THE EFFECT OF EXCHANGEABLE POTASSIUM ON K-Ar AGE VALUES OF ILLITE-SMECTITE

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Two different points of view:

There are two different schools of thought about chemical pre-treatment of clay before determination of age values by potassium-argon methods (conventional K-Ar dating and $^{40}Ar/^{39}Ar$ dating).

Two different points of view:

"As the effects of chemical treatments to remove carbonate, quartz, or organic material on the retention of Ar by illite are not known (Moore and Reynolds, 1997), we did not treat our samples."

Haines and van der Pluijm (2008) Clay quantification and Ar–Ar dating of synthetic and natural gouge: Application to the Miocene Sierra Mazatán detachment fault, Sonora, Mexico. *Journal of Structural Geology*, **30**, 525–538.

Two different points of view:

"Besides the obvious necessity of removing exchangeable K from smectitic surfaces, a correct technique to remove potassium from low-Ar retention sites at illite crystallite fringes seems to be the next crucial step toward correct measurement and interpretation of the K–Ar age of illite–smectite."

Szczerba et al. (2015) Molecular modeling of the effects of ^{40}Ar recoil in illite particles on their K-Ar isotope dating. *Geochimica et Cosmochimica Acta,* **159**, 162–176.

What Moore and Reynolds (1997) wrote:

"The rule is *do as little as possible to the sample before presenting it to the X-ray beam*. Use chemical treatments only as a last resort, and use as little physical treatment as possible because there is always the danger of changing, in some unanticipated way, these fragile phyllosilicates with large, reactive surfaces."

The origins of the two points of view:

- Moore and Reynolds were writing of requirements for the best possible determination of the structures of clay minerals.
- Szczerba and others were writing of requirements for the best possible determination of K-Ar age values of clay minerals.

Fundamental Assumptions of the K-Ar Method

(Dalrymple and Lanphere, 1969, Potassium-Argon Dating—Principles, Techniques and Applications to Geochronology)

4. "The rock or mineral has been a closed system since t_0; that is, there has been no loss or gain of K^{40} or Ar^{40} except for that which results from the radioactive decay of K^{40}."

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In this connection, it is of interest to note that Kulp and Engels (1963) were able to remove nearly 80 percent of the potassium from biotite by base exchange without seriously affecting the potassium-argon age. … Apparently the loss of potassium is a layer-by-layer process that also results in loss of argon."

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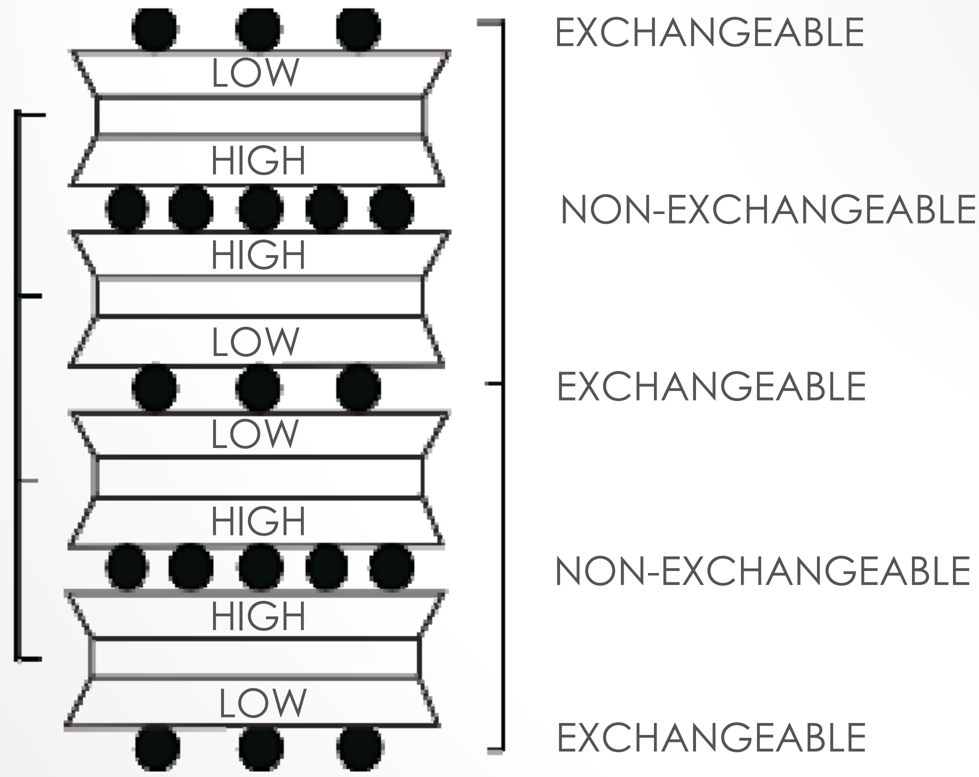
What is ‘exchangeable potassium’ in illite-smectite?

