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OBSIDIAN FROM HRAFNTINNUHRYGGUR, ICELAND: ITS LITHOPHYSÆ AND SURFACE MARKINGS[1]

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CONTENTS

HISTORICAL REVIEW

To the student of rocks the forms and relations of crystals and of crystal aggregates precipitated from a cooling magma are in large measure the expression of the physical conditions under which the magma solidified. This was thoroughly appreciated by the pioneers in petrology, who observed that as the physical conditions of freezing of such magmas varied, so also did the resulting products of crystallization, with respect both to the kinds of crystals formed (mineral composition) and to the habits and relations between the crystals (rock texture). Of the different kinds of crystals thus studied none has received more attention than the spherulites; and yet our knowledge of them is still incomplete, especially of the hollow spherulites or lithophysæ, the best examples of which have been found in the obsidian of Yellowstone National Park. These were studied many years ago by Iddings[2] in detail and with special reference to their mode of formation. At that time petrologists were not

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[1] Manuscript received by the Secretary of the Society April 20, 1915.
[2] U. S. Geological Survey, Seventh Ann. Report, 1885, pp. 253-295.

in accord as to the genesis of the lithophysæ. Von Richthofen had suggested in 1860 the name Lithophysen[3] (Greek λίθος, stone, and φῦσα, bubble) for the hollow spherulites in the Hungarian rhyolites, on the assumption that their formation is due to the expansion of gas bubbles which, liberated during the crystallization of the spherulites, are unable to escape from the viscous magma and hence force out the walls of a cavity, each successive bubble carrying a thin film (bubble) or shell of the magma into the cavity, and thus producing the concentric structure. During this process chemical reactions between the gases and the crystallized material of the spherulites take place and cause solution, recrystallization, and a general rearrangement of the original material precipitated from the magma. Zirkel[4] in 1876 practically adopted von Richthofen's hypothesis of chemical alteration. S. Szabó[5] and Roth,[6] on the other hand, considered that the lithophysæ are the result of chemical and mechanical alteration of solid spherulites, the soluble portions being removed chemically, the insoluble mechanically, with the exception of silica, which constitutes the major part of the lithophysæ. This view involves transfer of material away from the cavity, while according to von Richthofen's idea there is no such transfer, only rearrangement within the cavity. Still other views were held by von Hauer[7] and Weiss,[8] who considered that lithophysæ are hollow spherulites formed about the gas bubbles which escape from the cooling magma. Cross[9] concluded from his study of lithophysæ that the minerals, topaz and garnet, which occur therein, were "produced by sublimation or crystallization from presumably heated solutions, contemporaneous or nearly so with the final consolidation of the rock. The lithophysal cavities seem plainly caused by the expansive tendency of confined gases or vapors, while the shrinkage cracks in the walls and white masses of the Nathrop rock suggest the former presence of moisture."

Iddings found "that the lithophysæ in the obsidian of Obsidian Cliff, with their contents of prismatic quartz, tridymite, adular-like and tabular soda-orthoclase, magnetite and well crystallized fayalite, are of aqueo-igneous origin, and result from the action of absorbed vapors on the molten glass from which they were liberated during the process of crystallization consequent upon cooling." An arching of the layers around

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[3] Jahrb., K. K. Geol. Reichsanstalt, vol. 11, 1860, p. 181.
[4] U. S. Geol. Expl., 40th Parallel, vol. 6; Microscop. Petrography, 1876, p. 212.
[5] Jahrb., K. K. Geol. Reichsanstalt, vol. 16, 1866, p. 89.
[6] Beiträge zur Petrographie der plutonischen Gesteine. 1869, p. 168.
[7] Verhandl. K. K. Geol. Reichsanstalt, 1866, p. 98.
[8] Zeitschr. Deutsch. geol. Gesellschaft, vol. 29, 1877, p. 418.
[9] Am. Jour. Sci. (3), vol. 31, 1886, p. 432.

a lithophysa occurs frequently, and "at first sight it would seem that the expansion of a bubble of gas within the lava had occasioned the distention or displacement of its layers; but a careful study of portions of the rock which exhibit great distortion and plication of the layers makes it evident that in these cases the hollows occur beneath arches in the folds where there has been a local relief or diminution of pressure, which might allow the absorbed vapors to disengage themselves and to bring about the conditions which produce hollow lithophysæ in connection with spherulite development. In other words, the arching of the layers appears to have been the cause of the liberation of gases and the production of the cavity beneath, and not the result of expanding gases." The observed relations "leave no doubt that the spherulites and lithophysæ, in all their complexity of form and structure, are of primary crystallization out of a molten glass, which was gradually cooling and consolidating, and that, since its solidification, no alteration, chemical or mechanical, has taken place."

The work of Iddings on the Obsidian Cliff spherulites was so thorough and convincing that his conclusions have since been accepted and applied without reserve to all lithophysæ. In one particular, however, this generalization of the conclusions which hold primarily for the Obsidian Cliff rocks may not be warranted, namely, that in the formation of the cavities the expansion of the liberated gas plays no significant rôle. For the Obsidian Cliff lithophysæ the evidence probably justified the position taken by Iddings, that the cavities were formed by a kind of uniform tension in the viscous, cooling, and contracting magma (just as joints are formed in a later stage of cooling), and that at such points crystallization began and was accompanied by escape of gas into the cavity. But it is also possible that in other localities, as a result of slightly different conditions, the pressure of the escaping gas was a factor not only in enlarging the cavity, but also in its initial formation. We have thus two different hypotheses available: at the one extreme we find the total effect ascribed to hydrostatic tension or uniform pull developed by the shrinking of the magma during cooling; at the other, to the pressure of the gases set free on crystallization of the spherulites. In most cases it is probable that both factors, contraction of the cooling magma and gas pressure, have been active. The primary purpose of the present paper is to present evidence that in the case of the Icelandic lithophysæ the pressure of the liberated gas was an important factor in the development of the cavities. Incidentally the origin of certain etched surfaces of obsidian which resemble moldavitic markings will be considered.

THE HRAFNTINNUHRYGGUR OBSIDIAN

GENERAL DESCRIPTION

The obsidian specimens containing the lithophysæ were collected by the writer in 1909. Unfortunately lack of time and of transportation facilities permitted neither adequate field study of the occurrence nor the collection of a representative set of specimens. Only a few interesting random specimens were gathered to illustrate, as well as possible, the different types which occur.

The obsidian of Hrafntinnuhryggur forms a well developed, long ridge southeast of the volcano Krafla. It is not uniform in structure throughout, but ranges from dense black glass to a rock approaching pumice. Banding caused by an alternation of layers of the dense black glass with bands of semi-pumiceous or spherulitic material is characteristic of certain of the specimens. Near the west end of the ridge a small circular pond, resembling a shallow crater lake, occurs; and there the rock is apparently a breccia consisting of fragments of black obsidian glass (showing remarkable etched surfaces, which resemble those of the Bohemian moldavites and of certain desert rocks with etched surfaces) and of a white crypto-crystalline, siliceous substance.

The obsidian proper is a dense, black, brittle glass, remarkably uniform in character. Prismatic jointing was observed at several points and is of the ordinary columnar type. The obsidian glass takes a good optical polish, has a refractive index of about 1.500, and might possibly be serviceable as a source of material for making large telescope reflectors; its coefficient of expansion is probably low, in view of the high silica content. The fracture is conchoidal; in the field a single sharp blow of the hammer on a large uniform block a meter in diameter may spall off ashlars or shell-like pieces, which show most beautiful conchoidal fracture lines. The development of the two sets of lines—the one set concentric and emanating like wave-ripples from the point at which the blow was struck, the second set radiating from it in lines normal to the first—is so perfect and fascinating that the lack of transportation facilities is keenly felt by the geologist.

Under the microscope the obsidian glass is seen to be full of very minute crystallites of a colorless, prismatic mineral, not over 0.005 mm. in length and less than 0.002 mm. in width. The optical properties which could be determined on this mineral are: Refractive index, noticeably higher than that of the glass; birefringence, medium; extinction, apparently parallel to the elongation ($=\gamma'$). These properties are unfortunately not sufficient to identify the substance, but other and more precise data could not be obtained on the fine particles. Occasional minute, elongated bubbles (up to 0.05 mm. in length) were also observed.

The density (referred to water at 4° C. and to vacuum) of the obsidian is 2.387.

CHEMICAL CHARACTERISTICS

For the chemical analysis of the black obsidian I am indebted to Mr. J. B. Ferguson, of the Geophysical Laboratory, and express herewith my appreciation of his kindness. The material selected for analysis was part of specimen 88428,[10] a jet black glass free from spherulites and lithophysæ, but containing many of the minute crystallites noted above. The analysis is that of a fairly normal rhyolitic obsidian. Interesting and important is the presence of Cl and SO_3 in appreciable amounts. It will be shown later that the release of these volatile components in the magma had much to do with the formation of the lithophysæ, while the character of the physico-chemical system thus produced caused the simultaneous formation of crystals of fayalite and of tridymite at relatively low temperatures. This mineral association is not that of ordinary igneous rocks or lavas, but seems to be characteristic of lithophysæ in obsidian, notwithstanding the low content in oxides of iron (from 2 to 4 per cent). Thus in 1827 Gustav Rose discovered fayalite and tridymite in the lithophysæ of the obsidian from Cerro de las Navajas (analysis VI; $FeO + Fe_2O_3 = 2.20$ per cent); in 1885 Iddings found fayalite under similar conditions in the lithophysæ of Obsidian Cliff, Yellowstone National Park (analysis IV; $FeO + Fe_2O_3 = 1.63$ per cent).

