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MINERALOGY.—*Mullite, a silicate of alumina.*[1] N. L. BOWEN, J. W. GREIG, and E. G. ZIES. Geophysical Laboratory, Carnegie Institution of Washington.

INTRODUCTION

The compound $Al_2O_3 \cdot SiO_2$ occurring in the three forms sillimanite, andalusite, and cyanite has hitherto been regarded as the only compound of alumina and silica existing in nature. Of the three forms sillimanite has been accepted as the stable one under pyrogenetic conditions, but a recent study shows that it is necessary to make drastic modifications of existing conceptions in this regard. An investigation of the equilibrium relations of alumina and silica has shown that there is only one compound of these oxides stable in contact with liquid in the binary system.[2] This compound is $3Al_2O_3 \cdot 2SiO_2$ but crystals of it show such remarkable similarity with natural sillimanite that they have been identified with sillimanite by a number of workers examining synthetic mixtures and artificial products of various kinds.

The investigation noted above showed that this 3:2 compound is the only stable compound not only at the very high temperatures where liquid occurs in the binary system but also at temperatures as low as 1000°C. and probably much lower. In view of this fact it seemed to us that the compound could scarcely fail of occurrence in natural rocks though here again probably determined as sillimanite. The most promising material for the occurrence of the 3:2 compound

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[1] Received March 10, 1924.

[2] Papers reporting the results of this investigation were presented by Bowen and Greig at the recent meetings of the Geological Society of America and of the American Ceramic Society.. Journ. Amer. Ceramic Soc., April, 1924.

appeared to be the so-called sillimanite buchites or fused argillaceous sediments occurring rather frequently as inclusions in Tertiary intrusives of the Western Isles of Scotland. These have been noted by various writers, but those occurring in Mull have recently been the subject of a most interesting study in a paper by Dr. H. H. Thomas to whom we are greatly indebted for specimens of buchite.[3] It may be stated in advance that this material from Mull has fully justified our expectations.

The inclusions described by Thomas embrace the "sillimanite" buchites, which appear to be largely the product of direct fusion of phyllites, together with a number of varieties in which anorthite, hypersthene, and other minerals have been developed as a result of interaction of the inclusions and doleritic magma. It is the buchites proper that are of particular interest in the present connection. Of these we have examined two, one from Seabank Villa and the other from Nun's Pass. A chemical analysis of the latter is given by Thomas. The rocks consist principally of glass in which are embedded very rare plates of corundum and abundant minute prisms of a mineral having all the properties of sillimanite in so far as these can be measured in thin section. Careful measurements of the refractive indices of these crystals show, however, that the values are too low for sillimanite and, as will be shown more fully in the following, the crystals are to be identified with the compound $3Al_2O_3 \cdot 2SiO_2$. This compound has hitherto been recognized only in synthetic products. Its occurrence in natural rocks necessitates a mineralogical name and for this we propose the term, *mullite*, after the locality whence came the rocks in which it is here first identified, the Island of Mull.

PURE SYNTHETIC MULLITE

The pure compound $3Al_2O_3 \cdot 2SiO_2$ can be prepared by sintering a mixture of alumina and silica in the proportions demanded by the formula. A mass consisting exclusively of crystals of one kind is thus obtained, a fact which consitutes the best evidence of the composition of the compound. It is obtained also, together with other phases, in mixtures of alumina and silica in other proportions. In all these cases it has the same properties which are closely related to, yet distinct from, those of sillimanite. Comparison of their prop-

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[3] *On certain Xenolithic Tertiary Minor Intrusions in the Island of Mull (Argyllshire).* Quar. Jour. Geol. Soc., **78**: 229-260. 1922. See also the fine new map. Geol. Survey Scotland, Mull, sheet 44, 3d edition, 1923.

erties is best given in tabular form (see Table 1) but, by way of emphasizing the similarity in those properties most readily determined, it may be stated that both form prisms of nearly square cross section with a perfect cleavage whose trace is parallel to the shorter diagonal of this section. The plane of the optic axes is parallel to this cleavage and the elongation of the prisms is positive. Only when we turn to properties to which definite numerical values can be assigned do the differences become apparent, and even then they are not very great. The sillimanite from Delaware County, Pennsylvania, with which mullite is compared is one that we selected as being particularly pure and of which an analysis is given in Table 3.

TABLE 1.—PROPERTIES OF PURE MULLITE AND OF SILLIMANITE

		MULLITE	SILLIMANITE*
Crystal system		Orthorhombic	Orthorhombic
Prism angle $(110 \wedge 1\bar{1}0)$		89° 13′	88° 15′
Cleavage		‖010	‖010
Optic orientation		$c = \gamma$ and $b = \alpha$	$c = \gamma$ and $b = \alpha$
Refractive indices	γ	1.654	1.677
	α	1.642	1.657
Axial angle, 2V		+45°–50°	+25°–30°

* The optical properties were measured on the sillimanite from Delaware County, Pennsylvania, of which an analysis is given in Table 3. The prism angle is that ordinarily given for sillimanite in the text-books.

