THE REGENERATION OF AMPHIBOLES FROM THEIR MELTS AT NORMAL PRESSURE

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I. Introduction

E. Mitscherlich, P. Berthier and G. Rose have stated that amphiboles when fused do not recrystallize from their melts; instead pyroxenes[1] are formed. Analogous observations were also made by C. Doelter and E. Hussak (15), A Becker (9), F. J. Loewinson-Lessing(7)[2] and others. These observations tend to support the view that amphiboles and pyroxenes are heteromorphous varieties of one and the same substance. Such a view could be held only as long as the real rôle of "water" in amphiboles had not been explained, and consequently the principal difference between the minerals of the amphibole group and those of the pyroxene group still remained unknown.

More recently much has been accomplished by B. Gossner (16, 17), W. Kunitz (26) and B. Warren (36, 37)[3] leading toward the correct view concerning the constitution of the amphiboles. The latter determined the fine structure of certain amphiboles by means of *x*-rays, dispelling all doubts as to the rôle of H_2O in amphiboles. The experiments of the quoted authors proved that water is an unfailing constituent of amphiboles and enters their crystal lattice in the form of OH-groups.[4] The experiments of E. Posnjak and N. L. Bowen (30) show that the chief part of the H_2O is eliminated from the crystal lattice at one time, at the high temperature of about 900°.[5] They state that in the process of heating the amphibole (tremolite in the given case) it decomposes in accordance with a reaction of the following type:

$$\underset{\text{tremolite}}{H_2Ca_2Mg_5(SiO_3)_8} \rightarrow \underset{\text{pyroxene}^6}{2CaSiO_3 \cdot 5MgSiO_3} + SiO_2 + H_2O$$

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[1] On the basis of observations in nature, G. Rose (32) supposed that rapid cooling tends to prevent the crystallization of amphiboles and that with a slow cooling of the melt the amphibole must regenerate.

[2] F. J. Loewinson-Lessing acknowledged the important part played by H_2O in the formation of amphiboles and carried out some experiments (which were unsuccessful) with the passing of aqueous vapors above the melt during crystallization.

[3] One of the works (on the structure of anthophyllite) was published by Warren together with D. J. Modell (38). Concerning the constitution of amphiboles see also the article of H. Berman and E. S. Larsen (10).

[4] See also the roentgenographic determinations of F. Rodolico (31).

[5] See also the investigations of Kôzu, Ioshiki and Kani (24).

[6] According to N. L. Bowen (11) it must be a member of the series of solid solutions: diopside-clinoenstatite. But against this argument objections are raised, see for instance D. P. Grigoriev (21).

That is to say: while in the process of heating, the amphibole decomposes with the formation of pyroxene, silica and aqueous vapor. According to C. Doelter and E. Hussak (15) hornblende decomposes at a high temperature and produces augite, or olivine, and magnetite (and H_2O. Authors). According to Kôzu and Ioshiki (23), hornblende investigated by them melted at 1200° with the formation of crystals of rhombic pyroxene (?) and magnetite (H_2O is eliminated at a lower temperature). It is quite evident that in the fusion and crystallization of anhydrous melts no amphibole would form; synthesis of minerals of this group from dry melts is likewise impossible [N. L. Bowen and Posnjak (12)].

Fusion of amphibole under pressure in the presence of H_2O (conditions under which regeneration would take place) has not, as yet, been performed.

Recently D. P. Grigoriev (3, 19) and D. P. Grigoriev and E. W. Isküll (22) succeeded in obtaining amphiboles at normal pressure by experimenting with fluorine-bearing silicate melts.

Fluorine escapes from these melts only in part (not more than half of the primary content). It is present in these melts in all cases in a quantity sufficient for the building of molecules of minerals of the amphibole and mica groups, which crystallize from them.

In the crystal structure of amphiboles and mica obtained in such a manner, fluorine atoms occupy the spaces ascribed previously to OH-groups.[7] That is, there form fluorine-amphiboles and mica, which are known from nature.[8] The artificial production of amphiboles from silicate fluorine-bearing melts shows the methods to be chosen in order to regenerate amphiboles from their melts. Obviously the removed H_2O must be replaced by fluorine that remains partly in the melt.