The occurrence of an orthosilicate like olivine with tridymite is rare, if not unknown, in intrusive rocks. It is less rare in effusive rocks and indicates that physico-chemical conditions of equilibrium at the time of formation of the crystals may be very different even for magmas of the same general total chemical composition. The computed normative composition in such cases would be the same, but the actual modal composition may be totally different, thus emphasizing the difficulty of setting up a proper normative composition which even approximates the actual mineral composition of the rock.

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[10] The specimens described in this paper have been deposited in the U. S. National Museum; the number of the specimen is, in each case, its catalogue number in the National Museum.

	1	1*a*	2	3	4	5	6	7	8	9	10
SiO_2	75.01	1.250	75.12	73.40	74.70	75.52	75.23	76.91	75.25	76.68	74.80
Al_2O_3	12.27	.120	11.34	12.90	13.72	14.11	12.36	12.18	14.60	14.49	14.32
Fe_2O_3	0.80	.005	3.92	3.70	1.01	1.74	0.96	0.48	0.54	....	0.88
FeO	2.78	.039		....	0.62	0.08	1.24	0.92	1.60	1.09	1.00
MgO	0.08	.002	0.39	0.14	0.14	0.10	0.01	none	0.51	0.84	tr.
CaO	1.87	.033	1.73	2.35	0.78	0.78	1.00	0.92	1.06	1.53	1.26
Na_2O	3.36	.054	4.39	3.83	3.90	3.92	4.00	4.17	4.28	3.92	3.38
K_2O	2.80	.030	1.85	2.99	4.02	3.63	4.62	3.15	1.72	1.20	3.28
H_2O+	0.25	....	0.41	0.43	0.62	0.39	0.73	0.66	....	0.36	1.24
H_2O-	0.13	....	....	....	....	....	....	0.24	....	....	....
CO_2	....	....	....	....	....	....	....	....	....	....	....
TiO_2	0.33	.004	....	0.43	....	....	....	0.18	0.06	....	0.21
ZrO_2	....	....	....	....	....	....	....	....	....	....	....
P_2O_5	0.02	....	....	....	....	....	0.27	none	....	....	....
SO_3	0.07	.001	....	....	....	....	....	....	....	....	....
Cl	0.13	.004	....	....	....	....	....	....	....	....	....
F	....	....	....	....	....	....	....	....	....	....	....
S	0.02	....	....	....	....	....	....	none	....	....	....
MnO	0.06	.001	....	....	....	....	....	....	....	tr.	tr.
NiO	....	....	....	....	....	....	....	....	....	....	....
BaO	....	....	....	....	....	....	....	....	....	....	....
V_2O_3	....	....	....	....	....	....	....	....	....	....	....
MoO_3	....	....	....	....	....	....	....	....	....	....	....
FeS_2	....	....	....	....	0.40	0.11	....	....	....	....	....
	99.98 —0.02	sp. g., 2.387	100.00	100.17	99.91	100.38	100.42	99.81	99.62	100.11	100.37
	99.96										

1. Obsidian. Hrafntinnuhryggur, near Krafla, Iceland. J. B. Ferguson, analyst. I. 3″. 2. (3) 4.

1*a*. Molecular proportions of 1*a*.

2. Obsidian. Hrafntinnuhryggur, near Krafla, Iceland. R. Bunsen, analyst. Pogg. Annalen d. Chem. u. Physik, volume 83, 1851, page 212. I (II). 3 (4). ″2. 4.

3. Obsidian. Hlitharfjall, near Myvatn, Iceland. H. Bäckström, analyst. Geol. Fören. Förhandl., volume 140, 1891, page 663. I″. (3) 4. 2. 3.

4. Black obsidian. Obsidian Cliff. Yellowstone National Park. J. E. Whitfield, analyst. Described by J. P. Iddings. U. S. Geological Survey Annual Report, volume 7, 1885, page 291. I. (3) 4. 1 (2). 3 (4).

5. Red obsidian. Obsidian Cliff, Yellowstone National Park. J. E. Whitfield, analyst. Described by J. P. Iddings. U. S. Geological Survey Annual Report, volume 7, 1885, page 291. I. 3 (4). 1 (2). 3 (4).

6. Black obsidian. Cerro de las Navajas, Mexico. F. Baerwald, analyst. Described by C. A. Tearne, Zeitsch. Deutsch. Geol. Gesell., Berlin, volume 37, 1885, page 616. I. 4. 1″. 3″.

7. Pumice. Katmai Volcano, Alaska. George Steiger, analyst. G. C. Martin. Lab. Records, U. S. Geological Survey. I. 3 (4). (1) 2. ″4.

8. Dacite obsidian. Riviere des Vieux-Habitants, Guadeloupe. A. Pisani, analyst. Described by A. Lacroix. Mount Pelée. 1904, page 588. I. 3″. 2. 4.

9. Obsidian. Corinto, Nicaragua. J. Petersen, analyst. Neues Jahrb., 1898, volume 1, page 157. I. 3. 2. 4″.

10. Obsidian. Kawah-manoek Volcano, Preanger District, Java. Ledeboer, analyst. Described by R. D. M. Verbeek, Jb. Mijnw., volume 37, 1908, page 93. I. 3″. 2. 3 (4).

Norms computed from the above Analyses

	1	2	3	4	5	6	7	8	9	10
Q	39.90	35.52	32.7	34.9	36.7	32.34	37.80	39.78	43.92	39.48
or	16.68	11.12	17.8	23.4	21.7	27.24	18.90	10.01	7.23	19.46
ab	26.72	37.20	32.0	33.0	33.0	34.06	35.63	36.15	33.01	28.82
an	9.17	5.56	9.2	3.9	3.9	2.22	4.45	5.28	7.51	6.12
C	0.61	....	....	1.5	2.2	....	0.20	3.77	3.98	2.86
Na_2Cl_2	0.23	....	....	...	...	....	....	....	....	....
Na_2SO_4	0.14	....	....	...	...	....	....	....	....	....
di	....	2.42	2.2	...	...	0.99	....	....	....	....
hy	4.29	6.87	4.8	0.8	0.3	0.92	1.06	3.68	4.08	0.50
mt	1.16	....	....	1.4	0.2	1.39	0.70	0.70	....	1.39
il	0.61	....	....	...	...	....	0.30	0.15	....	0.46
hm	....	....	....	...	1.6	....	....	....	....	....
pyrite	....	....	....	0.4	0.11	....	....	....	....	....
ap	....	....	....	...	...	0.67	....	....	....	....

A comparison of these analyses, and especially of the norms computed from them according to the methods proposed by Cross, Iddings, Pirsson, and Washington, shows that they are all of the same general character. The Icelandic rocks contain a slightly larger amount of femic minerals than the other rocks, but the amount is not sufficient to place them in another class. It is interesting also to note that the analysis 2, by Bunsen, in 1851, agrees fairly well with the modern analysis 1 of the same rock. In the legend of the table of analyses the symbols, according to the quantitative classification of rocks proposed by Cross, Iddings, Pirsson, and Washington, are given. These symbols show that in nearly every case the rocks are located near the boundaries of the various subdivisions of the quantitative system.

If the obsidian of Hrafntinnuhryggur had crystallized under the physico-chemical conditions of a deep-seated rock, the mineral composition would probably have been: Quartz, about 40 per cent; orthoclase, about 16 per cent; oligoclase of average composition, Ab_3An_1, about 35 per cent (some of the albite substance would probably enter into solid solution with the orthoclase, but to what extent can not be predicted because of lack of information regarding these physico-chemical systems); aluminous amphibole, 6 per cent; titaniferous magnetite, 2 per cent, and a little apatite. The salts, Na_2Cl_2 and Na_2SO_4, indicated in the norm would probably be carried away in solution as part of the more soluble portion of the magma. It is, moreover, evident that the sodium would not be the only base in combination with these acid radicles as postulated in the norm. On the whole, experience has shown that in this persalane class of rocks the modal composition is not greatly different from the computed normative composition.