Conceptual definition: Exchangeable potassium is the potassium occurring as exchangeable cations on the external surfaces and within expanded interlayers of illite-smectite.

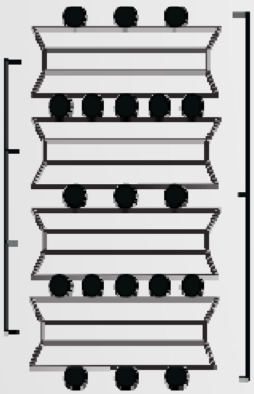


Modified from Shata *et al.* (2003) *American Mineralogist*, **88**, 748–762.

What is ‘exchangeable potassium’ in illite-smectite?

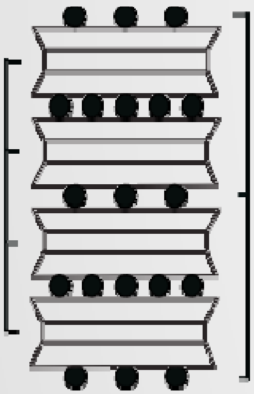
Conceptual definition: Exchangeable potassium is the potassium occurring as exchangeable cations on the external surfaces and within expanded interlayers of illite-smectite.

Operational definition: Exchangeable potassium is the potassium that can be removed promptly from illite-smectite by cation exchange with aqueous sodium.



From *The Clay Minerals Society Glossary for Clay Science Projects:*

"**cation exchange** a process whereby a cation bound to a site on a surface is replaced by a cation from a solution. In both phyllosilicates and zeolites, the cation may be located on either external surfaces or internal surfaces; thus, the full process may involve cations from the interior that diffuse toward the surface, and are in turn replaced by cations from the solution which diffuse inward. The term differs from solid-state diffusion primarily by time scale, where cation exchange occurs relatively quickly and solid-state diffusion requires a much longer period."



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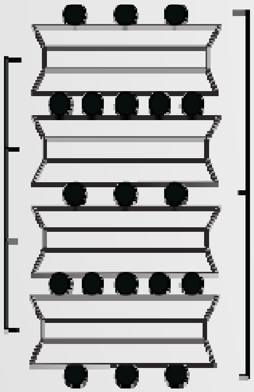

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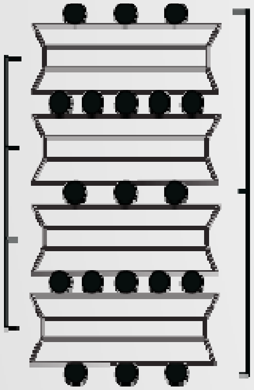
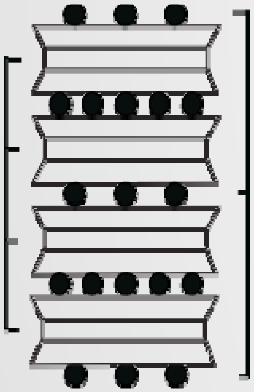


What potassium in illite-smectite is <u>not</u> 'exchangeable potassium'?

- In concept: Potassium in the non-expanded interlayers of illite-smectite is not 'exchangeable potassium' although such potassium is susceptible to sterically hindered cation exchange.



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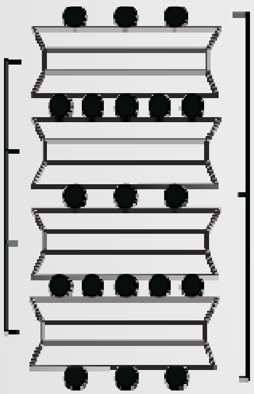
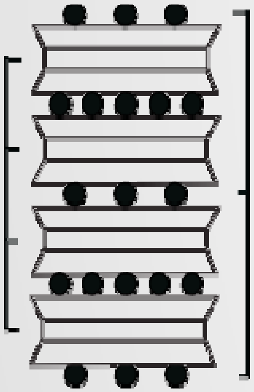
- In concept: Potassium in the non-expanded interlayers of illite-smectite is not 'exchangeable potassium' although such potassium is susceptible to sterically hindered cation exchange.

