

K-Ar AGE CONSTRAINTS ON THE ORIGIN OF MICACEOUS MINERALS IN SAVANNAH RIVER SITE SOILS, SOUTH CAROLINA, USA

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Abstract—K-Ar measurements were used in this study of upland Savannah River Site soils to distinguish between sorbed K and the K remaining in remnants of primary minerals. Study of sorbed K contributes to understanding further the interaction of alkali metals (Cs in particular) with the soils. Primary mineral K and the associated radiogenic Ar were studied to characterize soil mica with respect to its provenance and its relationship to hydroxy-interlayered vermiculite. K-Ar age values of Na-saturated clay fractions from five samples of these soils range in age from 270 to 370 Ma. After a moderate acid treatment (6% HNO₃ v/v, ~1 mol dm⁻³, 3 h, 80°C) of the clay fractions, K-Ar age values (270–325 Ma) were little changed on the whole, but they were more closely grouped near 300 Ma. Earlier work had shown that most of the K in these soils is found in material resistant to moderate acid extraction. The K-Ar age values show that this acid-resistant material is much older than any pedogenic minerals could be, even much older than the sedimentary parent rocks from which the soils were derived. These observations support earlier inferences by others that the K in these well leached soils is largely in remnants of primary muscovite from the parent sediments. Age values near 300 Ma suggest that the muscovite is largely from proximal Piedmont terranes of the Appalachian orogen, where the K-Ar relationship in most micas was set by Alleghanian tectonic processes late in the Paleozoic Era. The structural location of the K within mica, shown by the retention of the associated radiogenic Ar, is in contrast to the sorption-dominated behavior of the Cs and most of the Rb in these soils during pedogenesis. Stronger acid treatment (~6 mol dm⁻³ HNO₃, 3 h, 100°C) extracted substantial fractions of both the K and the radiogenic Ar from bulk-soil portions, indicating destruction of some of the primary mica. K-Ar age values for the sand-rich bulk soils were not useful for this study because the sand contains excess radiogenic Ar, probably in sand-sized vein quartz.

Key Words—Acid Extraction, Excess Radiogenic Argon, Hydroxy-interlayered Vermiculite, K-Ar Dating, Muscovite, Primary Mineral K, Provenance, Savannah River Site, Soil, Soil Clay.

INTRODUCTION

Since Dymond *et al.* (1974) used K-Ar dating to demonstrate the eolian origin of mica in Hawaiian soils, studies using measurements of radiogenic argon to constrain the origin of micaceous clay minerals in soil have been few (*e.g.* Mora *et al.*, 1998; Šucha *et al.*, 2001). Wilson (1999) pointed out that the contribution of inherited soil clays needs to be understood and he emphasized that K-Ar dating can be used to answer questions about the origin or provenance of mica in soils. In the acidic soils of the southeastern U.S., expanded 2:1 clay interlayers, formed by weathering of micas as a result of the high precipitation across the region, commonly contain intercalated hydroxy-aluminum polymers to form hydroxy-interlayered vermiculite (HIV) (Weed and Nelson, 1962; Bryant and Dixon, 1963; Rich, 1968; Fiskell and Perkins, 1970; Kirkland and Hajek, 1972; Barnhisel, 1978; Karathanasis *et al.*, 1983; Harris *et al.*, 1992). Harris *et al.* (1992) used high resolution transmission electron microscopy to find small zones of 1.0 nm lattice fringes occluded within

HIV and interpreted these zones to be remnants of primary mica from which the HIV had been derived.

Kaolinite and HIV are the predominant clay minerals in the near-surface soils of the Savannah River Site (SRS) in South Carolina (Kaplan *et al.*, 1997; Clark *et al.*, 1998; Segall *et al.*, 2000; Goto, 2001), where tritium and plutonium were produced for cold war era nuclear weapons from 1952 onward for three decades. Strong uptake of radiocesium by samples of these soils has been attributed to the presence of interlayer wedge zones in weathered-mica grains, where HIV grades into mica (Goto *et al.*, 2008a). Cation exchange sites within interlayer wedges are thought to be highly selective for Cs owing to size exclusion of more strongly hydrated cations (Rich and Black, 1964; Elprince *et al.*, 1977; Barnhisel and Bertsch, 1989).

During pedogenesis, naturally occurring stable Cs has been held rather effectively by the SRS soils while much of the K originally in the parent materials was leached away (Wampler *et al.*, 2012). Dilute HNO₃ solution (8% v/v, ~1.3 mol dm⁻³), at 80°C for 3 h, extracted much of the natural Cs from the soils but little of the K. About 90% of the K in test portions of five SRS soil samples remained in the solid residues after the acid extraction. Wampler *et al.* (2012) inferred that the K not extracted was in remnants of primary mica within HIV grains,

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never having participated in the mineral–water reactions of pedogenesis.

The present study had two main purposes. The first was to see if K-Ar measurements on HIV-bearing clay would confirm the inference of Harris *et al.* (1992) that the mica-like material within HIV originated from a mica precursor of the HIV. Such confirmation would support an interpretation by Wampler *et al.* (2012) that most of the K in SRS soils is in remnants of mica where it was not susceptible to acid extraction while most natural Cs now in the soil has been retained in interlayer wedge sites at the edges of the mica remnants. The key idea is that radiogenic Ar ($^{40}\text{Ar}_{\text{rad}}$) is associated with K remaining undisturbed in remnants of primary minerals and can thus be used to distinguish such structurally held K from K that has been released from silicate structures and has participated in mineral–water reactions during pedogenesis. The second purpose of the present study was to use K-Ar measurements for information on the provenance of the primary minerals in the SRS soils.

MATERIALS AND METHODS

Materials

The SRS study area is in the upper Coastal Plain of South Carolina, about 20 miles southeast of Augusta, Georgia. The area is underlain by some 300 m of Late Cretaceous to Miocene sediments composed of stratified quartz sand, clay, calcareous sediments, and conglomerates (Wyatt and Harris, 2004). These formations increase in thickness from northwest to southeast. Specific to the SRS, the parent sediments are overlain by well drained upland soils consisting predominantly of quartz sand while the clay fraction is dominated by kaolinite (Kaplan *et al.*, 1997; Findley, 1998). The temperate climate and relatively large amounts of precipitation have impacted the mineralogy of the soils (Looney *et al.*, 1990; Findley, 1998). Organic matter is typically confined to the top 15 cm of soil (Rogers, 1990).

The five samples examined in this study were collected from the Blanton, Fuquay, Lakeland, Orangeburg, and Vaucluse soil series (Table 1) and

were described by Findley (1998). The parent rocks of these upland soils are predominantly sandy Eocene and Oligocene sediments (Fallaw and Price, 1995; Prowell, 1996; Segall *et al.*, 2000). The quartz-rich sands are commonly micaceous (muscovite) and are interbedded with relatively thin layers of clay-rich finer sediment (Prowell, 1996).