SPHERULITES AND LITHOPHYSÆ

Attention has been given in the preceding paragraphs to the intimate relation between spherulites and lithophysæ and to the several different hypotheses which have been offered to explain the development of lithophysæ. In the Hrafntinnuhryggur obsidian all possible gradations occur between typical, compact, lithoid spherulites and typical lithophysæ with walls lined with minute crystallites, water-clear and very fragile. Pumiceous structures are also of common occurrence, but they are usually confined to definite bands and patches which alternate with streaks of black obsidian glass containing occasional large vesicular cavities. In the case of a wide band of glass these large cavities are more abundant in the immediate vicinity of the pumiceous layers and virtually disappear within a few centimeters. The gas cavities in both the pumiceous and adjacent bands are not spherical but tubular in shape, the direction of elongation being that of the lines of flow of the lava. This indicates that the lava during the period of its final flow was sufficiently viscous to prevent the escape of the free gas bubbles which it inclosed. The restriction of the gas bubbles to definite bands and parts of the mass might be considered to indicate that during the period of its flow the lava encountered physical conditions of such nature (especially release of pressure) that certain bands became supersaturated with volatile components, which were then released and formed bubbles. These could not migrate through the lava to any great extent because of its high viscosity. It is, however, conceivable and *a priori* more probable that the appearance of a pumiceous band is not the result of direct evolution of gas from that band alone, but that either before or during the eruption of the molten obsidian there was an accumulation of gas bubbles at certain points (magma hotter and less viscous, thus allowing freer circulation and concentration of evolved gas bubbles at favorable pockets near the margin of the magma chamber), and that on final outflow of the obsidian these foamy portions of the lava were drawn out and appear now as vesicular streaks, which serve to emphasize the lines of stiff viscous flow of the lava. On this hypothesis the amount of pumice accompanying a rhyolitic flow can not be considered to be indicative of the amount of gas given off by the obsidian. Most of the gas thus liberated from the solution no doubt escaped, and that which produced the pumice represents only a small part of the total amount contained originally in the molten obsidian.

Passing now to the spherulites, we find that they occur in typical development in several of the specimens. They range in size from a few tenths of a millimeter to over 5 millimeters in diameter. In the outcrop they are not evenly distributed through the rock mass, but are confined to certain bands or layers, thus indicating that in these bands crystallization took place more rapidly than in others. In the case of finely laminated flow banding, however, the spherulites cut across the banding. In no case was a suggestion of flow banding around a spherulite observed; this would occur were the spherulites older than the banding. In one instance the wall of a hollow spherulite was serrated as the result of a difference in behavior of the different bands with respect to crystallization and to attack by the volatile components released during the crystallization of the spherulite.

The relations outlined above suggest that the determinative factors in the development of the different structures which are now found in the obsidian—pumiceous, spherulitic, and lithophysal—were the physical conditions of cooling of the different parts of the lava, together with the amount and character of the volatile components dissolved in it. In order to show this clearly, six of the specimens collected at Hrafntinnuhryggur will be briefly described.

Specimen 88428 is a black compact obsidian glass, free from spherulites, but containing fine hairlike crystallites and minute bubbles 0.05 mm. in maximal length; also dark opaque grains scattered through it. Part of this specimen served for chemical analysis I and is described in sufficient detail above.

Specimen 88429 shows clearly the passage of obsidian glass to pumice. One end of the specimen is typical pumice, with silvery luster in the direction of elongation of the vesicles; the opposite end is of massive obsidian glass, with only occasional large cavities, which trend either approximately parallel with or transverse to the general lines of flow. The transverse cavities are much larger than the others and appear to be of the nature of rupture fissures—rather than elongated gas cavities—produced during the final stages of the cooling and flow of the lava as a result of the tensional stresses thereby developed.

Specimen 88430 presents another structural type which was developed during the period of cooling of the lava. Dull gray-black lithoidal bands and irregular masses alternate with bands and patches of black obsidian glass. The lusterless parts consist of spherulites which have crystallized from the glass. Under the microscope these spherulites are seen to be of two different types:

(1) Typical radial spherulites, with fibers radiating from a central point, or more commonly from a minute central bubble. The elongation of the fibers is α'; a distinct cross is visible between crossed nicols. The refractive indices are difficult to obtain accurately, but they lie between 1.520 and 1.540. The birefringence is medium to weak. Between many of the fibers are minute irregular cavities which greatly decrease the transparency of the spherulites. The determinations indicate that these spherulites are chiefly albite, with possibly a little admixed potash feldspar and also free quartz.

(2) Adjoining the radial spherulites are usually patches of substances of a deeper brown color and of slightly stronger birefringence and less pronounced radial spherulitic development. The elongation of the fibers in this material is not pronounced, but in those cases in which an elongation was apparent its character was γ'. The development approaches that of an aggregate of overlapping crystallites and grains too fine and too intimately intergrown for satisfactory determination. The refrac-

tive index is about 1.54. It is probable that these spherulites consist chiefly of quartz intergrown with some alkali-feldspar.

Not all of the spherulites in this specimen are entirely compact and gray-black in color. Portions of many of them are porous and then usually lighter in color and coarser grained. The appearance of such spherulites leads one to infer that gas was evolved during their crystallization, and that the volatile components thus set free acted on the spherulitic material of the walls and caused its recrystallization. In other words, each little spherulite, with its portion of volatile components, which were liberated during its crystallization and were inclosed in the thick viscous hot glass, may be likened to a chemical flask filled with appropriate reagents and crystal compounds and heated to such a temperature that certain chemical reactions take place. It is evident that the physico-chemical equilibrium conditions during the partial crystallization of a melted magma, from which appreciable amounts of volatile components are being liberated, are different from the equilibrium conditions obtaining in a system of the same total composition, but at a much lower temperature and containing the volatile components chiefly as vapor phases and the other components as crystallized units. The result of this shift in distribution of the elements from a homogeneous solution (magma) crystallizing at high temperatures to a heterogeneous system consisting of solid and vapor phases held at a lower temperature is a redistribution of the constituents in the solid phases, such that the mineral association which we encounter in the normally crystallized compact spherulites or in rhyolite or in granite is different from that of the hollow spherulites or lithophysæ. This difference will appear more clearly in the descriptions below, but it is essential that the fundamental difference in behavior and in stability relations of the two cases be emphasized.

In certain bands of this specimen the aggregate volume of the gas cavities is relatively large, but they are not elongated as in specimen 88429 and have the appearance rather of a spongy structure. The cavities here are associated with the spherulites and were evidently developed *in situ*.

In one larger cavity a white coating of clear, secondary hyalite was observed. This mineral is abundant in the more altered specimens of obsidian and pumice, especially in the specimens gathered at the small circular pond mentioned above. At this place highly siliceous solutions were evidently active and not only deposited hyalite but also alunite, and corroded the black obsidian glass in a remarkable manner, so that many of the fragments resemble in outer forms the Bohemian moldavites, whose origin is still in some doubt. The formation of these surface markings is discussed in a separate section below.

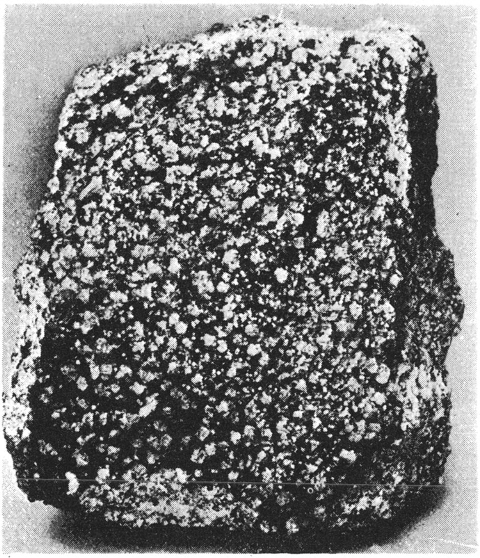

Figure 1.—*Obsidian containing radial Spherulites and bubble Cavities*

Specimen 88432. Two-thirds natural size

Specimen 88432, as shown in figure 1, is filled with spherulites, ranging in size from mere specks to kernels half a centimeter in diameter. The radial spherulites are usually white, as a result evidently of the action of the circulating solutions which deposited the alunite and hyalite in the adjoining gas cavities. The central part of many of the radial spherulites is still dark gray and unaltered. Under the microscope the secondary alteration is seen to be of the nature of a bleaching effect rather than of complete recrystallization, although there is evidence of partial recrystallization.

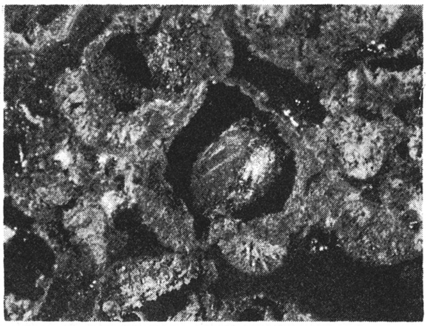

Figure 2.—*Lithophysæ with fluted Tongue of Obsidian projecting into hollow Cavity, shown in Center of Photograph*

Specimen 88433. Magnification, 15 ×

Specimen 88433.—In this specimen there are numerous cavities (0.5 to 8 mm. in diameter) partly filled with crystal fibers which radiate from the walls toward the center. They vary in size and often in shape; but when undisturbed by adjacent cavities they are roughly spherical in outline. On breaking open the cavities, one is impressed by the fact that the crystallized material does not completely fill them (figure 2); also that the crystals in the center of the cavity are coarser than those at the margins. The radial fibers are usually water-clear, and are capped and studded with tridymite crystals in twinned groups measuring up to

0.5 mm. in diameter. The supporting needles rarely measure over 0.02 mm. in thickness (see figure 3). Their optical properties, so far as could be determined, are: γ about 1.535, α about 1.530; birefringence weak; extinction oblique with $c:\gamma'$ from 0° to 28°; elongation is usually γ', but occasionally α'. The plane of optic axes is apparently normal to the elongation. Some of the needles have the appearance, between crossed nicols, of possessing exceedingly fine polysynthetic twinning. It was thought at first that this mineral was albitic plagioclase, but several of the above optical properties do not agree with those of albite and it is not certain that the mineral is a feldspar. The composition of the obsidian itself would indicate a feldspar. The tridymite has the usual characteristics: Tabular plates and thick prisms hexagonal in outline; weakly birefracting in irregular fine patches; refractive index slightly less than 1.480; plates grouped in characteristic twinned aggregates.