- In operation: Potassium that can be removed slowly from illite-smectite by acid treatment or base exchange is not 'exchangeable potassium.'



The significance of ‘exchangeable potassium’ in K-Ar dating of illite-smectite:

- In concept: Exchangeable potassium is not within a closed system and neither is the radiogenic argon formed by decay of ‘exchangeable potassium.’ The non-expanded interlayers of illite-smectite provide a closed system for potassium and argon.



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- In operation: 'Exchangeable potassium' should be removed from illite-smectite that is to be dated by the K-Ar method.

Some earlier studies:

Thompson and Hower (1973) An explanation for low radiometric ages from glauconite.

Aronson and Douthitt (1986) K/Ar systematics of an acid-treated illite/smectite: Implications for evaluating age and crystal structure.

Elliott, W.C. (1988) Ph.D thesis.

Clauer, N. *et al*. (1992) Effects of experimental leaching on Rb-Sr and K-Ar isotopic systems and REE contents of diagenetic illite.

Shata, S. (2000) Ph.D thesis.

Thompson, G.R. and Hower, J. (1973) An explanation for low radiometric ages from glauconite. *Geochimica et Cosmochimica Acta*, **37**, 1473–1491:

- Measured rate of extraction of potassium from glauconite samples in contact with warm 0.5 mol/L HCl solution.

- Considered the most rapidly extracted potassium, five to ten percent of total potassium, to be exchangeable potassium.

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.

- Applied the acid-dissolution method of Thompson and Hower (1973) to R1-ordered illite-smectite.

- Sodium-saturated the clay before beginning acid dissolution, so there is no information about exchangeable potassium the clay might originally have held.

Elliott, W.C. (1988) Bentonite illitization in two contrasting cases : the Denver basin and the southern Appalachian basin. Ph.D. Thesis, Case Western Reserve University.

- Tested the effect of acid treatment on the K-Ar age value of illite-smectite from the Denver Basin.

- Found no difference in age value relative to the same clay that had been treated by the methods of M. L. Jackson to remove carbonates and iron oxides—methods that leave clay sodium-saturated.

Clauer, N. *et al*. (1992) Effects of experimental leaching on Rb-Sr and K-Ar isotopic systems and REE contents of diagenetic illite. *Chemical Geology*, 103, 1–16.

- Separated 0.8–2 µm and <0.4 µm sub-fractions of an illitic claystone in distilled water.
- Treated portions of the sub-fractions with either HCl or NH_4Cl (both 1 mol/L, room temperature, 15 minutes).
- Found K-Ar age values of treated portions were no different than they were for the untreated portions.

Shata, S. (2000) Illitization and chloritization of illite/smectite and chlorite/smectite mixed-layer clays in high-grade diagenetic and very low-grade metamorphic environments of Gaspé Peninsula, Québec Appalachians, Canada: Problems and solutions. Ph.D. Thesis, McGill University.

- Separated clay size fractions (<2 µm and < 0.1 µm) without chemical treatment.
- Treated portions of the clay separates with warm *n*-alkylamine-hydrochloride solutions to intercalate alkylammonium ions.
- Determined K-Ar age values for untreated clay separates and for octadecylammonium-intercalated clay separates.

Samples of this study:

A318 <0.1 µm:
Burial diagenetic illite-smectite from the Lower Ordovician Cap Des Rosiers Group, Gaspé Peninsula, Québec.

TM29 <0.1 µm:
From the Middle Ordovician Deslandes Formation, but within the thermal halo of the McGerrigle Mountains Pluton, Gaspé Peninsula, Québec.

MAB-0101 ≤0.2 µm:
R3-ordered illite-smectite from altered gneiss, Johannes ore body, Malmberget, Sweden

Experiments of this study:

A318 <0.1 µm and two portions of TM29 <0.1 µm:

- Portions of the very fine clay not previously treated were treated for one hour with hot sodium acetate–acetic acid buffer solution (pH 5, 1 mol/L Na, solid/solution ratio 10–20 g/L). They were treated again with the buffer solution at room temperature for two days.
- Extracted potassium was measured.
- K-Ar age values of the sodium-saturated clays were determined.

