SYNTHESIS OF NORBERGITE AND CHONDRODITE BY DIRECT DRY FUSION

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ABSTRACT

Experiments were carried out in order to study the synthetic preparation of the minerals of the humite group by a single crystallization from a dry melt. The reaction products were identified by their optical properties and *x*-ray powder photograms. Below the melting temperature of magnesium fluoride the reaction between this compound and forsterite took place in a solid state. Artificial norbergite and chondrodite were obtained in which the hydroxyl groups were completely replaced by fluorine. The products were nearly or completely iron-free. Attempts to synthetize clinohumite and certain hypothetical upper members of the family failed, pure magnesium orthosilicate being obtained instead. Norbergite, chondrodite, and sellaite crystallized from a melt with a composition between sellaite and norbergite.

INTRODUCTION

Contrary to many common rock minerals which have been repeatedly prepared by the successful efforts of mineralogists and mineral chemists, the humite group, up to the present, seems to have gained only slight attention. The earliest attacks upon this problem were made by the famous French school of mineral chemists, nearly a century ago. Thus, Daubrée (1851, p. 627), by passing SiF_4 over MgO in a porcelain tube at dark-red heat, obtained a fibrous fluorine-bearing silicate, with a specific gravity equal to that of chondrodite, and showing a close chemical analogy with the last-mentioned mineral. Sainte-Claire Deville (1861), on the other hand, under similar circumstances reported only the formation of vitreous or crystalline silicates with a composition entirely different from that of chondrodite and humite.

In 1889 Doelter, in an important paper on mica synthesis, reported the occurrence of what he thought to be chondrodite in one of the experiments yielding no mica (1889, pp. 70–71). The synthesis was accomplished by dry fusion of actinolite ("Strahlstein"), nearly or totally devoid of alumina, with calcium fluoride and a little sodium fluoride. This result further led him to fuse Mg_2SiO_4 with a 5-fold amount of MgF_2 and a little Na_2F_2. The experiment resulted in the formation of yellow-brown rectangular grains, thought possibly to be humite (*op. cit.*, p. 72).

The next attack upon the problem was made by Jander and Fett in 1939. These authors carried out a series of hydrothermal experiments in bombs at different temperatures (360° to 600° C.) and pressures, starting from a mixture of the oxides MgO and SiO_2 with $H_2O+H_2F_2$, or MgF_2. The reaction products were identified by their *x*-ray diffraction patterns.

Jander and Fett claim that the presence of a minimum of 6% F_2 is necessary for the hydrothermal formation of chondrodite (1939, p. 158). Humite was also obtained by these authors in their experiments.

The chemical composition and atomic arrangement of the minerals of the humite group reveal interesting examples of close morphotropic and chemical relations existing between its members. Through the classical studies of Sjögren and of Penfield and Howe, and by Geijer's discovery of norbergite as the first member of the series, the chemistry of this group can be presented in the following way:

Norbergite,	$Mg(F, OH)_2 \cdot Mg_2SiO_4$;
Chondrodite,	$Mg(F, OH)_2 \cdot 2Mg_2SiO_4$;
Humite,	$Mg(F, OH)_2 \cdot 3Mg_2SiO_4$;
Clinohumite,	$Mg(F, OH)_2 \cdot 4Mg_2SiO_4$.

The crystal structures of the members of the humite group have been investigated by Taylor and West. They consist of slabs of the olivine structure and of magnesium hydroxide alternating with each other. In norbergite layers of $Mg(OH)_2$ alternate with layers of Mg_2SiO_4. In chondrodite two slabs of Mg_2SiO_4 are followed by one $Mg(OH)_2$, in humite every fourth slab is $Mg(OH)_2$, and in clinohumite every fifth slab. In natural humite minerals part of Mg^{2+} is always diadochically replaced by Fe^{2+} and by Mn^{2+}, and a part of OH^- by F^-.