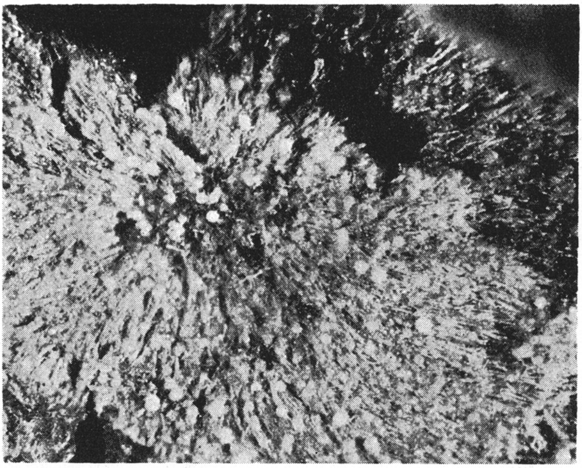

FIGURE 3.—*Tridymite Crystals supported by Needles of Feldspar (?) in recrystallized Lithophysa*

Specimen 88433. Magnification, 50 ×

The aspect of these lithophysal minerals and the manner of their grouping are such as to render untenable the hypothesis that they were crystallized directly from the cooling magma. A comparison of the lithophysæ of this specimen with the radial spherulites and the incipient lithophysæ of the specimens described above shows that the lithophysæ were originally spherulites with a gas cavity, but that they have been partly, and in some instances entirely, recrystallized by the action of the volatile components of the cavity at relatively high temperatures, the volatile components having been released during the initial crystallization of the spherulites. This is proved by several facts:

(*a*) The black obsidian glass can be seen at several points to have flowed into a lithophysal cavity whose walls had collapsed slightly. The inflowing obsidian was so stiff that it extended as a tongue of glass into the cavity (see center of figure 2 and figures 4 and 5). These tongues are of different shapes; they exhibit in cross-section the outline of the cracks through which they entered and are fluted longitudinally with straight grooves and lines which were impressed on them by the irregular outline of the crack shown in figure 5. They resemble the product obtained by the outflow, under great compression, of any viscous or plastic material, as iron, butter, or cheese, through an irregular orifice. The obsidian tongues on entering the cavities broke down and crushed the delicate lithophysal crystals extending from the walls. This proves that the major part of the recrystallization within the lithophysæ took place at a relatively high temperature, while the obsidian was still capable of stiff, viscous flow.

FIGURE 4.—*Radial Lithophysa, in part recrystallized*

Lithophysal cavity has collapsed slightly and is pierced by tongue of black obsidian. Specimen 88433. Magnification, 15 ×.

(*b*) The tridymite crystals have the form of hexagonal plates. These plates show the irregular birefracting areas characteristic of tridymite. The temperature of formation was accordingly above the inversion temperature, 120° C. Whether or not it was above 870°, the inversion temperature of quartz-

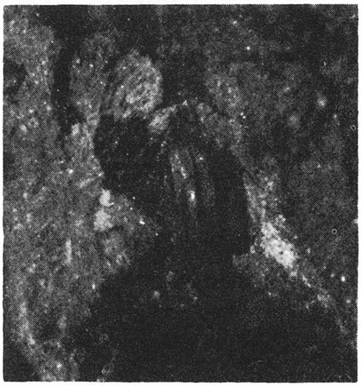

FIGURE 5.—*Sharply fluted Tongue of black Obsidian Glass projecting into lithophysal Cavity*

Specimen 88433. Magnification, 20 ×

tridymite, can not be determined from the data available. The presence of tridymite is not decisive evidence of a temperature of formation above 870°, for Fenner[11] has shown that it may crystallize as a metastable phase at relative low temperatures, especially in the presence of fluxes.

In some of the outer cavities a later ferruginous staining has been introduced, but this does not extend into the rock for any distance, as is evident from the fact that the cavities on a freshly fractured surface do not show the slightest trace of such staining.

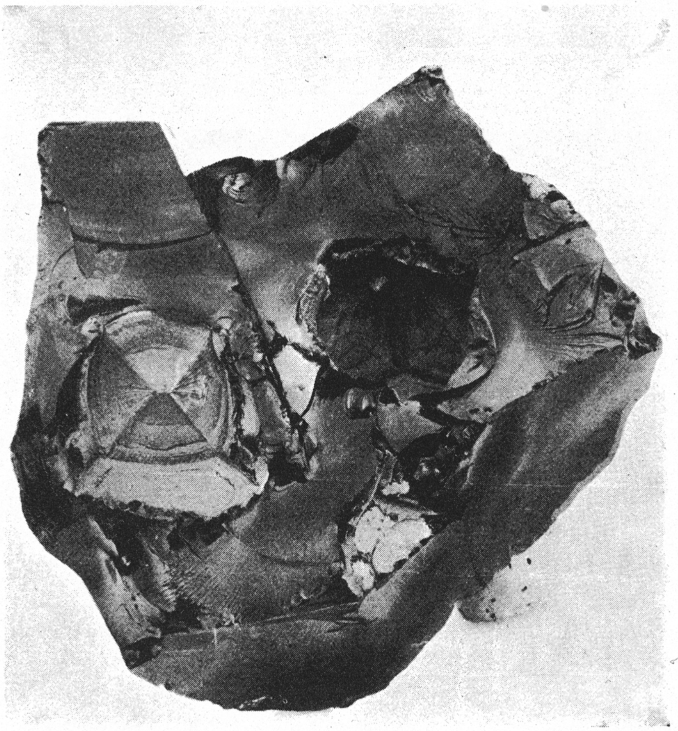

FIGURE 6.—*Remarkable Lithophysæ in Obsidian*

Cube-shape cavity. Specimen 88431. Two-thirds natural size

To recapitulate: Specimen 88433 proves definitely that crystallization of radial spherulites took place as a result of the action of gases at high temperatures, at which the obsidian was still soft and capable of flowing into cavities which had been sheared or had collapsed to a slight extent. The evidence of the presence of volatile components at high temperatures

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[11] Am. Jour. Sci. (4), vol. 36, 1913, pp. 331-384.

is as clear in the Icelandic material as in the Yellowstone Park occurrences.

Specimen 88431.—In this specimen we encounter lithophysæ of a shape and aspect which are unique. They are so remarkable that at first sight they do not appear to be spherulites. The cavities are in the shape of a cube about 25 mm. on a side, the walls of the cube having the appearance indicated in figure 6 and in the photomicrographs, figures 7 and 8. The inner walls are not perfectly flat, but show strong diagonal ribs passing from one corner of a cube face to the opposite corner, as though each cube face had not been quite fully developed into a plane, but still has superimposed on it four negative triangular tetrahexahedral faces; each four-sided pyramid thus formed points toward the center of the cube and not away from the center, as in the case of natural crystal bounded by tetrahexahedral faces. Between the strong diagonal ribs hollow depressions occur. From the apex of each four-sided pyramid fibers radiate toward the sides of the cube, as shown in figure 6. In addition to these lines of growth, a second set of structural lines and ridges and cracks is present, cutting the radiating lines at right angles and emanating as encircling waves from the center (see figure 7).

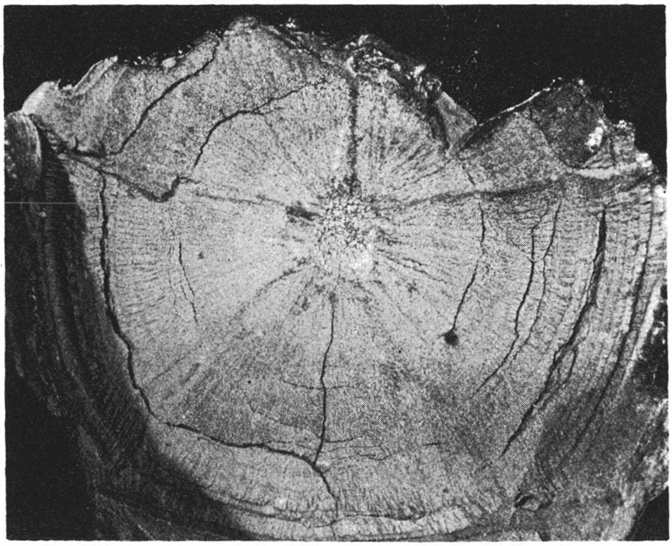

FIGURE 7.—*Lower Wall of Lithophysa on left side of Figure 6*

Shows character of crystallization. Specimen 88431. Magnification, 4 ×

On examining these cube faces still further, we find that any little irregularity on the one face is imaged in exactly the same relative position on the face immediately adjacent to it; thus in figure 6 we observe in the lithophysa on the left a sharply pointed facet on the diagonal rib in the lower left-hand corner of the vertical face; this facet appears on the horizontal face in precisely the same relative position and is shown faintly in the photograph. Much better examples of this phenomenon can be seen in the lithophysæ on the right side of figure 6, but they are not well reproduced in the photograph. The fact that any irregularity on the one face finds its counterpart on the face adjacent to it and intersecting it at the edge of the cube proves that the faces were originally together and were gradually forced apart as crystallization proceeded.

