

but a significant part of the variation is probably a result of experimental technique. These data suggest that it may be necessary to use both cation exchange capacity and surface charge density vs. mole % Al_2O_3 to test for errors in cation exchange capacity and surface area determination or for the presence of other minerals which would effect these characterizations.

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U.S. Geological Survey
Menlo Park
California 94025
U.S.A.

E. A. JENNE

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Effects of repeated NaTPB-alteration and K-fixation upon a phlogopite

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THE PARTICLE size of a phlogopite "weathered" in the laboratory by repeated K-removal and K-fixation was observed to decrease solely as a result of the "weathering" process. Structural expansion of the mica by hydrated cations during exchange reactions may produce strain sufficient to induce particle break-up (Brown and Newman, 1970). As particle size decreased, the extent to which interlayer potassium became non-exchangeable increased. This process of particle size reduction and its resultant effect on K-exchange properties of the mineral can occur equally well in both the laboratory and in nature.

To accomplish the "weathering," a 15-20 μ (e.s.d.) fraction of phlogopite, $(\text{K}_{0.92}[(\text{Mg}_{0.32}\text{Al}_{0.38}\text{Fe}_{0.13}^{2+}\text{Fe}_{0.01}^{3+}) \times (\text{Si}_{3.01}\text{Al}_{0.99})\text{O}_{10}\text{Cl}_{0.02}\text{F}_{1.10}(\text{OH})_{0.88}])^*$, was repeatedly cycled through successive K-extractions using NaTPB (sodium tetraphenylboron) solutions (Scott *et al.*, 1959, 1960a, 1960b, 1962a, 1962b, 1966, 1968), followed by K-fixation using N KCl solutions. Five cycles were completed, one cycle being denoted as the combination

of K-extraction and reintroduction of potassium into the mica (See Flow Chart, Fig. 1). In cycle 3, however, Mg-saturation followed K-removal, since more complete K-saturation was expected with Mg rather than Na as the complementary ion (Brown and Newman, 1970).

Equal amounts of mica and NaTPB mixed with 200 ml of N NaCl solution were agitated constantly with a magnetic stirrer. Alteration was continued until no more potassium could be removed. The rate of K-extraction was followed by analyzing for K and Na, representative mica samples taken periodically during the alteration period. The KTPB precipitate was removed from the samples using 4 washes with 70%(v/v)acetone-30%(v/v)N NaCl followed by 3 rinses with 70%(v/v)acetone-30%(v/v)water.

Potassium was "fixed" into the altered micas (the basal spacing collapsed from 12.2 to 10.1 Å) by washing the samples 4 times with N KCl solution; the samples were shaken overnight after each KCl application. After K-saturation excess KCl was removed with 3

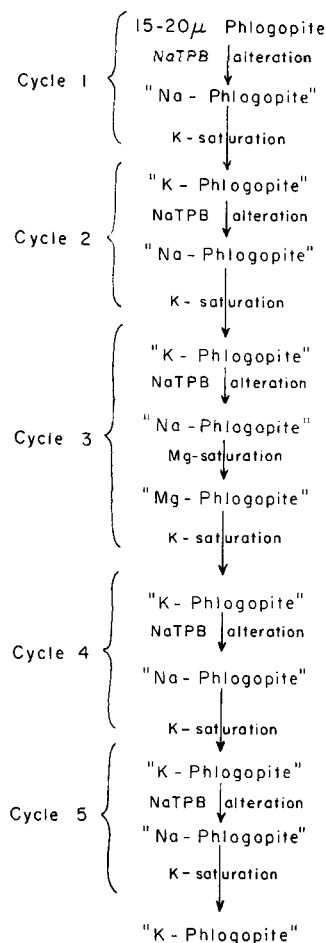


Fig. 1. Flow chart of the "weathering" process.

water washes and the samples were dried overnight at 105°C.

At the beginning of each cycle, (a) the samples were characterized chemically using atomic absorption for Mg, Fe (total), K, and Na analyses, and colorimetric techniques for Si, Al, and Fe²⁺ analyses (Pruden and King, 1969), (b) powder X-ray diffraction data were obtained using conventional techniques and a GE XRD 6 diffractometer and (iii) the percentage of particles greater than 15 μm was determined using sedimentation fractionation.

