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"FERROSILITE" AS A NATURAL MINERAL.

N. L. BOWEN.

ABSTRACT.

The crystallographic and optical properties of minute needles found in he lithophysae of an obsidian from Lake Naivasha, Kenya, correspond with hose of pure FeSiO₈ as determined by extrapolation in series of monoclinic pyroxenes. The occurrence of substantially pure FeSiO₈ as a natural mineral is rather unexpected since synthetic studies have suggested that reSiO₃ cannot occur as a crystalline compound. Critical examination of he results of synthesis shows, however, that the possibility of the forma-tion of substantially pure FeSiO₃ at decidedly low temperatures is not precluded. The needles may therefore be accepted as having substantially the composition $FeSiO_3$. It is proposed to extend the use of Washington's normative term "ferrosilite" to the naming of the natural mineral also and the name *clinoferrosilite* is therefore given to these crystals. Needles having the same properties have been found in the lithophysae of other obsidians, including the well-known example from Obsidian Cliff, Yellowstone Park.

The last paper from the pen of Henry S. Washington proposed, or rather reiterated his earlier proposal, that the normaive molecule FeSiO₃ should be named ferrosilite.¹ The term was thus put forth not as a mineral name but merely as a convenient designation of a theoretical end-molecule of metasilicate series, a molecule which it is often necessary to use in the recalculation of rock and mineral analyses. Nor did it seem likely that the name would ever be required as the designation of a natural mineral, for at approximately the same time there began to appear the results of a series of investigations of iron silicates all of which pointed to the conclusion that FeSiO₃ does not exist as a crystalline compound, a conclusion stated in substantially those words in the several papers setting forth these results.² With the ink scarcely dry on the

-: The system, MgO-FeO-SiO2, this Journal, 29, 151-217, 1935 (hereinafter referred to as "1935").

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N. L. Bowen.

latest of these papers it is somewhat disconcerting to find a mineral having properties that agree entirely with those of a monoclinic form of FeSiO₃ as indicated by a short extrapolation in the MgSiO₃-FeSiO₃ series of clino-pyroxenes and also in the CaFeSi₂O₆-FeSiO₃ series of like character.

The mineral was found in the lithophysae of a rhyolitic obsidian collected by me near Lake Naivasha, Kenya Colony, Africa, or more specifically, beside the road that skirts the south side of the lake and at a point approximately abreast of the western end of the southwest bay. The obsidian is almost entirely glassy (n = 1.488) but has occasional phenocrysts of anorthoclase with a maximum dimension of 1-2 mm. They have $\gamma = 1.532$ and $\alpha = 1.526$ and the extinction angles on the two cleavages are 2° and 8.5° respectively. In addition there are very rare rounded phenocrysts of fayalite upwards of 1 mm. in diameter, with α close to 1.82. They therefore approach pure Fe₂SiO₄.

In the hand specimen collected there was found also a small xenolith (diameter 4 mm.) consisting largely of olivine of a very different composition, viz. with about 70% Mg₂SiO₄. Associated with this olivine is a basic bytownite having nearly 90% anorthite, and a small amount of an undetermined pyroxene. The chemical characters of the obsidian are discussed on a later page where comparison is made with some other obsidians.

The spherulites are usually associated with the anorthoclase phenocrysts which have acted as nuclei for spherulitic crystallization. The small xenolith just described served in a like capacity. Some of the spherulites are solid but most of them are hollow lithophysae. The hollow variety may be as much as 1 cm. in diameter though usually much smaller.

MINERALS OF THE LITHOPHYSAE.

The minerals of the lithophysae are anorthoclase, cristobalite, magnetite, fayalite, biotite, and the mineral that has occasioned this note.

Anorthoclase rich in albite ($\gamma == 1.534$) was the first mineral formed in the lithophysae. It occurs as very minute, blocky crystals that are arranged about a central stem and give the aggregate effect of rods upwards of 0.3 mm. in length.

Cristobalite, the next mineral formed, occurs in small rosettelike groups about 0.2 mm. in diameter and has the properties typical of low-cristobalite. Neither quartz nor tridymite was found. The cristobalite and the anorthoclase make up the bulk of the lithophysal material.