The Blanton series is the most widespread soil series at the SRS (Rogers, 1990) and is characterized by a thick eluvial horizon that begins at a depth of ~10 cm and continues for >1 m. The horizon is extensively leached, having mostly sand and only small amounts of clay (Findley, 1998). The Fuquay series has an eluvial horizon just below the surface and is characterized by plinthite nodules (>5% by mass) in the B horizon (Findley, 1998). The Lakeland series is a soil made up almost entirely of unweathered quartz sand and is characterized by its almost complete lack of horizon development. The Orangeburg series has no eluvial horizon, has a reddish hue in the subsurface horizons, and generally has a finer texture than the other soils (Findley, 1998). The Vaucluse series has few distinguishable horizons and lacks an eluvial horizon depleted in colloidal materials (Findley, 1998).

The mass fractions of clay and K in these soil samples (Table 1) are as determined in previous studies. The mass fraction of HIV in each sample was calculated from the HIV contents of the clay fractions reported by Goto *et al.* (2008b), who used the formulae of Karathanasis and Hajek (1982) to calculate from X-ray diffraction (XRD) peak height ratios the amounts of HIV and quartz in the clay fractions as functions of the amount of kaolinite. To convert the results to mass fractions, gibbsite was assumed to account for ~10% of these clays, as reported by Kaplan *et al.* (1997) for Orangeburg and Blanton clay fractions. The amounts of HIV in the Orangeburg and Fuquay clay fractions calculated by Goto *et al.* (2008b), 20% and 25%, respectively, agree with HIV contents reported by Karathanasis *et al.* (1983) and Kaplan *et al.* (1997), respectively, for clay fractions of samples from the B horizons of these soil series. Kaplan *et al.* (1997)

Table 1. Soil samples.

Series	Sample number	— Location* —		Sampling depth* (cm)	Clay† (%)	K‡ (g kg ⁻¹)	HIV§ (%)
		SRP N	SRP E				
Blanton	35	33,348	54,468	25–51	2.1	0.56	0.9
Fuquay	42	87,219	37,347	122–153	17.8	1.36	4.5
Lakeland	2	95,318	82,743	51–76	7.3	0.73	1.8
Orangeburg	46	93,938	65,113	56–81	15.0	1.11	3.0
Vaucluse	12	95,572	48,098	66–91	1.5	0.27	0.5

* From Findley (1998). Locations are in Savannah River Plant coordinates.

† Average of values (percent by mass) from Findley (1998) and Goto *et al.* (2008a).

‡ From Wampler *et al.* (2012).

§ Percent by mass, calculated as described in the text.

reported 35% HIV in clay from the E horizon of Blanton soil, reasonably close to the 45% calculated by Goto *et al.* (2008b). That HIV is most abundant in the Blanton clay, from the shallowest of the five SRS samples, is consistent with numerous observations that HIV is particularly abundant in near-surface horizons of south-eastern U.S. soils (Harris *et al.*, 1992).

Preparation of clay and sand fractions

Goto (2001) prepared a clay fraction, $<2 \mu\text{m}$, from $\sim 25 \text{ g}$ of each of the five soil samples and found that these clays were composed mostly of kaolinite and HIV. For the present study, a portion ($<1 \text{ g}$) of each of Goto's clay fractions was saturated with Na by adding 15 cm^3 of 1 mol dm^{-3} sodium acetate-acetic acid buffer (pH 5.0) solution to a mixture of clay and deionized (DI) water. The mixture was shaken vigorously until the entire clay portion was re-suspended, and the suspension was centrifuged for 10 min at 2000 relative centrifugal force (RCF). After sodium saturation, the clay fractions were rinsed by dispersion in DI water and centrifuged. This sequence (rinsing and centrifuging) was repeated two or more times until only a small amount of clay became dispersed in DI water. This procedure produced a Na-saturated clay. A final suspension was poured into a Saran Wrap®-lined drying dish, placed in an oven set to 50°C , and dried overnight. Each dried clay residue was powdered in an agate mortar and weighed. Sand fractions were separated from $\sim 2.5 \text{ g}$ portions of the bulk soils by timed settling and decantation of material finer than $50 \mu\text{m}$ after pretreatment to remove cements and iron oxides. The procedures used were from Jackson (1969) and Kunze and Dixon (1986).

Acid extractions

Acid extractions of portions of the Na-saturated clay fractions were done with dilute HNO_3 (6% v/v, $\sim 1 \text{ mol dm}^{-3}$) prepared from trace-metal grade concentrated HNO_3 , in round-bottomed Savillex® vials of Teflon® (perfluoroalkoxy copolymer resin, PFA). Extractions were for 3.0 h at 80°C with shaking after 5 min, 15 min, and subsequent 15-min intervals. The mixtures were then centrifuged at 2000 RCF for 10 min. The solids separated by centrifuging were washed with deionized water, centrifuged, and dried overnight at 50°C (Naumann, 2010). The conditions used for acid extraction of the clay fractions were the same as those used for acid extraction of bulk soils by Wampler *et al.* (2012) except that the acid was slightly less concentrated (6% v/v instead of 8% v/v). Another set of acid extractions of the bulk soils, under substantially harsher conditions (50% v/v HNO_3 , $\sim 6 \text{ mol dm}^{-3}$, for 3.0 h at 100°C), had been done as a preliminary experiment, but the results of that experiment were not reported by Wampler *et al.* (2012) because of a problematic blank run for Cs. The K extracted in that experiment is reported below.

Potassium-argon determinations

In the present study, two methods were used to determine K-Ar age values for the five SRS soil samples, and materials derived from them (Naumann, 2010). A conventional method was used for the bulk soils, for residues from acid extraction of bulk soils, for the first set of K-Ar determinations of Na-saturated clays, and for the sand fractions. In this method, one portion of a sample was used for Ar isotope analysis and another portion was used for K determination. (An exception is that K values for the residues from the harsher acid extraction were calculated by difference, rather than determined directly.) K values for test portions of the bulk soils and for the sand fractions were reported by Wampler *et al.* (2012) and are used here. In the second method, applicable only to clays, a single portion of clay was used first for extraction of Ar, which was then analyzed isotopically. Then the solid material remaining after the Ar extraction was retrieved for K determination (Stephens *et al.*, 2007; Stroker, 2009; De Man *et al.*, 2010). This method was used for all work on acid-extracted clay and for duplicate determinations on two of the Na-saturated clays (Fuquay and Orangeburg).

For K determinations, solid materials were digested by a mixture of concentrated HF and HNO_3 in a clean PFA vial at $\sim 90^\circ\text{C}$ until all K-bearing solids were dissolved. After the digestion, excess acid solution was evaporated leaving nitrate salts. The nitrate salts from each test portion were dissolved in HNO_3 solution (0.1 mol dm^{-3}) containing CsCl (0.01 mol dm^{-3}) and transferred into a pre-weighed polyethylene bottle. More of the HNO_3 -CsCl solution was used to rinse the PFA vial and to fill the polyethylene bottle after each rinse solution had been transferred to the bottle. The mass of solution in the filled bottle was determined by weighing. Dilution was sufficient that the K in solution was $<2 \text{ mg kg}^{-1}$.