Actually, not quite the same mineral that was melted would be regenerated (fluorine amphibole instead of hydroxyl or hydroxyl-fluorine amphibole) but, after all, the problem of the regeneration of amphiboles from their melts at normal pressure[9] is solved in principle.

[7] In the mica, obtained by D. P. Grigoriev (4, 18) the fluorine content is 2.59%. E. F. Alexeeva and A. K. Boldyrev, who investigated this artificial mica by means of *x*-rays, supposed that OH in it is replaced not only by F, but also by OK-groups (instead of F, which is present in insufficient quantity). F. Machatschki (28), however, finds that in this case the lack in F is supplied only by oxygen.

[8] That the pure fluorine mica exists, one can be persuaded by examination of chemical analyses in Doelter's *Handbuch d. Mineralchemie*, Bd. II, 2. The complete replacing of OH by F in mica is well seen in the diagram of compositions of magnesium-iron-mica, which has been plotted by D. P. Grigoriev (4). The amphibole with large content of fluorine was described by J. Morozewicz (29).

[9] The hydrothermal synthesis of amphibole at low pressure was recently accomplished. See publications of K. H. Scheumann and W. Lüdke (27, 34, 35).

In order to regenerate amphiboles from their melts we attempted to fuse amphiboles with the addition of fluorine compounds. At the same time, in order to compare the results obtained, we fused amphiboles without such additions. Fusion was carried out in a cryptole furnace in graphite crucibles, at a temperature of about 1350°. The weight of each sample in all our experiments was 20 grams.

2. THE FUSION OF AMPHIBOLE FROM ILMEN MOUNTAINS

Hornblende found in veins in the Ilmen Mountains has been described by D. S. Beljankin (2). Its analysis, according to him, is as follows:

SiO_2	49.72
TiO_2	0.47
Al_2O_3	4.78
Fe_2O_3	4.48
FeO	5.66
MnO	0.38
MgO	14.08
CaO	12.73
Na_2O	2.93
K_2O	1.33
F	1.14
H_2O	1.33
	99.93

Calculating by Warren's method we arrive at the following formula:[10] $(OH,F)_{1.98}(Ca,Na,K)_{2.9}(Mg,Fe'', Fe''', Al, Ti)_5 (Si,Al)_8O_{22}$.

This amphibole may be classified among the common hornblendes and approaches the tremolite type.[11]

Under the microscope the mineral shows a pale green color with pleochroism: N_g=pale bluish green, N_m=green, and N_p=yellowish green; absorption $N_g > N_m > N_p$.

The elongation of the crystals is positive. The cleavage, typical for amphiboles, is clearly seen. The indices of refraction (determined by the immersion method) are:

$N_g = 1.635 \pm 0.003$,
$N_m = 1.622 \pm 0.003$,
$N_p = 1.614 \pm 0.003$,
$N_g - N_p = 0.021$.
Extinction angle $N_g \wedge c = 22°$; $2V = +70\text{–}75°$.

According to these data the amphibole is classed as a pargasite.

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[10] Aluminum was distributed between the groups of elements of magnesium and silicon in the following manner: $\frac{3}{5}$ were added to Mg and $\frac{2}{5}$ to Si.

[11] Compare the division of amphiboles into types by H. Berman and E. S. Larsen (10).

(a) Dry fusion.

The fused powder of the amphibole hardens to a granular mass (grain size up to 2 mm.). The color of the melt on fracture surfaces is gray. At the bottom of the melt, where the melt is adjacent to the crucible, globules of iron, that are reduced from the melt to a metallic state, are seen.