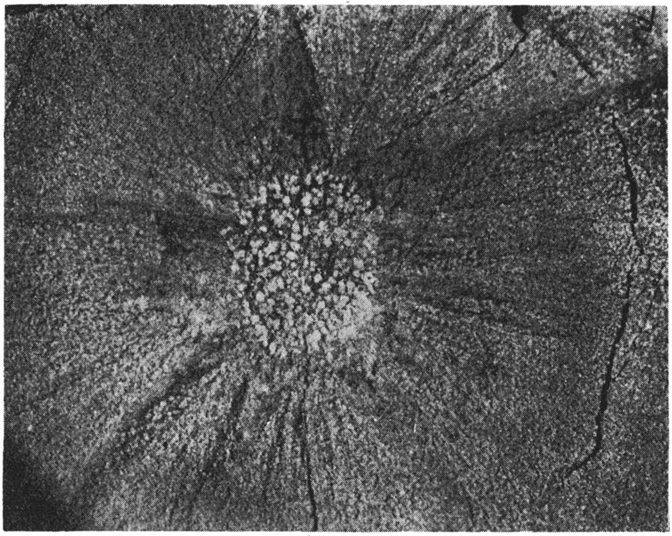

FIGURE 8.—*Enlarged central Part of Figure 7*

Shows decrease in granularity away from center. Specimen 88431. Magnification, 10 ×

Such pushing apart of a spherulite by the gas emitted during crystallization or by the pulling apart as a result of general hydrostatic tension is not unusual and would ordinarily be passed over unnoticed.

In the present instance the remarkable symmetry of the lithophysæ attracts attention, and the observer finds it difficult to picture the mechanism of such a process. When it is realized, however, that a cube can be considered to consist of a set of six four-sided pyramids (figure 9, negative tetrahexahedrons meeting in the center at their apices, the six cube faces being their bases), the geometry of the problem becomes clear. If, then, having started with a small spherulite and having caused it to fracture symmetrically as a result of the internal gas pressure along the lines of the pyramids of the cube, we then allow crystallization to proceed continuously with concomitant evolution of volatile components, which tend to force the rigid walls still farther apart, we obtain the present forms. Evidence that this has been the process of development is not lacking.

(1) The radius of curvature of the outer wall of the right side of the lithophysa on the right in figure 6 is variable. It is least in the center of the segment and becomes increasingly greater as the margin of the segment is approached; near the margin the curve of the outer wall shows a flexure. The edges of the lithophysal cube are very thin and only a thin film of crystallized material has been formed next to the glass, thus indicating that crystallization was active only a relatively short time at that point. The ratio of the thickness of the crystallized shell at the center of a segment to that of the crystallized film at its edge is of the order of magnitude of 50 to 1.

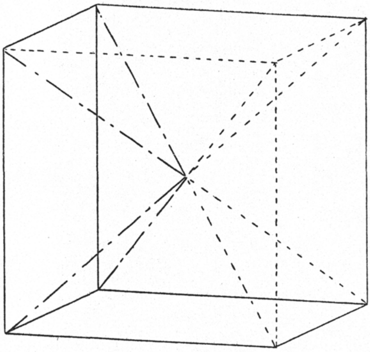

FIGURE 9.—*Diagrammatic Representation of Cube built up of six Pyramids*

The apices of the pyramids must meet at the center and their bases are the sides of the cube.

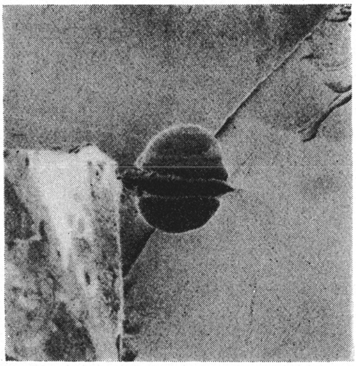

FIGURE 10.—*Ellipsoid-like lithophysal Cavity, with central Girdle of crystallized Material*

Specimen 88431. **Natural size**

(2) On one side of specimen 88431 a cavity, 9 mm. in diameter, occurs, out of which the crystallized material has fallen, except for a single equatorial groove (see figure 10). In this case it appears that the spherulite was not broken into halves until it had grown to an appreciable size, and that then it was forced apart along a single plane, thus elongating the sphere into an ellipsoid-like figure with a central girdle.

(3) A difference in age between the center and the margin of the exposed faces of the lithophysa is clearly indicated by the change in granularity of the recrystallized material. Beginning at the center (fig-

ures 7 and 8), we find the original radial spherulitic material covered with a crust of geode-like crystals measuring up to 0.2 mm. in diameter. These crystals decrease in size as we pass from the center toward the margin, where they are only a few hundredths of a millimeter in diameter. The majority of these lithophysal crystals are tridymite; they form clusters and rosettes similar in every respect to the tridymites of specimen 88432. The tridymite occurs in characteristic hexagonal plates, showing weak, irregular birefringence and low refractive index, $n \leq 1.480$. No quartz or cristobalite was observed with certainty. Extending into the tridymite crystals and holding them together is a radial, weakly birefracting mineral of much higher refractive index. It is probably identical with the fibrous, feldspar-like mineral which occurs in larger individuals in the cavities of specimen 88432, described above.

Scattered through the mass of tridymite crystals are small (0.05 to 0.1 mm. in diameter), sharply developed crystals of a honey yellow to yellow-brown mineral of the following optical properties: Refractive index α, considerably higher than 1.78, but noticeably less than 1.857; γ, slightly greater than 1.857. Optical character negative; birefringence strong; crystal system apparently orthorhombic. On a section practically normal to the obtuse bisectrix the angle between the crystal edges was found by measurement to be about 100°. All of these properties agree with those of fayalite, which also occurs in similar association in the Yellowstone Park lithophysæ. The angle noted above is probably that between (021) and $(0\bar{2}1)$, which is 99° 06′ for fayalite.

The relative abundance of the fayalite is remarkable when we recall that the total iron oxide content in the rock is less than 3 per cent. Similar relations were recorded by Iddings for the Yellowstone lithophysæ. The fayalite crystals decrease also in size from the center toward the margin of the lithophysal cube faces. The presence of fayalite and tridymite as the chief minerals formed indicates precipitation from a physico-chemical system different from that of the normal rhyolite magma; the system consisted largely, of course, of volatile components, which at the high temperatures attacked the crystals which had crystallized from the magma itself. These components were first set free on the crystallization of the spherulites, which in turn, at lower temperatures, were attacked by them, and changes were produced which resulted in new crystal phases more stable under the new conditions than the original crypto-crystalline substances of the spherulite. There is no evidence that during this recrystallization there was migration of material away from the cavity. The decrease in size of grain of the new crystals from the center to the margin indicates again that the gases acted for a much longer period at the center than at the margin; in short, the center is much older than the margin, and the gases active during the alteration were evidently those set free chiefly during the primary crystallization of the spherulites.

The evidence presented thus far proves that during the crystallization of the spherulites volatile components were active within the cavities; also that at the temperatures, at which the lava was still sufficiently molten to flow into very small cracks, the remarkable deformations described above were produced. Now the chemical analysis of this obsidian shows that it contains 0.13 Cl, 0.07 SO_3, and 0.27 H_2O—all volatile gases which would be set free, in part at least, on the crystallization of the silicates. It is not probable that either sodalite or noselite would be formed in the presence of so much quartz, and these are practically the only silicates containing NaCl or Na_2SO_4 which would be likely to be formed. We have seen, furthermore, that the escape of volatile components continued as crystallization proceeded and as the cavity was enlarged. The question arises: Did the pressure of this escaping gas force the cavity apart or was the main factor an external uniform tension developed on the shrinking of the magma?

