So far no other specimens have been investigated, that contain crystals large enough to permit the detection of such weak reflections. As the reflections are too weak for observance on powder photographs, it has not been possible to establish the frequency of occurrence of the two types of kalsilite.

Kalsilite joins the feldspar group of minerals in showing order-disorder of the Al and Si atoms and it is to be expected that further investigation of other minerals that carry Al and Si in four-fold coordination, such as nepheline, will reveal the occurrence of order-disorder. The prefixes *d*- and *o*- are suggested for the characterization of the disordered (*a* 5.15 Å) and ordered (*a* 8.9 Å) forms of kalsilite.

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# IDENTITY OF NOCERITE AND FLUOBORITE

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During an extensive investigation of the silicates and fluorides of calcium and magnesium performed in this Institute, we had the occasion to attempt the synthesis of a compound of the composition $Mg_3Ca_3O_2F_8$, which has been ascribed to the mineral nocerite. In the literature this rare mineral is described from only one occurrence in Nocera, Italy. It is found in volcanic tuffs, in geodes with abundant fluorite, and highly metamorphic inclusions of limestones which are locally dolomitic. Nocerite was described in these typical "piperno" tuffs for the first time by A. Scacchi (1), and repeatedly examined by other mineralogists (cf. Dana's "System of Mineralogy," 7th edition, vol. II. 1944, 1951, pp. 85 f.) Nocerite is hexagonal and is optically negative, with the refractive indices $\omega(Na)=1.5098$, and $\epsilon(Na)=1.4855$ (cf. F. Zambonini (2)); or $\omega=1.512$; $\epsilon=1.487$ (cf. E. S. Larsen (3)).

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Crystals of nocerite were subjected to an accurate *x*-ray examination by A. Scherillo (4). The most probable space groups were determined to be *C*6, or *C*6/*m*. The elementary cell constants are $a_0=8.84$ kX; $c_0=3.12$ kX. In view of the small amount of available pure crystal material, Scherillo was not able to make a complete chemical analysis. However, he discussed the evident difficulties in attempting to bring the formula usually ascribed to nocerite into harmony with the atomic groupings which should be postulated by the space groups indicated above.

All our attempts to synthesize a compound corresponding to the formula $Mg_3Ca_3O_2F_8$ have been in vain. In every case we only obtained mechanical mixtures of MgO, $MgF_2$, and $CaF_2$. No more successful were experiments in which were added small amounts of sodium compounds, which, according to some of the chemical analyses reported for nocerite, would make up one of the minor constituents of nocerite.

We then examined the behaviour upon heating of a sample of natural nocerite in order to study the kinetics of its supposed decomposition to the simple oxides and fluorides which are its constituents. The natural material of nocerite* is intimately intergrown with fluorite as shown by a microscopic inspection. Even with heavy liquids and centrifuging we have not been able to eliminate entirely the fluorite from our samples. Therefore, in the *x*-ray powder photographs the lines of $CaF_2$ are always distinctly identified. The mineral mixture of nocerite with some fluorite is thermally stable when heated for periods of thirty minutes each, at temperatures gradually increased from 300° to 900° C. When the temperature was raised in a closed platinum container to 1000° C., a partial fusion was observed, but the optical and *x*-ray characteristics of the resolidified material are identical with those of the initial mineral. The same results were obtained even by heating at the same temperature over night.

On the other hand, if the thermal exposure to about 900° was prolongated over several days, in an open platinum container, a progressively increasing loss in weight was observed which is accompanied by an irreversible, and finally complete chemical change. The *x*-ray powder patterns of the products treated in this manner show a gradual disappearance of the lines of nocerite and calcium fluoride, giving rise to entirely new lines with increasing intensities. After a sufficiently long exposure nothing of the initial minerals is preserved, and the examination of the new pattern gives the clear evidence that a mixture of

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* We owe two representative samples of nocerite from the original deposits of Nocera, Campania, to the kindness of Drs. C. Frondel (Harvard University), and A. Scherillo (Università di Napoli). To both gentlemen we express our sincere gratitude.

magnesium oxide and tricalcium borate has resulted (for the latter compound we referred to the chart No. $I/I_1$ 3-1089 of the collection of $x$-ray data of the *A.S.T.M.*). The conclusion is evident that nocerite cannot have the oxyfluoride composition given to this mineral by previous authors, but must contain boron which apparently has been entirely overlooked by them.

A spectrographic analysis of semi-quantitative character, which we owe to the courtesy of Professor Edward S. Foster, Jr., Physics Department, University of Toledo, has fully confirmed our assumptions by the fact that in the nocerite samples considerable amounts of boron have been identified, besides magnesium and calcium. The fluorine present in the mineral mixture with fluorite is much higher than that which would be combined with calcium in the form of $CaF_2$. It is therefore concluded that the mineral nocerite is not a simple magnesium borate, like kotoite (cf. T. Watanabe (5)), $3MgO \cdot B_2O_3$, or suanite, (cf. T. Watanabe (6)), $2MgO \cdot B_2O_3$, both from the Hol Kol Mine, Suan, North Korea.