Potassium in solution was determined by flame atomic absorption spectrophotometry. A Perkin Elmer model 3110 atomic absorption spectrophotometer was used to measure absorbance at 766.6 nm by K from aspirated sample solutions in an air-acetylene flame. The instrument was set to zero before aspirating a sequence of test solutions and reference solutions. During aspiration of each solution, ten 1.0 s measurements of absorbance were made and averaged. The measurement sequence was repeated from three to six times. K in each unknown test solution was calculated by linear interpolation of K content as a function of absorbance between points determined for reference solutions prepared by dilution of a gravimetrically determined amount of a KCl standard with the same HNO_3 -CsCl solution used to prepare the sample solutions.

For K-Ar analyses done by the single-portion method, $\sim 30 \text{ mg}$ of clay was weighed into a pre-weighed copper-foil capsule, and the capsule was closed by folding and crimping. After weighing, a set of such capsules was loaded into the Ar-extraction line. The line was then evacuated and the capsules were held under vacuum at

least overnight to remove adsorbed water and any associated atmospheric Ar. To extract Ar from a clay test portion, the capsule was heated step-wise with an externally wound resistance heater, which was made of insulated resistance wire wrapped around a fused-quartz tube, to a final temperature of ~860°C and held at that temperature for 15 min. This heating was sufficient to remove Ar from the sample clay, but did not melt the clay or the copper capsule. Follow-up heating of some capsules at ~1000°C showed that <1% of the $^{40}\text{Ar}_{\text{rad}}$ in the clay had not been released in the original heating. The capsules were later removed for K determinations as described above.

For the Ar isotope analyses done conventionally, the test portions (of bulk soils, bulk-soil extraction residues, sand fractions, and Na-saturated clay fractions) were heated in steps within an internal resistance furnace to a final temperature well above the ~1060°C melting temperature of copper, causing complete melting of the sample materials and release of gases to the vacuum line. However, even at this temperature, not all the Ar was easily released from the viscous melts of the quartz-rich bulk soils, bulk-soil residues, and sands. Repeated heating of some of the sand fractions showed that ~10% of the $^{40}\text{Ar}_{\text{rad}}$ had not been released from the viscous melt during the first heating.

During or after Ar extraction by either technique, a known amount of ^{38}Ar -enriched Ar with known isotopic composition was added to the gases released from the test material. The Ar was purified first by passing the gas mixture through two U-shaped gradient traps cooled by liquid nitrogen to remove water and CO_2 and then by contact with Ti metal (first hot, then cooling) to remove other reactive gases from the mixture. After purification, the Ar was analyzed isotopically with an Associated Electrical Industries, Limited (London, UK) type MS-10 mass spectrometer in the static mode. A chart recorder was used to record the output current from the mass spectrometer as a proportional voltage. The output was recorded across the mass range where the isotopes ^{36}Ar , ^{38}Ar , and ^{40}Ar were detected by the mass spectrometer. Minor hydrocarbon background signals at elementary mass to charge ratios (m/z) of 37, 39, and 41 were also

detected, and the signal at $m/z = 37$ was measured to allow minor corrections for hydrocarbon background at the positions of the Ar-isotope peaks. Mass discrimination was determined by isotopic analysis of Ar from air. Accepted values were used for isotopic compositions of terrestrial K and atmospheric Ar, and for the decay constants of ^{40}K , $\lambda_{\epsilon} = 0.581 \times 10^{-10} \text{ y}^{-1}$ and $\lambda_{\beta} = 4.962 \times 10^{-10} \text{ y}^{-1}$, as recommended by the International Union of Geological Sciences Subcommittee on Geochronology (Steiger and Jäger, 1977).

The accuracy of the K and Ar measurement procedures was confirmed by using them to obtain an age value of 95.1 ± 2.3 million years (Ma) for the interlaboratory reference glauconite sample GL-O (Odin *et al.*, 1982). Relative errors for calculated quantities were obtained by quadratic combination of relative error terms from the independent quantities used in the calculation, where the error term for each independent quantity is the estimated 2σ relative error times a factor (which may be unity) that depends on the functional relationship of the variables (Dalrymple and Lanphere, 1969, equation 7-1). The equation used to calculate error in apparent age includes a factor that accounts for the decreasing sensitivity of that error to error in $^{40}\text{Ar}_{\text{rad}}/\text{K}$ as apparent age increases, which was not included in Dalrymple and Lanphere's (1969) equation 7-1. The estimates of analytical error do not include an estimate of how 'sampling errors' (*i.e.* difficulty in taking equivalent small portions of soil materials for different measurements) may have affected the results.

RESULTS

Acid extractions

Acid extractions of subsamples of the bulk soils by Wampler *et al.* (2012) dissolved some of the solid material, including some of the K (Table 2, Figure 1). The amounts of $^{40}\text{Ar}_{\text{rad}}$ lost during acid extraction were not determined directly. Neither the decrease in mass of the solid nor the amount of K extracted during acid extraction of the clay fractions was determined.

Acid extraction of bulk soil under moderate conditions (8% HNO_3 , 80°C, 3 h) caused decreases in mass

Table 2. Effects of acid extractions on bulk soil mass and K content.

Sample	— Moderate extraction —			— Strong extraction —		
	Mass lost (%)*	— K extracted — (g kg ⁻¹)*	(%)†	Mass lost (%)*	— K extracted — (g kg ⁻¹)*	(%)†
Blanton 35	1.8	0.053	9.6	2.4	0.087	16
Fuquay 42	5.0	0.160	11.8	7.3	0.72	53
Lakeland 2	2.9	0.078	10.5	3.9	0.26	35
Orangeburg 46	5.4	0.128	11.5	8.8	0.38	34
Vaucluse 12	1.0	0.028	9.9	1.6	0.075	26

* Relative to the original mass of dried soil

† Relative to the original K content of dried soil

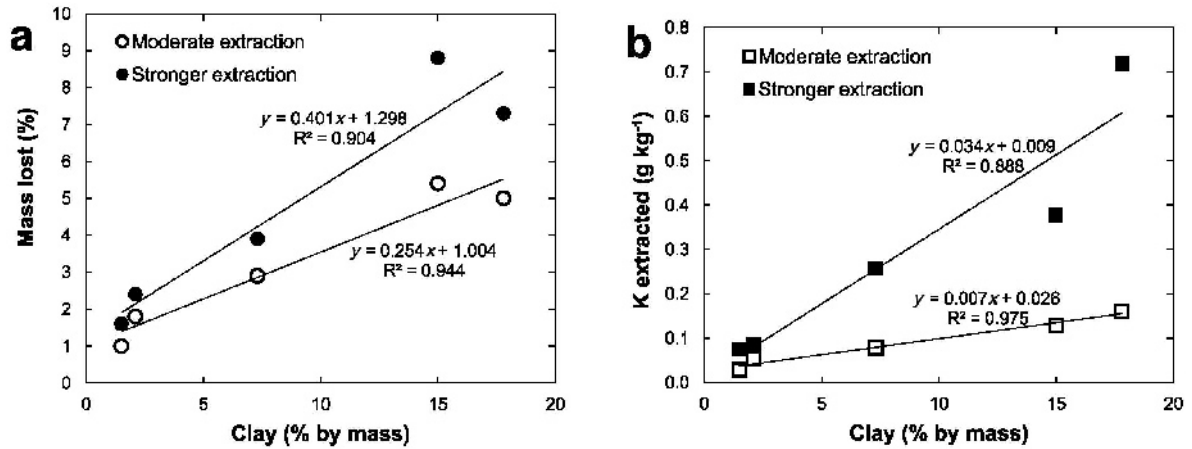


Figure 1. Correlations of mass lost during acid extraction (a) and of amount of K extracted by acid (b) with clay content of soil.

ranging from 1.0 to 5.4%. The decrease in mass and the amount of K extracted are both correlated with the clay content of the soil (Figure 1). Acid extraction of other bulk soil portions under harsher conditions (50% HNO₃, 100°C, 3 h) caused mass decreases ~50% greater, from 1.6 to 8.8%, also correlated with clay content. Nearly four times as much K was extracted under the harsher conditions than under the moderate conditions. The relative amount of soil K removed by acid extraction under moderate conditions was about the same for all samples, near 10%. The amount of K extracted is proportional to the amount of HIV in the soil (Figure 2).