Experiments of this study:

MAB-0101 ≤0.2 µm:

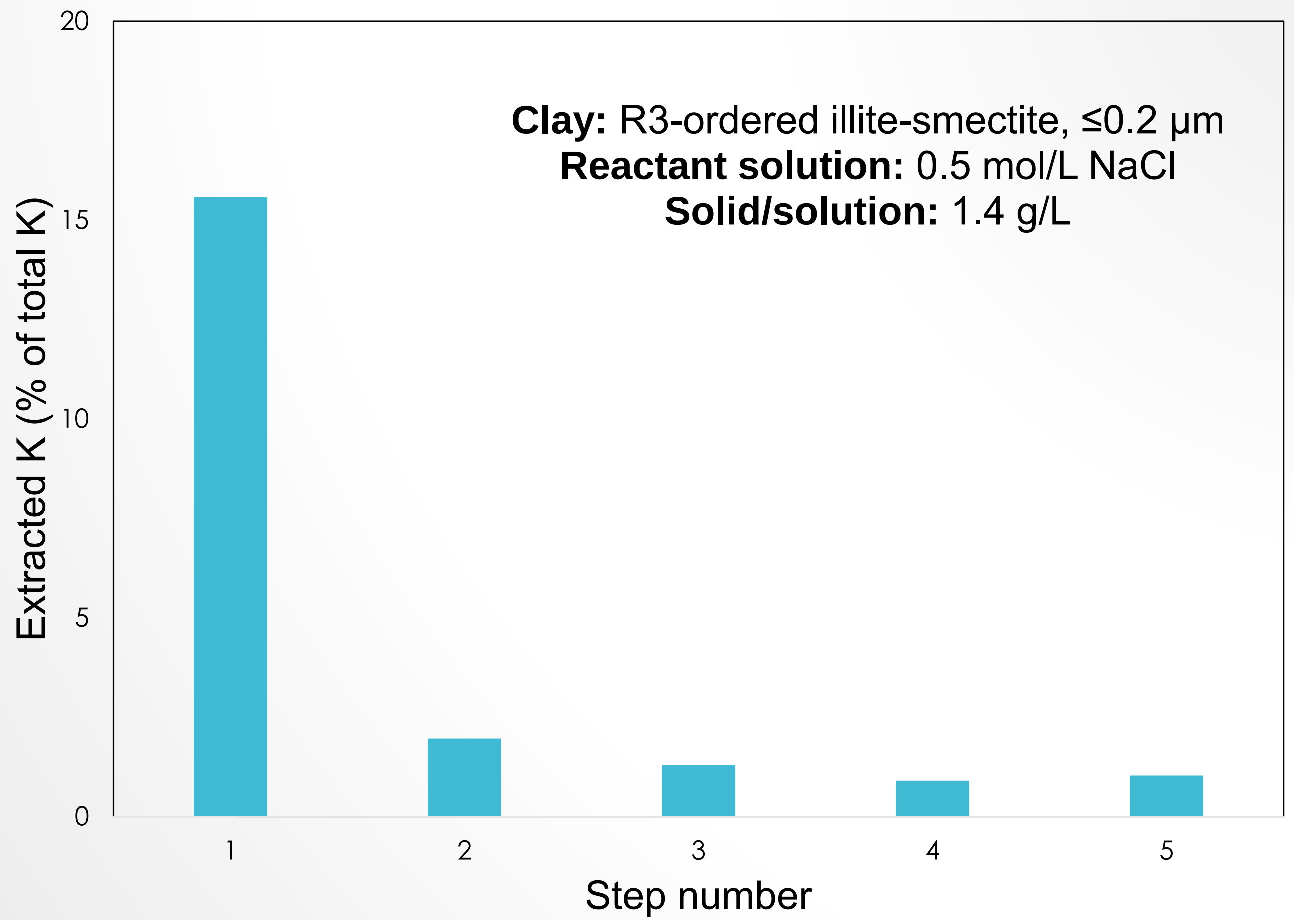
- A portion of the very fine clay, not previously treated, was treated five times with 0.5 mol/L NaCl solution at room temperature, solid/solution ratio 1.4 g/L.
- The potassium extracted in each step was measured.
- K-Ar age values of the untreated and the sodium-saturated clay were determined.

Results of this study:

Extracted potassium:

- Detailed results from MAB-0101 ≤0.2 μm show about 18% of the original potassium was exchangeable.

Potassium removed from MAB-0101 <0.2 µm during stepwise sodium-saturation treatment.



