

MINERALOGY and GEOLOGY

Infra-red Investigation of the Migration of Lithium Ions into Empty Octahedral Sites in Muscovite and Montmorillonite

IN work on the reaction of molten salts with layer-lattice silicates, it was found that molten lithium nitrate removed a large portion of the potassium from muscovite ($< 5\mu$) and lithium was fixed in a not readily exchangeable manner¹. It was suggested that lithium ions migrated into the vacant octahedral positions of the dioctahedral micas in a manner similar to that postulated previously by Hofmann and Klemen² and Greene-Kelly³ for lithium-saturated montmorillonite on heat treatment. X-ray diffraction measurements of the 060 spacing of muscovite treated with lithium showed no significant increase, whereas an increase might be expected in conversion of a dioctahedral composition to a trioctahedral composition. Attempts to apply the infra-red technique of Serratosa and Bradley⁴ for determination of the orientation of OH-bond axes to indicate formation of a trioctahedral composition were also unsuccessful.

Stubican and Roy⁵ observed that an increase in the amount of magnesium in octahedral sites in a muscovite-phengite series caused the absorption band with frequency 935 cm^{-1} to become more poorly defined. They allocated this band to $\text{H-O} \dots \text{X}^{3+}$ by comparison of spectra for minerals with their deuterated synthetic analogues, and showed that it moves from 935 to 910 to 827 cm^{-1} as the ions change from aluminium to gallium to iron. Serratosa⁶ has assigned the 915 cm^{-1} band in montmorillonite to $\text{H-O} \dots \text{Al}^{3+}$ on the basis that this band decreases in intensity at a rate concomitant with those of the stretching frequency (3,600 cm^{-1}) on heating to successively increased temperatures.

The dioctahedral compositions of the muscovite and montmorillonite structures provide each structural OH with two octahedral ion neighbours, predominantly aluminium in these two minerals. The effect of heavier octahedral neighbours or a greater number of neighbours on the OH bending frequency is considerable^{6,8}.

If lithium ions enter the empty octahedral sites in muscovite and montmorillonite, one would expect that the three octahedral neighbours (2 Al, 1 Li) of the OH would anchor it more firmly and lower its bending frequency. Fig. 1 shows superposed absorption records of the 5–2 μ fraction of (A) untreated muscovite (Delamica) and (B) the same material after treatment with molten lithium nitrate for 480 hr. The absorption feature appearing at 915 cm^{-1} in the untreated muscovite is absent after the treatment with lithium nitrate. In addition, the features at 828 cm^{-1} and 798 cm^{-1} are eliminated. Treatment of montmorillonite (Wyoming bentonite) with molten potassium nitrate at 350° C. did not affect the 915 cm^{-1} OH bending frequency, whereas treatment with molten lithium nitrate at 300° C. eliminated the band. These results give experimental verification of migration of lithium ions into empty octahedral sites in muscovite and montmorillonite as postulated previously.

A more detailed account of this work will be published elsewhere. We acknowledge helpful discussions with Dr. W. F. Bradley. The work was supported in part by a grant from the National Science Foundation (NSF G6063). The assistance of

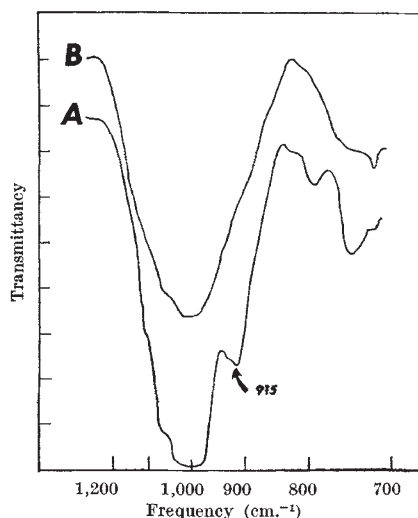


Fig. 1. Superposed infra-red spectra of muscovite (Delamica) (5–2 μ) (A) untreated and (B) treated with molten lithium nitrate at 300° C. for 480 hr.

Dr. John Amy and Marcia Dilling, Chemistry Department, in obtaining the infra-red spectra is gratefully acknowledged.

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¹ White, J. L., *Nature*, **174**, 799 (1954); *Proc. Fourth Nat. Conf. on Clays and Clay Minerals*, U.S. Nat. Acad. Sci.-Nat. Res. Coun. Pub. 456, 133 (1956).

² Hofmann, U., and Klemen, R., *Z. anorg. Chem.*, **262**, 95 (1950).

³ Greene-Kelly, R., *Clay Minerals Bull.*, **1**, 221 (1952); *Nature*, **170**, 1130 (1952).

⁴ Serratosa, J. M., and Bradley, W. F., *J. Phys. Chem.*, **62**, 1164 (1958).

⁵ Stubican, V., and Roy, R., abst. Pittsburgh, Pa., meeting of the Mineralogical Society of America (Nov. 1959); abst. Cleveland meeting of the American Chemical Society (April 1960).

⁶ Serratosa, J. M., *Amer. Mineral.*, **45**, 1101 (1960).

Mammoths in the Cotswolds

RECENT examples of fleeting opportunities provided to archaeologists, geologists and others by modern methods of excavation are common knowledge; all too often an opportunity passes before advantage can be taken of it. The following notes illustrate the fruits of sustained observation on one hand, and of good fortune on the other, which we have witnessed in the past year or so.

First, pits worked over a period at Great Chessells, near Bourton-on-the-Water, Glos., in a headwater tributary of the Windrush, were watched by Mrs. Helen E. O'Neil, because she was excavating a Romano-British site progressively destroyed by exploitation. She obtained from the gravels an important collection of mammoth teeth and two molars of woolly rhinoceros¹. They are comparable with material collected over many years from the lower gravels of the Summertown-Radley terrace of the Upper Thames and its tributaries around Oxford. The association united the headwaters of the headwaters of one such tributary, namely, the Windrush, with those of its confluence with the Thames.

Further, material of the same form as these molars of mammoth was recovered recently by one of us