K-Ar measurements

The results of K-Ar measurements (Table 3) show apparent ages of the untreated bulk soils that vary widely, from 370 Ma to 850 Ma (Figure 3). The age values of the Na-saturated clay fractions (averaged for duplicate runs) are smaller and more closely grouped, from 270 Ma to 370 Ma (Figures 3, 4). Potassium is

much more concentrated in the Na-saturated clay fractions, 0.52–0.83% by mass, than in the untreated bulk soils, 0.03–0.14% by mass. The difference in age value between bulk soil and clay is least for the Fuquay and Orangeburg samples. The Fuquay and Orangeburg samples contain 18 and 15% clay, respectively, and most of the soil K is in the clay fraction. The other samples have little clay and their bulk-soil age values are about twice the clay age values.

Potassium was less concentrated in the solid material after moderate acid extraction (8% HNO₃, 80°C, 3 h) of bulk soils, and ⁴⁰Ar_{rad} was either the same or less concentrated. The K-Ar age values for the solids remaining after this moderate acid extraction are greater than for the untreated bulk soils in four of five soils. However, the strong acid extraction (50% HNO₃, 100°C, 3 h) removed both K and ⁴⁰Ar_{rad} in sufficient amounts to cause them to be less concentrated in the solid residues than they were in the bulk soils. After the strong extraction, age values were greater for the Fuquay,

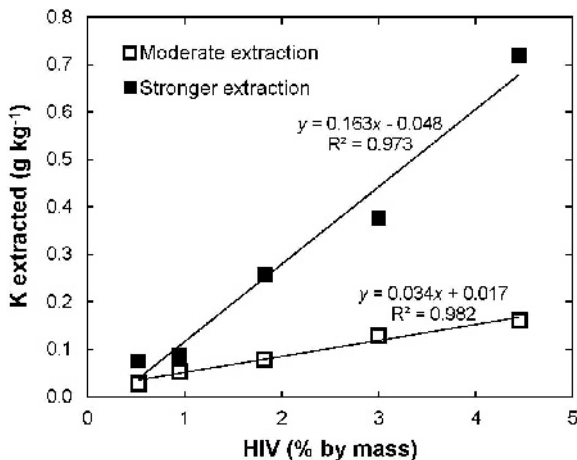


Figure 2. Correlation of amount of K extracted by acid with HIV content of soil.

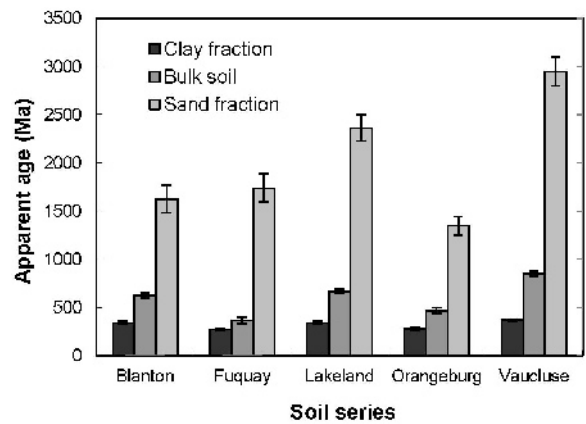


Figure 3. K-Ar age values of clay and sand fractions and bulk soil samples of five SRS soils. Average values of duplicate runs are plotted.

Table 3. K-Ar data.

Material	Test portions*		K [†] (mass %)	⁴⁰ Ar _{rad} (%) [§]	⁴⁰ Ar _{rad} (pmol g ⁻¹)	K-Ar age [‡] (Ma)
	K (mg)	Ar (mg)				
Untreated bulk soil						
Blanton	101.7	221.2	0.055±0.001	77	71±3	630±30
Fuquay	102.4	116.4	0.136±0.003	59	96±10	370±40
Lakeland	95.7	141.9	0.074±0.001	75	104±3	670±20
Orangeburg	104.0	137.0	0.111±0.002	74	103±8	470±40
Vaucluse	104.6	193.5	0.029±0.001	69	54±2	850±30
Bulk soil extracted with 8% HNO ₃ at 80°C						
Blanton	60.1	126.6 92.5	0.044±0.001	84 64	64±2 36±3	695±25 425±35
Fuquay	46.6	106.0 31.7	0.098±0.002	83 63	101±7 78±9	515±30 410±35
Lakeland	38.9	40.7	0.050±0.001	66	75±7	710±60
Orangeburg	37.5	96.2	0.101±0.002	87	105±7	520±30
Vaucluse	40.3	138.0	0.022±0.001	72	48±2	970±40
Bulk soil extracted with 50% HNO ₃ at 100°C						
Blanton		143.0	0.047±0.002	84	58±2	600±40
Fuquay		100.4	0.068±0.003	68	68±6	500±50
Lakeland		94.9	0.050±0.003	79	83±3	770±40
Orangeburg		87.0	0.080±0.004	74	93±6	570±40
Vaucluse		157.3	0.021±0.001	63	34±2	740±50
Na-saturated clay fractions						
Blanton	24.7	25.3	0.831±0.016	45	535±24	340±15
Fuquay	34.5	27.8	0.554±0.016	48	298±19	285±20
	85.1	85.1	0.634±0.010	56	309±5	260±10
Lakeland	30.2	29.6	0.561±0.012	31	365±20	340±20
Orangeburg	32.0	29.1	0.503±0.016	55	268±17	285±20
	40.6	40.6	0.527±0.009	64	263±9	265±10
Vaucluse	38.2	31.0	0.660±0.012	57	470±14	370±15
Clay fractions extracted with 6% HNO ₃ at 80°C						
Blanton	9.4	9.4	0.878±0.031	60	533±39	320±20
Fuquay	20.0	20.0	0.670±0.014	59	332±18	265±15
	60.3	60.3	0.660±0.010	69	364±7	295±10
Lakeland	20.9	20.9	0.741±0.015	56	456±20	325±15
	16.6	16.6	0.745±0.017	64	463±20	325±15
Orangeburg	19.1	19.1	0.584±0.013	64	296±19	270±20
	41.8	41.8	0.566±0.009	73	307±8	290±10
Vaucluse	19.1	19.1	0.903±0.020	62	537±22	315±15
Sand fractions						
Blanton	219.1	170.6	0.0067±0.0001	73	31±4	1630±150
Fuquay	220.6	119.6	0.0048±0.0001	64	24±3	1740±150
Lakeland	245.4	148.6	0.0051±0.0001	75	43±5	2360±140
Orangeburg	284.1	118.2	0.0077±0.0002	73	27±3	1350±100
Vaucluse	245.3	180.7	0.0032±0.0001	73	41±5	2950±150
Interlaboratory reference sample						
GL-O	16.3	16.7	6.85±0.19	96	1160±27	95.1±2.3

* K and Ar denote portions used for potassium determination and argon isotopic analysis, respectively.