In nature, on the other hand, the existence of a magnesium fluoroborate is well known. It is the mineral called fluoborite, to which is ascribed the general formula $Mg_3(BO_3)_2 \cdot 3Mg\,(OH,F)_2$. The compositions given in the literature (cf. Dana's "System of Mineralogy," 7th edition, vol II. 1944, 1951, pp. 369*f*.) differ only in their OH/F ratios. For example this ratio is 1.70 in the fluoborite from the Tallgruvan, Norberg district, Sweden (cf. P. Geijer (7)) but only 0.32 in a fluoborite from Selibin, Malaya (cf. R. W. Johnston and C. E. Tilley (8)), and intermediate, namely about 1.50 in fluoborite from Sterling Hill, N. J. (cf. L. H. Bauer and H. Berman (9), C. Palache (10)). Based on data measured on fluoborite occurrences of different composition, W. T. Schaller, (11) was able to calculate by extrapolation the optical and other constants for the pure F- and OH-end members of the fluoborite series. The calculated data for the pure fluorine fluoborite coincide nearly exactly with those measured by F. Zambonini for nocerite (see Table 1). It is,

TABLE 1

| | System | $\omega$ | $\epsilon$ | Optical Character | Density |
|---|---|---|---|---|---|
| Pure F-Fluoborite[1] | hexagonal | 1.502 | 1.487 | Negative | 2.98 |
| Nocerite[2] | hexagonal | 1.5098 | 1.4855 | Negative | 2.96 |

[1] Schaller.

[2] Zambonini.

therefore, plausible to consider that nocerite is identical with pure $Mg_3(BO_3)_2 \cdot 3MgF_2$.

The data given in the literature for the constants of the elementary cell of the Norberg fluoborite (high in OH) are $a_0 = 9.05$ kX; $c_0 = 3.09$ kX (cf. G. Aminoff, in P. Geijer (7)), and for the fluoborite also from Norberg: $a_0 = 9.06$ Å; $c_0 = 3.06$ Å (cf. Y. Takeuchi (12), who gives the space group $C^2_{6h} = C6_3/m$). They are evidently very near to those measured by Scherillo for nocerite (see above). From the $x$-ray data obtained in our laboratory of the nocerite samples available to us, we calculated the following constants of the elementary cell: $a_0 = 8.82$ Å; $c_0 = 3.10$ Å, in good agreement with those indicated by Scherillo. The slight deviations from the reported data for fluoborite are probably due to the fact that they refer to a crystal phase in which more than half the fluorine is replaced by hydroxyl anions.

The identification of the nocerite sample which we examined, with a mixture of fluoborite and calcium fluoride also easily explains the phenomena observed after heating in open platinum containers in direct contact with the air. Under these conditions the calcium fluoride is evidently gradually changed to calcium oxide which in turn reacts with the fluoborite. Tricalcium borate is the reaction product, and magnesium oxide and magnesium fluoride are set free. Further, the magnesium fluoride is partially changed to magnesium oxide (cf. M. M. Sychev (13).

To confirm our hypothesis here submitted concerning the true composition of nocerite, we synthesized the pure compound $3MgO \cdot B_2O_3 \cdot 3MgF_2$. It is easily prepared by solid state reaction from mixes of the powders of the constituents at a temperature slightly above 1000° C.

In Table 2 the spacings are given for the most important lines of the $x$-ray powder photographs. For comparison, those of nocerite, of synthetic $Mg_3(BO_3)_2 \cdot 3MgF_2$, and of fluoborite from Sterling Hill, N. J., are tabulated. The identity of the two first patterns is evident. The lines in the third are shifted to smaller $2\theta$ angles, corresponding to the widening effect of the substitution of fluorine by hydroxyl anions. It may also be that the slight differences between the spacings of the nocerite diagram and that of the synthetic pure compound $Mg_3(BO_3)_2 \cdot 3MgF_2$, which are nearly within the limits of error, may be caused by a very small content of OH in the natural nocerite.

## CONCLUSIONS

It is concluded that the mineral nocerite originally described as a complex oxyfluoride of calcium and magnesium, with the formula $Mg_3Ca_3O_2F_8$, is in reality a complex fluoroborate of magnesium, con-

TABLE 2

| *h k l* | Nocerite* | | Synthetic $Mg_3(BO_3)_2 \cdot 3MgF_2$ | | Fluoborite from Sterling Hill | |
|---|---|---|---|---|---|---|
| | *d*(Å) | *I* | *d*(Å) | *I* | *d*(Å) | *I* |
| 100 | 7.63 | mw | 7.60 | mw | 7.70 | mw |
| 110 | 4.40 | m | 4.40 | m | 4.44 | m |
| 200 | 3.82 | vw | 3.82 | vw | 3.86 | vw |
| 210<br>101 | 2.89 | mw | 2.88 | mw | 2.92 | mw |
| 300<br>111 | 2.55 | m | 2.54 | ms | 2.56 | m |
| 201 | 2.40 | m | 2.40 | ms | 2.42 | m |
| 220 | 2.20 | vw | 2.19 | w | 2.22 | vw |
| 310<br>211 | 2.12 | ms | 2.12 | ms | 2.13 | m |
| 400 | 1.911 | mw | 1.910 | mw | 1.922 | w |
| 221 | 1.796 | m | 1.796 | ms | 1.806 | m |
| 320<br>311 | 1.750 | mw | 1.750 | m | 1.762 | mw |
| 410 | 1.667 | w | 1.665 | w | 1.680 | w |
| 401 | 1.625 | w | 1.626 | w | 1.638 | w |
| 002 | 1.550 | w | 1.550 | mw | 1.558 | mw |
| 500<br>321<br>102 | 1.524 | w | 1.524 | mw | 1.534 | mw |
| 330<br>411<br>112 | 1.466 | m | 1.466 | ms | 1.477 | m |
| 420<br>201 | 1.444 | w | 1.443 | mw | 1.453 | w |

* After deduction of the $CaF_2$ lines.

taminated by fluorite. It is identical with the synthetic product of the composition $Mg_3(BO_3)_2 \cdot 3MgF_2$ which is the F-end member of the series of complex compounds of the fluoborite group corresponding to the general formula $Mg_3(BO_3)_2 \cdot 3Mg(OH,F)_2$. The term nocerite, therefore, in spite of its evident priority, should be placed into synonymy with fluoborite, this latter name being used for the whole isomorphous series.

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