

POTASSIUM-DEPLETED MUSCOVITE. PART I. PREPARATION
USING FILTRATION PROCESS FOR TREATMENT WITH
MOLTEN LITHIUM NITRATE¹

by

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ABSTRACT

The reaction between molten lithium nitrate and muscovite does not go to completion in a single treatment because of the equilibrium restriction imposed by the presence of potassium in the melt. An apparatus consisting of a stainless steel vessel with a porous stainless steel filter, valve and vacuum connections was designed to eliminate this restriction and to provide for more complete removal of the equilibrium melt in each successive treatment.

Macroscopic swelling of the muscovite in the molten lithium nitrate was observed after prolonged treatment. x-Ray diffraction examination of samples of solidified melt revealed intracrystalline swelling in the muscovite.

INTRODUCTION

The weathering process in micas is accompanied by a loss of potassium and an increase in water (Denison, Fry and Gile, 1929). This relationship has been recognized through chemical analysis of differentially weathered micas. x-Ray diffraction properties of the weathering products of mica have been used as criteria for establishing weathering sequences. But such series are always uncertain because of the lack of contiguity of the series members. This results from the impossibility of sampling a specific mica throughout its natural weathering sequence. Therefore, different formations which have been exposed to weathering for different lengths of time are sampled at essentially the same geologic instant. Their characteristics are used as evidence of the course of alteration of crystal structure during weathering.

The laboratory equivalent of a contiguous weathering series for micas has been approached through the removal of interlayer potassium by mass action replacement. Leaching with aqueous salt solutions (Barshad, 1948; Mortland, 1958) or with potassium complexing solutions (De Mumbrum, 1959) has been successful for biotites, but has not been satisfactory for muscovite. Treatment with molten salts (White, 1956) has removed more potassium from a muscovite. The extent of potassium removal was found to increase with increasing

¹ Journal Article no. 1510, Purdue University Agr. Exp. Sta., Lafayette, Indiana.

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ratio of melt to muscovite, indicating that replacement of the potassium was limited in degree of completion by a quasi-equilibrium reaction. This paper describes a filtration technique for overcoming the equilibrium restriction by periodic replacement of the melt.

The authors gratefully acknowledge the support of the National Science Foundation in this research by a grant (NSF G-6063) through the Purdue Research Foundation (PRF 2007).

EXPERIMENTAL

Preparation of Muscovite

The mineral used in this study is a mechanically delaminated muscovite obtained as Delamica from English Clays Lovering Pochin and Company, Ltd., St. Austell, Cornwall, England. This is a representative dioctahedral muscovite with practically all of the isomorphous substitution in the tetrahedral layer. It is essentially pure as obtained, the principal impurity being a small amount of kaolinite. Its chemical properties have been described elsewhere (White, 1956).

From the original sample, the 5–2 μ (equivalent spherical diameter) fraction was separated using successive dispersions, sedimentations, and decantations. This fraction was dialyzed, then dried from the suspension by evaporating most of the water at room temperature by circulating air around the dialysis tubing, and oven-drying at 105°C for 24 hr.

Filtration Apparatus

In preliminary experiments a medium porosity fritted Pyrex glass filter was used for leaching small samples (Spain, 1958). Molten lithium nitrate was allowed to flow by gravity through a 60 ml funnel containing the muscovite, the rate being about 50 ml in 2–3 hr. The principal disadvantages of this method were cracking of the glass funnel due to thermal shock or reaction of the glass with lithium melt, or both.

A modified apparatus consisting of a stainless steel vessel with a porous stainless steel filter was designed to eliminate these objections (Fig. 1). The apparatus consists of a tripod-supported body of 18–8 stainless steel with a cylindrical internal cavity at the bottom of which is a micro metallic porous filter made of 304 stainless steel and having maximum pore size of 2 μ . Filtration was controlled by a copper-bronze "B" gas valve below the filter.

Initial attempts at gravity filtration were unsuccessful, probably owing to blockage by entrapped air. Once the filter was saturated with melted lithium nitrate, the filtration proceeded successfully although rather slowly. Because of the small difference in specific gravity between the Delamica and the lithium nitrate melt, the Delamica failed to sediment, remaining rather loose and fluffy after gravity filtration. This limited the amount of molten lithium nitrate which could be added for the succeeding treatment.

In order to hasten filtration and secure more complete removal of the melt, a vacuum trap was constructed and connected by copper tubing to the outlet valve of the filter vessel, the entire apparatus being confined within the muffle of the furnace at 300°C. The vacuum was supplied by an aspirator connected to the vacuum trap by a copper tube inserted under the furnace door. Application of vacuum reduced the filtration time from about 2 hr to less than 10 min and produced a filter cake that was obviously freer of melt.

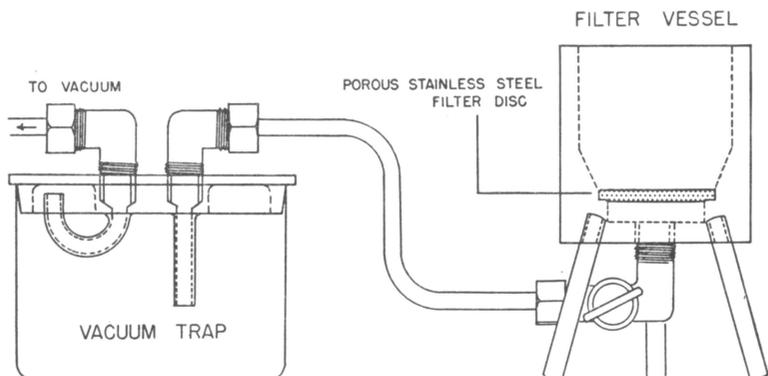


FIGURE 1.—Schematic diagram of stainless steel filter vessel and vacuum trap for repetitive treatment of mica with molten lithium nitrate.