[†] K values for the untreated bulk soils and for the sand fractions are from Wampler *et al.* (2012). K in the residues from acid extraction of bulk soils with 50% HNO₃ at 100°C was not determined directly but was determined by difference, using the measured amounts of K extracted.

[‡] Age values have been rounded to the nearest 10 Ma for bulk soils, for residues from acid extraction of bulk soils, and for sand fractions, and to the nearest 5 Ma for clays and acid extracts of clays. The corresponding error values have been rounded upward to end in 5 or 0.

[§] Percentage of total ⁴⁰Ar that is radiogenic argon.

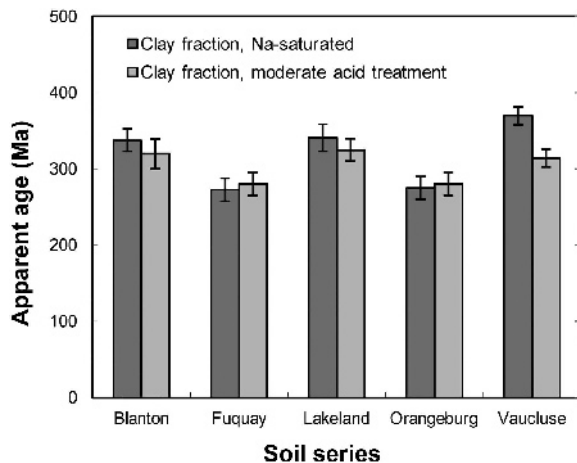


Figure 4. K-Ar age values of clay fractions before and after moderate acid extraction. Average values of duplicate runs are plotted.

Orangeburg, and Lakeland residues relative to the bulk soils, but the value for the Vaucluse residue was substantially smaller than that for the bulk soil.

The age values of the clay fractions are for the most part 300 ± 40 Ma for both the Na-saturated clay fractions and the clay residues after moderate acid extraction. The mass fraction of K was greater in all these residues than in the Na-saturated clay, and the specific amount of $^{40}\text{Ar}_{\text{rad}}$ was also greater in all but the Blanton clay residue. The K-Ar age values of the sand fractions are large and variable (1350–2950 Ma). The errors are unusually large owing to the small quantities of measured K and $^{40}\text{Ar}_{\text{rad}}$.

INTERPRETATIONS

Effects of acid extractions

Soil mass decreases during acid extraction owing to dissolution of acid-soluble minerals such as gibbsite and Fe (oxyhydr)oxides, to partial dissolution of silicate minerals such as kaolinite and HIV, and to replacement of heavier ions (for example, K^+ and $\text{Mg}(\text{H}_2\text{O})_6^{2+}$) by hydrogen ions. The mass losses during both the moderate and strong acid extractions of bulk soil are correlated with the clay content of the soil sample. However, the mass losses are disproportionately greater for the two samples with smallest clay contents and for the Orangeburg sample, which is unusual among these samples in having sufficient Fe oxide to give the sample a red color. These observations indicate that most of the acid-soluble material is in the clay fraction but that some acid-soluble material, notably the Fe oxide in the Orangeburg sample, was removed by the pretreatment before size separation (Goto, 2001).

The approximate proportionality of amount of K extracted to soil clay content, in both the moderate and strong extractions (Figure 1), indicates that the K

extracted came mostly from the clay in the soil. The even closer proportionality of extracted K to HIV content (Figure 2) implies that the extracted K was present within HIV before extraction, consistent with earlier inferences that nearly all of the cation exchange capacity (CEC) of these soils is due to HIV (Goto *et al.*, 2008a) and that the non-exchangeable K in these soils is largely in small mica remnants within weathered-mica grains that are now largely HIV (Wampler *et al.*, 2012). Acid extraction removes exchangeable K, and the strong acid extraction at 100°C apparently removed part of the “primary mineral K” (as defined by Wood and DeTurk, 1940) also. About one third (on average) of the K and about one fourth of the $^{40}\text{Ar}_{\text{rad}}$ were removed by the stronger acid treatment, which suggests that roughly one fourth of the primary K-bearing material in the soil was destroyed.

For four of the five clay fractions, the moderate acid extraction caused no significant change in age value, which indicates that any exchangeable K on the original clay had been replaced by Na before the K-Ar measurements. On average, K and $^{40}\text{Ar}_{\text{rad}}$ are ~15% more concentrated in the clay residues after moderate acid extraction than they were in the clay before extraction, if the anomalously large change for K in the Vaucluse clay fraction is not considered. These data indicate that acid extraction under these conditions effectively removed the acid-soluble components of the clay fraction such as gibbsite, which constitutes ~10% of the clay fractions of these soils (Kaplan *et al.*, 1997; Goto *et al.*, 2008b). As acid dissolution removed materials that do not contain K (gibbsite, perhaps some kaolinite), the proportion of non-exchangeable K in insoluble materials (such as remnants of mica within HIV grains) became larger compared to the mass of the residual solid.

Significance of the age values

The apparent ages for the clay fractions offer a possible interpretation which is that the K and radiogenic Ar remaining in clay fractions is within remnants of detrital muscovite that was in the parent Tertiary sediments—mica remnants that were not yet transformed to other phyllosilicates such as HIV or kaolinite during soil-forming processes. This interpretation is supported by the similarity of the K-Ar ages of these SRS clays to the K-Ar ages of muscovite-rich sediment samples from the Georgia kaolin belt (191–412 Ma, Hassanipak, 1980) and to K-Ar ages of weathered muscovites also from the Georgia kaolin belt (113–374 Ma, Elser, 2004). The similarity of the age values of the SRS clays to those of the detrital muscovite suggests that the provenance of the mica in the parent sediments was essentially the same as that of the micas in the somewhat older kaolin-belt sediments. That the age values center on 300 Ma suggests that the muscovite in both was from the proximal part of the Appalachian Mountain belt. The Alleghanian Orogeny was an extensive tectonic event during which metamorph-

ism and plutonism produced micas and reset the K-Ar clocks of many older Appalachian micas to near zero late in the Paleozoic Era, ~300 Ma (Dallmeyer *et al.*, 1986; Hatcher *et al.*, 2007).