Magnetite was apparently the next mineral formed. It is present only in very small amount and forms perfect octahedra about 0.005 mm. across.

Favalite occurs as clear amber crystals, tabular || 100 after their usual habit in lithophysae. They are upwards of 0.5 mm. in their greatest dimension and 0.02 mm. thick, and are decidedly the largest individual crystals in the cavities. No detailed study of them was made but their index a was found to be nearly if not quite as high as that of the Rockport favalite. from which fact it is to be inferred that they deviate but little from the theoretical composition Fe₂SiO₄. The fayalites are perched upon cristobalite and occasionally include the magnetite octahedra. They are therefore for the most part of later formation than these two minerals but cristobalite and probably magnetite continued to grow during a part of the period of formation of fayalite, for cristobalite rosettes are found attached to the basal parts of favalite crystals. Distal portions of the favalite crystals are, on the other hand, always free from perched crystals of any kind. Though present in relatively large crystals there is ordinarily no more than one crystal of favalite to a cavity and their actual proportion is therefore very small.

Biotite occurs as tabular crystals of hexagonal outline with a diameter of about 0.01 mm. and a thickness one fourth as great. It is optically negative with 2V very small. The index γ is close to 1.675, and α is about 1.605, values that indicate its approach to a pure iron end-member of the micas. Twinning on the base is common and the acute bisectrix makes an angle of about 3° with the normal to the base.

Finally we have the mineral which has not been noted hitherto among natural or synthetic products. It occurs in needle crystals about 0.05 mm. long and 0.005 mm. in transverse dimensions. They are transparent and nearly colorless though there is a trace of the amber tone of the fayalites. In larger crystals they might prove to be as strongly colored as the fayalite. They protrude into the cavities in a manner which suggests that they are the latest mineral to form, yet it is to be noted that, of the three minerals biotite, fayalite, and the needles under discussion, no one has been found perched upon another. It is possible, therefore, that biotite

 $\mathbf{482}$

 $\mathbf{483}$

485

N. L. Bowen.

and the needles were essentially contemporaneous with each other and with the later stage of fayalite growth.

The needles have properties which mark them as a pyroxene. They are invariably twinned on 100 and usually the twinning is repeated several times, a condition that renders it difficult to get exact values for some of the optical properties. The extinction angle $c_{\Lambda\gamma}$ is 34.5 ± .5. The refractive index $\gamma =$ $1.794 \pm .002$ and $a = 1.763 \pm .002$. It is impossible to be sure which is the lower, the minimum index observed when the needles lie on the clinopinacoid or the index of the transverse ray when they lie on the orthopinacoid, but the latter seems to be a shade lower. From these facts it may be stated that β is nearly equal to a, the optic axial angle 2V very small, and the plane of the optic axes is probably || 100. The small size, the needle habit, and the prevalence of twinning prevent the verification of these properties by means of an interference figure. Several crystals were mounted for goniometric measurement and three of them gave reasonably satisfactory measurements of interfacial angles in the prism zone. A series of values is as follows: 89°8', 90°46', 45°18', 44°32', 44°48', 45°26', 44°31', 44°32', 45°18', 45°29'. These are typical of the angles in the prism zone of pyroxene crystals showing a combination of unit prism with ortho and clinopinacoids and, if reliance may be placed on averages, indicate prism angles of 89°10' and 90°50'. Terminal faces are present but no satisfactory measurements were obtained from them.

PROPERTIES OF MONOCLINIC FeSiO₃ AS INDICATED BY EXTRAPOLATION.

The series of pyroxenes extending from hedenbergite, CaFeSi₂O₆, towards FeSiO₃ has been prepared synthetically and the optical properties have been studied (1933, pp. 260-1). It is necessary to grow the crystals at a low temperature because they crystallize in the wollastonite form at high temperatures. The material is therefore too fine-grained for detailed optical measurements. However, the indices γ and α were measured for all compositions from hedenbergite to CaSiO₃ 20 per cent, FeSiO₃ 80 per cent by weight. Extrapolation to 100 per cent FeSiO₃ gives the values $\gamma = 1.790$, $\alpha = 1.763$ with a possible error that is difficult to evaluate but is about $\pm .003$.