Method of Treatment

Approximately 15 g of 5–2 μ Delamica was mixed with crystalline, reagent grade lithium nitrate to promote contact between particles, placed in a 600 ml stainless steel beaker in a muffle furnace at 300°C, and stirred frequently. After 12 hr, the molten lithium nitrate–Delamica mixture was transferred to a stainless steel filter vessel and filtered. Thereafter, the equilibrium melt was filtered off every 12 hr and 75 g of fresh molten lithium nitrate was added with stirring.

Test samples were removed at 166, 254, 355 and 409 hr by allowing small increments of filter cake to solidify on a stainless steel spatula. These samples were suspended in water, washed free of lithium, and solvated with ethylene glycol; the effects of potassium removal on expansion characteristics were determined by x-ray diffraction measurements of the d -spacings.

At the completion of the molten salt treatment, the potassium-depleted Delamica, with the lithium nitrate remaining after filtration, was suspended in de-ionized water. Free lithium and other salts were removed by dialysis in a small-batch condenser-type dialyzer constructed by placing dialysis tubing within a condenser jacket. About 100 ml of suspension was placed in the central dialysis tubing and mechanically agitated with a spiral glass rod stirrer. De-ionized water in the jacket was replaced thoroughly every 15 min

by a timer-controlled solenoid valve. The concentration of free salts was measured by flame photometric determination of lithium in the supernatant liquid of a centrifuged aliquot of suspension. Dialysis was considered complete when the free Li concentration reached less than 1 ppm in the suspension liquid.

RESULTS AND DISCUSSION

The diffraction patterns (Fig. 2) of the Delamica before treatment and after the treatment intervals illustrate the progressive and complete disappearance of the intensity maximum at 10 Å which is characteristic of the

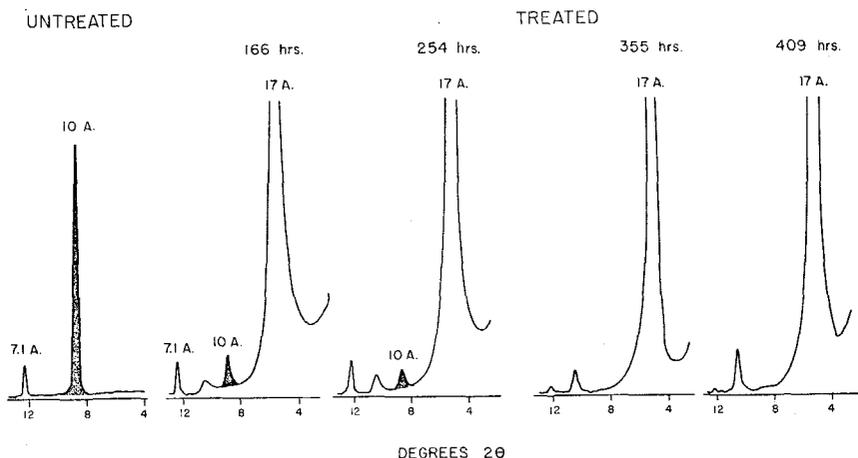


FIGURE 2.—Diffractometer tracings of muscovite reacted with molten lithium nitrate at 300°C for varying periods of time. The samples were solvated with ethylene glycol; the unreacted mica gives a peak at 10 Å (stippled) while the reacted mica gives an expanded spacing of 17 Å, Cu K_{α} radiation.

unexpanded d_{001} spacing of muscovite. Simultaneously, a diffraction maximum appears at 17 Å corresponding to the spacing of a 2 : 1 lattice expanded by 2 layers of ethylene glycol molecules. This change was accompanied by a reduction in total potassium content from 7.45 percent in the untreated Delamica to 0.70 percent after 409 hr treatment.

Intracrystalline expansion of the muscovite in the LiNO_3 melt was studied by making x-ray diffractometer tracings of the solidified melt. Portions of the LiNO_3 melt containing the reacted mica were poured into aluminum foil molds and maintained at 300°C for several hours. This permitted the mica flakes to sediment to the bottom of the mold with a considerable degree of preferred orientation. The mold containing the melt was then allowed to cool and the aluminum foil was stripped from the melt tablet and the bottom

surface of the tablet used as the diffracting surface. Diffractometer tracings of the tablet (Fig. 3) show the expanded spacing of 11.3 Å for the reacted mica in addition to the 10 Å spacing of the unreacted muscovite.

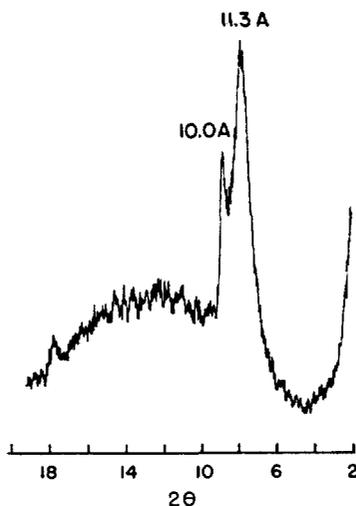


FIGURE 3.—Diffractometer tracing of preferentially oriented muscovite flakes in solidified lithium nitrate after treatment for 174 hr at 300°C. Intensity maximum at 11.3 Å shows presence of expanded material; 10 Å peak is typical of unexpanded mica.

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