The consistency of age values between treated and untreated clay fractions is interpreted to indicate that the SRS clays contain micaceous interlayers or micaceous remnants that harbor K in sites where it is not exchangeable even though the clay fractions are composed primarily of kaolinite and HIV. These sites holding non-exchangeable K within mica interlayers are where ^{40}K has decayed to ^{40}Ar in a confined system that has been closed since diffusive loss of Ar from mica (resetting) ceased during exhumation of the orogenic belt where the mica crystals formed. Thus, removal of exchangeable K from the clays by Na saturation has made the clay into a useful K-Ar clock that is not appreciably affected by moderate acid extraction. The clay-fraction age values show variability; the parent materials of the SRS soils probably had varying provenances within the Appalachian orogenic belt. Thus, the age values of muscovite in Tertiary sediments vary from place to place, reflecting variability in the erosion and transport of mica from the Appalachian Blue Ridge and Piedmont provinces to be deposited as Tertiary sediments of what is now the Coastal Plain.

Bulk soil age values are larger and more variable than clay age values (Figure 3). The magnitude and variability of the age values could be due to variable proportions of detrital phases of old provenance or to the presence of excess $^{40}\text{Ar}_{\text{rad}}$ (Dalrymple and Lanphere, 1969) in some soil particles larger than clay. The first alternative is unlikely in view of the scarcity of ancient (Grenvillian) terrane in the proximal Appalachian orogenic belt and to the absence of K-bearing minerals other than muscovite in these soils. K-feldspar originally in the parent sediments has long since been replaced by kaolinite, and the muscovite in the Tertiary sediments has age values <400 Ma. Vein quartz from the Appalachian Piedmont contains excess $^{40}\text{Ar}_{\text{rad}}$ (Rama *et al.*, 1965; Awuah and Wampler, 1982). K-Ar age values of such quartz may be extremely large because Ar trapped in fluid inclusions is largely unsupported by K. Prowell (1996) reported that the coarsest phase of the upland unit at the SRS is characterized by gravels consisting of vein quartz. The presence of excess $^{40}\text{Ar}_{\text{rad}}$ in sand-sized vein quartz could substantially shift apparent age values of the bulk soils. The K-Ar age values for the sand fractions of these soils (1350–2950 Ma) are explained by the presence of excess $^{40}\text{Ar}_{\text{rad}}$ in the sand.

DISCUSSION

The mineralogy of the SRS soils, especially the clay fractions, is important for interpreting the results of K-Ar studies. From the study of Goto (2001), the clay fractions

of these SRS soils are composed of kaolinite, Al-hydroxy interlayered vermiculite, gibbsite, and in most cases quartz. This mineral assemblage is consistent with clay fractions of other highly weathered soils in the southeastern U.S. (Weed and Nelson, 1962; Rich, 1968; Fiskell and Perkins, 1970; Barnhisel, 1978; Karathanasis *et al.*, 1983; Harris *et al.*, 1992). The soil mineralogy provides insight to soil properties such as CEC and soil pH, which in turn provide context for understanding sorption and release of anthropogenic metals in these soils.

Like clay fractions of other HIV-bearing coastal-plain soils of the southeastern U.S. (Kirkland and Hajek, 1972; Harris *et al.*, 1992), the clay fractions of the upland SRS soils do not contain mica or feldspar detectable by conventional XRD analyses (Kaplan *et al.*, 1997; Clark *et al.*, 1998; Goto, 2001). The parent materials of these soils are highly mature clastic sediments, largely muscovite-bearing sands in which original K-feldspar has been replaced by kaolinite (Prowell, 1996). Direct evidence that muscovite has weathered to kaolinite and vermiculite in soils of the region has been provided by scanning electron microscopy (*e.g.* Elliott *et al.*, 1997; Segall *et al.*, 2000). Along with dominant kaolinite, XRD of clay fractions by Segall *et al.* (2000) revealed clay-sized HIV mostly in the uppermost parts of cores that extended for tens of meters through soil and sediment at the SRS. In contrast, significant illite was found only in the deeper parts of these cores. In total, these observations provide sound support for the hypothesis that the K in the clay fractions of the SRS soils is in highly weathered grains of what were once muscovite but which are now mostly HIV.

The finding of Appalachian mica-like K-Ar age values for the soil clay fractions is strong support for the presence of remnant muscovite in the clay (which has no detectable feldspar). The finding is consistent with the observation by Harris *et al.* (1992) of mica remnants occluded within HIV and supports their inference that the HIV in U.S. southern coastal plain soils is a mica derivative. The observation that acid extraction at 80°C removed little if any of the K from the clay fractions and had no significant effect on the age values of four of the five clay fractions supports the idea that the K is in remnants of muscovite. Not only is muscovite much more resistant to K-release than trioctahedral mica (Leonard and Weed, 1970), Al-rich dioctahedral clays are notably resistant to acid extraction. Thompson and Hower (1973) and Aronson and Douthitt (1986) found that extraction with dilute acid at 80°C removes strongly bound K from micaceous interlayers of glauconite and illite only very slowly. Derkowski *et al.* (2009) showed that authigenic Fe clays (glauconitic) are removed by stronger acid treatments (3 mol dm⁻³ HCl at ~100°C), which causes the age values of the residues to be greater than the glauconite age values when acid-resistant, older Al-rich detrital material is present. That is consistent with the effect of

stronger acid extraction on the bulk soils at 100°C observed in the present study.

The K-Ar age values of this study, before and after acid extractions, are significant to understanding the sorption and release of other alkali metals as well as K by the SRS soils. At low concentrations of Cs and Rb, illite is highly selective for Cs and Rb relative to K (Brouwer *et al.*, 1983). The SRS soils are similarly selective for these cations relative to K, as shown by the relatively high Cs/K and Rb/K ratios seen when acid extraction under moderate conditions removed most of the Cs and Rb that had been sorbed by these SRS soils during pedogenesis (Elliott *et al.*, 2009; Wampler *et al.*, 2012). Because the K-Ar age values strongly support the presence of mica remnants in the soils, they also support the hypothesis that interlayer wedge sites in highly weathered mica grains, where the structural layers of remnant mica splay to become those of HIV, provide the microenvironment where Cs and Rb are selectively sorbed and fixed by these soils (Wampler *et al.*, 2012).

The K-Ar age values support the inference that Cs is concentrated in interlayer wedges in an additional way. Large Cs ions almost certainly could not have migrated into closed mica interlayers that have retained similarly large radiogenic Ar atoms. If migration of Cs into mica interlayers (Evans *et al.*, 1983; Comans and Hockley, 1992) can be ruled out, the interlayer wedges are the only microenvironment within the weathered-mica grains where Cs ions reasonably could have become fixed.

Unlike the clay fractions, for which saturation with Na should have removed exchangeable K, the untreated bulk soils presumably contained some exchangeable K, up to ~10% as indicated by the fraction of total K removed by moderate acid extraction (Table 2). Removal of the exchangeable K caused age values to be greater after the acid extraction in four of the five cases, but the differences are widely variable and the difference for the fifth sample (Blanton) is in the wrong sense. These problems are attributable to large uncertainties in the measurement of $^{40}\text{Ar}_{\text{rad}}$ in bulk soils and their extraction residues, which is probably due both to difficulty in extracting all of the Ar from molten quartz and to non-uniform distribution of excess $^{40}\text{Ar}_{\text{rad}}$ -bearing vein quartz in the small test portions used. The age values themselves are not meaningful given the contribution of excess $^{40}\text{Ar}_{\text{rad}}$ from vein quartz. Only the age values of the clay fractions, which presumably have no vein quartz, are useful for interpretation. These age values demonstrate that moderate acid treatment is suitable as a pretreatment for K-Ar study and does not release ^{40}Ar from the closed primary mica interlayer system.