As the construction of the idealized structures of the humite minerals can be carried out merely by stacking together unit blocks of Mg_2SiO_4 and $Mg(OH)_2$, it was thought to be worthwhile to try to carry out the synthesis of the minerals proper by direct coupling of the lattice units. Seeing that OH^- in these lattices is partly replaced by F^-, experiments were carried out in order to try to produce hydroxyl-free members of this group by dry fusion of forsterite and magnesium fluoride at atmospheric pressure. The synthetic minerals, if obtained, were thought to be comparable with the fluorine-bearing amphiboles produced by Bowen and Schairer (1935), and with similar phlogopites and hornblendes obtained by Grigoriev (1934, 1935), and by Grigoriev and Isküll (1937). In case of humite minerals, however, attention must be paid to the fact that the $Mg(OH)_2$ has a lattice of the cadmium iodide type, while MgF_2 has the symmetrically coordinated rutile structure. The complete replacement of OH^- by F^- in the lattice would thus be expected to correspond to a decrease in polarization.

APPARATUS AND REAGENTS

The forsterite used in the experiments was obtained from a dunite sample from Almklovdalen in Søndmøre, Norway. The mineral was separated from the crushed rock sample by means of Clerici solution. Its properties were determined as follows:

FeO	6.67%
MnO	0.07%
Sp. gr.	3.199–3.202
	$\alpha = 1.648$
	$\beta \sim 1.669$
	$\gamma = 1.688$
Composition:	$Fo_{90}Fa_{10}$.

A magnesium fluoride preparation ("gefällt, doppelt gereinigt") of Riedel-de Haën, Berlin, was used. The determination of its properties gave the following results:

FeO	0.12%
MnO	0.00%
	$\omega = 1.377$
	$\epsilon = 1.388$.

In all, 16 fusions were carried out. For the first experiments, 1–3, a high temperature furnace with silicon carbide heating units was used, and the charges were placed in platinum crucibles. The temperatures were measured with a Pt-PtRh thermoelement. All other fusions were carried out in a cryptole furnace in small graphite crucibles. In this case, the temperatures were measured with an optical pyrometer. In all these experiments the charge was heated to 1600°–1700° C., and the values given below will represent the average temperatures in this range. One gram of forsterite was weighed out for every fusion, and an amount of MgF_2, calculated to give the charge the desired composition, was carefully mixed with the former. After the fusion, the crucible was allowed to cool down in the furnace. The reaction products were studied in thin sections. Refractive indices of the compounds formed were determined by the immersion method. The error in these determinations is ± 0.002. In addition, axial angles were determined with the universal stage when possible, with an error of $\pm 2°$. The compounds were identified by comparing their *x*-ray powder photograms with those of the natural minerals.

EXPERIMENTS

2. A mixture with the composition of norbergite was heated for 1 hr. at 1290° C. and allowed to cool down in the furnace for 1 hr. The product obtained was a loose light brown powder. Forsterite and magnesium fluoride had completely disappeared. The mass was homogeneous, and the determination of the refractive indices gave: $\alpha > 1.550$, $\gamma < 1.595$. The diffraction pattern obtained from the reaction products was identical with that of natural norbergite.

3. The composition of the charge was the same as in Exp. 2. Now, the mixture was heated for 2 hrs. at 1350° C. and allowed to cool down as above. The reaction product consisted of a partly sintered light brown powder with refractive indices: $\alpha > 1.550$, $\gamma < 1.595$. The product was homogeneous and the powder photograms proved the presence of norbergite.

6. A third charge of norbergite was heated for 2 hrs. at 1620° C. and allowed to cool down overnight. The cake was crystalline and consisted of white lath-shaped crystals up to 2 mm. long. Megascopically, small blebs of graphite could be distinguished in the mass. The parts of the cake next to the walls and the bottom of the crucible contained small rounded iron globules. The hardness of the crystals was approximately 6. They did not gelatinize, or dissolve, when treated with boiling concentrated or dilute hydrochloric acid. The determination of the refractive indices revealed the presence of three different phases with the following indices:

(1) $\alpha = 1.564$, $\beta \sim 1.567$, $\gamma = 1.592$;
(2) $\alpha \sim 1.591$, $\gamma \sim 1.630$;
(3) $\alpha \sim 1.641$, $\beta \sim 1.655$, $\gamma = 1.667$.

The greatest part of the reaction products consisted of the phases (1) and (2), amounting to approximately 40% and 50% of the total mass, respectively, while the amount of the third phase was about 10% of the total mass.