Mullite was synthesized as long ago as 1865 by Sainte-Claire Deville and Caron.[4] They passed SiF_4 over a mixture of alumina and silica at a bright red heat and obtained crystals which had the composition given under I and II, Table 2. We have repeated the experiment and find that the crystals have refractive indices identical with those of pure mullite made by other methods.

Vernadsky separated crystals of mullite from Sèvres porcelain by means of hydrofluoric acid and analyzed the crystals. He found the composition given under III, Table 2. On the basis of these results he assigned the formula $11Al_2O_3 \cdot 8SiO_2$ to his own and to Deville's crystals.[5]

Cox separated the crystals from a burned fire clay and analyzed them with results given under IV and V, Table 2.[6] He accepts Vernadsky's formula.

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[4] Ann. Chim. Phys. **5**: 114. 1865.

[5] Bull. Soc. Min. France **13**: 270. 1890.

[6] A. H. Cox, Geol. Mag. (Decade 6) **5**: 61. 1918.

All of these analyses agree in placing the composition somewhat more siliceous than the 3:2 ratio yet not so siliceous as the 11:8 ratio. In view of the fact that mullite crystals are particularly prone to carry small inclusions of the siliceous liquid in which they grow, this small excess of silica is probably not to be regarded as representing a real departure of the crystals themselves from the 3:2 ratio.

TABLE 2.—ANALYSES OF MULLITE BY EARLIER INVESTIGATORS

	I	II	III	IV	V	$3Al_2O_3 \cdot 2SiO_2$
	DEVILLE		VERNADSKY	COX		
SiO_2	29.1	29.5	29.7	30.07	28.89	28.2
Al_2O_3	70.9	70.2	70.3	69.93	71.11	71.8

TABLE 3.—COMPOSITION OF NATURAL SILLIMANITE

	I	II	III
SiO_2	37.08	36.70	37.1
Al_2O_3	63.11	62.73	62.9
Fe_2O_3	0.09	0.63	
	100.28	100.06	100.0

I. Sillimanite from Delaware County, Pennsylvania. U. S. National Museum No. 9752. E. G. Zies analyst. TiO_2 is less than 0.01 percent.

II. Sillimanite from Romaine, Quebec.* E. W. Todd analyst.

III. Theoretical $Al_2O_3 \cdot SiO_2$.

* Walker and Parsons. Univ. of Toronto Studies, Geol. Series No. 16, 1923, p. 36.

MULLITE FROM SEABANK VILLA, ISLAND OF MULL

As we have already stated, the natural example of this compound, to which we wish to direct attention here, occurs as minute crystals embedded in glass. It would thus appear to be unfavorable material for the establishment of a species, but as a matter of fact it can readily be separated from the glass. This was accomplished by allowing the powdered buchite to stand over night in *cold* hydrofluoric acid which completely decomposes the glass without affecting the crystals (Vernadsky's method). After decanting the HF a little concentrated H_2SO_4 is added and the mass warmed to decompose fluorides. A little HCl is then added, followed by dilution with water. The remaining powder is then caught on a filter paper, well washed, and the filter paper burned off. In this manner a powder of a delicate lilac pink is obtained which proves on examination under the microscope to consist of clean, sharp crystals of mullite with no foreign material other than very rare plates of corundum. The optical determinations and chemical analyses were made on powder so obtained.

The refractive indices of these crystals are higher than those of pure synthetic mullite, an effect to be attributed to their content of TiO_2 and Fe_2O_3, as is also their pink color. The determined values are given in Table 5, and in Fig. 1.

The chemical composition of this natural mullite is given in Table 4.

TABLE 4.—ANALYSES OF MULLITE

	I	II	III
SiO_2	28.2	29.04	29.36
Al_2O_3	71.8	69.63	69.05
Fe_2O_3		0.50	0.86
TiO_2		0.79	1.12
MgO			0.10
Na_2O		0.18	
K_2O		0.06	
	100.0	100.20	100.49

I. Theoretical composition $3Al_2O_3 \cdot 2SiO_2$.

II. Mullite from Seabank Villa, Island of Mull. (Contained 0.51 per cent corundum and 0.1 per cent rutile which were determined separately.) E. G. Zies analyst.

