THE MINERALS OF OBSIDIAN CLIFF, YELLOWSTONE NATIONAL PARK, AND THEIR ORIGIN

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INTRODUCTION

This study was undertaken with two objects in view; first, to determine and describe the minerals that are found in the cavities in extrusive volcanic rocks. and, second, to obtain, if possible, information on the character and action of solutions given off by magmas. The results of my study of the minerals of Obsidian Cliff, Yellowstone National Park, are here given, and it is expected that other investigations will follow as material becomes available.

No field examination of the occurence was possible, and this paper is based upon a study of the extensive suite of specimens in the United States National Museum, including the material collected and described by the late Dr. J. P. Iddings.[1] A number of specimens from similar occurrences in California, Utah, Mexico, and Lipari Islands were examined for comparison.

The minerals in the cavities of volcanic rocks may be considered as the final products of chemical reactions, and may be expected to furnish some evidence as to the original nature of the solutions. In the case of flow rocks, the physical environment can be determined with a fair degree of certainty. The physical chemistry of solutions at high temperatures and pressures has been determined to some extent by Smits,[2] Centnerswer,[3] Niggli,[4] and Morey,[5] and will not be discussed at this time.

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[1] U. S. Geol. Surv., Mon. 32, pt. 2, 1899.

[2] A. Smits, Zeits. f. Phys. Chem., vol. 51, 1905, p. 193; vol. 52, 1905, p. 498; vol. 54, 1906, pp. 498, 512; vol. 67, 1909, p. 464; vol. 76, 1911, p. 445.

[3] M. Centnerswer, Zeits. f. Phys. Chem., vol. 46, 1903, p. 427; vol. 61, 1908, p 356.

[4] P. Niggli, Neues. Jahrb. f. Min., 1914, p. 69; Zeits. f. Anorg. Chem., vol. 76, 1912, p. 161; vol. 77, 1912, p. 321; also Niggli and Morey, Journ. Amer. Chem. Soc., vol. 35, 1913, p. 1086.

[5] G. W. Morey, Journ. Amer. Chem. Soc., vol. 39, 1917, p. 1174.

OBSIDIAN CLIFF

The Obsidian Cliff, which is so well known for the beauty and delicacy of its lithophysae and the minerals found in them, flanks the road leading from Mammoth Hot Springs to the Norris Geyser Basin, on the west. Iddings describes it as follows:[6]

Obsidian Cliff is at the northern end of Beaver Lake, in the Yellowstone National Park, about 11 miles south of Mammoth Hot Springs. It forms the eastern wall of a narrow cut in the plateau country through which Obsidian Creek flows at an elevation of 7,400 feet. The cliff extends for half a mile, rising from 150 to 200 feet above the creek and falling away gradually to the north; the upper half is a vertical face of rock, the lower portion a talus slope of the same material.

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The cliff presents a partial section of a surface flow of obsidian which poured down an ancient slope of rhyolite from the plateau lying to the east. * * *

The exact point at which this obsidian broke through the older rocks and reached the surface has not yet been discovered; but that forming Obsidian Cliff has evidently flowed down from the high plateau in a northwest direction into a preexisting valley, the planes of flow in the lava clearly indicating that it has crept down the slope back of Obsidian Cliff and accumulated in the bottom of a channel between rhyolite hills.

The detailed petrography of this occurrence has been given by Iddings, so it is not my purpose to discuss that phase of the subject; the mineralogy shows some interesting features touched upon but casually by him, and will be considered in this paper.

GENERAL DESCRIPTION OF THE ROCKS OF THE AREA

The rhyolitic rocks of the Yellowstone National Park are wholly extrusive. They are superficial flows in the form of nearly horizontal sheets which vary but little in chemical composition but show a multiformity of physical aspects. Lithoidal and glassy facies are both abundant. The color varies as much as the physical fabric and ranges from a very light gray through shades of gray and brown to black, while some phases are red or mottled, as the variety called marekanite. The rocks are usually porphyritic and, even in some of the hyaline facies, phenocrysts of feldspar or, more rarely, quartz are present. In some areas vesicular or lithophysal rocks are abundant and it is often in these that a variety of minerals of unusual interest is found. These reach their maximum development in the flow making up the Obsidian Cliff and here the relationship of the minerals to one another and to their matrix is most apparent.

OBSIDIAN

The obsidian of Obsidian Cliff is a dark, glassy rock with conchoidal fracture, entirely typical of all other obsidians in appear-

[6] J. P. Iddings, 7th Ann. Rep. U. S. Geol. Surv., 1888, p. 255.

ance, and usually free of phenocrysts, though those found elsewhere in the park show well-formed crystals of feldspar scattered through a glassy groundmass. The rock presents all gradations from that purely hyaline to a lithoidite, with but a minor amount of glass. One of the features to first attract attention is the abundance of stony spherulites scattered through the glass, sometimes singly, sometimes aggregated into bunches, and often coalesced to form well-defined layers parallel to the planes of flow. In some specimens the glass carries hollow spherulites lined with a white coating of crystalline material, either sparsely disseminated or so abundant as to make up the bulk of the rock.

The distribution of the spherulites in zones parallel to the flow structure at once suggests that the glass varies somewhat in its physical or chemical properties. The boundary between the laminae rich in these bodies and those free from them is quite sharp in some specimens and in others gradational. The larger spherulites occupying a position in these bands of stony matter are often semihollow and seem to be the result of spherulitic crystallization that has been carried to a more advanced stage. The luster of the larger ones is dull and the structure more earthy than that of the small, compact bodies, and their entire mass is porous owing to minute, closely-spaced cavities. In these spherulitic bands the small spherulites, joined together to form a line, usually pass through the center of the larger, open bodies, frequently dividing them into halves, and at their intersection, the material of the smaller ones, usually rather glassy, changes to a more granular texture.

Tenne[7] first brought out the fact that spherulites are but special cases of the crystallization of obsidian glass. A comparison of the following analyses given by Iddings[8] will show the chemical similarity of the glass and the spherulites.

Analyses of obsidian and spherulites from Obsidian Cliff

	Obsidian	Spherulites
	Per cent	*Per cent*
Silica (SiO₂)	74.70	76.70
Alumina (Al₂O₃)	13.72	11.98
Ferric oxide (Fe₂O₃)	1.01	1.45
Ferrous oxide (FeO)	.62	....
Iron disulphide (FeS₂)	.40	....
Manganous oxide (MnO)	Trace.	....
Lime (CaO)	.78	.39
Magnesia (MgO)	.14	
Soda (Na₂O)	3.90	3.89
Potash (K₂O)	4.02	4.73
Ignition	.62	.66
	99.91	99.80

[7] C. A. Tenne, Zeits. d. Deutsch. Geol. Gesell., 1885, p. 610.