In thin section the mass was found to consist of colorless subhedral or anhedral lath-like crystals measuring from 0.02 to 2.3 mm. in length. One poorly-developed direction of cleavage, parallel to the elongation of the crystals, was found in some cases. Hematite blebs were present, and narrow graphite and hematite strings, parallel to the elongation, were often found in the crystals. Two different phases were easily distinguished under the polarizing microscope, one of them with extinction parallel to the elongation; in the other, the maximum elongation angle observed, as measured from the trace of the outline, was 30°. Twinning was present in many grains; the twinning plane was parallel to the elongation. Sometimes laths with higher refractive indices and inclined extinction were found to be surrounded by a shell with lower refraction and parallel extinction. The axial angle, $2V_\gamma$, of the latter was 44° while that of the kernel was large. All the phases were optically biaxial, positive. The *x*-ray diffraction pattern of the reaction products was exceedingly similar to those of natural norbergite and chondrodite. From the above properties, the products consist of norbergite, chondrodite, and forsterite.

12. Still another norbergitic charge was treated as in Exp. 6. Also in this case the cake was crystalline, but the crystals were smaller than in

the previous experiment. Only in the part next to the bottom of the crucible could small white subhedral laths be seen in the cake; while the upper portion consisted of a white mass of small anhedral grains, with occasional blebs of graphite and layers of hematite, which were parallel to the surface of the charge and gave the whole a herringbone structure. On the free surfaces the cake had a pearly luster. Small iron globules adhered to the surfaces close to the walls of the crucible. The hardness of the cake was about 6. The determination of the refractive indices again revealed the presence of three compounds, viz.

80% with $\gamma \sim 1.590$,
5% with $\gamma \sim 1.630$,
15% with $\gamma \sim 1.668$.

The percentages are approximate.

In thin section, a few subhedral laths were found, measuring up to 0.7 mm. in length. They were biaxial, positive, and sometimes twinned, the twinning plane being parallel to the elongation. One poorly developed cleavage direction, parallel to the elongation, was occasionally observed. The axial angle was large. The maximum extinction angle observed, as measured from the trace of elongation, was 24°. The main part of the material, however, was present as small anhedral grains of uniform orientation, their elongation being vertical to the bottom of the crucible. The extinction was parallel to the elongation. The diffraction pattern was, again, similar to those of natural norbergite and chondrodite. To judge by their properties, the reaction products include norbergite, chondrodite, and forsterite.

7. The charge of this experiment had the composition of chondrodite. It was heated for 3 hrs. at 1640° C. and allowed to cool down for 5 hrs. The resulting cake was coarsely crystalline and consisted of white lath-shaped crystals with a hardness of about 6. They were not decomposed when boiled with dilute or concentrated HCl. Graphite and occasional pellets of iron adhered to the parts next to the crucible.

Under the polarizing microscope the mass was found to consist of colorless elongated lath-like crystals, some of which were euhedral and showed the characteristic olivine-like outline. In these extinction was parallel to the elongation. The length of all grains was between 0.4 and 0.8 mm. The major part consisted of subhedral laths, with occasional twinning and cleavage cracks parallel to the elongation. The maximum extinction angle observed in these grains, measured as in previous cases, was 14°. Both compounds were biaxial, positive, and the axial angle of the latter, $2V_{\gamma}$, was 68°–70°. The interstices of the laths consisted of small anhedral grains with somewhat lower refractive indices, finely disseminated graphite, and hematite. The determination of the refractive indices gave the reaction products the following approximate composition:

10% with $\gamma \sim 1.620$;
60% with $\alpha \sim 1.611$, $\beta \sim 1.620$, $\gamma = 1.640$;
30% with $\beta \sim 1.654$, $\gamma \sim 1.668$.

The *x*-ray powder photogram of the reaction products was similar to that obtained from natural chondrodite. According to their properties the reaction products consist of chondrodite and forsterite.

