

NOTES AND NEWS

OH-F EXCHANGE IN FLUORINE PHLOGOPITE

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INTRODUCTION

Synthetic fluorine micas have assumed an important part in the literature of crystal chemistry, and the substances themselves are now commercial products. In the commercial operation the intergrowth of crystals and the bonding action of any residual melt make it difficult to split off all the usable mica. Noda, *et al.* (1) have successfully used mild hydrothermal leaching to break up the aggregates or dissolve (or devitrify) the intercrystal bonding material. This also appeared to increase the ease of splitting of the mica, and its flexibility.

Temperature-weight decrease curves of treated products suggested (by the appearance of low temperature weight loss) the formation by the hydrothermal treatment of a small amount of hydroxyl-phlogopite. A sudden increase of gas evolution at 850° C. from a heavily treated product was observed when it was heated in an evacuated vessel. This is probably proof of the formation of hydroxyl-phlogopite, because natural hydroxyl-phlogopite showed similar behavior in the same vessel (1). Romo and Roy (2) have studied the exchange of F⁻ for (OH)⁻ in various layer minerals and found that in many cases actual replacement of OH by F in the lattice at low temperatures appeared unproved, although large amounts of F⁻ ions were removed from solution, and (OH)⁻ released.

Thus, it was our intention to approach the equilibrium exchange product from the F-rich end. If extensive solid solution exists between the F and OH mica—as many analyses would suggest—it should be possible to obtain partial replacement in the F-mica lattice of the F⁻ by OH⁻.

EXPERIMENTAL PROCEDURE

Cleaned splittings of F-phlogopite were broken up in a blender, and “glassy” particles were elutriated off. The small clean splittings were ground in a blender; and particles below <2 μ e.s.d. were collected and dried at 110° C.

This material was reacted with water and dilute KOH solutions in

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silver-lined Morey bombs at temperatures between 200° and 500° C. for periods ranging from 3 to 30 days. The products were examined petrographically and by *x*-ray diffraction.

RESULTS

The data obtained are tabulated in Table 1. Below 300° C. with water or .44 N KOH there appeared to be no effect on the F-mica. However, at 275° C. with 1.74 N KOH, and above 400° C. with both .44 N and 1.74 N KOH it was found that each mica diffraction maximum was resolved into a doublet. Since one set of lines remained the same throughout, and the new lines were always the same, it was clear that the F-mica was reacting to give the same new phase—in different amounts depending on the condition of the runs.

Table 1. DATA ON HYDROLYSIS OF F-PHLOGOPITE

Reagent	Temp. (°C.)	Pressure (Kg/cm ²)	Time (Days)	Products*
H ₂ O	240	s.v.p.	18	No change detected
H ₂ O	460	700	3	No change detected
H ₂ O	460	700	19	No change detected
H ₂ O	460	700	29	No change detected
0.44 N KOH	235	s.v.p.	6	No change detected
0.44 N KOH	425	350	9	Two micas. ~40% new phase
0.44 N KOH	425	350	13	Two micas.
1.74 N KOH	425	350	13	Two micas. ~40% new phase
1.74 N KOH	425	350	8	Two micas. 40% new phase
1.74 N KOH	275	s.v.p.	15	Two micas. 20% new phase

* The % conversion is estimated very roughly from the ratio

$$\frac{I_{00l}(\text{OH-mica})}{I_{00l}(\text{F-mica})}$$

for $l=3$ and 5 .

Products treated with water up to 460° C. for 29 days showed no change when examined by the *x*-ray diffraction method. Also, no change was observed in products treated at room temperatures up to 90 days with 0.9 N or 0.45 N KOH.

At first it was not at all easy to determine what the new phase was. The only *x*-ray data—including data obtained by us on natural phlogopites (containing iron)—suggested that, if anything, OH-phlogopite would have a very slightly smaller basal spacing than the fluorine analogue.