CONCLUSIONS

Measurements of K and radiogenic Ar in association with extractions that do not affect the radiogenic Ar-bearing primary minerals in soils provide important

information about the location and past behavior of K in the soils. K-Ar age values of SRS soil clay fractions are those of remnants of primary mica in the clay, because exchangeable K was removed before age determination.

Acid extraction under moderate conditions removes the exchangeable K from bulk portions of the SRS soils and accounts for modest increases in K-Ar age values observed for most of the bulk soils after such extraction. The bulk-portion age values themselves are meaningless owing to the presence of excess $^{40}\text{Ar}_{\text{rad}}$ in vein quartz. Measurements of K and Ar isotopes indicate that treatment of bulk soils with 50% HNO_3 at 100°C is strong enough to release some of the nonexchangeable K, and thus $^{40}\text{Ar}_{\text{rad}}$, from the primary mica sites.

Age values of clay fractions did not change significantly in response to moderate acid extraction (6% HNO_3 at 80°C) because exchangeable K had been removed by pretreatment. The measurements show that little if any K and $^{40}\text{Ar}_{\text{rad}}$ were lost from the clay during these extractions. The approximately 300±40 Ma apparent ages of the clay fractions indicate that the nonexchangeable K within the soils has been in closed systems throughout the sedimentary and pedogenic processes responsible for the present-day soils and give strong support to the idea that this K exists in muscovite remnants within weathered-mica grains that are now largely HIV. Furthermore, the lack of exchange of K and the retention of $^{40}\text{Ar}_{\text{rad}}$ within the interlayers of such primary mica supports the idea that wedge sites adjacent to the mica interlayers are where Cs accumulates by selective sorption in these soils.

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REFERENCES

- Aronson, J.L. and Douthitt, C.B. (1986) K/Ar systematics of an acid-treated illite/smectite: implications for evaluating age and crystal structure. *Clays and Clay Minerals*, **34**, 473–482.
- Awuah, A.K. and Wampler, J.M. (1982) Variability of argon and helium in quartz and calcite vein minerals from sedimentary and metamorphic rocks. *Georgia Journal of Science*, **40**, 19.
- Barnhisel, R.I. (1978) Analyses of clay, silt, and sand fractions of selected soils from Southeastern United States. *Southern Cooperative Series Bulletins* No. **219**, University of Kentucky, Lexington, Kentucky, USA.
- Barnhisel, R.I. and Bertsch, P.M. (1989) Chlorites and hydroxyinterlayered vermiculite and smectite. Pp. 729–788 in: *Minerals in Soil Environments*, 2nd edition. (J.B. Dixon and S.B. Weed, editors). Soil Science Society of America, Madison, Wisconsin, USA.

- Brouwer, E., Baeyens, B., Maes, A., and Cremers, A. (1983) Cesium and rubidium ion equilibria in illite clay. *Journal of Physical Chemistry*, **87**, 1213–1219.
- Bryant, J.P. and Dixon, J.B. (1963) Clay mineralogy and weathering of red-yellow podzolic soil from quartz mica schist in the Alabama Piedmont. *Clays and Clay Minerals*, **12**, 509–521.
- Clark, S.B., Bryce, A.L., Leuning, A.D., Gariboldi, J., and Serkiz, S.M. (1998) Factors affecting trivalent f-element adsorption to an acidic sandy soil. Pp. 149–164 in: *Adsorption of Metal by Geomedia: Variables, Mechanisms, and Model Applications* (E.A. Jenne, editor). Academic Press, San Diego, California, USA.
- Comans, R.N.J. and Hockley, D.E. (1992) Kinetics of cesium sorption on illite. *Geochimica et Cosmochimica Acta*, **56**, 1157–1164.
- Dallmeyer, R.D., Wright, J.E., Secor, D.T., and Snoke, A.W. (1986) Character of the Alleghanian orogeny in the southern Appalachians: Part II. Geochronological constraints on the tectonothermal evolution of the eastern Piedmont in South Carolina. *Geological Society of America Bulletin*, **97**, 1329–1344.
- Dalrymple, G.B. and Lanphere, M.A. (1969) *Potassium-Argon Dating: Principles, Techniques, and Applications to Geochronology*. W.H. Freeman and Company, San Francisco.
- De Man, E., Van Simaey, S., Vandenberghe, N., Harris, W.B., and Wampler, J.M. (2010) On the nature and chronostratigraphic position of the Rupelian and Chattian stratotypes in the southern North Sea Basin. *Episodes*, **33**, 3–14.
- Derkowski, A., Śródoń, J., Franus, W., Uhlík, P., Banaś, M., Zieliński, G., Čaplovičová, M., and Franus, M. (2009) Partial dissolution of glauconite samples: implications for the methodology of K-Ar and Rb-Sr dating. *Clays and Clay Minerals*, **57**, 531–554.
- Dymond, J., Biscaye, P.E., and Rex, R.W. (1974) Eolian origin of mica in Hawaiian soils. *Geological Society of America Bulletin*, **85**, 37–40.
- Elliott, W.C., Savin, S.M., Dong, H., and Peacor, D.R. (1997) A paleoclimate interpretation derived from pedogenic clay minerals from the Piedmont province, Virginia. *Chemical Geology*, **142**, 201–211.
- Elliott, W.C., Krogstad, E.J., and Wampler, J.M. (2009) A comparison of Cs/K mass ratios in select micas, soils and kaolins from the Southern Appalachian Piedmont and coastal plain. *Geochimica et Cosmochimica Acta*, **73**, A326.
- Elprince, A.M., Rich, C.I., and Martens, D.C. (1977) Effect of temperature and hydroxy aluminum interlayers on the adsorption of trace radioactive cesium by sediments near water-cooled nuclear reactors. *Water Resources Research*, **13**, 375–380.
- Elser, A.M. (2004) The provenance and weathering of muscovite from the Georgia kaolin deposits. PhD thesis, Georgia State University, Atlanta, Georgia, USA.
- Evans, D.W., Alberts, J.J., and Clark, R.A. (1983) Reversible ion-exchange fixation of cesium-137 leading to mobilization from reservoir sediments. *Geochimica et Cosmochimica Acta*, **47**, 1041–1049.
- Fallow, W.C. and Price, V. (1995) Stratigraphy of the Savannah River Site and vicinity. *Southeastern Geology*, **35**, 21–58.
- Findley, M. (1998) Characterizing the environmental availability of trace metals in soils at the Savannah River Site. M.S. thesis, Clemson University, Clemson, South Carolina, USA.
- Fiskell, J.G.A. and Perkins, H.F. (1970) Selected Coastal Plain soil properties. *Southern Cooperative Series Bulletin*, No. **148**, University of Florida, Gainesville, Florida, USA.
- Goto, M. (2001) Development of a quantitative model for binding cesium to SRS soils. MS thesis, Georgia Institute of Technology, Atlanta, Georgia, USA.
- Goto, M., Rosson, R., Wampler, J.M., Elliott, W.C., Serkiz, S., and Kahn, B. (2008a) Freundlich and dual Langmuir isotherm models for predicting ¹³⁷Cs binding on Savannah River Site soils. *Health Physics*, **94**, 18–32.
- Goto, M., Rosson, R., Wampler, J.M., Elliott, W.C., Kahn, B., and Serkiz, S. (2008b) A quantitative model for binding Cs-137 on SRS soil. WSRC-STI-2008-00114, Westinghouse Savannah River Company, Aiken, South Carolina, USA.
- Harris, W.G., Morrone, A.A., and Coleman, S.E. (1992) Occluded mica in hydroxy-interlayered vermiculite grains from a highly-weathered soil. *Clays and Clay Minerals*, **40**, 32–39.
- Hassanipak, A.A. (1980) Isotopic geochemical evidence concerning the origin of Georgia kaolin deposits. PhD thesis, Georgia Institute of Technology, Atlanta, Georgia, USA.
- Hatcher, R.D., Bream, B.R., and Merschat, A.J. (2007) *Tectonic map of the Southern and Central Appalachians: a tale of three orogens and a complete Wilson cycle*. Geological Society of America Memoir **200**, pp. 595–632.
- Jackson, M.L. (1969) *Soil Chemical Analysis – Advanced Course*. Published by the author, Madison, Wisconsin, USA.
- Kaplan, D.I., Bertsch, P.M., and Adriano, D.C. (1997) Mineralogical and physicochemical differences between mobile and nonmobile colloidal phases in reconstructed pedons. *Soil Science Society of America Journal*, **61**, 641–649.
- Karathanasis, A.D. and Hajek, B.F. (1982) Revised methods for rapid quantitative determination of minerals in soil clays. *Soil Science Society of America Proceedings*, **46**, 419–425.
- Karathanasis, A.D., Adams, F., and Hajek, B.F. (1983) Stability relationships in kaolinite, gibbsite, and Al-hydroxyinterlayered vermiculite soil systems. *Soil Science Society of America Journal*, **47**, 1247–1251.
- Kirkland, D.L. and Hajek, B.F. (1972) Formula derivation of Al-interlayered vermiculite in selected soil clays. *Soil Science*, **114**, 317–322.
- Kunze, G.W. and Dixon, J.B. (1986) Pretreatment for mineralogical analysis. Pp. 91–99 in: *Methods of Soil Analysis, 2nd edition, Part 1 - Physical and Mineralogical Methods* (A. Klute, editor). American Society of Agronomy, Madison, Wisconsin, USA.
- Leonard, R.A. and Weed, S.B., (1970) Mica weathering rates as related to mica type and composition. *Clays and Clay Minerals*, **18**, 187–195.
- Looney, B.B., Eddy, C.A., Ramdeen, M., Pickett, J., Rogers, V., Scott, M.T., and Shirley, P.A. (1990) Geochemical and physical properties of soils and shallow sediments at the Savannah River Site. WSRC-RP-90-1031, Westinghouse Savannah River Company, Aiken, South Carolina, USA.
- Mora, C.I., Sheldon, B.T., Elliott, W.C., and Driese, S.G. (1998) An oxygen isotope study of illite and calcite in three Appalachian Paleozoic vertic Paleosols. *Journal of Sedimentary Research*, **68**, 456–464.
- Naumann, T.E. (2010) K-Ar age values of bulk soil samples and clay fractions: Effects of acid extraction and implications for the origin of micaceous clay in Savannah River Site soils, South Carolina, USA. MS thesis, Georgia State University, Atlanta, Georgia, USA. http://digitalarchive.gsu.edu/geosciences_theses/27
- Odin, G.S. et al. (1982) Interlaboratory standards for dating purposes. Pp. 123–150 in: *Numerical Dating in Stratigraphy, Part I* (G.S. Odin, editor). John Wiley & Sons, Chichester, UK, 630 pp.
- Prowell, D.C. (1996) *Geologic map of the Savannah River Site, Aiken, Allendale, and Barnwell Counties, South Carolina*.