9. Another charge with the compositon of chondrodite was heated for 2 hrs. at 1600° C. and allowed to cool down for 3 hrs. The products consisted of white lath-shaped crystals, this time with many inclusions consisting of small pellets of iron, blebs of graphite and, occasionally, hematite. Megascopically, the cake had a gray color. In thin section, the silicate material was found to form a colorless irregular mass of subhedral lath-like crystals with a maximum length of 0.7 mm. A few cleavage cracks parallel to the elongation of the laths were observed. No twinning was present. Some of the grains had extinction parallel to the elongation, while in other grains the maximum extinction angle observed, measured from the trace of elongation and of the cleavage cracks, was 33°. All the material was optically biaxial and positive. The determination of the axial angle of some grains gave $2V_\gamma$ of 72°–74°. The refractive indices for the main portion of the material were: $\alpha = 1.607$, $\beta = 1.620$, $\gamma = 1.640$. In addition, material was present with $\gamma \sim 1.665$. The powder photograms of the reaction products were identical with that of natural chondrodite. The reaction products evidently consist of chondrodite and a little forsterite.

8. The charge had the composition of clinohumite. It was heated for 3 hrs. at 1650° and allowed to cool down overnight. The cake consisted of small white irregularly shaped crystals, not acted upon by hydrochloric acid. Inclusions of metallic iron, graphite, and hematite were present. In thin section, a network was visible, consisting of short subhedral colorless laths 0.2 to 0.3 mm. in length, and containing numerous inclusions of the material stated above, as blebs or finely disseminated matter. Cleavage cracks parallel to the elongation were sometimes present. No twinning could be established. The extinction was parallel to the elongation. The material was biaxial, positive, with a large axial angle. Its refractive indices were: $\alpha = 1.633$, $\beta = 1.644$, $\gamma = 1.664$. The powder pattern given by the reaction product corresponded with that of forsterite. By its properties, the compound obtained in this experiment is magnesium orthosilicate.

10. Another charge of clinohumitic composition was heated for 2 hrs. at 1640° C. and allowed to cool down overnight. Megascopically, short lath-shaped white crystals, graphite, and metallic iron were found to be present in the cake after fusion. The cake was quite brittle, and no thin section of it could be prepared. The determination of the refractive indices yielded the following results: $\alpha = 1.632$, $\beta = 1.644$, $\gamma = 1.664$. The powder pattern was similar to that of forsterite. The reaction product, according to its properties, is magnesium orthosilicate.

15. The charge had, again, the composition of clinohumite. It was heated for 2 hrs. at 1600° C. and allowed to cool down overnight. The properties of the reaction products were similar to those in the previous experiment. The determination of the refractive indices revealed the presence of two compounds, viz.

$$5\% \text{ with } \alpha \sim 1.610,$$
$$95\% \text{ with } \alpha = 1.631, \quad \beta = 1.644, \quad \gamma = 1.663,$$

the percentages being approximate. The powder diffraction pattern was similar to that of forsterite. The reaction products consist of magnesium orthosilicate, with minor amounts of chondrodite.

In order to study the possibility of obtaining hypothetical members of the humite group, some of which have been supposed to exist according to Bragg (1937, p. 153), the following experiments were carried out, starting with smaller and greater amounts of forsterite than is known to enter into the formulas of the known minerals in this group.

16. The charge had the composition $MgF_2 \cdot \frac{1}{2}Mg_2SiO_4$. It was heated for 2 hrs. at 1600° C. and allowed to cool down overnight. Megascopically, the cake was composed of white lath-shaped crystals with hematite and graphite blebs, and a large number of iron globules on the surfaces next to the walls of the crucible. The crystals were neither gelatinized, nor dissolved, when treated with boiling hydrochloric acid.

Three different crystalline substances were found to be present in a thin section of the cake. The mass consisted of colorless slender subhedral laths, ranging from 0.06 to 3.9 mm. in length, and of smaller more euhedral rectangular grains with the form of thick prisms. Twinning was often present, especially in the smaller grains, and cleavage cracks parallel to the elongation of the grains were usually observed. By the determination of the extinction angles the presence of two different substances was established, one of which had extinction parallel to the elongation, while the maximum extinction angle observed in the other, measured as in the above experiments, was 33°. Both compounds were often intergrown, in which case the center of the grain was usually twinned and had inclined extinction and higher refraction, while the shell consisted of material with parallel extinction and lower indices of refraction. Both were biaxial, optically positive. The axial angle, $2V_\gamma$, of the former compound was 63°, and that of the latter one 42°–48°. The determination of the refractive indices gave following results:

$$\begin{aligned}&(1)\quad \alpha \sim 1.552, \quad \beta \sim 1.560;\\ &(2)\quad \alpha \sim 1.575, \quad \beta = 1.588, \quad \gamma = 1.604.\end{aligned}$$

The main part of the reaction products consisted of the substance with the lower refraction.