[8] J. P. Iddings, U. S. Geol. Surv., Mon. 32, pt. 2, 1899, p. 426.

LITHOIDITE

Through an increase in the proportion of stony structure, there is a complete gradation of the glassy obsidian into a rock entirely crystalline, though usually microcrystalline—the lithoidite. In this rock the groundmass is partly minutely crystalline, partly aphanitic, and through it are sometimes scattered phenocrysts of feldspar or quartz. The aphanitic facies are colored some shade of brown or dark gray, while the crystalline portions are usually light gray, so that this contrast of colors gives the rock a distinctively mottled appearance. Scattered throughout the mass are irregular cavities lined with minute crystals, causing it to appear rough and harsh to the touch. As the aphanitic portions become more visibly granular, the entire rock becomes more uniformly gray in color, and the irregular cavities give way to those more symmetrical. These cavities are often of extreme delicacy and beauty, especially in those facies of the lithoidite that are decidedly laminated.

Although this rock is usually placed among the rhyolites, it differs from the true rhyolites in its mineralogical composition. It may be chemically classed as a *soda-rhyolite*, but none of the calculated normative minerals of rhyolite are found in its mode. This is brought out by the following analysis by J. E. Whitfield,[9] and the calculated norm and mode of the rock.

Analysis of Lithoidite, Obsidian Cliff

	Per cent
Silica (SiO_2)	75.50
Titanium oxide (TiO_2)	none
Alumina (Al_2O_3)	13.25
Ferric oxide (Fe_2O_3)	1.02
Ferrous oxide (FeO)	.91
Manganese oxide (MnO)	none
Lime (CaO)	.90
Magnesia (MgO)	.07
Lithia (Li_2O)	.06
Soda (Na_2O)	4.76
Potash (K_2O)	2.85
Phosphorus pentoxide (P_2O_5)	none
Sulphur trioxide (SO_3)	.32
Water (H_2O)	.41
	100.05

Norm and mode of Lithoidite, Obsidian Cliff

Norm	Per cent	Mode	Per cent
Quartz	34.2	Tridymite	34.5
Orthoclase	17.2	Natrosanidine	61.6
Albite	40.3	Fayalite	2.7
Anorthite	4.4	Hematite	1.0
Corundum	.6	Hornblende	.8
Hypersthene	1.1		
Magnetite	1.4		

[9] U. S. Geol. Surv., Bull. 150, 1898, p. 160.

Under the microscope the lithoidite has a texture and habit strongly individual and peculiar. It is made up of radiated masses of feldspar needles arranged haphazardly or aligned in rows. The interstices between these masses are in turn lined or completely filled with crystals of tridymite, which is more coarsely crystalline than the feldspar in which it occurs in the form of nests or lenses. Scattered through the rock are well formed crystals of fayalite. The hornblende always forms very minute crystals, which are scattered through the mass or arranged along the flow lines and apparently represent the microlites in the glassy phase of the rock.

Very little of the excess silica shown in the norm is present as quartz, but occurs almost entirely in the form of tridymite, both in the cavities and in the groundmass. The normative albite and ortho-clase are largely combined to form sanidine, or, more properly, natro-sanidine, while the ferrous iron is contained for the most part in the fayalite. The other constituents are largely in the minute crystals of what is probably hornblende.

LITHOPHYSAE

Both the obsidian and the lithoidite carry abundant hollow cavities lined with crystalline matter. These, for the reason that they sug-gested bubbles formed by expanding steam, were called *lithophysae* by Von Richthofen. In their simplest form they are hollow cavities in the glassy obsidian, lined with a thin coating of crystalline matter which is shown by close inspection to be made up of minute rods of white or gray feldspar with small pellets of white, waxy cris-tobalite (pl. 4, fig. 2). The boundary between the glass and the crystalline lining of the cavities is sharply defined and the hollow spheres often break easily from the glass, leaving a smooth, clean cavity. The simple forms become more complex when the crust is made up of partially concentric leaves, or when fibers of feldspar almost completely fill the cavities. In the latter case they approach the solid spherulites in character, although in this type of lithophysae the radial fibrous structure is decidedly more pronounced than in the solid bodies (pl. 4, fig. 3). When the rock becomes more lithoidal, especially in those facies having a banding of glassy and stony mat-ter, the lithophysae increase in size, are irregular in outline, and complex in structure (see pl. 1). It is apparent that the larger lithophysae, like the simpler forms, are intimately connected with the stony spherulites, since they are usually aligned with them and in many cases appear to be but special instances of spherulitic crys-tallization. Frequently the lithophysae form on only one side of a line of spherulites, but less often on both sides, so that the stony matter passes through the cavity as a median plane without other

change in appearance than becoming somewhat lighter in color and duller in luster.

Although the line of demarkation between the larger lithophysae and the glass is sharp, they can not be removed as easily as can the simpler ones. The material in the larger forms is dull in appearance, radiated textures are not so apparent, and the pellets of cristobalite give way to bright aggregates of tridymite. Well-defined crystals of fayalite are common in this type.

The lithophysae attain their greatest complexity and beauty in the completely lithoidal rock. (See pl. 2.) Perhaps the simplest of the types found are sharply defined circular areas of crystalline feldspar and tridymite that form the walls of flattened cavities. These become more complex through an arrangement of the crystals in concentric rings, as many as 50 of which have been noted in some specimens (pl. 3). Finally, in the most complex types, the growth of these ridges is somewhat similar to that of the petals of a rose.

The materials of the groundmass of the lithoidite and the lithophysae are similar, but the crystals of the latter are much larger and bounded by crystal faces.

In cross section the lithophysae of the lithoidal rock are narrow, lenslike bodies with the concentric rings of crystals on both top and bottom. Some have a flat floor with a low-domed roof in which the rings are on the floor only while the arrangement of the crystals on the roof is entirely haphazard. In general structure the walls are finely laminated and rather sandy with the larger crystals confined to the inner surface of the cavity. In minor details the lithophysae vary greatly, but in general the preceding description covers the main types.