In a microscopic examination the melt appears to consist wholly of pyroxene crystals, which are colorless and have the form of thick tablets. The cleavage proper to pyroxenes is clearly seen. The elongation of the crystals is positive. The indices of refraction, determined also by means of the immersion method, are:

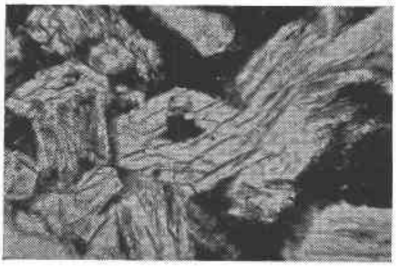

FIG. 1. The regenerated amphibole. One crystal is normal to [001]. ×150.

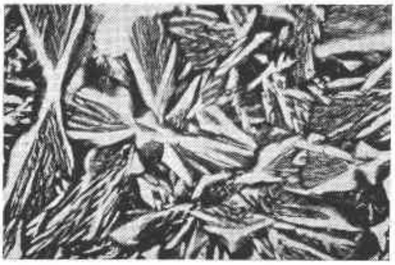

FIG. 2. The regenerated amphibole showing skeleton-growth. ×65.

$$N_g=1.664\pm0.003,$$
$$N_m=1.655\pm0.003,$$
$$N_p=1.652\pm0.003,$$
$$N_g-N_p=0.012.$$
Extinction angle $N_g \wedge c=40°$, $2V=+60°$.

(b) Fusion with fluorine.

We had at our disposal only one fluorine compound suitable for our experiments, namely, calcium fluoride. Therefore, the amphibole was fused with 5% (by weight) of calcium fluoride. Thus 2.43% F and 2.57% Ca were introduced into the melt. The powder of amphibole and CaF_2 were carefully mixed and then fused in the manner described above.

The melt thus obtained appeared crystalline and had a radiating structure. The maximum size of a single crystal was 3 mm. The color of the melt was pale gray, slightly greenish. In parts adjacent to the crucible globules of reduced iron were formed.

Under the microscope, from the general aspect and character of the cleavage (Fig. 1) the product obtained is clearly an amphibole.

The elongated crystals of the mineral form radiating aggregates.

In some areas of the thin sections of the melt, not entire crystals, but only skeletons of amphibole crystals can be seen (Fig. 2). The spaces between the crystals are filled with a dark opaque substance.

Under the microscope the amphibole is colorless. The elongation of the crystals is positive. The indices of refraction (determined by means of the immersion method) are:

$$N_g = 1.603 \pm 0.003,$$
$$N_m = 1.590 \pm 0.003,$$
$$N_p = 1.586 \pm 0.003,$$
$$N_g - N_p = 0.017.$$

The angle $2V = +55\text{–}60°$, extinction angle $N_g \wedge c = 17°$.

According to these data the newly formed amphibole differs greatly from the original mineral. Particularly striking is the difference in the indices of refraction.

The changes in the properties of the amphibole are probably due to the following circumstances:

1. Reduction of nearly all the iron present in the hornblende to metal. The newly formed amphibole is poor in iron.
2. Replacement of the eliminated Fe by Ca, which was introduced as CaF_2.
3. Total replacement of OH by F.
4. The possible elimination of some oxides from the melt at high temperature (e.g., those of the alkalis).

The reduction of the Fe content, as is known, must decrease the indices of refraction and birefringence; this may be observed in the newly formed amphibole. The same holds true of F, as shown by N. L. Bowen and J. F. Schairer for the synthetic amphiboles that they have obtained (13).[12] The action of Ca is as a rule, not very strong. The rôle of alkalis is in this case not definitely established.

3. THE FUSION OF OTHER AMPHIBOLES

In order to convince ourselves that besides the thoroughly investigated amphibole from Ilmen Mountains, other amphiboles are also liable to regeneration, we performed some fusion experiments with two other amphiboles: (1) an amphibole from Sliudjanka collected by D. P. Grigoriev in the year 1931 and which probably approaches pargasite, (2) an amphibole from Chertanysh (near Miass, Ural Mts.) which has been labelled in the Mining Museum under the name of actinolite (No. 808–3 of the fundamental collection).