The data represented in Fig. 2 show that the initial rate of native K-removal from the phlogopite was extremely slow compared with subsequent release of "fixed" potassium (Ellis and Mortland, 1959; Brown and Newman, 1970). Although the initial rates of release of the "fixed" potassium were the same for cycles 2-5, the total amount of potassium which could be removed decreased considerably with each succeeding cycle. In cycle 1, sixteen days were required before no further loss of potassium was observed. The total potassium remaining in the mica at the end of cycle 1 (not shown in Fig. 2) was 1.91%.

The increased difficulty of complete K-removal with each succeeding cycle is attributed to the decreasing particle size. (No chemical change was observed after cycle 1 when a small amount of ferrous iron was oxidized and the layer charge lowered slightly). By the end of cycle 5 nearly all of the mica was reduced to less than 15 μm, with some of the particles in the less than 1 μm range (Table 1).

No single factor can be cited for the irreversibility of the K-exchange reaction—irreversible in the sense that the properties of the original mica are not reconstituted with K-fixation. Any one, or all, of various factors previously suggested may contribute to the observed behavior: (a) reduction of layer charge during the alteration (Ellis and Mortland, 1959), (b) reduction of crystal perfection as indicated by slightly larger basal spacings of the K-saturated alteration products than for the original

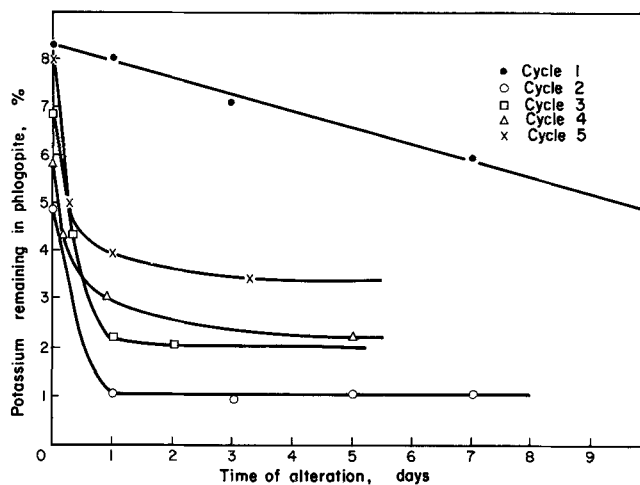


Fig. 2. Rate of potassium release from phlogopite.

Table 1. Interlayer cation content and percentage of particles greater than 15μ at the beginning of each cycle

Cycle	Moles of interlayer cations per half unit cell (K-saturated)			Percent of particles greater than 15μ
	K	Na	Total charge	
1	0.92	0.00	0.92	83†
2	0.45	0.45	0.90	56
3	0.68	0.20	0.88	32
4	0.80*	0.09	0.89	—
5	0.76	0.12	0.88	17
6	0.73	0.15	0.88	7

*Some Mg present (see Flow Chart) added to the K value.

†It is expected that the true value for $>15\mu$ particles is close to 100%; however, the sedimentation method used allowed a small percentage of $15\text{--}20\mu$ particles to be included in the $<15\mu$ fraction.

mica (Brown and Newman, 1970), or (c) water molecules trapped in the interlayer region during K-fixation which facilitate the Na-K exchange reaction in the altered mica (Barshad, 1954).

Similar results have been reported by Scott (1968) for the effect of particle size on potassium exchangeability. However, particle size reduction was obtained by dry grinding of the micas prior to NaTPB alteration. Thus, a question remained concerning the relationship between the observed decreases in K-exchangeability and the adverse effects of grinding on mineral structure.

Following cycle 5, over 40% of the potassium in this phlogopite was non-exchangeable, indicating a particle size effect greater than Scott (1968) observed with phlogopite but similar to the maximum effect obtained with muscovite. The greater K-retention of this phlogopite is attributed to its high fluorine content ($\sim 5\%$), which causes an affinity for potassium similar to that of dioctahedral micas (Rausell-Colom *et al.*, 1964; Newman, 1969).

With the phlogopite used in this experiment, a slight reduction in net negative charge on the layers was observed during the first 11 days of alteration (cycle 1), only one quarter of which could have resulted from ferrous iron oxidation. Repeated K-removal and fixation did not reduce the layer charge below that occurring initially.

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M. B. McBRIDE*

SALLY WENTWORTH ROSSI†

Department of Land Resource Science

University of Guelph

Guelph, Ontario, Canada

*Present address: Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48823, U.S.A.

†Present address: Istituto di Chimica Agraria, Università delgi Studi, Via S. Giacomo 7, 40126 Bologna, Italia.