A PETROGRAPHIC STUDY OF ARTIFICIAL SILLIMANITE

by

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INTRODUCTION

The scope of this thesis is limited to that of a petrographic study of Sillimanite and the minerals occuring with it. But as this work is subsidery to the work of the Bureau of Mines, in the study of Sillimanite as a refractory and also that the preparation and the testing of the resultant materials often throws light on the crystallization of the melts; a few paragraphs will be taken to describe the way the material was prepared and also the way it was tested after preparation. For a fuller account, F.W. Schroeder's thesis must be consulted.

Realizing the need for a refractory material that will withstand the severe conditions of the electric furnace, the Bureau of Mines has investigated Sillimanite to see how nearly it will fill the requirements of such a refractory. An ideal refractory for use in the electric furnace would have the following specifications. 1. The cone fusion temperature should not be lower than cone 35 or about 1750° Centigrade. 2. It should be able to stand a load at high temperatures. Some refractorys that have a high fusion point fail at much lower temperatures when subjected to high pressure. 3. As the electric furnaces have comparatively enormous fluctuations in temperature over a short period of time, an ideal refractory would have a small temperature coefficient of expansion.

If this were not the case the bricks would crack or split an undesirable process called spalling. 4. After the bricks are prepared and are in place as the lining of a furnace their volume should remain nearly constant. 5. It should be chemically inert so as to withstand the chemical action of slags, metals and furnace gases. 6. It should be hard enough to withstand the abrasion of circulating metals and dense enough to resist penetration of slags. 7. It should have low heat conductivity in order to minimize radiation losses and low electrical conductivity in order to minimize power losses by short circuiting.

PREPARATION OF ARTIFICIAL SILLIMANITE

Natural occurences of Sillimanite have not as yet been found in quanities to be used to be used on a commercial scale. To obviate this difficulty the Bureau of Mines undertook the preparation of artificial Sillimanite from alumina and china clay. In preparing artificial Sillimanite the Higgins type electric furnace was used (Fig.1). This furnace has a capacity of 300 pounds of fused material. As china clay and alumina have low electrical conductivities, the material must be heated almost to it's melting point before it becomes appreciably conductive. In charging the furnace, a layer from 4 to 6 inches deep, consisting of the china clay-alumina mixture to which 5 to 10 percent sawdust is added, is laid down. The object of the sawdust is to make the mass porous enough to allow the escape of any gas that may be formed.

A crushed carbon train is built up between the electrodes. The shell is then filled up with charge and the power turned on. Power input varies between 40 and 60 K.W. during the course of the melt. A low E.M.F. of from 30 to 50 volts is first used which must be increased as th carbon train burns out. At times the potential difference must be raised as high as 150 to 175 volts. However the conductivity of the charge increases with the temperature and the melt ends with an E.M.F. of approximately 80 to 90 volts. The electrodes are then withdrawn and the melt allowed to cool. After cooling the fused clay is taken from the furnace and the unfused material broken from around it. These materials are then crushed and sampled for testing. (Fig. 2, shows chart for typical melt).

METHODS OF TESTING

Methods of testing are as follows: 1. Chemical Analysis of the melts are made in the laboratory of the Bureau of Mines. The scheme of analysis was developed by Mr. Barrett and Mr. J.L. Sullivan, fellowship men in the Bureau of Mines. 2. Cone Fusion Tests. Material made into cones by grinding it and binding with gum arabic. These prepared cones from the melts are then compared with standard Orton Cones. 3. Load Test. The object of this test is to determine the temperature at which a standard 9 inch brick will fail when subjected to a compressive load of 25 pounds to the square inch. 4. Spalling Tests. The bricks are heated and then immersed in cold water. The amount of cracking is then

noted.

MINERALOGY OF SILLIMANITE AND ASSOCIATE MINERALS

Sillimanite belons to the andalusite group of minerals. It was named after Professor Benjamine Silliman of New Haven (1779 - 1864). Sillimanite is a definate compound represented by the formulae Al_2SiO_5 or $Al_2O_3.SiO_2$. It consists of 36.8 percent silica and 63.2 percent alumina. Crystallographically Sillimanite crystallizes in the orthorhombic system, forms prismatic faces, striated and rounded. Commonly occurs in long parallel groups, passing into fibrous and columnar massive forms which are sometimes radiating. Cleavage: b (010) very perfect. Fracture uneven. Hardness is between 6 and 7. Specific Gravity is between 3.23 and 3.24. Luster is vitreous approaching sub-adamantine. Color hair-brown, grayish brown, grayish white, pale olive-green. Transparent to translucent. Sillimanite is biaxial optically positive, sometimes distinctly pleochroic and double refraction strong. Axial plane is parallel to b (010). Axial angle and indices are variable, 2V = 20° (approx.) = 1.638. = 1.642. = 1.653. The conditions which Sillimanite can form magmatically have been determined by J. Morozewicz.[1] In the magmatic mixture $RO.mAl_2O_3.nSiO_2$, if magnesia or iron are absent where m = 1, and n is greater than 6, Sillimanite is developed. Shists of the above composition are found in nature with Sillimanite crystals in them.