The fusion of these amphiboles, without additions, leads to the forma-

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[12] Cf. also the statements of W. Kunitz concerning the magnesium-iron mica. See also the data of D. P. Grigoriev (4).

tion of pyroxenes that, in optical character, resemble those described above. Fusion with 5% CaF_2 resulted in the production of an amphibole and the same dark opaque substance which had been observed in the melts of the amphiboles from the Ilmen Mts.

We shall not describe the fused products of these amphiboles as they present nothing new in comparison with the results of the first experiment. They interest us insofar as they confirm the correctness and importance of the methods we have chosen for the regeneration of amphiboles.

4. *X*-RAY STUDY

From the powder of one of the specimens of regenerated amphiboles ("Amph-5") *x*-ray diffraction patterns have been obtained by V. I. Mikheev. The *x*-ray study was carried out in the Roentgenographic Laboratory of the Mining Institute.[13]

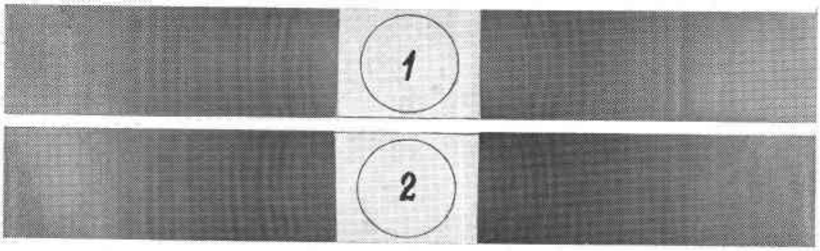

FIG. 3. *X*-ray diffraction patterns of natural (1) and regenerated (2) amphiboles.

The *x*-ray diffraction pattern of "Amph-5" is shown in Fig. 3 (2), and Fig. 3 (1) shows the pattern obtained from the natural amphibole from the Ilmen Mts. The latter pattern has been obtained from V. N. Doobinina's diploma work.

Pattern "Amph-5" shows 44 pairs of lines. The diffraction pattern obtained from natural amphibole shows 47 pairs of lines. The spacings between the corresponding pairs of lines of these patterns are identical. The relative intensities of the lines coincide in 39 cases; some deviation in five cases may be explained as due to the difference in the chemical composition of the newly formed amphibole in comparison with the natural amphibole (in no case was the position of a line changed but only its intensity). The absence of some lines in the patterns of the artificial amphibole in comparison with those that may be observed in patterns of the natural mineral, is probably due to the conditions of exposure. The

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[13] *X*-ray diffraction patterns were obtained with $K\alpha\beta$ radiation of iron by means of a Hadding tube. For callibration the powdered "Amph- 5" was mixed with NaCl.

complete identity of the patterns of the natural and artificial amphiboles is well observed in Fig. 3. Hence the x-ray patterns confirm the conclusion that the newly formed mineral is truly an amphibole and that the structures of natural and artificial amphiboles are wholly identical.

5. Conclusion

Thus our experiments show:

(1) That only pyroxenes (monoclinic) crystallize from the dry melts of the investigated amphiboles.

(2) That amphiboles crystallize from their melts with fluorine additions, but they have their chemical composition somewhat altered.

(3) That to produce amphiboles from their melts the presence of fluorine (or OH) is required. This had formerly been shown by N. L. Bowen and E. Posnjak, but only inferentially.

(4) That fluorine acts in the melts the same way as the OH-group does, and occupies its space in the crystal structure of the amphiboles that crystallize from these melts.

(5) That our hypothesis regarding the possibility of replacing OH by F has been fully verified by experiments with silicate melts.

In conclusion it must be noted that fusion of amphiboles with fluorine additions had already been performed by C. Doelter (14) in 1888. According to him the fusion of alumina-bearing amphiboles with NaF and MgF_2 gave as a result magnesium-mica, and similiar fusions of amphiboles which contained no alumina lead to the formation of augite and olivine. C. Doelter added the fluorine compounds in very large quantities (particularly MgF_2). Hence it becomes obvious why our experiments give different results. It is likewise true that the purpose of the experiments of C. Doelter was quite different, namely, the artificial production of mica.

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