It is evident that where gas bubbles are formed in a magma the vapor pressure of the gas has been sufficient to overcome the internal pressure of the magma; also that simple vacua of regular bubble shape in a viscous magma would be difficult to form. Field experience and laboratory practice have shown that, in such instances where the magma is inclosed between frozen walls and shrinkage occurs on cooling, cracks (joints) develop rather than bubbles disseminated evenly through the magma. Reduction of hydrostatic pressure in the liquid favors the formation of gas bubbles just as does the opening of a siphon bottle containing carbonated water. Bubbles may begin to form, moreover, when the liquid becomes supersaturated with respect to the gas. Increase of uniform pressure raises the saturation limit with respect to the dissolved gas; conversely, reduction of uniform pressure lowers the saturation limit and favors the escape of the gas. Gravity, furthermore, is a factor which would tend to close any vacuities disseminated through the magma. On cooling, it would seem, then, that a magma inclosed in a solid shell would tend to shrink away from the roof and to leave cracks rather than simple bubbles. The formation of bubbles is facilitated if there be a point of discontinuity in the liquid (differences in potential). This is given in the case of gas in the magma reaching supersaturation near some nucleus, such as a minute crystal or spherulite. It is less easy, if not impossible, to explain the formation of a vacuum bubble in a moving viscous liquid.

Another fact which bears on the present problem is the increase in solubility of gas in a liquid with falling temperature. The effect of this, if pronounced, would be, in the case of a simple bubble, a reduction in its size with lowering temperature. Opposing such reduction, however, is the hydrostatic tension which develops in the central portion of the magma on cooling and which tends to enlarge the bubbles. The ultimate effect which these opposing forces may have had on the bubbles in Iceland obsidian is not known, but the fact that the cavity was lined with crystallized material would tend to retard the magmatic resorption of the gas, and thus tend to produce larger cavities than otherwise.

To summarize the conclusion briefly: Gas escaping from the magma on crystallization was an active factor in the development of the lithophysæ in the obsidian from Hrafntinnuhryggur. It caused recrystallization and aided to a large extent in enlarging the cavity as crystallization proceeded. The amount of energy required to effect the observed recrystallization in the cavities need not have been great, because the energy necessary for the solution of the spherulite crystals first formed was probably largely offset by the energy liberated during the crystallization of the lithophysal minerals. The shrinkage of the viscous lava on cooling tended, of course, to reduce the uniform hydrostatic pressure; but the chief effect of such reduction on the size of the bubble cavities was to increase the rate of evolution of gas from the magma (reduction of solubility of gas in magma under reduced pressure). Shrinkage of the magma alone without evolution of the inclosed gas would tend to produce cracks (joints) bearing some relation to the inclosing walls. That the magma contained abundant gas, however, is proved both by the presence of pumiceous layers and by the recrystallizing action of the gas on the walls of the cavity. The conclusion seems, therefore, warranted that in the Hrafntinnuhryggur obsidian, and probably in most obsidians, the pressure of the gas set free from the magma as a result of crystallization and also of reduction of hydrostatic pressure induced by the shrinking of the central portions of the magma on cooling has been an important factor in the development of the lithophysæ. To ascribe the total effect to the uniform pull or tension developed by shrinkage of the cooling magma is not an adequate hypothesis to account for the different facts and relations which have been observed.

SECONDARY MINERALS AND ETCHING PHENOMENA PRODUCED BY HOT CIRCULATING SOLUTIONS

Although not strictly germane to the theme of this paper, it may be of interest to describe the effects produced by hot solutions on the more porous and exposed portions of the obsidian. As noted above, both hyalite and alunite were deposited from these solutions on the walls of bubble cavities. In specimen 88434 the gas bubbles adjacent to the spherulites are usually coated with minute water-clear crystals of a substance which is evidently a secondary mineral introduced by circulating solutions after the solidification of the obsidian; this mineral agrees in its optical properties with alunite. The largest crystals measure less than half a millimeter in diameter and are bounded by the basal pinacoid and by rhombohedral faces, which are triangular in shape. Basal cleavage is distinct and gives rise to a distinct semipearly luster on the basal pinacoid. As a result of this cleavage, it is an easy matter to obtain sections normal to the optical axis, on which then the uniaxial, optically positive interference figure of a mineral of medium to fairly strong birefringence is visible. Rhombohedral cleavage is also present, but is poorly developed. The refractive indices were measured by the immersion method: ω about 1.575, ϵ about 1.595; birefringence about 0.020. Hardness apparently 3 to 4. Slightly soluble in hydrochloric acid, but to a greater degree in sulphuric acid. In the HCl solution potassium was found to be present; also sulphuric acid. On heating in a closed tube, the mineral decrepitates and emits a white cloud of sulphurous fumes. This material heated on charcoal before the blow-pipe gives, after moistening with dilute cobalt nitrate solution, the characteristic blue color test for aluminum. The density was found by immersion of a clear crystal in Klein's solution to be 2.73. These properties agree with those of alunite, and the determination as such may be considered reasonably certain. The alunite appears to have been formed during the later stages of precipitation of the hyalite. Compared with hyalite, it is present in small amounts. The small geodes of alunite, when examined under high powers,[12] glisten and sparkle with the crystal faces of this mineral and are exceedingly beautiful. The same mineral occurs in the more completely crystallized rhyolite of specimen 88434, which is likewise banded and full of gas-bubble pores.

It is of interest to inquire into the character and the temperature of the solutions from which the hyalite and alunite were deposited. In this connection one feature is of special interest: The obsidian fragments and blocks which are associated with the hyalite and alunite occurrences are

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[12] For the examination of extremely minute crystals in the hand specimen, the following method has been found satisfactory: Use a binocular magnifying glass (magnification, 65 ×) and view object illuminated by a strong electric light, partly inclosed in a brass holder mounted on a universal arm, which is attached to binocular stand and can be moved in any direction, thus enabling the observer to illuminate at will any particular crystal from any desired direction.

still unaltered, but their surfaces are deeply etched, pits and narrow grooves cutting into the surfaces 3 or 5 and even to 15 mm. (see figure 11, specimen 77616, and figure 12, specimen 88435). These markings vary in shape and size from semicircular grooves, which have been well characterized as lunar crater forms by G. P. Merrill,[13] to straight channels not unlike the marks left by an engraver's tools. The distribution of the various markings, both regular and irregular, follows no discernible order; and the question of the mode of formation of such remarkable etch phenomena is of interest especially because of the similarity of these markings to those which are found on the moldavites of Bohemia, which have been described in great detail by F. E. Suess,[14] who considers them to be of extraterrestrial origin.

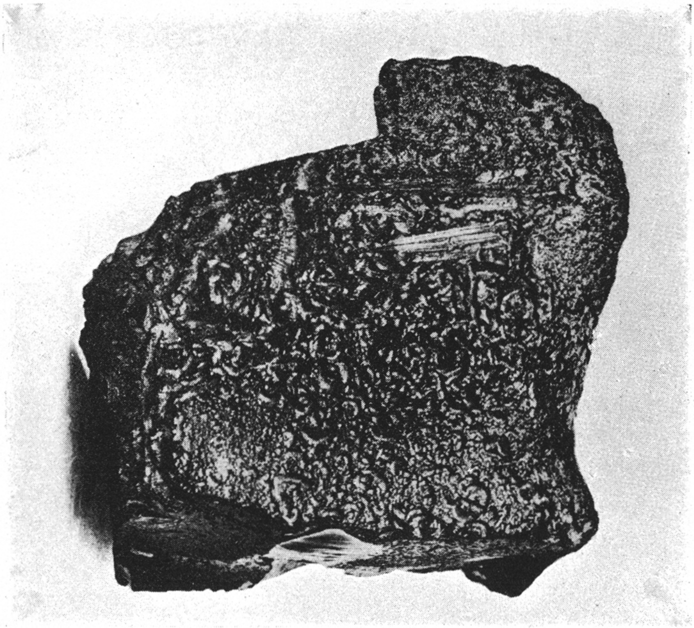

FIGURE 11.—*Etched Surface of Obsidian Glass, moldavitic in Character*
Specimen 77616. Two-thirds natural size

In the present case the origin of the etch figures is clearly shown by the records contained in the present suite of specimens. The following facts have a direct bearing on the problem: (1) The etching is evidently the work of hot and probably alkaline solutions. This is inferred from

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[13] Proc. U. S. National Museum, vol. 40, 1911, p. 485.

[14] Jahrb. d. K. K. Geologischen Reichsanstalt, vol. 50, 1900, pp. 193-382.

the obvious connection between the deposition of hyalite (specimen 88435) and the etch pits. In figure 12 a face of obsidian is shown from which a crust of hyalite was broken off. The surface shows etched grooves and markings like the lines on a turtle shell; they were obviously formed during the deposition of the hyalite. A careful study of the entire specimen under a binocular microscope leads to the conclusion that the solutions actually bored into the obsidian and continued to do so until a protecting crust of hyalite was formed. The irregular distribution of the etch channels seems to be, in part at least, the result of the irregular precipitation of hyalite from an exceedingly mobile medium, probably a hot solution with admixed vapors; in short, from hot volcanic emanations which escaped from the intruded but still hot magma mass. In view of the high silica content of the obsidian, 75 per cent, it is probable that the etching solutions were alkaline and not acid. A glass bottle of the composition of obsidian should be an excellent retainer for even hot acid solutions. It is significant that the greater part of the hyalite was deposited before the alunite. This may indicate a gradual change in the composition of the volcanic emanations by the increased concentration of sulphuric acid.