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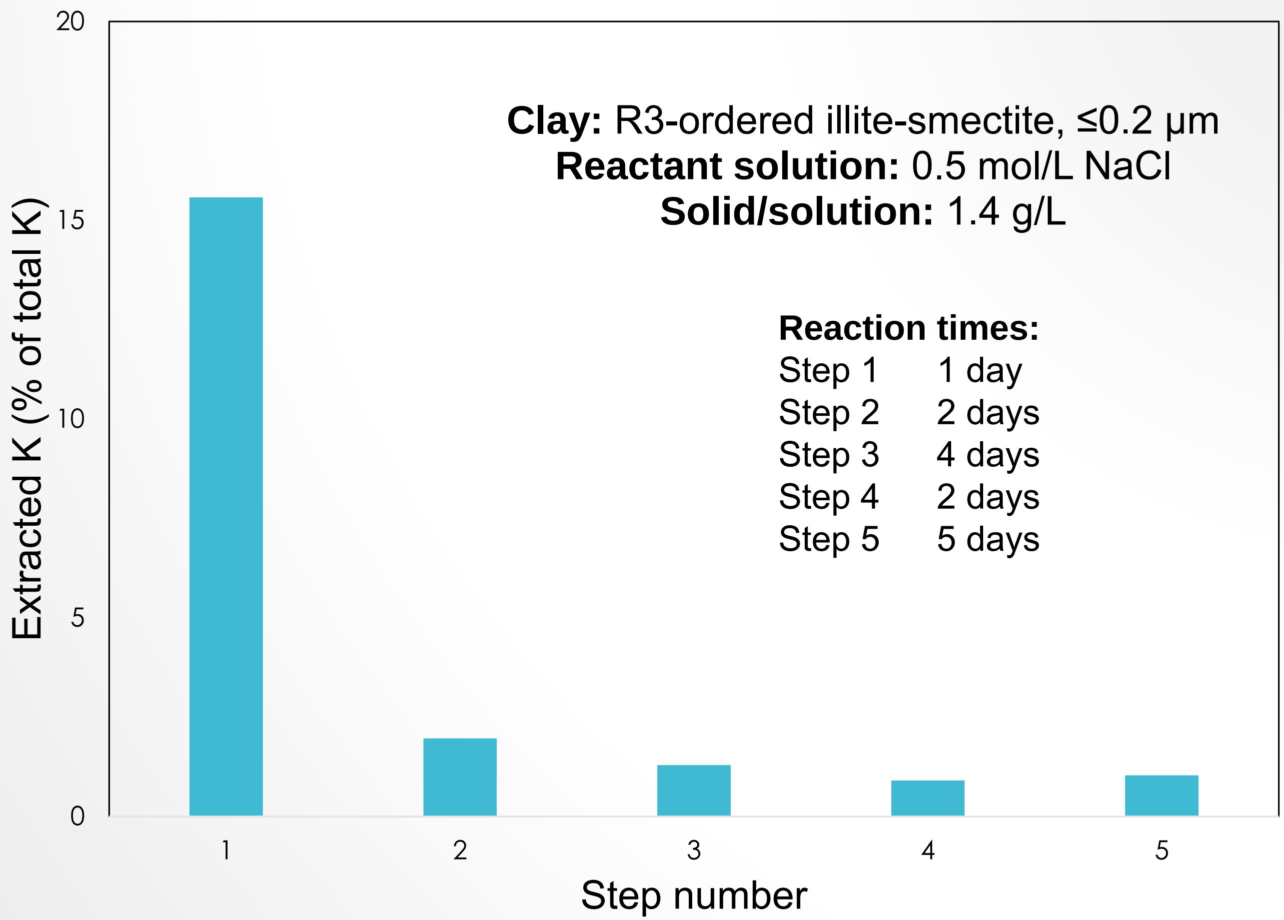

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- 12% of the potassium was extracted from A318 <0.1 µm.
- Extracted potassium from the two portions of TM29 <0.1 µm represent 41% and 39% of the original potassium.

Results of this study:

K-Ar age values:

- The K-Ar age values of untreated portions and sodium-saturated portions of the very fine clays are presented in the following slides.

- Observed decreases in the ratio of potassium to radiogenic argon are compared to the amounts of potassium extracted during sodium saturation.

A318 <0.1 μm

from the Early Ordovician (488–468 Ma) Cap Des Rosiers Group
Gaspé Peninsula, Québec

	Potassium as K (mass %)	K-Ar age value (millions of years)
Untreated	2.22	378
Octadecylammonium-intercalated	1.94	419

- From Salah Shata's Ph.D. thesis, McGill University

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Sodium acetate buffer solution-treated	2.96	417

- The increase in potassium content upon treatment with the buffer solution indicates destruction of components other than the K-bearing clay.