1. Data of Geochemistry.

Corundum crystallizes in the hexagonal system. It is often twinned and the crystals are usually rough or rounded. Parting c (0001), sometimes perfect, but interupted. Fracture uneven to conchoidal. Hardness is equal to 9. Specific Gravity varies between 3.95 and 4.10. Luster is Adamantine to vitreous, sometimes pearly. Color blue, red yellow, brown, gray, and nearly white. Optically uniacial negative, often shows a tendency towards a biaxial anomoly. Index of refraction = 1.767 to 1.768 and = 1.759. Corundum is a definate compound represented by the formulae Al_2O_3, aluminium = 52.9 percent and oxygen = 47.1 percent. In nature it often occurs in crystalline rocks, such as granular limestone and dolomite, gneiss, granite, mica slate and chlorite slate. In the alumosilicate magma with the general formulae $RO.mAl_2O_3.nSiO_2$ the following rules are found to apply.[1] First is magnesia and iron are absent, and the value of n lies between 2 and 6, the excess alumina will crystallize wholly as corundum; but if n is greater than 6, Sillimanite, or Sillimanite and corundum will form.

The striking difference between corundum and Sillimanite are the differences in index of refraction which makes a very easy separation possible by imbedding the crushed fragments of the minerals in an oil of known index of refraction which lies between that of Corundum and Sillimanite. In thin sections Sillimanite is characterized by its high interference colors while the interference colors of Corundum are low.

1. Data of Geochemistry.

Another test which makes the separation easy under the microscope is the determination of the interference figure. Sillimanite is biaxial positive and Corundum is uniaxial negative. In a Sillimanite matrix corundum stands out in a rough high relief. In crystal habit the two minerals differ markedly, the fibrous structure of Sillimanite is readily distinguished from the granular texture of corundum.

The binary eutectic for alumina and silica is represented by (Fig.3). The curve is self explanatory showing the temperatures of formation of the different minerals. Any quartz that is formed in these melts is of the amorphous variety having an index of refraction close to trydimite and is termed glass.

PETROGRAPHY OF THE DIFFERENT MELTS

The numbers assigned to the various melts are those used by the Bureau of Mines. They are not in numerical order but are arranged in the order that they were prepared and treated. The first group of melts, were attempts to get the true Sillimanite proportions by mixing charges of theoretical Sillimanite proportions, (Al_2O_3 = 63 percent. SiO_2 = 37 percent). As these melts did not give the calculated results, another group of melts were started. This time the first melt contained increasing amounts of silica until Sillimanite proportions were obtained. In studying the different thin sections it was desirable to know the part structure played in producing a good brick and also the type of structure

which gave the best results. An attempt to explain the factors that control structure is also made. Chemical analysis are given for the different melts and the tests (whereever made) on the resultant bricks are also given.

MELT 27

This melt was mad up of theoretical Sillimanite proportions. The melt contained a large amount of ferro-silicon which when made up into bricks had an explosive effect, thus making the bricks unsuitable. It was found that on adding several pounds of iron turnings to the liquid mass at the end of the melt, that these turnings would settle thru the melt gathering the ferro-silicon and concentrate it at the bottom of the furnace. An analysis of Melt 27 is given below.

UNFUSED		FUSED	
SiO_2	44.65	SiO_2	41.67
Al_2O_3	51.66	Al_2O_3	54.20
Fe_2O_3	2.30	Fe_2O_3	2.11
CaO	1.10	CaO	1.76
MgO	0.29	MgO	0.26

CONE FUSION TEST

Unfused mixture	Cone 36
Fused mixture	Cone 30

MELT 27 (A)

A remelt of Melt 27 was made in order to eliminate the ferro-silicon. During the process of remelting considerable silicon was volatilized which is shown by a comparison of the analysis.

MELT 27		MELT 27 (A)	
SiO_2	41.67	SiO_2	35.73
Al_2O_3	54.20	Al_2O_3	61.54
Fe_2O_3	2.11	Fe_2O_3	2.36
CaO	1.76	CaO	0.87
MgO	0.26	MgO	0.21

A brick from Melt 27 (A) was tested and shown to fail due to it's bond. The difference in bonds between the interior and exterior of of the bricks from the furnace is due to a recrystallization of the Sillimanite on the exterior of the brick.

A thin section made of Melt 27 (A) shows that the melt is made up of long rather thick fibers of Silliman-ite which lay in parallel directions A great deal of glass is contained in this melt, the glass has an index of refraction below that of Canada Balsom (1.54).

MELT 33

The material used to make up this melt was a mixture of residues taken from all previous melts. Eight bricks were made from this melt varying in size of grog, amount of bond added, and the heat treatment was varied. All the bricks failed between Cones 15 to 18 when subjected to load tests.