Large, more or less porous spherulites that are obviously transitional between the stony spherulites and the lithophysae, are abundant in the obsidian from the east bank of the Firehole River near the Madison River. These are made up entirely of rodlike feldspar crystals and tridymite plates with occasional intertelluric feldspar and quartz phenocrysts embedded within their mass. They have a rude, concentric structure and usually show large cracks resembling shrinkage cracks, that are lined with loosely coherent, sandlike tridymite crystals. These spherulites appear to be the result of a progressing crystallizing process that started from a nucleus and spread outward through the glass and engulfed some of the phenocrysts.

ORIGIN OF THE LITHOPHYSAE

There have been two general hypotheses proposed to account for the lithophysal structure in obsidians and the materials contained

in them. Von Richthofen[10] first explained them as a result of expanding gas bubbles while the rock was in a molten or plastic state, the disengagement and expansion of the gas being brought about by the release of pressure due to the eruption of the magma. This hypothesis has found supporters in Von Hauer,[11] Zirkel,[12] Weiss,[13] Cross,[14] and Iddings.[15] A second hypothesis is that of Szabo [16] who considered the lithophysae to be the remains of solid spherulites from which much of the material had been removed by chemical means, leaving the lithophysal minerals as an insoluble remainder. This theory was supported by Cole.[17] A chemical examination of these bodies and of the accompanying glass by Tenne,[18] however, demonstrated that they were identical, and, therefore, that no removal of material is involved. The lithophysae are rather a special type of crystallization of obsidian glass.

MINERALS OF THE LITHOPHYSAE

The minerals identified in the cavities and lithophysae of the Obsidian Cliff lavas are, in order of their abundance, feldspar, tridymite, cristobalite, fayalite, and quartz. Numerous minute needles associated with the feldspars may be hornblende.

Feldspar.—In numerous spherulitic lavas, glassy phenocrysts of feldspar are abundant, but this is not the case in the flows of Obsidian Cliff proper. Here the feldspars are largely confined to the spherulties and lithophysae. In the glassy obsidian, the cavities are lined with, or sometimes partially filled by a white, semifibrous coating, which, in the larger cavities becomes more pronounced and under the microscope resolves itself into an aggregate of prismatic orthoclase crystals arranged in parallel position. The constituent groups are sometimes straight, sometimes curved, while occasionally they show delicate branching forms. These feldspar groups are beautiful objects under the microscope (pl. 4, fig. 1), but only in the very coarsest ones can the arrangement be discerned with the naked eye. Twinning is sometimes developed but the twinning law could not be determined with any amount of certainty. The rodlike crystals are terminated by a single glassy crystal that seems to be untwinned. The feldspars in the more glassy portions of the flow contain small white pellets of cristobalite disseminated throughout

[10] F. von Richthofen. Jahrb. k. k. geol. Reichsanstalt, vol. 11, 1860, p. 180.

[11] Karl von Hauer, Verhandl. k. k. geol. Reichsanstalt, 1866, p. 98.

[12] Ferdinand Zirkel, U. S. Geol. Expl. 40th Par., vol. 6, Microscopical Petrography, 1876, p. 212.

[13] Ch. E. Weiss, Zeits. d. Deutsch. Geol. Gesell., vol. 29, 1877, p. 418.

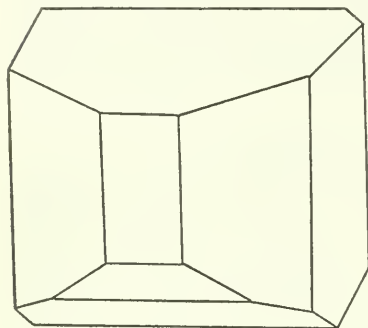[14] Whitman Cross, Amer. Journ. Sci., ser. 3, vol. 31, 1886, p. 432.

[15] J. P. Iddings, 7th Ann. Rep. U. S. Geol. Surv., 1888, p. 279.

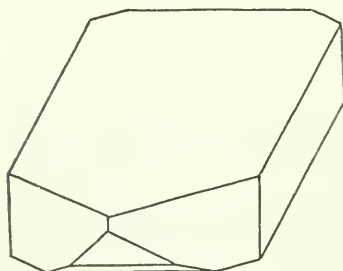[16] Joseph Szabo, Jahrb. k. k. geol. Reichsanstalt, vol. 16, 1886, p. 89.

[17] Grenville A. J. Cole, Quart. Journ. Geol. Soc. London, May, 1885, p. 162.

[18] C. A. Tenne, Zeits. d. Deutsch. Geol. Gesell., 1885, p. 610.

their mass and scattered over the surface. In the large lithophysae or in the more lithoidal rock the cristobalite is replaced by crystalline aggregates of platy tridymite, and here the rodlike feldspar gives way to rather coarse crystal forms. Where the feldspar crystals are large enough to be determined crystallographically, two types are recognizable. One with the normal prismatic habit has the forms (001), (110), (101), and (100) (fig. 1a), and another with an unusual platy habit, is tabular parallel to (001) and has the form (100) absent and (101) reduced to a narrow face or entirely missing (fig. 1b). The first type is normal in that the plane of the optic axis is perpendicular to (010) and has a dispersion of ρ greater than v. The second type, which forms beautiful glassy crystals in the lithoidite, is usually much larger than the first, is less abundant, and in most cases the plane of the optic axis is the normal one for feldspar, but at times the sanidine orientation is encountered. 2V is small, v is greater than ρ, $\alpha=1.518$, $\beta=1.525$, $\gamma=1.527$. These indices are near those of orthoclase but the analysis given by Iddings shows the crystals to be a sodium-bearing orthoclase with a ratio of Na : K of almost 1 : 1. The crystals show a small extinction angle with the edge cb when lying upon the base. They are eminently suitable for optical work and evidence of microperthitic intergrowth, although carefully sought for, could not be found, unless an orthopinacoidal blue chatoyancy is evidence for heterogeneity.

Fig. 1.—Two habits of feldspar from the lithophysae of Obsidian Cliff

Tridymite.—Tridymite is very common, not only in the cavities and lithophysae but also in the groundmass of the lithoidite. Practically all of the quartz shown in the norm of the rhyolite appears in the form of tridymite in the mode of its crystalline phase. Large crystals are never found, 0.5 millimeter being perhaps the average size. In the larger lithophysae it is present as simple hexagonal plates and can be readily distinguished from the feldspar, which it often resembles, by its decidedly lower index of refraction. Tridymite plates in parallel position are common, but twins are rare if not entirely absent. This is rather remarkable when the rarity

of single crystals in the many other occurrences where twins are the rule is noted.