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Untreated	2.22	378
Octadecylammonium-intercalated	1.94	419
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- The K-Ar age value increased by 10%. The ratio of potassium to radiogenic argon decreased by 10%.

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- The K-Ar age value increased by 10%. The ratio of potassium to radiogenic argon decreased by 10%.
- 12% of the potassium was extracted.
- The results support the idea that little, if any, radiogenic argon is associated with exchangeable potassium.

MAB-0101 ≤0.2 μm

Illite-smectite from altered gneiss, Johannes ore body, Malmberget, Sweden

	Potassium as K (mass %)	K-Ar age value (millions of years)
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Sodium chloride-treated	6.1	838

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- About 18% of the original potassium was exchangeable.

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Untreated	7.7	759
Sodium chloride-treated	6.1	838

- The K-Ar age value increased by 10%. The ratio of potassium to radiogenic argon decreased by 12%.
- About 18% of the original potassium was exchangeable.
- Experimental error may account for the difference between 18% and 12%, or some ‘non-exchangeable K and its radiogenic argon may have been extracted, or the exchangeable K was associated with one-third as much radiogenic argon as was the non-exchangeable K.

TM29 <0.1 μm

from the Middle Ordovician Deslandes Formation, but within the thermal halo of the McGerrigle Mountains Pluton Gaspé Peninsula, Québec

	Potassium as K (mass %)	K-Ar age value (millions of years)
Untreated	2.11	159
Octadecylammonium-intercalated	0.46	296

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- The small potassium content of the octadecylammonium-intercalated clay is due to replacement of K that was in "expandable illite" by alkylammonium ions.

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- The small potassium content of the octadecylammonium-intercalated clay is due to replacement of K that was in "expandable illite" by alkylammonium ions.
- There are two aspects of the reduction of K content: (1) removal of K, and (2) increase in mass of the solid phase as K (molar mass 39.1 g/mol) is replaced by octadecylammonium (270.5 g/mol).

TM29 <0.1 μm

	Potassium as K (mass %)	**K-Ar age value (millions of years)**
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Sodium acetate buffer solution-treated	1.59	290

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Octadecylammonium-intercalated	0.46	296
Sodium acetate buffer solution-treated	1.59	290
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- Potassium content decreased upon treatment with the buffer solution, but not nearly as much as it decreased upon intercalation of octadecyammonium.

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- K-Ar age values increased 82% upon treatment with the buffer solution, and the ratio of potassium to radiogenic argon decreased 48%.

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- K-Ar age values increased 82% upon treatment with the buffer solution, and the ratio of potassium to radiogenic argon decreased 48%.
- Extracted potassium was only 40% of the original potassium.

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Sodium acetate buffer-treated second portion	1.40	294

- K-Ar age values increased 82% upon treatment with the buffer solution, and the ratio of potassium to radiogenic argon decreased 48%.
- Extracted potassium was only 40% of the original potassium.
- The difference between 40% and 48% is likely due to experimental error. Weighing error can be large for very fine clay.

Conclusions of this study:

- Very fine illite-smectite separated from rock without chemical treatment can have exchangeable potassium that is a significant fraction of the total potassium.

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- Little if any of the exchangeable potassium on the studied clays was associated with radiogenic argon.

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- Very fine illite-smectite separated from rock without chemical treatment can have exchangeable potassium that is a significant fraction of the total potassium.
- Little if any of the exchangeable potassium on the studied clays was associated with radiogenic argon.
- Clay prepared for mineralogical study without chemical pre-treatment should have its exchangeable potassium removed before K-Ar measurements begin.

Recommendations for further study:

- Do similar K-Ar measurements of coarser clay separates for comparison.

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- Do K-Ar measurements on fine clay after each of a set of repeated treatments with sodium solution over an extended time period, to pinpoint when radiogenic argon in significant quantity begins to accompany the extracted potassium.

Recommendations for further study:

- Do similar K-Ar measurements of coarser clay separates for comparison.
- Do K-Ar measurements on fine clay after each of a set of repeated treatments with sodium solution over an extended time period, to pinpoint when radiogenic argon in significant quantity begins to accompany the extracted potassium.
- When possible to do so, measure both extracted potassium and extracted argon—a more sensitive way to pinpoint when radiogenic argon in significant quantity begins to accompany the extracted potassium