CHEMICAL ANALYSIS

SiO_2	32.18
Al_2O_3	63.80
FeO	3.17
CaO	0.51
MgO	0.25

Two thin sections were made of this melt, one on the rim or exterior of the melt which proved to be a mixture of Sillimanite and Corundum, in some places the rim showed as much as 90 percent of Corundum. The thin section taken from the center of the melt was compose of Sillimanite and an isotropic substance which resembled unfused china clay. The character of the Sillimanite is apparently different than that in Melt (27 A) as the individual crystals crystals show an interlocking contrasted to the parallel nature of them in the first melt. A photomicrograph of Melt 33 is shown in (Fig. 6).

MELT 28

Melt 28 was made of 75 percent alumina and 25 percent silica. A brick made from this melt was subjected to three load tests without causing failure. The brick was unchanged at Cone 26. This brick was apparently the proper sillimanite mixture to be suitable for the refractory requirements.

CHEMICAL ANALYSIS

UNFUSED		FUSED	
SiO_2	31.75	SiO_2	29.50
Al_2O_3	65.82	Al_2O_3	68.14

CONE FUSION TEST CONE 38

The structure of this melt is exceedingly close. It is cryptocrystalline in texture and shows that the crystallization of the Corundum took place in a number of centers and may have broken up the crystallization of the Sillimanite. If the corundum acts as an obstacle to Sillimanite crystallization it should be distributed at regular intervals and the Sillimanite crystals should end at a corundum center. In this section that is apparently the case. At some places the structure shows an overlapping of Sillimanite crystals on those of Corundum giving it a mixed crystal texture. Brick from Melt 28 shows no modification from the melt. The strength of the brick evidently came from the original texture of the melt. A photomicrograph of Melt 28 is shown in (Fig.7). This photograph shows the mixing of the Sillimanite and Corundum crystals.

MELT 41

Another melt was attempted to try and reproduce the texture found in Melt 28. A brick from this melt sheared at Cone 16.

CHEMICAL ANALYSIS

UNFUSED		FUSED	
SiO_2	33.54	SiO_2	30.70
Al_2O_3	62.66	Al_2O_3	66.14
FeO	2.67	FeO	3.16

CONE FUSION TEST CONE 38

Melt 41 is composed entirely of Sillimanite. It is of the long bladed variety composed of parallel crystals. No Corundum is in evidence, in this section, so the crystallization of the Sillimanite proceeded without interuption. Photomicrograph of Melt 41 is shown in (Fig. 8).

ALUMINA-SILICA SERIES

After the failure of Brick 41 it was decided to start with pure alumina and make each successive melt higher in silica until the desired proportions were reached. This would throw light on the amount of Corundum needed to favorably influence the structure of the melts and also over what range between the compound Sillimanite and pure Corundum that this desired structure could be reproduced. The first melt, that of pure alumina, is designated as Melt O.

MELT O

This melt showed traces of carbon in chemical analysis. No bricks or tests were made of this material.

Under the microscope the melt is seen to be composed wholly of corundum. The individual crystals are microscopic in size. A photomicrograph of this melt is shown in (Fig. 9).

MELT 44

This melt was made up of 90 percent alumina and 10 percent silica.

The section taken of this melt is composed wholly

of Corundum. In this melt the first appearance of a peculiar structure is seen. This structure is seen in the next three succeeding melts. The Corundum assumes beautiful patterns that correspond to the patterns of snow flakes. The Corundum evidently started crystallizing from a center and built up around it in concentric squares.

MELT 52

Melt 52, the amount of silica was increased so that the melt showed the following chemical analysis.

CHEMICAL ANALYSIS

SiO_2	11.56
Al_2O_3	86.64
FeO	1.80

CONE FUSION TEST	CONE 39 to 40
LOAD TEST	CONE 31

A thin section of this melt showed very little variation from the section made of Melt 44. It consisted wholly of corundum, which assumed the peculiar texture noted in Melt 44. A photomicrograph of Melt 52 is shown in (Fig. 10).

MELT 53

In Melt 53 the silica was increased so that the chemical analysis showed 12.9 percent silica.

CHEMICAL ANALYSIS

SiO_2	12.9
FeO	1.5
Al_2O_3	85.6

As none of the material from this melt was made into bricks, there is no data as to the tests it would withstand.

A thin section of this melt was very little different from that of Melt 52. The section was composed wholly of Corundum which crystallized out in the same manner as noted in Melt 44 and Melt 52. A photomicrograph of this melt is shown in (Fig. 11).

MELT 54

In Melt 54 the silica proportion was increased until the chemical analysis showed 14.5 percent silica.

CHEMICAL ANALYSIS

SiO_2	14.5
Al_2O_3	83.3
FeO	2.2

CONE FUSION TEST	CONE 39
LOAD TEST	CONE 31

A thin section of this melt is composed cheifly of Corundum altho a few needles of Sillimanite are in evidence. This is the first appearance of Sillimanite as far as the thin sections have been examined. The

Corundum does not have the texture that it assumed in the three previous melts but resembles the structure in the melt composed of pure alumina (Melt 0). A photomicrograph of Melt 54 is shown in (Fig. 12).

MELT 55

In Melt 55 the silica proportion was increased until the chemical analysis showed 18.2 percent silica.