III. Mullite from the crowns of glass pots. N. L. Bowen, analyst. Fe_2O_3 and TiO_2 by M. Aurousseau.

The other buchite examined, the analyzed material from Nun's Pass, is not significantly different from the Seabank Villa example just discussed. Treatment with HF does not, however, yield as clean a product of mullite. A considerably greater quantity of corundum as well as rather abundant minute needles of rutile are left with the mullite. It was on this account that the product obtained from the Seabank Villa buchite was used for analysis, though, no doubt in the absence of better material, the composition of the mullite in the Nun's Pass buchite could have been determined by appropriate treatment. The refractive indices were measured, however, and found to be appreciably higher than those of the Seabank Villa mullite, in fact not significantly different from those of the pot-crown crystals immediately to be described.

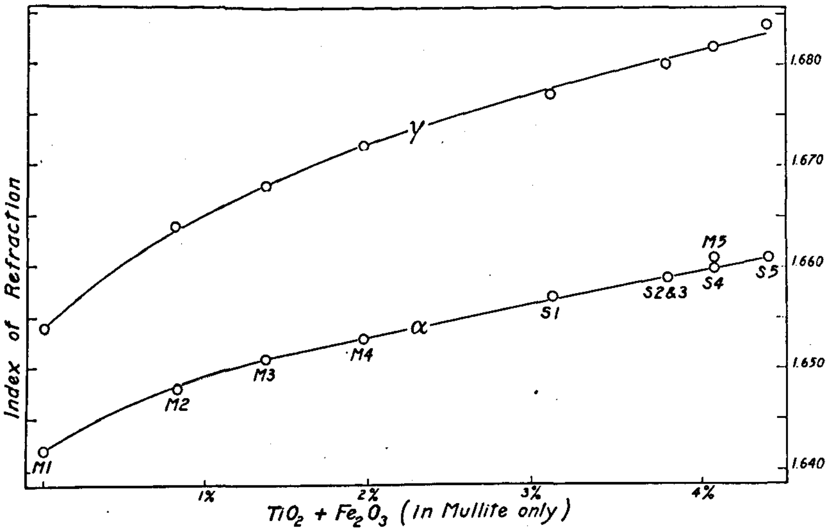

Fig. 1.—Relation between the refractive indices of various mullites and sillimanites. M1, M2, etc. = mullite I, mullite II etc. of Table 5. S1, S2, etc. = sillimanite I, sillimanite II, etc. of Table 6.

TABLE 5.—REFRACTIVE INDICES OF MULLITES

	I	II	III	IV	V
γ	1.654	1.664	1.668	1.672	1.682
α	1.642	1.648	1.651	1.653	1.661

I. Pure mullite $3Al_2O_3 \cdot 2SiO_2$.

II. Eitel's crystals (made aluminothermically, exact composition unknown).

III. Natural mullite from Seabank Villa, Island of Mull. Analysis under II, Table 4.

IV. Mullite from pot crowns. Analysis under III, Table 4.

V. Mullite from glass pots (G. V. Wilson). Composition unknown.

TABLE 6.—REFRACTIVE INDICES OF SILLIMANITES

	I	II	III	IV	V
γ	1.677	1.680	1.680	1.682	1.684
α	1.657	1.659	1.659	1.660	1.661

I. Sillimanite from Delaware County, Pennsylvania. Analysis under I, Table 3.

II. Sillimanite from Romaine, Quebec. Analysis under II, Table 3.

III. Sillimanite from Morlaix, France. Exact composition unknown.

IV. Sillimanite from Saybrook, Connecticut. Exact composition unknown.

V. Sillimanite from Saybrook, Connecticut. Exact composition unknown.

MULLITE FROM THE CROWNS OF GLASS POTS

All wares made from clays develop mullite crystals when heated to a sufficiently high temperature. If the ware carries but little iron or titanium the mullite crystals approach pure synthetic mullite very closely in properties and therefore in composition. When much iron or titanium is present a considerable amount of these may enter into the mullite crystals with corresponding effect on their properties. Some material sent us by Mr. Donald Ross of the Findlay Clay Pot Company proved to be of the latter kind. It came from the crowns of covered pots used in the manufacture of glass during several months. The mullite crystals in this have refractive indices much higher than those of pure mullite but still appreciably lower than any sillimanite. A quantity of these crystals was separated from the glass matrix by the method already described and the clean crystals so obtained were used for determination of the refractive indices and for chemical analysis. It is to be noted that the crystals frequently contain minute tubular inclusions of the liquid (glass) in which they grew, which is highly siliceous, and these should tend to throw the composition of the analyzed sample a small distance on the silica side of the actual composition of the crystals. The results of analysis are given in Table 4. The crystals are plainly mullite containing considerable amounts of titanium and iron. Their optical properties are given in Table 5 and in Fig. 1.