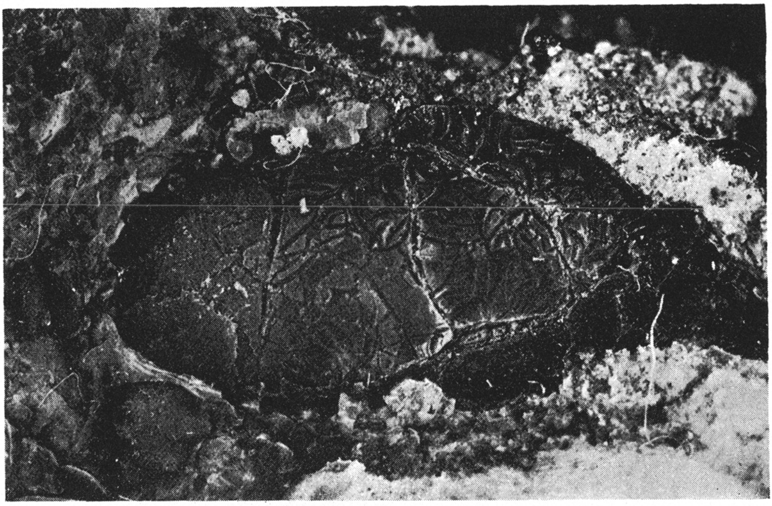

FIGURE 12.—*Etched Surface of a small Obsidian Fragment*

The surface was protected in part by a coating of hyalite circulating solutions which reached the obsidian along cracks in the hyalite mantle. Specimen 88435. Magnification, 10 ×.

(2) Experiments in etching both crystals and glasses have shown that the nature of the etched surface produced is dependent on the kind of

etching medium and on the character of the surface etched. The etching process is not unlike the abrasive action of sand-laden winds on exposed rock surfaces in deserts.[15] The attacking acid solution etches in the direction of least resistance and the material is carried away in solution. The solution currents form whirls and eddies, and thus favor unequal attack even on a perfectly homogeneous surface. Furthermore, any irregularities in the surface or material are emphasized by the solutions. An examination of the surface of the obsidian of the most uniform specimen, 88428, shows the presence of fine point irregularities, in the shape usually of minute triangular-shaped areas, as though at such points the cohesion of the obsidian was different from that of the surrounding points; this difference finds expression in the character of the surface of fracture obtained on the splitting off of the glass chips. Such points of unique cohesion are probably the minute bubble cavities which are scattered through the glass and are visible in thin obsidian splinters under the microscope. These points and cavities offer favorable points of attack for the etching solutions, which, as the dissolving action proceeds, continue to enlarge the cavities, and thus possibly to produce lunar crater forms on some of the specimens. Another explanation of these forms is that they are etched enlargements of original half-moon fracture cracks, produced by striking the glass fragment a sharp blow. The distinct wavelike lines, both radial from and concentric to the point of impact of a blow which fractures a piece of obsidian, are lines which exert a directive influence on the attacking solution, and thus give rise to certain types of the remarkable etch forms which we observe. Still another kind of crack requires mention, namely, the shrinkage rupture cracks, as shown in specimen 88429, described above. Into these fissures the solutions enter and tend to enlarge them. In the case of strain in the glass the solutions probably etch most rapidly along the lines of maximum strain, and this again tends toward irregularity of etching on the exposed surface.

In addition to these factors inherent in the etched material, any foreign substance, as a precipitate, attached to the surface serves as an obstruction to the acid streams of the solvent and forces them to flow along certain paths. Attention has been called above to the effect of precipitated hyalite in this direction. Observation proves that the pitted character of some of the slightly etched surfaces is not due to a spongy layer of original bubble cavities which have been exposed by subsequent fracturing.

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[15] V. Goldschmidt and F. E. Wright: Neues Jahrb., Beilage Bd. xvii, 1903, pp. 355-390; Beilage Bd. xviii, 1904, pp. 335-376.

(3) The matter of internal strain noted above is significant for two reasons: (*a*) its directive influence on the etching solutions, and (*b*) the light which it throws on the former history of the fragment under examination. In the case of a large mass of obsidian, the internal strains set up on very slow cooling are virtually compensated at the period of their formation, so that the chilled product is a remarkably well annealed mass of glass far superior in this respect to the best optical glass.

Strain birefringence in the large fragments of the obsidian (specimen 88428) is hardly detectable even in the largest splinters, which are sufficiently transparent for observation. Around the radial spherulites (specimens 88432 and 88433) no strain birefringence could be detected in the adjacent glass in the thin section. This proves a very perfect state of annealing. On the other hand, the small etched fragments of obsidian in specimen 88435, which were found near the pond noted above and at some distance from the main obsidian mass, are in a state of severe strain. Small splinters of these fragments show gray interference colors and uneven distribution of the regions of differential compression and tension. The strain in these fragments is apparently even greater than that produced on heating a small splinter of the annealed obsidian in a Bunsen burner to a temperature of 1,000° or 1,200° C. and then quenching it in water. This proves clearly that the fragments are not simply fragments of the annealed obsidian mass which have been broken off and transported to their position and there etched, but that they were cooled very rapidly from a high temperature to relatively low temperatures. The natural inference is that they are shattered ejectamenta of the obsidian magma after the manner of the bombs of less siliceous magmas, or that they represent fragments of the outer chilled crust of the obsidian magma. The distribution of the strain phenomena indicates the first rather than the second inference. On the assumption that these fragments represent bombs, the irregular rupture shrinkage cracks are readily explained. A study of the types of volcanic bombs ejected by rhyolitic magmas and of the distribution of strain in them would be of interest in this connection. It is also important to note that on heating the obsidian in the Bunsen burner the obsidian tends to evolve gas bubbles and thus to become pumiceous. The tendency toward pumiceous development in some of the etched specimens has been noted above.

THE MOLDAVITES

In view of the great similarity between the etched surfaces of obsidian fragments at Hrafntinnuhryggur and those of the tektites, especially the moldavites of Bohemia, which have been considered to be of extraterrestrial origin, it is of interest to examine the strain phenomena in specimens of moldavites. Moldavites are fragments of a green-colored glass which occur in certain gravels in Bohemia, especially near Budweiser and Treibitsch, and are characterized by remarkable surface markings similar to those described above. The distribution of the moldavites is not unlike that of Indian arrow-heads in the Middle West. The moldavites occur here and there, but never in any manner indicative of their origin. They approximate in composition a rhyolite glass high in silica. Because of their abnormal distribution and remarkable surface markings, Suess concludes, following a suggestion of R. D. M. Verbeek,[16] that they are meteoritic in origin, derived possibly from the moon. H. S. Summers,[17] in a recent study of obsidianites, concludes that the chemical evidence also indicates that they are of meteoritic rather than of volcanic origin. G. P. Merrill,[18] on the other hand, presents evidence against the necessity for considering the moldavites to be of extraterrestrial origin because of their external surface markings. The present study tends to confirm and to strengthen the objections advanced by Merrill.

With a proper choice of solution and temperature, it should be relatively easy on rapidly chilled specimens of glass of moldavite composition to reproduce the surface markings and thus to produce artificial moldavites. This Professor Merrill has shown to be possible by simple means, namely, by suspending fragments of obsidian or glass in hydrofluoric acid vapor. The mode of occurrence of the Hrafntinnuhryggur fragments is a good example of the result of the process at work in nature on a large scale.

Two instances may be cited to prove that etching phenomena of this type can be produced on other materials: (*a*) In the course of experiments on the etching of cleavage fragments of calcite, the writer observed etch pits and channels in process of formation on the under side of the fragment immersed in a weak solution of hydrochloric acid in a beaker.[19] (*b*) On a specimen of stalactite from Luray, Virginia (U. S. National Museum specimen 88436), the surface is pitted and grooved with shallow markings across the concentric layers not unlike some of the markings on the moldavites.

Passing now to the consideration of strain phenomena exhibited by the moldavites, we may first direct our attention to the different effects which result from the various physical conditions under which strain is

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[16] Jahrboek van het Mijnwesen in hederlandish Oostindie. vol. xx. 1897. p. 235. Amsterdam.

[17] Proc. Roy. Soc. Victoria. vol. 21. pt. 2. 1909. p. 428.

[18] Proc. U. S. National Museum. vol. 40, 1911, p. 485.

[19] Neues Jahrbuch, Beilage Bd. xviii, 1904. p. 340.

produced in cooling glass. These are well known in the glass industry and apply with equal force to the cooling of a silicate glass of moldavitic or rhyolitic composition, provided proper allowance be made for differences which arise because of high silica content. On the cooling of a mass of glass heated to a high temperature, the outer portions of the mass in contact with air chill most rapidly and contract, but on so doing meet with resistance from the hot interior mass. This shrinkage against strong counter-resistance produces radial compression in the marginal shell, which, because of the rapid cooling, quickly becomes so stiff that appreciable movement is no longer possible; the material thus sets under a state of permanent radial compression. The central portion contracts, in turn, on cooling and tends to draw away from the now rigid incasing shell. Tensile stresses normal to the boundary surfaces are thus set up and the material soon acquires a permanent set under tensile strain. The net result of such rapid cooling is therefore an outer zone of radial compression which decreases rapidly toward the center of the mass; it becomes zero (neutral band or band of no strain) and passes finally into a wide central region of tensile stresses.

