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## PETROLOGIC RESULTS OF A STUDY OF THE MINERALS FROM THE TERTIARY VOLCANIC ROCKS OF THE SAN JUAN REGION, COLORADO<sup>1</sup>

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### 1. GEOLOGIC SETTING

BY ESPER S. LARSEN

This paper gives only a brief statement of those features of the Tertiary volcanic rocks of the San Juan region that bear rather directly on the mineralogic problem under discussion. For additional information the reader is referred to the recent bulletin of Cross and Larsen.<sup>2</sup>

The Tertiary volcanic rocks overlie rocks that range in age from pre-Cambrian to Oligocene, and the volcanic rocks themselves range in age from Miocene to Quaternary. They form a great pile that is about 100 miles across and that exceeds 5,000 feet in thickness over much of this area. They have been studied in some detail and have been mapped as stratigraphic units within the San Juan area. The generalized section that follows omits some smaller units and subdivisions not essential to the problems of this series of papers.

Quaternary andesite. A single small body.

Erosion to mountain topography.

Pliocene (?):

Hinsdale volcanic series:

Andesite. Local domes, mostly in New Mexico.

Andesite-basalt. Mostly flows.

Rhyolite. Flows and tuffs.

Los Pinos. Breccias with some flows. Latite-andesite.

Erosion to peneplain.

Miocene (?):

Fisher latite-andesite.

Erosion to mountain topography.

Miocene:

Potosi volcanic series:

Piedra rhyolite.

Erosion to mountain topography.

<sup>1</sup> Published with permission of the Director of the U. S. Geological Survey.

<sup>2</sup> Cross, Whitman, and Larsen, E. S., A brief review of the geology of the San Juan region of southwestern Colorado: *U. S. Geol. Survey, Bull.* **843**, 1935.

Huerto andesite.

Alboroto quartz latite.

Erosion to mountain topography.

Sheep Mountain andesite.

Treasure Mountain quartz latite.

Erosion to mountain topography.

Conejos andesite.

Erosion to a mountain topography.

Silverton volcanic series with several subdivisions.

Erosion to mountain topography.

San Juan tuff.

Erosion.

Lake Fork andesite.

The rocks older than the Potosi occupy a relatively small area, chiefly in the western part of the region, and they are in general too much altered for a detailed study of their minerals. The rocks of the Potosi series are the most widespread. They had a total estimated volume of 5,600 cubic miles and are composed of about equal proportions of rhyolites (including quartz latites) and andesitic rocks. The Fisher and Hinsdale rocks are widespread but had a much smaller volume than the Potosi rocks.

Each of the subdivisions of the Potosi is made up of many flows and clastic layers. The three rhyolite and quartz latite members are made up largely of regularly layered flows and tuff beds that spread over very large areas. Few centers for their eruption have been found. The rocks of all three of these members vary considerably in texture and composition, but are chiefly rhyolites and quartz latites, with a few local thin andesite layers. The two younger andesitic members (Sheep Mountain and Huerto) are more local in occurrence and chaotic in structure than the rhyolitic members, and are piled up about local centers. The Conejos andesite is a thick widespread formation. The andesite members also vary considerably in composition and texture and carry local bodies of quartz latite or even rhyolite.

The Fisher rocks were piled up about several volcanic centers. They range from quartz latite (not far from rhyolite) to pyroxene andesite, or rarely to basalt. As a group, they are characterized by large phenocrysts. These phenocrysts are plagioclase, hornblende, and pyroxene in the andesites; these same minerals together with biotite in the quartz latites; and orthoclase, plagioclase, and biotite, with or without hornblende and quartz, in the rhyolitic rocks.

The Hinsdale members occur in rather scattered, relatively thin bodies and were extruded from a number of centers. The andesite makes up a group of volcanic domes in northern New Mexico, south of the San Luis Valley, and ranges from cristobalite latite to basalt. The Hinsdale ande-

site-basalts occur in thin widespread flows that resemble plateau basalt on a small scale. They are basalts in the southern part of the area but are olivine and quartz-olivine andesites and basalts in the northern part.

The San Juan area is probably the largest body of volcanic rocks that has yet been studied in detail. It is well exposed in deep canyons and is therefore favorable for a study such as the present one. In the course of the study and mapping, many thousands of specimens were collected and sectioned, and more than 100 analyses of rocks were made, chiefly in the laboratory of the United States Geological Survey. These analyses were carefully selected to represent the various rocks in the mapped units. Twenty-three analyses of minerals separated from the rocks have been made by Mr. F. A. Gonyer, of the Department of Mineralogy and Petrography at Harvard University.