In the large, hollow spherulitic lithophysae, composed of fibrous feldspar and tridymite the latter mineral is usually grouped in spherical aggregates resembling the cristobalite pellets but with a rough surface and more vitreous luster. These groups of tridymite are attached to the feldspar rods and project into the cavity or into the spaces between the crystals of feldspar. One gains the impression from an examination of this occurrence that the tridymite is a somewhat later formation than the feldspar. In the lithophysae of the lithoidite also the tridymite appears to be later than the feldspar since it forms radiating groups of plates perched upon stubby feldspar crystals (see fig. 2, and pl. 4, fig. 4). In the cracks of the large spherulites of the Firehole River obsidians, the tridymite is dusted over the surface and is undoubtedly the last mineral to form. Some of these masses of radiating rods carry phenocrysts of quartz and feldspar of intertelluric origin which are likewise dusted over with tridymite plates where they project into a crack.
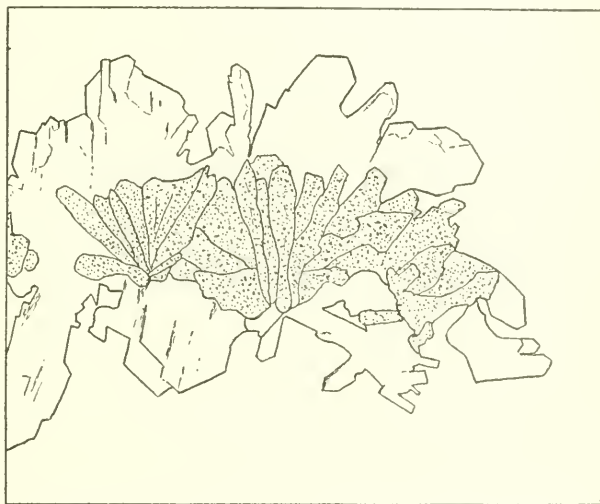

FIG. 2.—SECTION OF RING IN LITHOPHYSAE SHOWING THE RELATION OF THE TRIDYMITE (WHITE) TO THE FELDSPAR (STIPPLED). CAMERA LUCIDA SKETCH.   ×40

Apparently the feldspars of these bodies grew rather rapidly while the tridymite formed more slowly.

Cristobalite.—The cristobalite is found only in cavities in the wholly glassy rock where it is abundantly, though not always conspicuously, associated with feldspar. It is never found with the coarser feldspar crystals and is evidently confined to the upper and thinner portions of the flow. It forms small white pellets smoother than those of the tridymite groups, which are scattered over the surface or through the body of the feldspar crusts (pl. 4, figs. 2 and 3). Clear, honey-yellow crystals of fayalite are often associated with it. Under the binocular microscope the cristobalite shows a fine, drusy surface made up of crystals which are usually too small

to distinguish except through high magnification. The larger groups are white and have a waxy luster, while the smaller ones are somewhat more translucent. The groups are irregularly rounded and show no suggestion of crystal form.

Under the microscope the pellets of cristobalite are seen to be made up of radiating laths with low birefringence. The surface is composed of minute octahedral or larger dodecahedral crystals, the latter being usually flattened and very much resembling the hexagonal plates of tridymite, from which they can be distinguished only by their higher indices of refraction. The mean refractive index of cristobalite is 1.486 with a birefringence too low to give a recognizable interference figure, and in thin sections is so feeble that close inspection is necessary to differentiate it from glass.
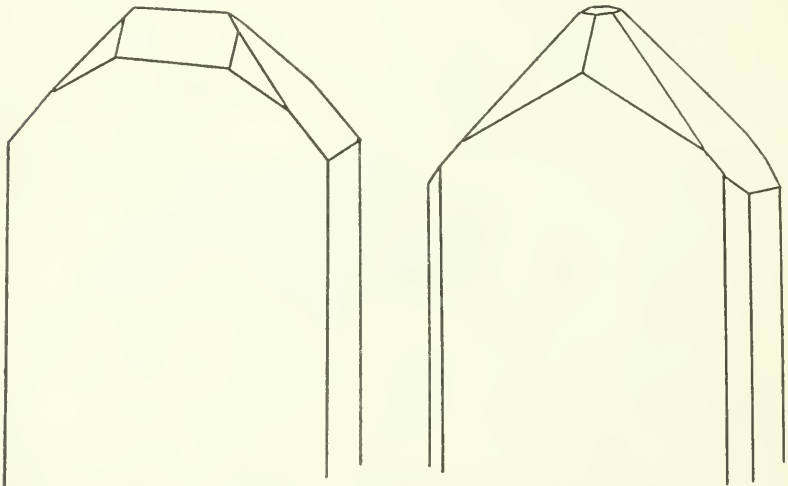

FIG. 3. CRYSTAL HABIT OF FAYALITE FROM THE LITHOPHYSAE OF OBSIDIAN CLIFF

The optical properties and general physical appearance of the cristobalite are near those of the tridymite, and the similarity is heightened by the presence of the cristobalite as flattened dodecahedral crystals showing angles of 120 degrees. This striking similarity raised a doubt as to the actual presence of two distinct minerals in the rocks. A sample of the white pellets was submitted to R. W. G. Wyckoff of the geophysical laboratory, Carnegie Institution of Washington, for X-ray examination. His comparison of its pattern with that of the synthetic form, definitely determined the mineral to be cristobalite.

Fayalite.—Fayalite is present in all parts of the flow, but never in abundance. Fresh, unaltered crystals, a millimeter or less in length and of a fine, honey-yellow color, are found in the upper portions of the flows in association with cristobalite and fibrous

feldspar. Their small size and light color makes them inconspicuous objects which are easily overlooked. In habit they are flat plates tabular to the macropinacoid (100) with the edges modified by narrow faces of (120), (111), (101), and (010) (figs. 3, 4). The indices of refraction are high. The crystals are weakly pleochroic; Y is light brown, X light grayish brown. The optical orientation is X=b, Y=c, Z=a; the broad front pinacoid gives an obtuse bisectrix figure with the plane of the optic axis parallel to the base.