OTHER EXAMPLES OF MULLITE CRYSTALS

Two other examples of mullite crystals will serve to complete the series. One of these was prepared by Eitel by an aluminothermic method. The crystals so obtained were believed to be sillimanite but careful measurement of the refractive indices by Eitel gave values much lower than those of sillimanite and only a little higher than those of pure mullite. The exact composition is unknown but observed pleochroism[7] indicates some content of TiO_2 and Fe_2O_3 and both γ and α fall at the same composition on Fig. 1, thus indicating a $TiO_2 + Fe_2O_3$ content very close to 1 per cent.

The other example was described by G. V. Wilson and comes from glass pots. Mr. Wilson has kindly sent us several specimens of glass-pot crystals and among these we find one lot of crystals whose refractive indices correspond exactly with those published by him. These indices are, as noted by Wilson, the same as those of silli-

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[7] W. Eitel, Zeit. anorg. Chem. **88**: 173. 1914.

manite from Saybrook, Connecticut, within the limits of error of measurement.[8] That these crystals are not sillimanite, however, we could state on the basis of the method of their formation alone, but we have also proved that they are not, in the absence of sufficient material for chemical analysis, by means of thermal tests which establish that they are mullite.

The refractive indices suggest a content of TiO_2 + Fe_2O_3 upwards of 4 per cent (see Fig. 1). The notably strong pleochroism is, no doubt, connected with the comparative richness in these oxides.

THE MULLITE SERIES

In the foregoing we have discussed individual members of a series of mullites of varying TiO_2 + Fe_2O_3 content. The series is best brought out in the plot of refractive indices against composition, Fig. 1. This plot emphasizes the remarkable convergence of the properties of mullite upon those of sillimanite as the TiO_2 + Fe_2O_3 content of the mullite increases, until finally the two are, for practical purposes, no longer distinguishable in crystallographic and optical properties. Chemical and thermal properties must then be resorted to. One exception is to be noted in the matter of optical properties, namely, that when mullite has indices close to those of sillimanite it is always markedly pleochroic with γ violet-pink, β and α colorless. Thomas remarks upon this unusual pleochroism in "sillimanite." Present indications are that it is characteristic of mullite. It should be noted that even the optic axial angle, which is quite large (45°–50°) in pure mullite, becomes smaller in other members of the series. In crystals of mullite with the higher amounts of TiO_2 + Fe_2O_3 it is sensibly the same as in sillimanite.

Several different sillimanites showing a range of indices have been placed on the plot and tabulated in Table 6. The variation of indices in sillimanite itself is no doubt connected with variation of content of Fe_2O_3 + TiO_2, but in only two of those given have optical properties and chemical composition been determined on the same material. These are the sillimanite from Delaware County, Pennsylvania, which is very near the theoretical composition, and that from Romaine, Quebec, which contains a greater quantity of Fe_2O_3 (see Table 3). The other sillimanites plotted have not been analyzed. The scale of TiO_2 + Fe_2O_3 given on the plot applies only to mullite and not, of course, to sillimanite.

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[8] Trans. Soc. Glass Tech. **2**: 189. 1918.

It cannot be too strongly emphasized that there is no transition in composition from mullite to sillimanite. Their remarkable similarity in crystallographic properties would lead one to expect a series of solid solutions but all crystals made in the laboratory or found in nature have been either the one or the other with nothing intermediate.

GENETIC ASPECTS

In the identification of mullite in these high-temperature contact rocks, buchites, the findings of the laboratory are confirmed. Mullite is the stable compound of alumina and silica at high temperatures. Present indications are that mullite will be found in other contact rocks particularly in those that have been strongly heated. When the limits of stability of mullite and sillimanite have been determined these minerals will, no doubt, prove useful temperature indicators in geology.

SUMMARY

Having found, in the course of an investigation of the system, alumina-silica, that $3Al_2O_3 \cdot 2SiO_2$ is the only compound stable at high temperatures, we anticipated that this compound would be found in rocks of the appropriate composition when formed at high temperatures. We therefore examined some sillimanite buchites, so-called, from the Island of Mull, kindly supplied us by Dr. H. H. Thomas, and found that the "sillimanite" is really the $3Al_2O_3 \cdot 2SiO_2$ compound for which we accordingly propose the name, *mullite*.

The optical properties of pure mullite have been determined, as well as those of a series of mullites of varying TiO_2 and Fe_2O_3 content mounting to about 4 per cent. The properties show a remarkable similarity with those of sillimanite, the members of the series highest in $TiO_2 + Fe_2O_3$ being practically indistinguishable from sillimanite in optical properties. Chemically, however, the two compounds, mullite and sillimanite are always distinct and in spite of their crystallographic similarity there is no solid solution series between them.

Mullite will, no doubt, be found in other rocks. Its presence in some rocks and that of sillimanite in others will afford useful information regarding the relative temperatures of formation of the rocks.