In the MgSiO₃-FeSiO₃ system all clino-pyroxenes from clino-enstatite to the composition MgSiO₃ 30, FeSiO₃ 70 wt. per cent were prepared synthetically. These were more satisfactory for optical measurement because they could be grown at a higher temperature. All three refractive indices and the extinction angles were determined. An indication of the values of these properties at a composition still richer in FeSiO₃ was obtained by preparing a monoclinic pyroxene by inversion of a natural orthorhombic variety. This natural pyroxene has small quantities of other oxides and a rather considerable amount of MnO but by grouping MnO with FeO an approach to the value for a pyroxene with 87 per cent $FeSiO_3$ was obtained (1935, pp. 197-199). Extrapolating the curves determined by these several values we find for the composition FeSiO₃ $\gamma = 1.794$, $\alpha = 1.760$ (probably $\pm .003$) and β very close to a. In the case of the extinction angle it is clear that a maximum value occurs at an intermediate composition but unfortunately the only composition that lies any significant distance on the $FeSiO_3$ side of the maximum is this product obtained by inversion of the natural pyroxene. Extrapolation is therefore somewhat uncertain. All that can be said is that the extinction angle of monoclinic FeSiO₃ should be a little less than 36°.

When these extrapolated values are compared with the measured values for the lithophysal mineral, viz. $\gamma = 1.794$, a = 1.763, β sensibly = a and $c_{\Lambda}\gamma = 34.5^{\circ}$, it is plain that one would conclude immediately that the mineral is substantially pure FeSiO₃ crystallized as a monoclinic pyroxene. Added to this is the fact that the prism angle is about 90°50' and that this value differs from that for the more familiar diopside-rich pyroxenes (92°50') in exactly the manner one would expect, for a slag pyroxene with some 80 per cent FeSiO₃ has been found to have a prism angle with the appropriate intermediate value 91°20'.³

The case for identifying these crystals as pure or substantially pure FeSiO_3 would thus seem to be complete and there the matter might be allowed to rest were it not for the fact that synthetic studies had led to the conclusion that FeSiO_3 has no existence as a crystalline compound. It is in order now to review the evidence pointing to that conclusion.

⁸Bowen, N. L.: J. Wash. Acad. Sci., 23, 83-87, 1933.

484

-experimental studies bearing upon the existence of $FeSiO_3$.

In the system, FeO-SiO₂, no crystalline compound of the composition FeSiO_3 occurs at liquidus temperatures, the only compound being Fe_2SiO_4 . This fact does not preclude the



Fig. 1. Equilibrium diagram of mixtures of metasilicate ratio of the system, CaO-FeO-SiO₂. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium.

possibility of the existence of FeSiO_3 at lower temperature, but a test of that possibility made by crystallizing at 660° a but a test of that possibility made by crystallizing at 660° a glass approaching FeSiO_3 in composition revealed that the principal product even at that temperature was Fe_2SiO_4 (1932, principal product even at that temperature was Fe_2SiO_4 (1932, m general agreement with those made upon natural material, it would appear that no great change of solid phase equilibrium the time, the possibility still remains open, of course, that at

still lower temperatures FeSiO_3 could form. Moreover, it is not impossible that in thus devitrifying the glass the hightemperature equilibrium was obtained metastably and that even at 660° a metasilicate should form.

In the system, CaO-FeO-SiO₂, there are two series of metasilicate solid solutions, the one wollastonitic, the other hedenbergitic. The former series is definitely limited to compositions with less than about 76 per cent FeSiO₃ but the latter--and these are typical monoclinic pyroxenes—extends somewhat hevond this composition at high temperatures (about 980°) and there are indications that it extends to compositions still richer in $FeSiO_3$ as the temperature is lowered (1933, p. 213). This fact is indicated in the equilibrium diagram, Fig. 1, by the curve XR, sloping to the right downward but shown as a broken curve because the degree of slope is not known. It is not impossible that the curve XR has such a shape that it meets the FeSiO₃ side of the diagram at some temperature. If this be true then below that temperature FeSiO₃ could exist as stable crystals of monoclinic pyroxene. Therefore the results of this system likewise fail to prove the non-existence of $FeSiO_3$ at some low temperature.