The larger lithophysae of the glassy rock contain fayalite crystals that are larger and stouter, and with a fine chestnut brown color. Many of them have a red and green iridescence on the surface, giving a metallic sheen. These larger crystals, under the microscope,
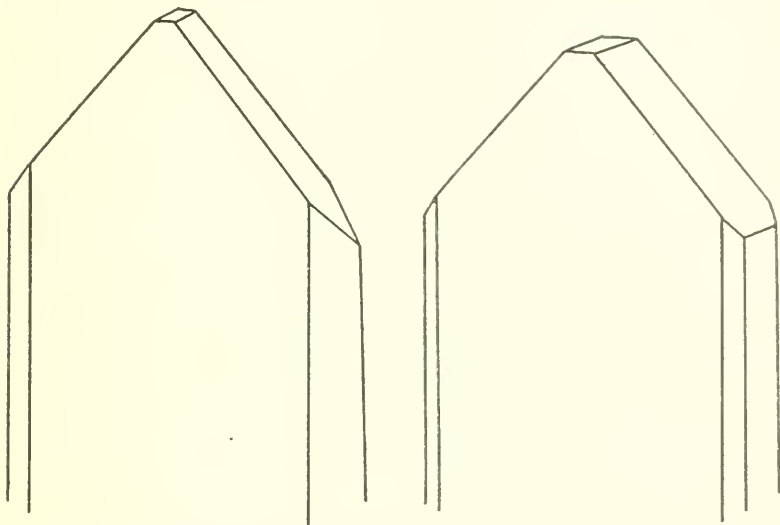

FIG. 4.—CRYSTAL HABIT OF FAYALITE FROM THE LITHOPHYSAE OF OBSIDIAN CLIFF

have the same optical properties as the smaller, except that the pleochroism is fainter in shades of chestnut brown. Many of the crystals show a coarse cross grating on the surface, the lines being parallel to the faces (010) and (001), apparently due to cleavage.

The fayalite crystals are exceptionally sharp and the faces bright. The measured angles are as follows:

Measured angles of fayalite crystals

Face	φ	ρ
001		0
010	0	90
100	90	90
101	90	51° 33′
120	47° 16′	90
031	0	49° 10′
111	65° 22′	51° 00′

Fayalite is also present in the lithophysae of the lithoidite where the crystals are somewhat more prismatic in habit and are usually wholly or in part altered to hematite. In all cases it forms larger crystals than any of the associated minerals.

Quartz.—Quartz is not uncommon as phenocrysts in some of the Yellowstone rhyolites but is far less abundant than feldspar. In the lavas of Obsidian Cliff, however, it is absent except for minor amounts in some of the lithophysae of the lithoidite where it occurs as small prismatic crystals. In one specimen a cavity carried small crystals of quartz with small plates of tridymite dusted over them. These quartz crystals are trapezohedral in type and hence apparently of the low temperature form.

DISTRIBUTION OF THE MINERALS

The relation of the minerals to their position in the flow was not studied in the field, but certain associations suggest a vertical distribution. Iddings describes the surface of the flow as pumiceous, passing in depth into a glass rich in cavities but barren of minerals. Below this is a zone of glass carrying simple lithophysae made up of fibrous feldspar and cristobalite. As more stony matter is encountered, corresponding to greater depths, the lithophysae become larger, the feldspar crystals stouter, and the cristobalite is replaced by tridymite. This phase passes over to the lithoidite (representing a still deeper zone) in which the feldspar occurs in well-defined crystals and the tridymite as large, single individuals. Presumably the quartz-bearing lithophysae are from the lowest or thickest parts of the flow, but hand specimens do not show any direct evidence of this. Fayalite is present in all zones; in the upper it is clear yellow to brown and is fresh, while in the lower it is wholly or in part altered to hematite.

The type of silica mineral to form seems, therefore, to be dependent upon the position within the flow. Since the comparatively slight increase in pressure in such a flow would produce but a negligible effect upon the silica inversions involved, and since the temperature of consolidation in different parts of the flow was essentially the same, some other factor has determined which form shall be produced. As we are dealing with the metastable forms, the time factor may have been an important one.

TEMPERATURE OF FORMATION OF THE MINERALS

In a specimen of the hyaline obsidian carrying numerous lithophysal cavities (No. 2235 of the Iddings Collection), a small tongue of glass several millimeters long and shaped like a fish-hook projects through the crust into the cavity. This tongue is similar to those

described by Wright[19] from Hrafntinnuhryggur, Iceland. It has a double significance in demonstrating that the crystals formed while the glass was still somewhat viscous, while its distinctive fish-hook shape suggests that it was forced into the cavity by pressure. Thus, though still rather viscous, the preservation of the delicate structure of the lithophysae shows that the mass must have been essentially at rest. The temperature of formation then must have been somewhere near the point of solidification of the glass. Brunn found that obsidian from Lipari no longer flowed at 800° C. For a fresh magma still charged with volatile constituents, the temperature must be somewhat lower. In some specimens of lithophysae, trapezohedral quartz takes the place of the more common tridymite as an apparently primary crystallization. These facts would suggest a temperature of formation of the minerals as somewhere in the neighborhood of 500° C. This is, of course, much below the quartz-tridymite and tridymite-cristobalite inversion points,[20] and the last named minerals must have formed as unstable phases.

ORIGIN OF THE MINERALS

The first mode of origin that suggests itself is the transportation of the materials in aqueous solution from the outside into the cavity, much after the manner in which zeolites are formed. Because of the relatively slight solubility of these minerals, even at somewhat elevated temperatures, a considerable volume of solvent would be required. Glass is easily susceptible to hot aqueous solutions and if the origin of the minerals had actually occurred in this manner, a decided alteration would be apparent. The glass, however, is perfectly fresh to the very walls of the lithophysae. If aqueous solutions were inadequate, then perhaps the materials were transported in gaseous solution whose mineral content was in the form of easily volatile compounds. But such a process involves an abundant supply of fluorine, chlorine, or other mineralizers, and, although sought for, no evidence of these constituents in any large quantity was found.

It is difficult to conceive any origin whereby the materials were introduced into the cavities from outside, or to escape the conclusion that the materials making up the minerals originated within the cavity itself. Iddings[21] has already pointed out that "these lithophysae, composed of prismatic quartz, tridymite, soda-orthoclase, fayalite, and magnetite (to which should be added cristobalite), are of aqueo-igneous origin and have been produced by the action of the

[19] F. E. Wright, Bull. Geol. Soc. America, vol. 26, 1915, p. 255.

[20] Clarence N. Fenner, Amer. Journ. Sci., vol. 36, 1913, p. 331.

[21] J. P. Iddings, 7th Ann. Rep. U. S. Geol. Surv., 1888, p. 283.

absorbed gases upon the molten glass from which they were liberated during the crystalization consequent upon cooling."

Below is given the normative composition of the glass, spherulites, and lithophysae, calculated from the analyses given by Iddings,[22] a comparison of which will show the close relationship between them and immediately suggest the origin of the minerals from the glass.