CHEMICAL ANALYSIS

SiO_2	18.2
Al_2O_3	79.6
FeO	2.2

No tests were made on this material.

A thin section of this melt shows a structure that closely approaches that of Melt 28. The section is composed of Sillimanite and Corundum. Most of the slide shows a mixed crystal effect that is well brought out in the photomicrograph (Fig. 13). This section also shows a segregation of the Corundum into bunches. Where Corundum occurs in this manner it assumes the structure noted in Melt 52 and Melt 53. From the appearance of this section and comparing it to the thin section of Melt 28 it appears that this melt would make a very good brick.

MELT 56

In Melt 56 the silica content has been increased to 23.1 percent according to the chemical analysis.

CHEMICAL ANALYSIS

SiO_2	23.1
Al_2O_3	74.8
FeO	2.1

No tests were made on the material from this melt.

The thin section of this melt shows corundum to be quite plentiful with increasing amounts of Sillimanite. The texture is still cryptocrystalline. A photomicrograph of this melt is shown in (Fig. 14).

MELT 57

In Melt 57 the silica content was increased until the chemical analysis showed 33 percent silica.

CHEMICAL ANALYSIS

SiO_2	33.
Al_2O_3	65.2
FeO	1.8

No tests were made of this material.

In the thin section, Melt 57 is seen to be composed wholly of Sillimanite which shows a parallel fibrous structure, somewhat interwoven. In the photomicrograph (Fig. 15) the structure of the melt is very well shown.

MELTS 58, 59 AND 60

These three melts do not vary much in thin section except as to the arrangement of the Sillimanite crystals. The sections are made up wholly of Sillimanite which is coarsely crystalline and is not suitable for refractory material.

Photomicrographs of Melts 59 and 60 are shown in (Figures 17, 18 and 19).

SUMMARY

1. The worth of the polarizing microscope in the study of non-opaque refractory materials has proved to be as valuable as the study of polished sections is to the Metallographer. The type of crystallization, the constituents of a melt, and the structure are all avenues of study which can be accomplished best with the aid of thin sections.

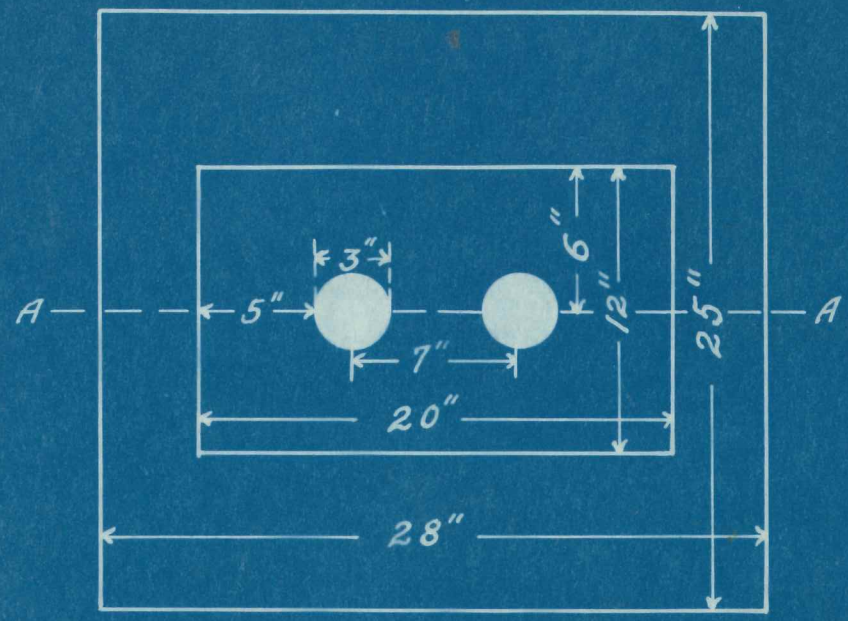
2. As there is undoubtedly a magmatic segregation within the melt, during the process of crystallization, is shown by the concentration of alumina in one part of the melt and the concentrations of silica in another part.

3. That the most essential thing about the crystallization of a melt to produce good refractory material is the structure. Every good brick examined showed a cryptocrystalline structure.