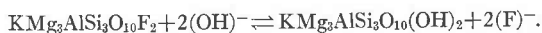
The basal spacing (001) of fluorophlogopite was measured and found to be $9.98_4 \pm 0.005 \text{ \AA}$, while the spacing for the new diffraction peak was $10.15_4 \pm 0.01_7 \text{ \AA}$, i.e., $0.17 \pm 0.02 \text{ \AA}$ larger than that of fluorophlogopite.

About this time the data of Yoder and Eugster (3) were made available to us. They reported that the 001 spacing¹ of synthetic OH-phlogopite is approximately 0.17 \AA larger² than synthetic F-phlogopite. This difference was immediately seen to be essentially identical to that given above. Further, the relative intensity data also lent support to this view. In the newly formed phase the intensity of the 002 and 004 reflections appeared to be considerably (more than $2\times$) stronger compared to 001 and 003 in the original F-mica. From the above paper it can be seen that this is the case when synthetic OH-phlogopite is compared with synthetic fluorophlogopite.

The infra-red absorption spectra did not prove to be useful as a direct measure of the extent of OH replacement. Only in the "most-reacted" samples was evidence obtained for a broad absorption band with a maximum near 3μ rather than 2.75μ .

Powder diffraction data obtained with $\frac{1}{3}^\circ$ 2θ /min scanning rate in which ± 0.01 2θ precision is obtained showed that in the various samples the two spacings were essentially constant although the ratio of the sets of intensities varied greatly depending upon the amount of conversion. In the "most reacted" run approximately equal amounts of the two phases were formed.

These data indicated unambiguously that under the conditions of reaction very little solid solution exists between the two end members and that we have a true exchange reaction of the type.



Estimates from the intensity ratios of F to OH reflections of the amount of conversion indicated that approximately twice as much conversion occurs in the same time at 425° C. as at 275° C. , temperature being more important than the change in concentration from 0.44 N to 1.7 N KOH. Due to the number of possible complications³ no attempt was made to assign significance (as far as reaction kinetics are concerned) to the differences in extents of conversion.

In conclusion it can be said that these data indicate that there is no (or very little) partial solid solution between F-phlogopite and OH-

¹ Assuming for simplicity a one-layer cell in all cases.

² See the difference in 003 and 005 spacings in tables of d values for (OH) and F phlogopite in paper cited. Agreement of actual d values with ours is also excellent.

³ For example, partial leaking, effect of change of concentration of (OH) ion by reaction, effect of differing amounts of unweighed reactants, etc.

phlogopite at temperatures below 450° C.; and that if desired, F-micas could be converted to OH-mica by mild hydrothermal treatment in KOH solutions. It also indicates in connection with the data of Romo and Roy (*loc. cit.*) that at room temperature exchange by partial substitution of F for OH in the mica lattice should be very limited and that the "decomposition-reaction" mechanism for the fixation of F⁻ by micas is the more likely explanation. This poses a problem in connection with the genesis of phlogopites which may appear to contain large amounts of both fluorine and hydroxyl.

ACKNOWLEDGMENT

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A NEW OCCURRENCE OF EUCOLITE NEAR WAUSAU, MARATHON COUNTY, WISCONSIN

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Eucolite, a rare sodium-zirconium silicate, which has not been recorded before from north-central Wisconsin, was found in lujaurite while making a laboratory and thin section study of the rocks from an area 8 miles west of Wausau, Marathon County. Only 3 other localities for eucolite are known in the United States, and this is the first, as far as the writers are aware, in which the mineral is associated with the finer grained, aegirine-rich variety of nepheline syenite.

The syenites and nepheline syenites in the area are the latest in the series of the complex, crystalline rocks of Huronian age, which form a portion of the Canadian Precambrian shield, extending southward into Wisconsin. Both have aplitic and pegmatitic phases. Emmons (1953, p. 71-87) believes that the syenite and nepheline syenite occur as dikes along shear zones; and that the nepheline syenite originated by the replacement and recrystallization of granite, in an apparent roof-section of a batholith, effected by sodic feldspar solutions derived from the unmixing of potassic feldspars of the wall rocks.

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