Normative composition of obsidian, spherulites, and lithophysae

	Obsidian	Spherulites	Lithophysae
	Per cent	*Per cent*	*Per cent*
Quartz	36.72	33.48	37.32
Orthoclase	21.68	27.80	23.45
Albite	33.01	32.48	35.63
Anorthite	3.89	.95	1.11
Corundum	2.24	-----------	0.41
Hypersthene	0.30	-----------	-----------
Magnetite	0.28	-----------	-----------
Hematite	1.60	1.44	1.44

These bodies, are in fact, as other investigators have pointed out, but special types of crystallization of obsidian. It only remains to determine the mechanics of a crystallization that will give rise to unstable forms of silica and the other characteristic features of lithophysal structure.

We have already seen that the lithophysae are closely related to the spherulites. Since they are but one step advanced, they must have their beginnings in spherulitic crystallization. Iddings has shown that the crystallization of the spherulite began in the separation of a microlite from which the further crystallization proceeded in all directions. If its environment was rich in dissolved water, this would be liberated and begin its work of solution immediately. The glass, being easily soluble, will be readily attacked, but a saturated solution of glass will be supersaturated with respect to the crystalline phases and one or more of them must crystallize out. In Figure 5 the relation of the silica minerals to temperature and solubility is given. The actual value of the solubility of these minerals is of course not known, but their relative solubility is known from their stability relations. Glass, being the least stable, is the most soluble, followed in turn by cristobalite, tridymite, and, finally by quartz, the stable phase, which is the least soluble. A solution at the temperature and concentration X (fig. 5), for instance, in contact with glass, would then be supersaturated with respect to all the crystalline phases of silica; cristobalite, tridymite, and quartz, and one or more of these must separate out in crystalline form. The fact that all three crystalline phases are apparently stable in contact with each

[22] 7th Ann. Rep. U. S. Geol. Surv., 1888, p. 291.

other suggests that the solubility curves do not lie very far apart, for the rate of transformation of an unstable to a stable phase is dependent upon their relative solubilities. A great difference in solubility brings about a rapid transformation to the stable phase. The difference in solubility as shown by the curves in the diagram is, therefore, probably somewhat exaggerated.

The form which actually separates out is, in the absence of nuclei, determined by which ever nucleus first forms. It is obviously necessary for the solution to be supersaturated with respect to the stable phase before the less stable form can possibly separate out. Further, the unstable forms are likely to appear only if their solubility is not greatly different from that of the stable forms. This is a further indication that the solubility of the silica minerals is
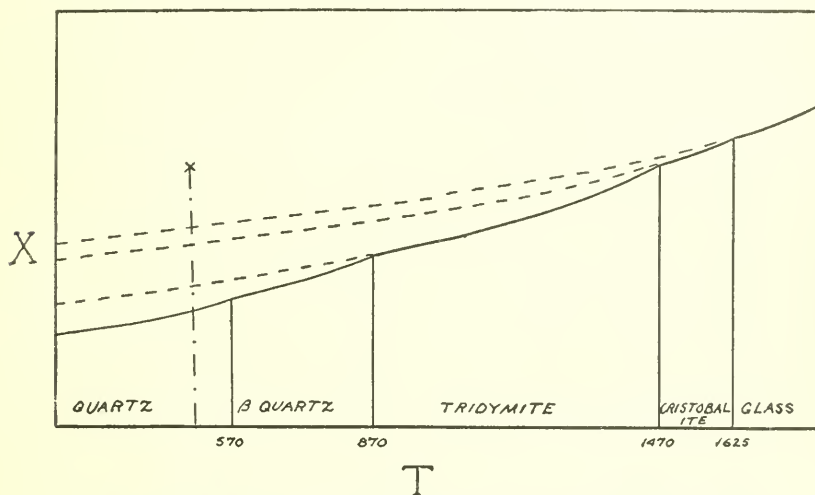

Fig. 5.—Diagram showing relative solubility of the forms of silica

not very greatly different. In fact, judging from the ease with which the unstable phases of silica form, their solubility is very nearly the same. If this actually be the case, it may even be possible for the unstable phase to form in equilibrium with the stable, provided the former produces large crystals while the latter separates as very fine particles. This apparent ambiguity is due to the fact that the smaller particles have a higher vapor tension and hence a greater solubility than the larger, and may even equal in solubility the larger crystals of the unstable phase. This, of course, can only happen if the solubility of the two phases differs but slightly.

It is well known that the various allotropic modifications may be obtained from a solution by merely varying the conditions of crystallization. The theory of allotropy proposed by Smits[23] is based

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[23] A. Smits, Zeit. Physik. Chem., vol. 82, 1913, p. 657.

upon the idea that the different modifications are all present in the solution in equilibrium with each other. In the supersaturated solution it is possible for the metastable nucleus to be first formed. If the rate of change to attain equilibrium is small or if cooling is sufficiently rapid, or if both of these conditions maintain, it is easily possible for an unstable form to separate out. To some extent, therefore, the phase to form is conditioned by the rate of cooling. From Ostwald's principle of the succession of the phases of a metastable system, we would expect to find a tendency for the silica to pass from glass through the intermediate unstable phases cristobalite and tridymite to reach the stable form quartz. In that portion of the flow where the escape of the solvent was rapid, the least stable crystalline phase, cristobalite, could form, and, in the absence of prolonged action, persist. Where the action of the solvent is continued for a longer period, the somewhat more stable form, tridymite, could form, and, finally, where the action is of sufficiently long duration, the stable form quartz might be attained. This does not imply that cristobalite is first formed to be later transformed into tridymite and quartz, for this certainly is not the case. The various forms of silica once produced, persist with great tenacity, and the use of mineralizers is usually required to change one into the other.

Whether the solution attacking the glass was liquid or gaseous can not be determined with certainty. At the low pressure and comparatively high temperatures prevailing, they were probably gaseous. The thickness of lava above the solutions was not sufficiently great to cause pressure high enough to keep the solutions liquid at the temperature of the flow, and the slight concentration of the solute probably had only a small, perhaps negligible, effect upon the boiling point of the solution. Just how competent gases are to dissolve silicate glass at a temperature of about 500° C. can not be told precisely at this time, but undoubtedly some solution does take place. Certain lines of evidence indicate that the solubility of silica in gaseous water may be fairly great at comparatively low temperatures. The solubility, however, need not be great nor the amount of solvent large, for the solvent in a case such as this simply acts as a catalyzer. Its action is continuous. As rapidly as the crystalline phase separates from its supersaturated solution, the solvent is capable of dissolving more glass, this process continuing until the transformation is complete or until the escape of the solvent stops the reaction. In this manner the final effect of a small amount of solvent can well be the transformation of a considerable bulk of glass into crystalline matter.

