material was different after treatment applies to all nine treated portions of the paleosol clay fractions, not just to the two for which there is clear evidence of decrease in mass after one hour of treatment. The sense of mass change for the seven others cannot be established with the available data, but consideration of the probable response of the smectitic interlayers of the Ilt-Sme and of the originally K-rich contracted interlayers of the Ilt-Sme and mica to TPB treatment (the entire process described as "TPB treatment in the published article) allows some useful estimates of the sense and magnitude of the mass change experienced by each treated portion.

Estimated upper limits for the fractional mass change caused by changes in the interlayer cation of each kind of interlayer affected by TPB treatment can be calculated simply by assuming full saturation of that kind of interlayer by one species before TPB treatment and full saturation by NH_4^+ after TPB treatment, provided that a reasonable estimate of the amount of the species displaced by the reaction is available. For example, the mass change caused by replacement of all the K^+ in ideal muscovite (9.8% K by mass) with NH_4^+ would be a decrease of a bit more than 5%, because the mass of NH_4^+ is a bit less than one-half that of K^+. The mass of added NH_4^+ would be 9.8% × 18.04/39.10 = 4.5% of the mass of the original muscovite, and the mass decrease would be 9.8% − 4.5% = 5.3%.

Consider also the mass decrease caused by replacement of Ca^{2+} in Ca-montmorillonite by NH_4^+ if the interlayer Ca content were 0.2 atoms per $O_{10}(OH)_2$, corresponding to only 1.9% by mass of such bi-hydrated montmorillonite. The mass of two NH_4^+ ions is so near that of Ca^{2+} (36.08/40.08 = 0.90) that the mass decrease due to change of the interlayer cation would be negligible, 0.10 × 1.9% = 0.19%. The situation is quite different, however, if the hydration of the interlayers is considered. The interlayer water of bi-hydrated Ca-montmorillonite accounts for about 15% of its mass (Fleury et al., 2013). The fine clay (<1 μm) of LSC-16N was mostly R0 Ilt-Sme. Its low K content (2.51%) indicates that roughly one-half of the interlayers of its Ilt-Sme were expandable. This clay fraction had been coagulated with a solution that would have left Ca^{2+} as the predominant interlayer cation, so it is reasonable to consider the interlayer-water content of the untreated clay to have been nearly one-half that of bi-hydrated Ca-montmorillonite—say 7% by mass. After replacement of the Ca^{2+} by Na^+ during K extraction and then replacement of most if not all the Na^+ by NH_4^+ during quenching, the TPB-treated clay would have held much less water because of the weak attraction of NH_4^+ for water. It is reasonable to expect that this clay fraction lost roughly 5% of its mass as interlayer water that had been held during air drying of the untreated clay but was not held during air drying of the TPB-treated clay.

The Ilt-Sme of the LSC-16N fine clay also experienced exchange of Na^+ for some of the K^+ in its originally contracted interlayers while reacting with NaCl-NaTPB solution. The evidence for this is the larger age value of the portion tested after one hour of TPB

treatment than before, interpreted as a consequence of extraction of K and its associated radiogenic Ar from relatively young Ilt-Sme while older detrital muscovite was little affected. The mass decrease owing to replacement of K^+ by NH_4^+ would have been the mass of K extracted times 0.539 (i.e., 1 − 18.04/39.10). The mass of K extracted in one hour is unknown, but almost certainly was a modest fraction of the original K content, 2.51%. The relative mass decrease owing to replacement of K^+ by NH_4^+ in the one-hour-treated LSC-16N fine clay was probably less than 1%. Consideration that some water probably accompanied the NH_4^+ in the air-dried clay suggests that replacement of K^+ by NH_4^+ should have had negligible effect on this clay fraction.

Although there are many uncertainties, the above considerations suggest that significant decreases in mass of the paleosol clay fractions, when compared in air-dried form, could have occurred upon TPB treatment because of loss of a substantial amount of water from expandable interlayers of Ilt-Sme and because of replacement of K^+ by NH_4^+ in originally contracted interlayers of muscovite. Such decreases should not have been more than about 5%, however, and that only for the Ilt-Sme rich fine fraction of LSC-16N because of its smectite-rich Ilt-Sme. Pure muscovite might lose about 5% of its mass, but muscovite probably was not more than about 30% of any of the tested clay fractions.

Consideration of apparent increases in radiogenic Ar content require looking elsewhere for a cause of significant mass decreases. The radiogenic Ar content of the LSC-16N < 1 μm clay TPB treated for one hour was 20% larger than that of the untreated clay, and the radiogenic Ar content of the LSC-16N 2–5 μm clay TPB treated for one hour was 10% larger than that of the untreated clay fraction. Radiogenic Ar content was not greater after TPB treatment for any other clay fraction. The two anomalous increases could be a result of analytical mistakes, but, because they occurred for fractions of the same paleosol whose Ilt-Sme is smectite rich, a more likely explanation for the large increases in radiogenic Ar content is that these original clay fractions contained substantial amounts of a soluble substance that had not rinsed out of the smectitic clay.

The causes of mass decrease greater than a few percent discussed above—loss of water from smectite interlayers of Ilt-Sme and presence of soluble material in the untreated clay—should have become manifest during the first hour of TPB treatment, thus affecting all three treated portions of a clay fraction equally, regardless of treatment duration. For this reason, although differences in K content are not reliable indicators of the K extracted from any original clay fraction, the differences in K content among the three treated portions of any clay fraction should be reliable (within a few percent, relatively) indicators of the differences in amounts of K extracted in treatments of different duration. Thus, the additional amounts of K extracted in the treatments subsequent to the one-hour treatment can be estimated with confidence by inspection of the decreasing K values shown on Fig. 2 for the three successively longer treatments of any paleosol clay fraction.

Reference cited:

Fleury M., Kohler E., Norrant F., Gautier S., M'Hamdi J. & Barre L. (2013) Characterization and quantification of water in smectites with low field NMR. *The Journal of Physical Chemistry*, **117**, 4551−4560.