CONVERSION OF PLAGIOCLASE TO NEPHELINE

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THIS communication reports the conversion of anorthite rich plagioclase to nepheline by the cation exchange reaction with sodium chloride. Two different conditions are employed: (*i*) reaction in the solid-state (around 750° C.) (Duffin, 1964), (*ii*) reaction in molten sodium chloride (at 900° C.). In molten sodium chloride, the oligoclase is found converted to a mixture of albite and nepheline.

METHOD

In one case the powdered mixture (200 mesh) sodium chloride (2·5 g) is mixed with the plagioclase (0·1 g) and maintained at 750° C. in a platinum crucible for 48 hours. In the other case, the mixture is heated to 900° C. and is maintained molten for 4 to 8 hours. After the interval, the cooled material is washed with water on a sintered glass septum, till free of chloride. The solid remaining undissolved is found to be nepheline and utilised for further investigation. Calcium is detected in the washings and is estimated by EDTA titrations using calcein as indicator.

ANALYSIS

The plagioclase feldspar used in this investigation is a phenocryst from the dolerite dyke of Nandydurg Mine of Kolar Gold Fields. The oligoclase used is from the acid charnockite of Halagur (Bangalore District).

The composition of the anorthite rich plagioclase is as follows:

$Na_2O = 3{\cdot}55\%$, $CaO = 13{\cdot}65\%$, $K_2O = 0{\cdot}22\%$, $Al_2O_3 = 31{\cdot}05\%$, $SiO_2 = 51{\cdot}3\%$, corresponding to that of 67% anorthite. The oligoclase has the composition $Na_2O = 6{\cdot}15\%$, $CaO = 4{\cdot}9\%$, $K_2O = 0{\cdot}35\%$, $Al_2O_3 = 25{\cdot}52\%$, $SiO_2 = 59{\cdot}92\%$ (30% anorthite). The product obtained from the ion exchange reaction of anorthite has the composition: $Na_2O = 18{\cdot}65\%$, $Al_2O_3 = 30{\cdot}71\%$, $SiO_2 = 50{\cdot}51\%$. The calcium and potassium content of nepheline obtained from the reaction in molten sodium chloride is below detection. The estimated lime content in the washed solution is 13·6% of the original sample. This indicates that nearly complete substitution of calcium occurs when the exchange is carried out with oligoclase.

INFRARED SPECTRUM

The I.R. spectrum is made use of to identify the different phases. The spectra of 67-anorthite (I), the converted material (II), and that of a natural sample of nepheline (III) are presented in Fig. 1. The spectrum of nepheline obtained from the solid-state reaction is identical with that of the natural sample. It is also clear from the spectrum that the nepheline obtained by the reaction is free of unconverted feldspar.