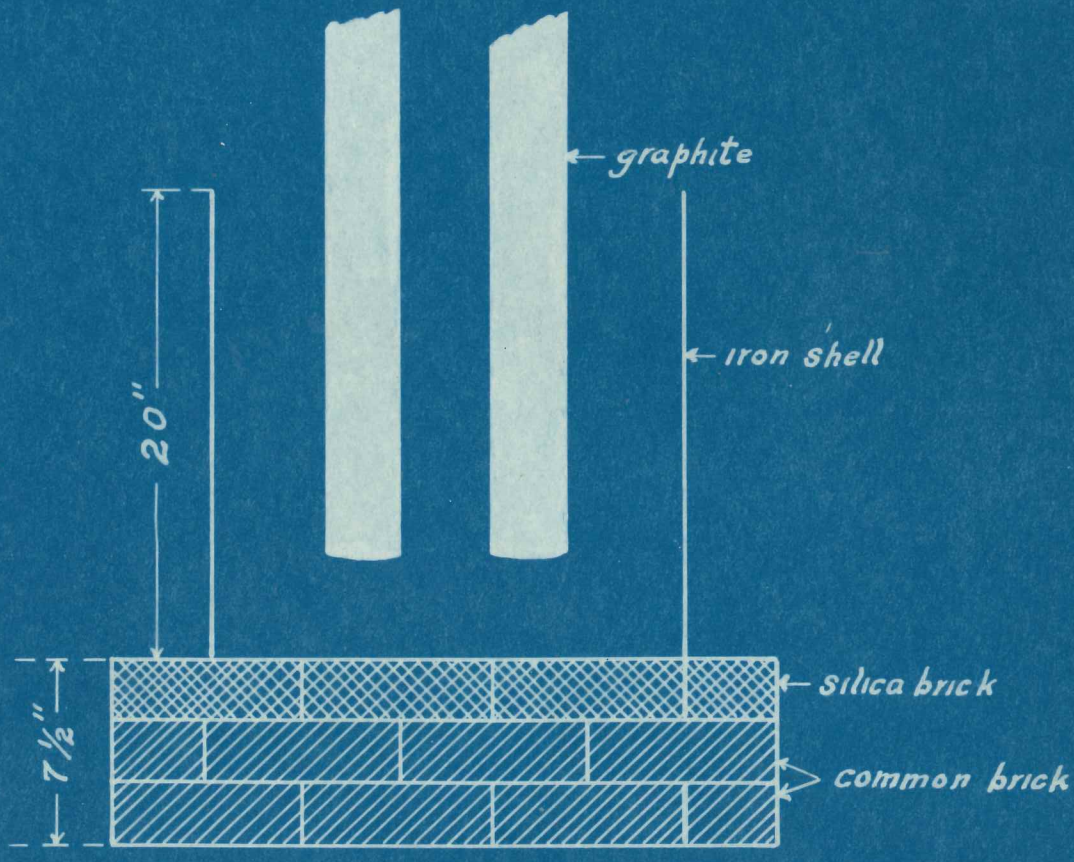
4. That this structure may or may not be effected by the crystallization of the corundum within the melt. The best bricks were made from melts which showed an intergrowth between corundum and sillimanite. Corundum evidently broke up Sillimanite crystallization in these bricks. In other sections corundum and sillimanite are found concentrated in different areas showing that the mere presence of corundum does not mean that it will produce a favorable structure.

5. In the study of Sillimanite melts from a petrographic standpoint, it seems advisable to the author that a number of thin sections should be prepared from

each melt. As the crystallization undoubtedly varies in different parts of the melt, the study of one section is often misleading even when typical samples are chosen. It is beyond the scope of this thesis to make such a detailed study, however the results obtained evidently point toward the generalizations stated above.