The feldspars have apparently separated from the solutions before the quartz, tridymite, cristobalite, or fayalite, for invariably these last minerals are perched upon the feldspar crystals. They

are, too, large and more perfectly developed. This suggests also that iron and silica are comparatively more soluble under these conditions than the feldspar. It is interesting to note that Niggli [24] found that crystals forming in the " pq region," that is, by direct crystallization of the solid phase from the gaseous solution, were many times larger than those formed from the liquid solution. Larsen [25] noted that in the rocks of the Creede District the quartz and orthoclase formed nests in a fine grained groundmass in which these later minerals were enormously larger than those of the groundmass, a condition again suggesting that the crystals were formed from gaseous solution.

RELATION OF WATER TO THE CRYSTALLIZATION OF FLOWS

The effect of dissolved gases to reduce the viscosity of a melt and thus to favor crystallization is already well known. The solvent action of the escaping gases upon the glass, with its concomitant separation of crystalline phases has not been emphasized as a means of bringing about a crystalline mass. It seems probable that the action of what appears at first sight to be an almost insignificant amount of water vapor upon highly acidic rocks, like those of Obsidian Cliff, can, under favorable circumstances, cause an almost complete crystallization. There are several facts that seem to bear out the importance of this action. First there is the prevalence of tridymite and cristobalite in the acidic flow rocks, not only in the cavities but in the groundmass as well. This fact was first clearly brought out by Larsen.[26] In his studies of the rocks of the Creede District he showed that these two minerals were relatively more important than quartz. The inconspicuousness of both in thin section have made them easily overlooked and their presence is probably more widespread than is generally believed for it is only recently that the wide distribution of these minerals has been recognized. The second fact is the characteristic structure of many of the rhyolites and related rocks that manifests itself in a rough appearance and feeling of harshness, due to the numerous small cavities lined with tridymite and feldspar crystals. The well-known tendency of anhydrous melts of silica and the alkali feldspars to form glass rather than to crystallize, suggests that the mineralizers are a most important factor in bringing about crystallization in acidic flows. It might be mentioned also that in some of the most successful mineral syntheses, the action of water vapor upon glasses has been employed. It therefore appears that this

[24] P. Niggli, Centr. f. Min., Geol. u. Pal., 1912, p. 331.

[25] E. S. Larsen, U S Geol. Surv., Bull. 718, 1923, p. 21. See especially plate 6, fig. A.

[26] Idem, p. 47.

action of gases upon viscous melts or glasses is of primary importance in bringing about the crystallization of the lavas, and may, in fact, be largely responsible for the crystalline character of their flows.

DESCRIPTION OF PLATES

PLATE 1

Large lithophysae and spherulites in obsidian glass. These lithophysae are made up of feldspar rods and globular aggregates of tridymite crystals.

PLATE 2

Lithoidite showing different forms of lithophysae. These lithophysae are made up of sanidine and tridymite. The black crystals scattered through the lithophysae are fayalite.
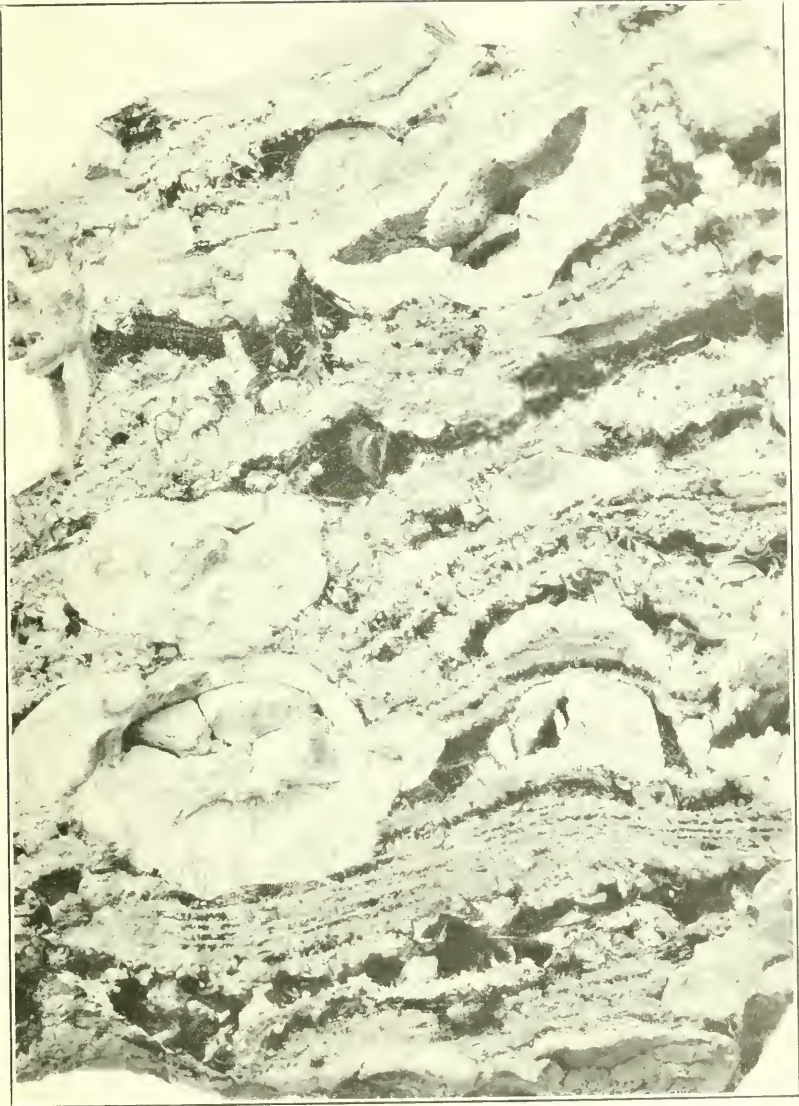
PLATE 3

Lithophysae in lithoidite with numerous rings. The rings are made up of tridymite and feldspar, while the black crystals are fayalite.