In the system, MgO-FeO-SiO2, pure synthetic clinopyroxenes with an FeSiO₃ content up to 70 per cent were prepared. No indication was obtained that this concentration of FeSiO₃ approached the maximum possible value. The limitation was imposed rather by the fact that it was impossible to produce a homogeneous glass with more than 70 per cent FeSiO₃, and glass was the initial material from which the pyroxenes were prepared. In the absence of glasses richer in reliance was placed upon a natural orthorhombic pyroxene very rich in FeSiO₃ from which a clino-pyroxene was readily prepared by heating it until it inverted. Furthermore, it was this natural material or its inversion product that was used to fix parts of the curves KY and CY of Fig. 2. In particular the position of the point V, where they intersect, was determined entirely with the aid of this material, which deviated considerably from the pure MgSiO₃-FeSiO₃ mixtures. Comment upon this feature of the work was made at the time as follows. "As a result of such observations the in general agreement with those made upon natural material, it would appear that no great change of solid phase equilibrium

486

487



489

is introduced by the presence of the foreign oxides in the natural minerals. Again, the fact that curves CY and KYcome together at Y in the appropriate manner suggests that although portions of these curves were determined with the aid of natural minerals the position of the curves on the actual diagram for pure iron-magnesium silicates would not be significantly different and that we are justified in presenting the diagram so determined as that of the pure iron-magnesium silicates." (1935, p. 171.)

Now it is possible that this comment arose from an oversanguine attitude. The considerable amounts of foreign oxides present in the natural minerals may have made a greater difference than was supposed. Perhaps the curve CY would prove to be more nearly straight and the curve KY might be found to fall more rapidly to lower temperatures at its iron-rich end, if pure synthetic minerals could be prepared and were used for investigation. The result might be that the field marked clino-pyroxenes should spread across the diagram and have a definite intercept on the FeSiO₃ side of the diagram at some low temperature. Therefore it must be admitted again that, while a number of features pointed in that direction, nevertheless no absolute proof has been obtained of the non-existence of FeSiO₃ as stable monoclinic crystals at some low temperature.

STABILITY OF THE PYROXENE CRYSTALS FROM THE LITHOPHYSAE.

On the other hand, even when these admissions are made, there still remains the incontrovertible fact that $FeSiO_3$ is unstable at high temperatures, and if the crystals from the lithophysae are really pure or substantially pure $FeSiO_3$ it should be possible to bring about their dissociation into olivine and SiO_2 simply by heating them. This is readily accomplished in pyroxenes of both the Ca-Fe series and the Mg-Fe series when they are raised above the temperature at which they are stable. Accordingly a study was made of the behavior of the crystals from the cavities. To do this it was necessary to work with the mixture of minerals obtained by breaking out the whole contents of the lithophysae. The study was made by heating such material in evacuated, sealed, silicaglass tubes in order to avoid oxidation of the ferrous minerals, and as an additional precaution a small piece of pure iron was

placed in the tube. The product was examined under the microscope to observe such changes as the pyroxene needles had undergone. Without detailing all the results it may be stated that after heating at 960° for 7 hrs. individual needles showed locally, but only locally, a tendency to become opaque. This change may be due to formation of the two phases fayalite and SiO₂ with their great difference of refractive index, but the change is certainly not as definite as that in related iron-rich pyroxenes, for in these the presence of the two phases after heating can be established with certainty Even when heated for an hour at 1070°, at which temperature much of the feldspar-cristobalite aggregate was converted into glass, no unquestionable formation of fayalite and SiO₂ from the pyroxene needles could be made out. Such temperatures are well above those at which any possibility of stability of FeSiO₃ can be admitted, for it will be recalled that, even when the diagrams (Figs. 1 and 2) are modified in the manner which has been suggested as not impossible, the range of stability of FeSiO₃, if there be any, must lie at decidedly lower temperatures.