The interstices between the laths were filled with small anhedral grains and their aggregates, characterized by their high negative relief.

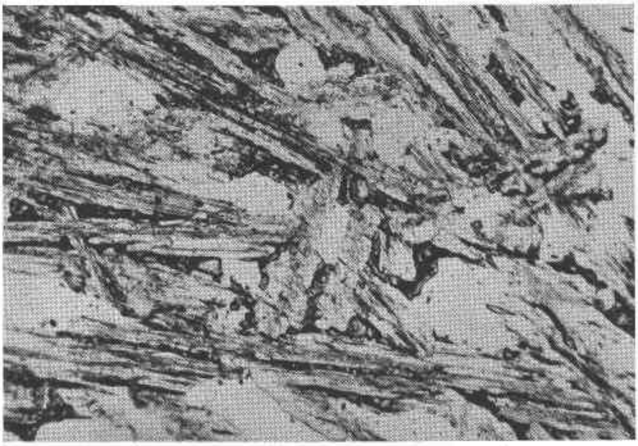

Fig. 1. Laths of synthetic norbergite and chondrodite (light gray) with irregular grains of sellaite (dark gray) in thin section. Exp. 16. Magn. 27×. 1 nicol.

A few grains were observed which developed forms similar to a four-pointed star. This compound was optically uniaxial, positive. According to its properties, it is recrystallized magnesium fluoride, or sellaite.

A photomicrograph of the reaction products is presented in Fig. 1.

From the x-ray powder photogram, the presence of magnesium fluoride could be further established among the reaction products, while the pattern in other respects was similar to that yielded by natural norbergite. From the above properties, the reaction products consist of norbergite, chondrodite, and sellaite.

11. A mixture with the composition of $MgF_2 \cdot 8\frac{1}{2}\ Mg_2SiO_4$ was heated for 2 hrs. at 1640° C. and allowed to cool down overnight. The reaction products consisted of small white crystals, iron pellets, and graphite, as

in the above experiments. The last-mentioned mineral, as small inclusions in the mass, was quite common. The determination of the refractive indices of the crystals gave: $\alpha = 1.633$, $\beta \sim 1.644$, $\gamma = 1.663$. The powder photogram of the substance was similar to that of forsterite. The above properties reveal the reaction product to consist of this compound.

14. A charge of similar composition as in Exp. 11 was heated for 2 hrs. at 1600° C., and allowed to cool down overnight. Megascopically, the cake was composed of small white crystals with inclusions of iron, hematite, and graphite. Due to the numerous inclusions, the color of the cake was gray. In thin section, it was found to consist of colorless crystalline matter with much opaque material. The crystalline substance was present in form of usually small anhedral (length 0.02 to 0.14 mm.) grains. The outlines of the more well-developed grains were similar to those of olivine crystals. Neither cleavage or twinning was present; the extinction was parallel to the elongation, and the crystals were biaxial, positive. The determination of the refractive indices gave: $\alpha = 1.633$, $\beta \sim 1.645$, $\gamma = 1.663$. The axial angle, $2V_\gamma$, was 80°–84°. The x-ray diffraction photogram proved the presence of forsterite.

13. In this experiment, the charge was highly forsteritic, with the composition $MgF_2 \cdot 17Mg_2SiO_4$. The mixture was heated for 2 hrs. at 1600° C. and left to cool down overnight. The cake consisted of very small white crystals. Due to the occurrence of numerous graphite and iron inclusions, the mass had a dark gray color. The determination of the refractive indices yielded the following values: $\alpha = 1.633$, $\beta = 1.644$, $\gamma = 1.664$. The x-ray diffraction pattern of the reaction products was similar to that of forsterite, thus proving the presence of this compound as resulting from the experiment.