- U.S. Geological Survey, Washington, D.C., USA.
- Rama, S.N.I., Hart, S.R., and Roedder, E. (1965) Excess radiogenic argon in fluid inclusions. *Journal of Geophysical Research*, **70**, 509–511.
- Rich, C.I. (1968) Hydroxy interlayers in expansible layer silicates. *Clays and Clay Minerals*, **16**, 15–30.
- Rich, C.I. and Black, W.R. (1964) Potassium exchange as affected by cation size, pH, and mineral structure. *Soil Science*, **97**, 384–390.
- Rogers, V.A. (1990) *Soil survey of the Savannah River Plant area, parts of Aiken, Barnwell, and Allendale Counties, South Carolina*. U.S. Dept. of Agriculture, Soil Conservation Service, Washington, D.C., USA.
- Segall, M.P., Siron, D.L., and Colquhoun, D.J. (2000) Depositional and diagenetic signatures of Late Eocene–Oligocene sediments, South Carolina. *Sedimentary Geology*, **134**, 27–47.
- Steiger, R.H. and Jäger, E. (1977) Subcommittee on Geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth and Planetary Science Letters*, **36**, 359–362.
- Stephens, E.C., Anderson, J.R., Gullet-Young, C., Wampler, J.M., and Elliott, W.C. (2007) Age of the Ocmulgee Limestone (Georgia Coastal Plain) based on revised methodology for the K-Ar age of glaucony. *Southeastern Geology*, **45**, 15–24.
- Stroker, T. (2009) K-Ar dating of authigenic illite: integrating the diagenetic history of the fluvial Williams Fork Formation, Mesaverde Group, Piceance Basin, NW Colorado. MS thesis, Colorado School of Mines, Golden, Colorado, USA.
- Šucha, V., Šrodoň, J., Clauer, N., Elsass, F., Eberl, D.D., Kraus, I., and Madejová, J. (2001) Weathering of smectite and illite-smectite under temperate climatic conditions. *Clay Minerals*, **36**, 403–419.
- Thompson, G.R. and Hower, J. (1973) An explanation for low radiometric ages from glauconite. *Geochimica et Cosmochimica Acta*, **37**, 1473–1491.
- Wampler, J.M., Krogstad, E.J., Elliott, W.C., Kahn, B., and Kaplan D.I. (2012) Long-term selective retention of natural Cs and Rb by highly weathered coastal plain soils. *Environmental Science & Technology*, **46**, 3837–3843.
- Weed, S.B. and Nelson, L.A. (1962) Occurrence of chlorite-like intergrade clay minerals in Coastal Plains, Piedmont, and Mountains soils of North Carolina. *Soil Science Society of America Proceedings*, **26**, 393–398.
- Wilson, M.J. (1999) The origin and formation of clay minerals in soils: past, present and future perspectives. *Clay Minerals*, **34**, 7–25.
- Wood, L.K. and De Turk, E.E. (1940) The absorption of potassium in soil in non-replaceable forms. *Soil Science Society of America Proceedings*, **5**, 152–161.
- Wyatt, D.E. and Harris, M.K. (2004) Overview of the history and geology of the Savannah River Site. *Environmental Geosciences*, **11**, 181–190.

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