Two explanations of the results obtained may be mentioned. The first is that the crystals have substantially the composition FeSiO₃, were formed at a low temperature at which they were stable, and exhibit a reluctance to dissociate into fayalite and SiO_2 that is much greater than that shown by related ironrich pyroxenes. The second is that the crystals, in spite of the remarkable approach of their properties to those indicated for pure FeSiO₃, nevertheless carry considerable amounts of other oxides which give them a stability not shared by FeSiO₃, the extraneous oxides being of such a nature as to produce compensatory effects upon the optical properties, with, say, MnO lowering the indices and perhaps Fe_2O_3 and TiO_2 raising them approximately the same amount. If the second explanation represents the truth then, of course, no significance is to be attached to the discussion of possible modification of the determined diagrams, since this discussion arose from the finding of these natural crystals and from acceptance of the evidence indicating that they have substantially the composition FeSiO_3 . It is regrettable that it should be necessary to leave our

It is regrettable that it should be necessary to near has knowledge of these crystals thus incomplete. This paper has been written principally to advertise their existence and the special problem they present, in order that mineralogists and petrologists may seek them in other occurrences where they night be obtained in such quantity as to permit accurate deternination of all their properties, chemical as well as physical. From a large quantity of the Naivashan obsidian it is probable that a separation could be made of material adequate in quality and quantity to solve the problem. Unfortunately I have only one hand specimen of average size.

OCCURRENCE IN OTHER OBSIDIANS.

The mineral has been sought in the lithophysae of other obsidians and was found in three of them, but unfortunately none of these is as promising a source of pure material in quantity as is the Naivashan rock itself.

The three other obsidians in which it was found are the following:

- 1. Obsidian from Coso Mountains, California, collected by A. L. Day.
- Obsidian from Hrafntinnuhryggur, Iceland, collected by F. E. Wright.
- 3. Obsidian from Obsidian Cliff, Yellowstone National Park, collected by J. P. Iddings.

In the lithophysae of the Coso Mountains obsidian the pyroxene needles are rather numerous but are excessively small and would be readily overlooked were one not making a special search with the aid of immersion liquids found by previous experience to be most favorable for their detection. In the lithophysae from Hrafntinnuhryggur⁴ they are very rare and also rather minute. Of Obsidian Cliff material a large quantity was examined, especially of that containing large lithophysae, without finding any of the pyroxene needles. In one specimen with small lithophysae (specifically U. S. National Museum No. 2232) they are present in small amount but the largest individual crystals approach the African crystals in size.

In all examples the crystals occur in the same manner as in the Naivashan rock and their optical properties are the same, within the limits of error of measurement on material some of which is none too favorable.

Crystals of this particular pyroxene thus appear to be of widespread occurrence in the lithophysae of obsidians. Though they are quantitatively of minor importance, a name for them

⁴Wright, F. E.: Bull. Geol. Soc. Amer., 26, 255-286, 1915.

is desirable and further introduction of new terms will be avoided if Washington's "ferrosilite" is accepted, though perhaps *clinoferrosilite* is preferable since there may be an orthorhombic equivalent. Even though the crystals eventually prove to contain, as suggested above, fair amounts of other oxides. it does not seem probable that the quantity will be large enough to invalidate the use of the name of the end member, just as a considerable amount of albite (up to 10 per cent) may be present in a plagioclase and yet the name anorthite be acceptable for it.

CHEMICAL COMPOSITION OF THE OBSIDIANS.

It is of interest to compare the chemical composition of the four obsidians in which the proxene needles have been found. Their analyses are given in Table I. Two of these are by E. S. Shepherd, made in connection with his studies of gases in rocks. His new analysis of the black obsidian from Obsidian Cliff merits special mention because it shows significant differences from old analyses of that rock. Potash is notably higher in the new analysis as is silica also, whereas alumina is lower, with the result that no corundum appears in the norm although a considerable amount shows in the norm of the old analysis.5

There is nothing especially unusual in the composition of the Naivashan obsidian. The content of FeO is small, a fact of particular interest in connection with the presence of fayalite as phenocrysts. Evidently iron orthosilicate may form as early crystals even though present in small amount. This obsidian occurs in a region of highly sodic rocks including pantellerites, and, though its own alkalis are substantially those of "normal" obsidians, the formation of fayalite as early crystals is a character that links it with pantellerite. Fayalite occurs as phenocrysts in this rock type in Pantelleria.⁶ The rocks in which Soellner found fayalite phenocrysts do, however, contain FeO in such quantities as to render the crystallization of that phase less unexpected.⁷ Among the East African associates of the Naivashan obsidian a fayalite-bearing phonolite has been described by Campbell Smith. He has also

⁵ See Washington's Tables, U. S. Geol. Surv., Prof. Paper 99, p. 63.