PLAN



ELEVATION SECTION ON A-A

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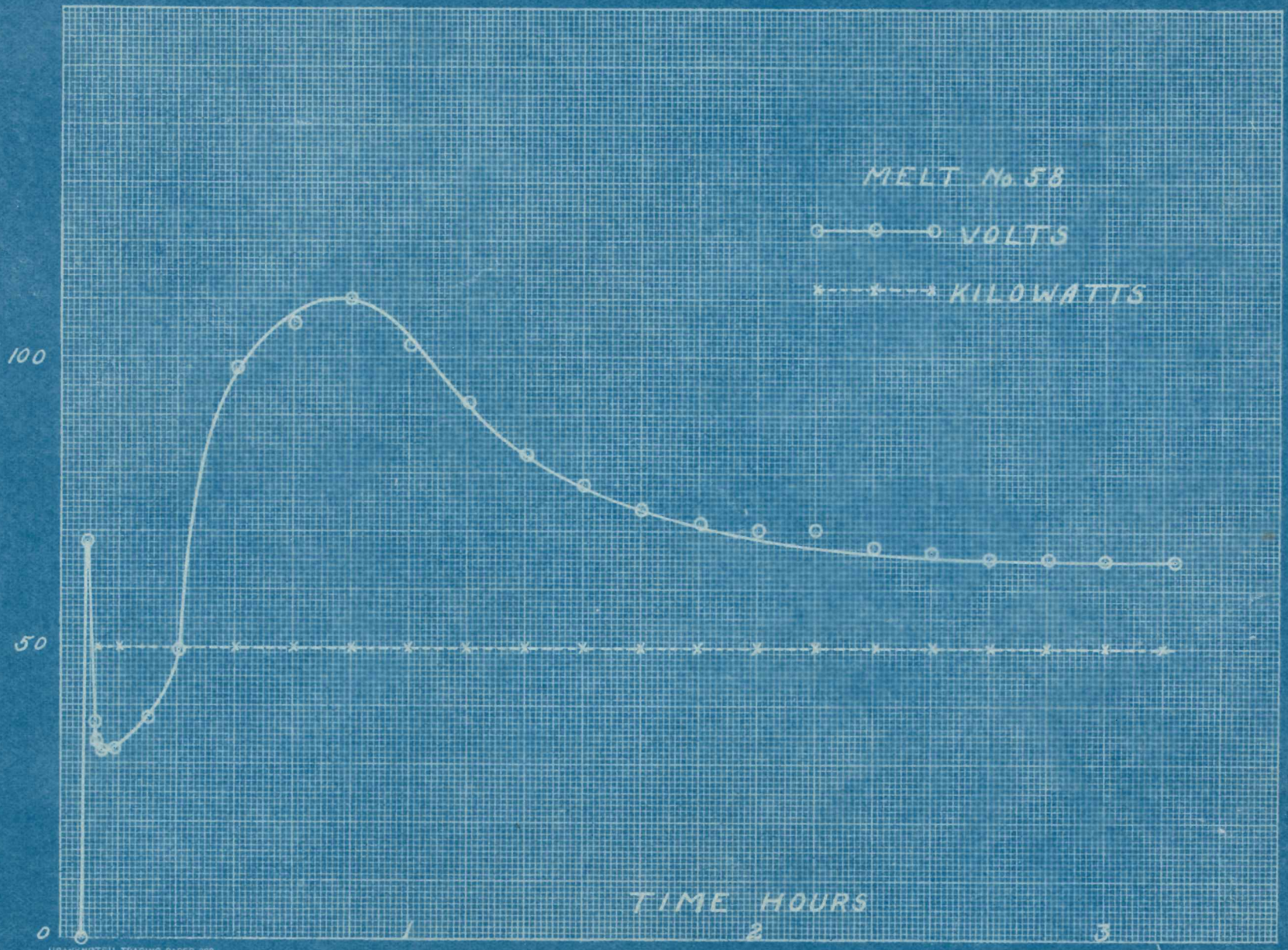
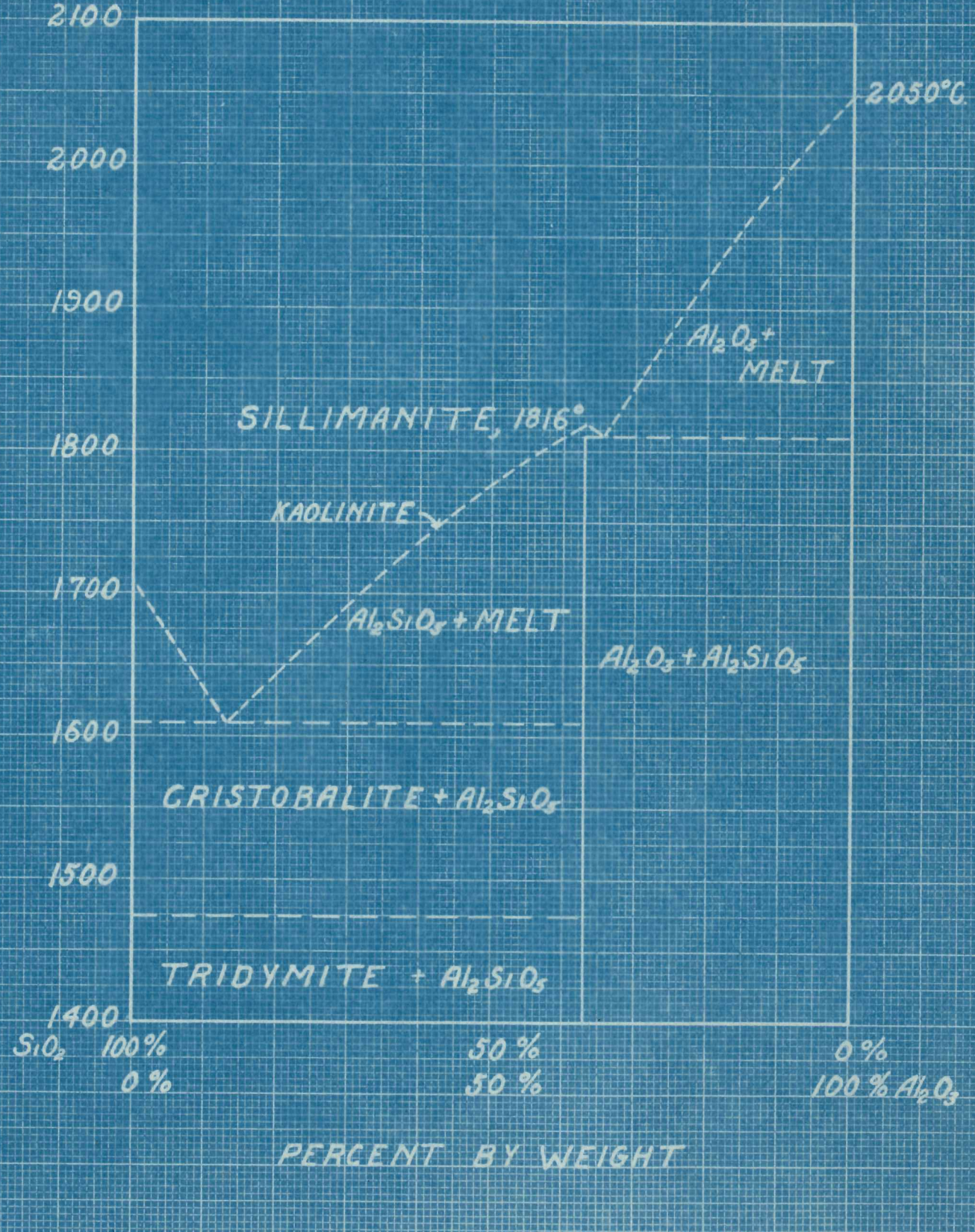


SILICA - ALUMINA DIAGRAM

Rankin & Wright, Am. Jour. Science, Vol. 189, 1915. with later modifications.