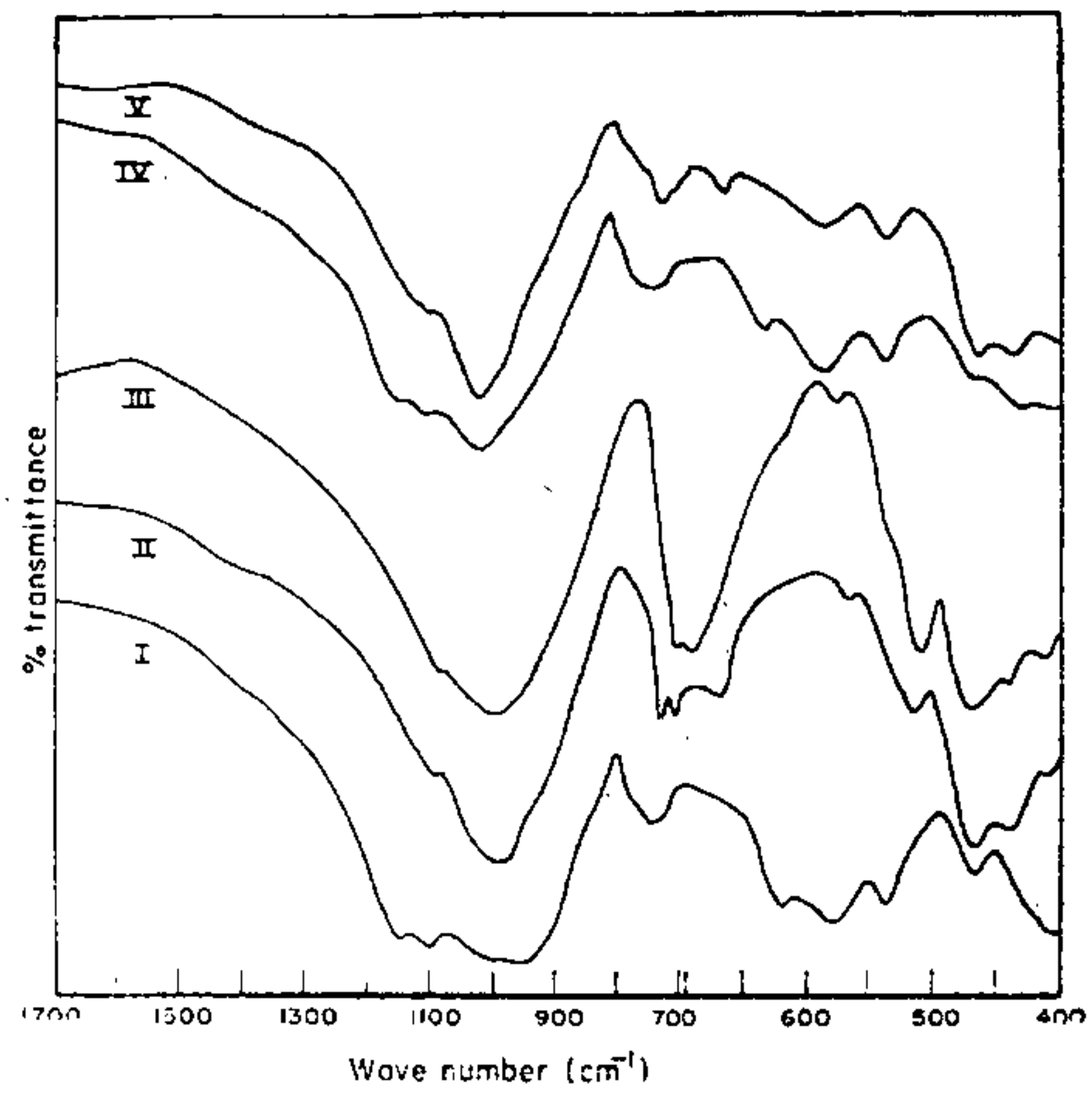

FIG. 1. Infrared spectrum. I, 67% anorthite; II, Converted sample; III, Nepheline (from Rajasthan); IV, 30% anorthite; V, Converted sample from 30% anorthite.

The spectrum IV is of the oligoclase while V is that of the same material heated in molten sodium chloride. Spectrum V indicates that the product is a mixture of albite and nepheline.

DISCUSSION

The conversion of anorthite to nepheline takes place by the cation exchange reaction as:

$$CaAl_2Si_2O_8 + 2NaCl = 2NaAlSiO_4 + CaCl_2.$$

It follows that the cation exchange is accompanied by the rearrangement of the silicate framework. In many reactions of aluminosilicates, it is envisaged that the substitution

of Ca^{+2} or Na^{+} occurs along with the addition or removal of Al^{+3} or Si^{+4} from the silicate framework. From the present set of experiments, it is evident that during the exchange of cations of unequal charges, the rearrangement of the silicate structure occurs in preference to the substitution or depletion of Al^{+3} or Si^{+4}. This is much more important in the case of 67% anorthite for which the reaction can be represented as :

$NaCa_2Al_5Si_7O_{24} + 4NaCl = Na_5Al_5Si_7O_{24} + 2CaCl_2$ ($NaAlSi_3O_8 : 2CaAl_2Si_2O_8$).

This results in a nepheline with Si : Al ratio of 1·4 with a lower sodium content. It is known that the natural samples of nepheline contain excess of Si over the theoretical amount and the variation in Si : Al ratio varies up to 1·4 (B. Mason, 1966). Therefore, such cation exchange reactions may be occurring in nature as well, resulting in nepheline of higher silica content.

The resemblance of the infrared spectrum of the natural sample of nepheline and that from the solid-state reaction is very striking. This clearly indicates the formation of nepheline by such solid-state reactions in nature. The natural samples of nepheline contain more of K^{+} and Ca^{+2} as impurity. The difference in the spectrum II and III (650–750 cm.$^{-1}$ and 400–450 cm.$^{-1}$ region) is due to the presence of these ions. On the other hand, nepheline obtained from the molten sodium chloride is completely devoid of K^{+} and Ca^{+} ions. Therefore, the I.R. absorption bands are clearly split. The same situation exists in the I.R. spectrum of albite and microcline (Lyons, 1967).

It may be expected that by heating plagioclase in molten potassium chloride gives rise to kaliophillite. But, it is observed that cation exchange takes place only to a certain extent (2·0% K_2O is taken by 67-anorthite, in molten KCl). This can be atributed to the difference in size of Ca^{+2} and K^{+}. In the case of sodium chloride melt, initially complete substitution of Ca^{+2} by Na^{+} in plagioclase takes place readily. Consequently, the silicate framework rearranges to accommodate another ion of Na^{+}. The initial substitution of K^{+} can be expected to be very slow. On the other hand, kaliophillite may be formed by heating celsian in molten KCl. Due to the non-availability of clesian, this has not been attempted.

1. Duffin, *Min. Mag.*, 1964, **33**, 812.
2. Lyons, R. J. P., *Physical Methods in Determinative Mineralogy*. Ed. J. Zussman, Academic Press, N.Y., 1967, p. 371.
3. Mason, B., *Principles of Geochemistry*, John Wiley and Sons, Inc., N.Y., 1966.

A NOTE ON AN INVARIANT OF SPHERICALLY SYMMETRIC SPACE-TIMES

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IN our recent investigations of spherically symmetric metrics, we have found that for the most general spherically symmetric metric

$$ds^2 = -Adr^2 - Bd\Omega^2 + Cdt^2 + 2Ddrdt,$$
$$d\Omega^2 = d\theta^2 + \sin^2\theta\, d\phi^2, \qquad (1)$$

where A, B, C, D are functions of r and t alone, the quantity

$$I = \frac{f_1 f_4 - f_5^2}{f_2 f_3} \qquad (2)$$

is an invariant under arbitrary non-singular transformations $(r, t) \to (\bar{r}, \bar{t})$ preserving spherical symmetry. Here f_1, f_2, f_3, f_4 and f_5 are the independent non-vanishing components of the curvature tensor R_{hijk} in the notations of Takeno[1] as given by

$$f_1 = R_{1212} = \frac{R_{1313}}{\sin^2\theta}, \quad f_2 = R_{1414}, \quad f_3 = \frac{R_{2323}}{\sin^2\theta},$$
$$f_4 = R_{2424} = \frac{R_{3434}}{\sin^2\theta}, \quad f_5 = R_{1224} = \frac{R_{1334}}{\sin^2\theta}. \qquad (3)$$

Since the variation of the gravitational field from point to point is mainly brought out by the curvature tensor, this invariant I is of interest. As we have found, this also seems to have a good geometrical interest.

Firstly, we have found that for all the solutions of the field equations

$$R_{ij} = 0 \qquad (4)$$