^o Soellner, J.: Z. Krist., **49**, 144, 1911. ^{The} Khagiar and Gelkhamar types mentioned by Soellner have been analyzed by Washington, J. Geol., 22, 706, 1914.

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Analyses of Obsidians Showing "Clinoferrosilite" as a Lithophysal Mineral.

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-	. 1	2	3	4
iΩ,	75.55	75.01	76.78	75 .92
1203	12.31	12.27	12.09	12.31
le ₂ O ₃	0.69	0.80	0.56	0.40
eO	1.17	2.78	0.81	0.68
IgO	0.04	0.08	0.10	0.08
aO	0.23	_1.87	0.57	0.59
a ₂ O	4.55	3.36	3.79	4.26
GO	4.69	2.80	4.93	4.36
I_2O+	0.15	0.25	0.12	0.98
<u>1</u> 0—	none	0.13	0.08	
1O ₂	0.13	0.33	0.08	0.06
rO_2			0.01	0.01
P_2O_5	0.01	0.02	0.09	0.15
O ₃		0.07	····	0.06
	0.21	0.13	0.05	0.00
	0.28	0.02	0.15	0.14
	0.04	0.02	0.00	0.02
4n0	0.04	0.00	0.02 none	0.02
a0	• • • •		none	nr n d
120 · · · · · · · · · · · · · · · · · · ·				
	100.05	99.98	100.29	100.02
	- 0.16	- 0.02	- 0.10	— 0.08
				
	99.89	99.96	100.19	99.94
D	1.488	1.485	1.485	1.485
	Norn	ns		
	1	2	3	4
<u>.</u>	327	38.8	34.8	33.0
2. · · · · · · · · · · · · · · · · · · ·	27.8	167	28.9	26.1
1	35.1	28.3	32.0	36.1
n	00.1	9.2	1.7	1.4
	0.4	0.3		
V	1.4	4.3	1.1	1.1
nt	0.9	1.2	0.7	0.7
·····	0.3	0.6	0.1	0.1
D			0.2	0.3

Obsidian. Lake Naivasha, A. Willman analyst, with fluorine determination by E. S. Shepherd.

Obsidian, Hrafntinnuhryggur, J. B. Ferguson analyst in F. E. Wright, op. cit.

Obsidian, Obsidian Cliff, Yellowstone National Park, E. S. Shepherd analyst.

4. Obsidian, Coso Mts., California, E. S. Shepherd analyst.

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Note: In the norms fluorite, halite, thenardite and such normative minerals were computed but they have been omitted from the statements as given above. No. 1 has more fluorine than lime (in equivalents) and it has been necessary to assume a little NaF in addition to CaF2.

493

studied obsidians from the vicinity of Lake Naivasha but they are of somewhat different type from that here described, a difference which is substantiated by my own collection of obsidians from that area.⁸ The high content of halogens in the Naivashan obsidian is characteristic of rocks of the area, a fact that will be brought out in a later publication describing them.

The four obsidians given in Table I, taken as a group, seem to possess no unusual character that marks them off from obsidians in general. The Coso Mountains example is lowest in FeO yet clinoferrosilite has developed rather abundantly in The characters and conditions that favor its lithophysae. formation of that crystalline phase are thus matters for future determination.

ACKNOWLEDGMENTS.

I wish to thank Dr. H. E. Merwin for guidance in the goniometric measurement of the small needles and Dr. E. S. Shepherd for permission to publish the two analyses of obsidians made by him and also for his determination of fluorine in the Naivashan obsidian. It is a pleasure also to acknowledge the work of the University of Minnesota laboratory for rock analysis established by Professor Grout. The analysis executed by A. Willman is from that laboratory.

⁸ Smith, W. Campbell: Quart. J. Geol. Soc. London, 87, 1931, p. 249 for fayalite phonolite, p. 219 for obsidians.

GEOPHYSICAL LABORATORY,

CARNEGIE INSTITUTION OF WASHINGTON.