It is obvious that the relative intensities of the strain thus set up and the relative widths of the zones of compression and of dilatation depend on the composition and size of the glass mass, on the initial temperature of heating, and on the rate and conditions of cooling. Experiments have shown that in ordinary glasses the temperature region at which the viscosity of the material becomes so great that differential strains may persist for a period of time is between 250° and 450° C. Above 500° practically all differential stresses are relieved by flow of the material, while at 250° the movement in the material is so sluggish that a very long period of annealing is required to produce an appreciable relief of stress differences. At a still lower temperature the glass is so rigid that under small loads it behaves as an elastic solid and the forces of restitution set up as a result of the strain suffice to restore the material to its initial configuration on release of the load; in short, strictly speaking, the glass is no longer viscous, according to the established definition of the term. At ordinary temperatures the glass is so rigid, or its viscosity so great, that a state of strain may persist in it for geologic ages, as tests on obsidians have shown. It is evident, therefore, that the state of strain of a glass fragment may well serve as an indicator of the conditions under which it cooled.

The strain phenomena in glass are not apparent under ordinary conditions of observation, but they can be rendered visible by simple optical methods, which in this respect function as does the developer on the photographic plate. The optical effects resulting from strain were first studied in detail by Brewster in 1814, at a time when only the simplest of optical apparatus was available and but little was known of double refraction. Notwithstanding this, Brewster deduced from a series of ingenious experiments many of the fundamental laws of the optical behavior of glass strained either mechanically by differential pressure or tension or as a result of non-uniform heating or cooling. Brewster found that a plate of glass under load is birefracting; that the optical effect produced is sensibly proportional to the intensity of the strain; that a plate of glass under differential compression behaves optically as a uniaxial negative crystal with its principal axis in the direction of the acting load, while under differential tension it acts as an optically positive uniaxial crystal; that in a glass plate cooled quickly from a high temperature a permanent strain is imparted which is at maximum intensity next to the outer surfaces (zone of compression), and which, decreasing toward the center, reaches a neutral band and passes then into a zone of tension in the central part of the plate; that compression produces retardation, while dilatation causes acceleration of the transmitted light waves.

Since Brewster's time improvements have been made in the methods of observing and measuring strain birefringence, but these refinements are not required in the present problem. To study the distribution of strain in an irregular glass fragment, the only apparatus required is two crossed nicols and a sensitive tint plate. This is easily obtained by removing condenser, objectives, and eyepiece from the microscope and observing the fragment immersed in a liquid of the same refractive index. For this purpose a small crystallizing dish or beaker is well suited as a container, and benzol, with refractive index approximately 1.50, as an immersion liquid. The purpose of the refractive liquid is to overcome the annoying surface reflections from the glass surface, which tend to disturb and to mask the interference phenomena resulting from strain.

Returning now to the moldavites, we have three possibilities to consider:

(1) The moldavites are etched fragments of a large mass of slowly cooled obsidian. In this case, as we have seen above, little, if any, strain is present. Between crossed nicols the fragment is practically isotropic.

(2) The moldavites are volcanic ejectamenta which were originally molten, but were chilled rapidly during contact with the air. In this case they should show a considerable amount of strain, with an outer zone of compression, an intermediate zone of no strain, and a central region under dilatational strain.

(3) The moldavites are meteoritic in origin. In the case of meteorites the conditions are unique. The meteor enters the earth's atmosphere as a very cold body. The frictional resistance of the atmosphere very quickly raises the temperature of the exposed surface of the meteorite to the melting region. Such melted portions are then brushed off, with the result that only a thin crust of the molten matter is left on the meteorites when they reach the earth's surface. The period of flight through the atmosphere is of such short duration that the center of the meteorite does not become appreciably heated. According to Professor Merrill, to whom the writer is indebted for a statement of the conditions which obtain during the fall of a meteorite, the only recorded instance in which a meteorite was touched immediately after it had reached the earth's surface showed that the meteorite was "stone cold." The result of such conditions of flight and local surficial heating is intense local strain analogous to the strains set up on inserting a large piece of glass into a hot Bunsen flame. The glass fragment commonly cracks into pieces, or small chips spall off analogous to exfoliation shells on rocks exposed to sudden changes in temperature. The outer forms of stony meteorites indicate that they have been subdivided in this manner.

The distribution of the strains set up under such conditions can be readily obtained by inserting the edge of a cover glass or object glass into a Bunsen burner. If care be taken to avoid fracturing, the edge of the glass plate melts, while the center and opposite edge are still cold. Examination of the plate after cooling shows the presence of a very narrow marginal band under intense compressional strain, which decreases in the direction of the center and passes through a neutral line into a zone of tensional strain, which soon reaches a maximum and then diminishes gradually and practically disappears near the center. The glass plate usually breaks asunder later near the line of maximal tensional strain.

Examination of moldavite specimens from Bohemia[20] showed a distribution of strain identical with that described above for conditions of cooling postulated under case 2, namely, those of a highly heated or molten mass of glass chilled rapidly. The small etched obsidian fragments from Hrafntinnuhryggur (specimen 88435) exhibit the same distribution of strain. In the moldavite specimens the strain is distributed in such a manner as to indicate that they are not fragments of a large mass of annealed glass (obsidian or artificial glass) or single meteorites, but rather fragments resembling in character the spatters or splashes of molten obsidian described above. It should be noted, however, that the meteoritic origin of the moldavites is not absolutely disproved, for it is

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[20] The writer is indebted to Professor Merrill for the loan of these specimens.

conceivable that all of the outer zone of intense compression and part of the inter zone of dilatation have been etched away, and only the central core of the original fragment is left. It does, however, prove that the present surface markings of the moldavites are not original surface markings produced on the fragment during its flight through space. This conclusion is in agreement with the inferences which have been drawn by Professor Merrill from the etching phenomena.

It may be noted that in highly siliceous glasses the birefringence developed for a given load is less than that developed under similar conditions in ordinary, less siliceous glasses, which have much higher coefficients of expansion.

SUMMARY

The obsidian at Hrafntinnuhryggur, near Myvatn, Iceland, is of special interest to the geologist because of the unusual opportunity it offers for the study of the effects resulting from the physico-chemical conditions of cooling. In the present paper the formation especially of spherulitic, lithophysal, and pumiceous structures is discussed; certain remarkable surface markings resembling the pits and grooves on moldavites are also described briefly. They were produced by the etching effect of hot volcanic emanations on fragments of obsidian glass.

The evidence given above indicates that in the formation of the lithophysæ gases were active. These volatile components, which were released from the magma during the crystallization of the radial spherulites, attacked part of the material of the spherulites; new crystal compounds, as tridymite and fayalite, were formed which bespeak conditions of formation different from those under which the original spherulites were crystallized. The pressure of the liberated volatile components aided materially in the original formation and subsequent enlargement of the lithophysal cavities. The general hydrostatic tension (external pull) resulting from shrinkage of the central part of the cooling magma probably aided in this development, but the inclosed gas pressing against the walls of the cavity was also an important factor.

Volatile components set free during the crystallization of a spherulite may either escape along minute cracks and spaces in the spherulite to its margin and there form a bubble in the viscous magma or the viscosity of the magma may be such that the internal gas pressure forces asunder the spherulite. In the first case the presence of the gas bubble adjacent to the spherulite hinders the further growth of the spherulite at that point, with the result that the spherulites with adjacent bubble cavities are well developed, as in specimens 88430 and 88432, described above. In the second case it is important to note that the forcing apart of the cavity was a very slow process. The first rupture took place when the spherulite was small; the rigid walls of the cubical or irregularly shaped cavity thus formed were constantly forced apart, but continued to grow as crystallization advanced. The edges of the cube were thin and in contact with the magma, which, however, was probably so thick and viscous that less resistance was offered to the slow forcing apart of the walls of the spherulite than to the formation of gas bubbles adjacent to the spherulite. Examples of this phenomenon are shown by specimen 88431. It is not possible to determine from the scant evidence at hand the several quantitative factors which are essential to the formation of the type of lithophysal cavities of specimen 88431.

Evidence is also presented which shows clearly that the deeply etched surfaces on irregular fragments of the obsidian are the result of etching by hot circulating solutions from which large amounts of hyalite were deposited. Minute crystals of alunite were also deposited during a later stage of circulating solutions. The close resemblance of the surface-etching phenomena thus produced to the surfaces of moldavites and other tektites is emphasized; also the mechanics of the etching process by which such extraordinary forms are obtained. The distribution of strain within the moldavites is considered briefly. The conclusion is reached that neither the external form of the moldavites nor the distribution of strain within them can be considered to be an indication of their extraterrestrial origin, as has been stated by Suess. This conclusion is identical with that recently advanced by Merrill, and the above evidence serves to strengthen the position taken by him.

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Notes