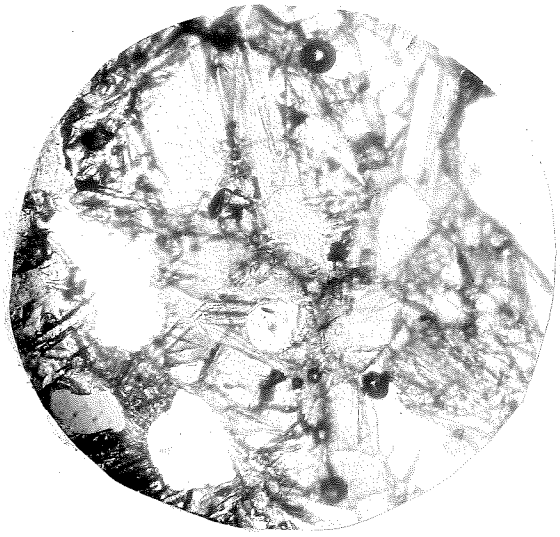


Fig. 5.

Fig. 6.

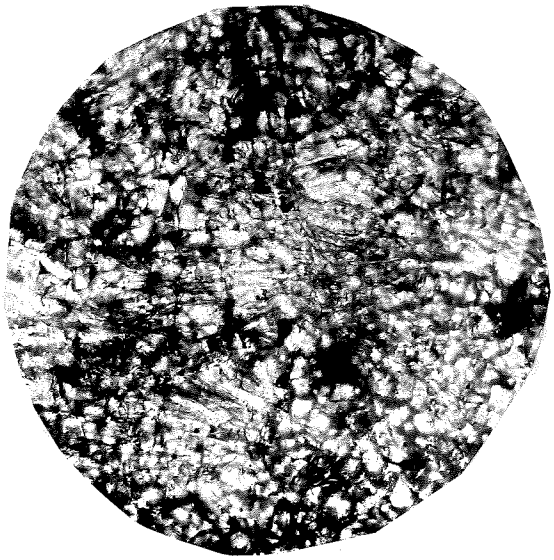


Fig. 7.

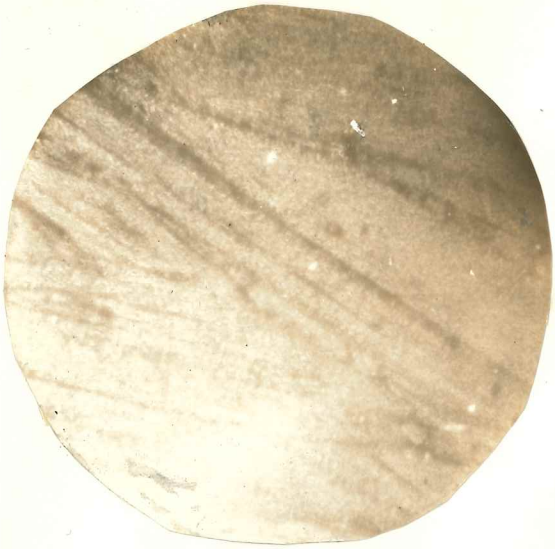


Fig. 8.

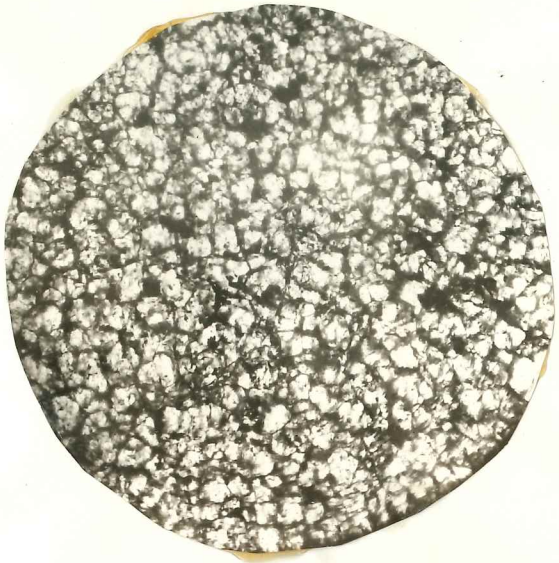


Fig. 9.