PLATE 4

FIGS. 1. Feldspar crystals in parallel growth, out of lithophysal cavity. ($\times$ 40)
2. Cristobalite pellets in lithophysal cavity. ($\times$ 6)
3. Cristobalite pellets and feldspar rods in small lithophysae. ($\times$ 6)
4. Tridymite, feldspar, and fayalite in small lithophysae. ($\times$ 6)
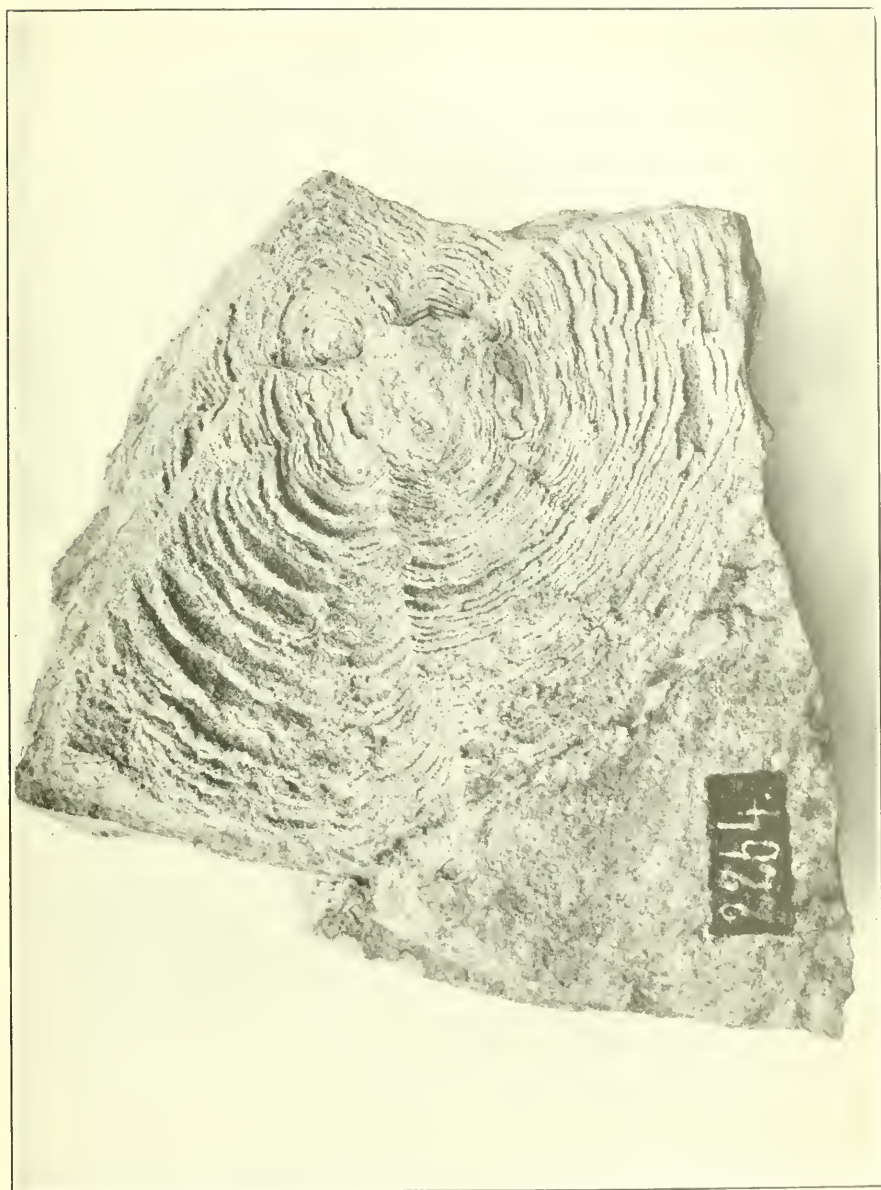
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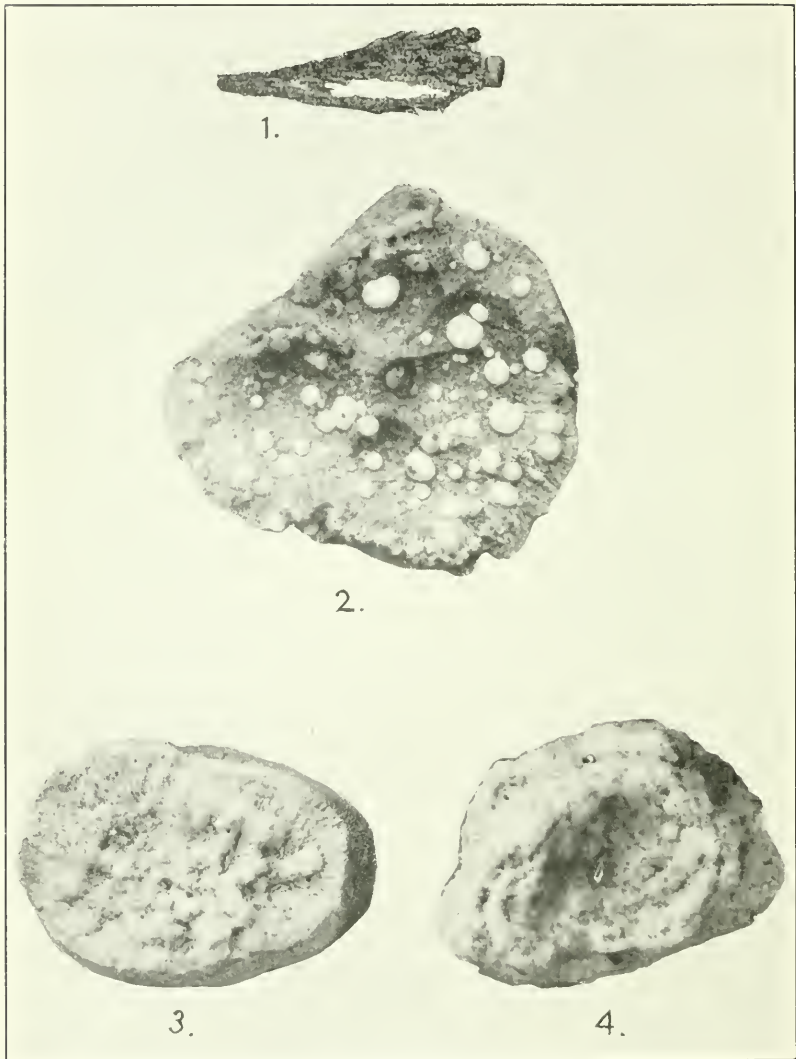
FOR EXPLANATION OF PLATE SEE PAGE 18

THE MINERALS OF OBSIDIAN CLIFF

THE MINERALS OF OBSIDIAN CLIFF

THE MINERALS OF OBSIDIAN CLIFF

FOR EXPLANATION OF PLATE SEE PAGE 18