Discussion of Results

The experiments described above seem to make apparent that, in some cases at least, it is possible to produce synthetic minerals belonging to the humite group by simple crystallization from a dry melt. As the products are different from the natural minerals which always contain hydroxyl groups, replacing a part of the fluorine, it seems to be appropriate to call the water-free synthetic products obtained fluor-norbergite and fluor-chondrodite, respectively. No experiments have been made with melts of the composition of humite. The attempts to produce clinohumite and certain hypothetical upper members of the group have thus far failed, magnesium orthosilicate being obtained instead. In these cases the amount of MgF_2 present was too small to produce an easy melting of the charge, as is seen by the properties of the reaction products and by the incomplete separation of the metallic phase. It seems to be evident, from these experiences, that the artificial preparation of clinohumite, if at all possible, must be tried at temperatures exceeding that necessary for the melting of forsterite.

It also seems to be apparent that the reaction between forsterite and magnesium fluoride will take place even at temperatures below the melting points of these compounds. Thus, in experiments 2 and 3, these components disappeared during the heating of the charge for one or two hours at 1290°–1350°, norbergite being formed instead. The reaction has evidently taken place in a solid state.

To judge from the above experiments, there seems to occur a general tendency towards an easier crystallization of the silicate phase, and a more complete separation of the reduced iron phase, with an increase in the MgF_2 content of the melt.

An explanation of the simultaneous formation of the humite minerals with different compositions and, likewise, of magnesium orthosilicate in melts with clinohumitic composition, may be found in the occurrence of metallic iron among the reaction products. In the highly reducing atmosphere in the furnace, the iron present in the forsterite lattice is reduced to metal and, thereby, an excess in SiO_2 in the melt is brought about. The iron is removed, in most cases evidently completely, and pure magnesium compounds crystallize from the melt. As the composition of the charges was calculated under assumption that a diadochic replacement of Mg^{2+} by Fe^{2+} would result in the reaction products, the mineral composition of the crystallized melt is often more complicated than can be expected from the composition of the charge. In experiments yielding only forsterite, an excess of MgF_2 was present in the melt. As renewed checking of the refractive indices of the reaction products did not reveal the presence of any grains with indices below 1.500, it must be assumed that MgF_2 either has escaped from the melt or is camouflaged by graphite abundantly present in the cakes; or, that a reaction has taken place between magnesium fluoride and carbon, leading towards the formation of magnesium carbides.

Special attention must be paid to Exp. 16. Here the reaction products consisted of fluor-norbergite with minor amounts of fluor-chondrodite. The excess of MgF_2, in this case, crystallized from the melt in the form of sellaite. Consequently, no intermediate step between sellaite and norbergite seems to be possible.

No direct comparison of the refractive indices can be made between the natural humite minerals and those artificially produced, due to the lack of chemical analyses in the latter case. As to the natural humite minerals, Larsen (1928, pp. 354–359) found a tendency towards a decrease in the indices of refraction with the increase in the fluorine content. A similar conclusion was made also by the present writer (Rankama, 1938, p. 91), on a later occasion. In the amphibole group, Bowen and Schairer (1935, p. 549) noted that the refractive indices of synthetic fluor-amphiboles are lower than those in the hydroxy-amphiboles. Their observation was further verified by Grigoriev and Isküll (1937, p. 173), in regard to a regenerated amphibole rich in fluorine.

In the present case, all the products obtained are completely devoid of water. Consequently, nothing can be said as to the effect of fluorine and water on the refractive indices in the humite group. The indices of refraction of synthetic magnesium fluor-norbergite agree with the values given in literature for the natural mineral, and thus would indicate that the iron compounds were not completely reduced. In Exp. 16, on the other hand, the exceptionally low refractive indices of both norbergite and chondrodite may be explained by the complete reduction of the iron compounds to metallic iron.

The magnesium orthosilicate obtained in the experiments is evidently very pure, to judge from its optical properties. Its indices of refraction are decisively lower than those of the forsterite used in the fusions. In experiments yielding magnesium orthosilicate as the main or single component, the refractive indices seem to be even a little lower than those reported in the handbooks for pure magnesium orthosilicate. This would, perhaps, suggest a partial replacement of O^{2-} by F^{-} in the lattice.

By the complete replacement of the hydroxyl groups in the lattices of norbergite and chondrodite by fluorine, the chemical resistance power of the compounds evidently will increase. The synthetic fluor-norbergite and fluor-chondrodite are insoluble in hydrochloric acid of any concentration, while the natural humite minerals are easily gelatinized by this acid.

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