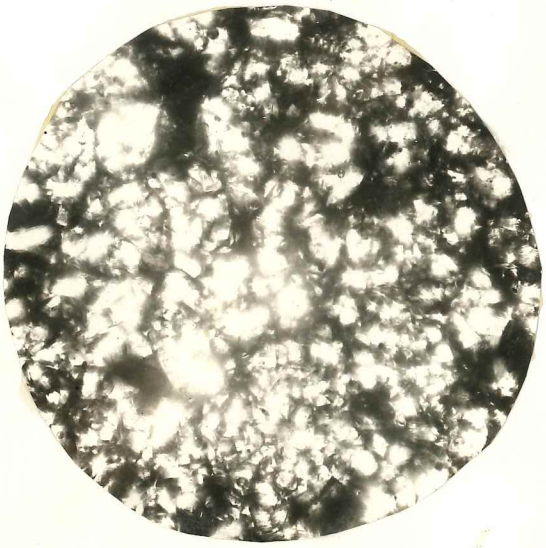


Fig. 10.

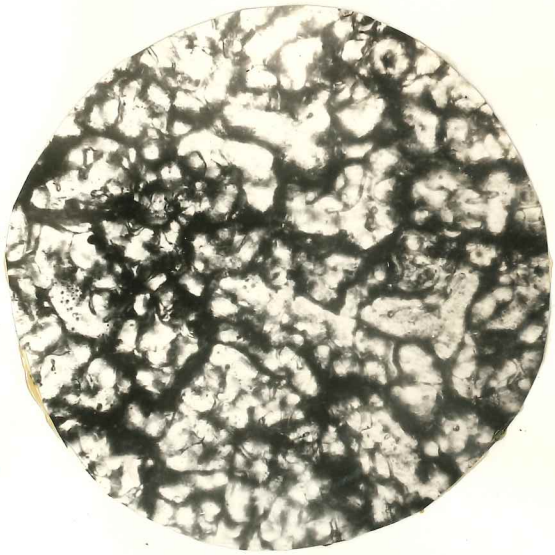


Fig. 11.

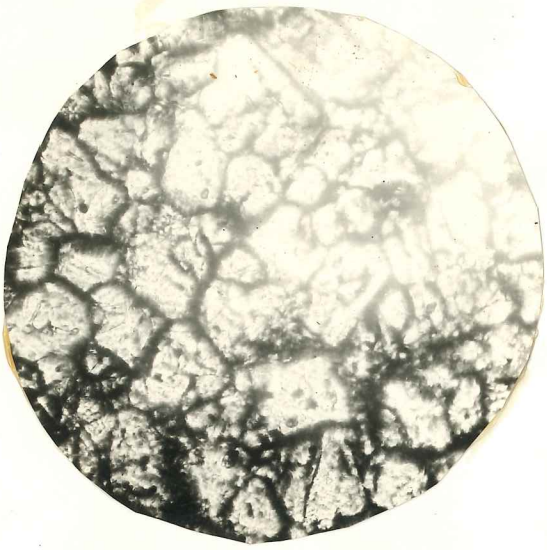


Fig. 12.

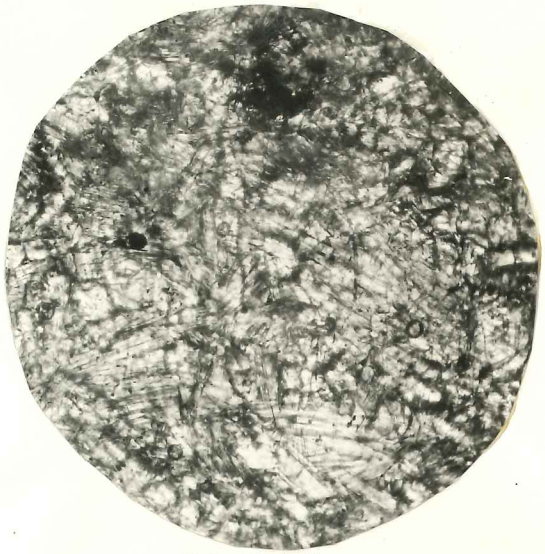


Fig. 13.

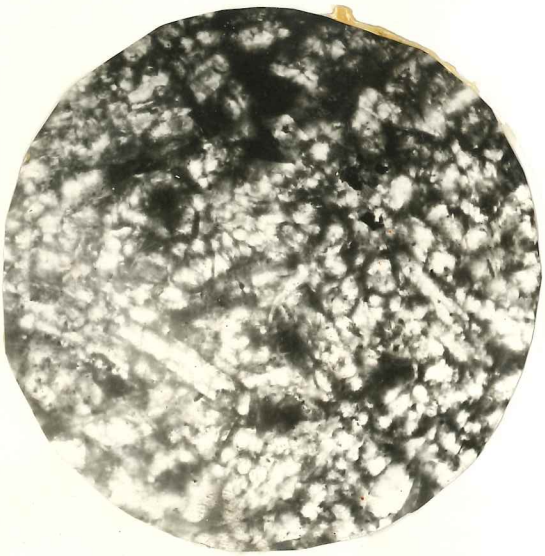


Fig. 14.

Fig. 15.

Fig. 16.

Fig. 17.

Fig. 18.