These volcanic rocks represent an excellent petrographic province, and the same types, chemically and in large part texturally and mineralogically, recur again and again. Variation diagrams of the rocks—plotted against  $\frac{1}{3}\text{SiO}_2 + \text{K}_2\text{O} - \text{FeO}$  (total iron) — $\text{MgO} - \text{CaO}$  to place the rocks quantitatively between basalt and rhyolite—show surprisingly regular curves and the eleven major formations fit essentially the same variation diagram.

Taking everything into consideration, the San Juan region offers an unusually favorable opportunity for the study of the petrologic significance of the minerals of a series of volcanic rocks of the ordinary lime-alkali series.

Lavas are favorable for a study of the crystallization of igneous rocks because they afford a series of naturally chilled rocks that are somewhat similar to those formed experimentally by quenching in the laboratory.

## 2. THE SILICA MINERALS

BY ESPER S. LARSEN

The San Juan lavas offer a favorable opportunity for a study of the silica minerals, for all three forms—quartz, tridymite, and cristobalite—are common in these lavas, and the rocks have been studied with some care in order to identify these minerals.

### RELATIVE ABUNDANCE OF QUARTZ, TRIDYMITE, AND CRISTOBALITE

Tridymite has commonly been considered to be a rather rare mineral, but in the San Juan lavas it is present in somewhat greater amount than quartz. It makes up as much as one-fourth or more of some of the rocks. It is estimated to be the third mineral in abundance in the San Juan lavas as a whole, and is exceeded in amount only by feldspar and pyroxene. An estimate of the quantity of tridymite in the San Juan lavas

is 350 cubic miles, or enough to cover the State of Massachusetts with a uniform layer 250 feet thick. The quantity of quartz is nearly as great as that of tridymite.

Cristobalite that can be determined with the microscope is a fairly widespread mineral in the lavas, but it very rarely makes up more than a small fraction of 1 per cent of any lava. Cristobalite, as determined by *x*-ray methods by Dr. C. S. Hurlbut,<sup>3</sup> is the chief silica mineral of the spherulites and submicroscopic parts of the rhyolitic rocks, and such cristobalite is nearly as abundant as tridymite.

In other younger lavas of the western United States I have found tridymite and cristobalite about as abundant and widespread as in the San Juan region, and specimens of such lavas from other parts of the world seem to show a similar amount. It seems, therefore, that tridymite is a rather common and abundant mineral in young lavas and that it should be given more emphasis in our textbooks on mineralogy and petrology, and in the literature in general. Cristobalite has been considered a very rare mineral—a mineral curiosity—but in the San Juan region, as shown by the microscope, it is present in small amount in about a tenth of the lavas. It is equally common in fresh lavas that I have seen from other localities.

#### QUARTZ

Quartz is present in the granular intrusive rocks, as phenocrysts in the lavas, and in the groundmass. It is the only silica mineral in the intrusive rocks, except those which were intruded very near the surface.

Quartz phenocrysts are relatively scarce in the San Juan volcanic rocks; they are present in nearly as large a proportion of the basaltic lavas as of the quartz latite and rhyolite lavas. They are rare in the andesites. The quartz phenocrysts in the basalts, although conspicuous, never make up more than 2 per cent of the rock. Almost all of them are associated with olivine phenocrysts, and they are invariably much resorbed and have a narrow reaction rim of small augite rods. A photomicrograph of a typical quartz phenocryst is shown in Fig. 1. The resorption may be complete and leave only the reaction rim of augite rods. The quartz basalts described by Iddings<sup>4</sup> from the Tewan Mountains, New Mexico, are from the southern extension of the San Juan volcanic province. The name Tewan Mountains cannot be found on any map of New Mexico that I have seen, but Iddings' description shows clearly

<sup>3</sup> Hurlbut, C. S., *x*-ray determination of the silica minerals in submicroscopic intergrowths: *Am. Mineral.*, vol. 21, pp. 727-730, 1936.

<sup>4</sup> Iddings, J. P., On a group of volcanic rocks from the Tewan Mountains, N. Mex., and on the occurrence of primary quartz in certain basalts: *U. S. Geol. Survey, Bull.* 66, 1890.

that his rocks came from the Valles Mountains and White Rock Canyon, west of Santa Fe.

The quartz phenocrysts are most commonly 1 to 2 millimeters across. They have all the appearance of typical phenocrysts, but there has always been doubt as to their origin. If they represent partly resorbed inclusions from a sandstone or older igneous rock, no remnants of the inclusions were found, and none of the other minerals that should have been associated with the quartz are present. Their distribution in any given flow appears to be uniform. The magma must therefore have been

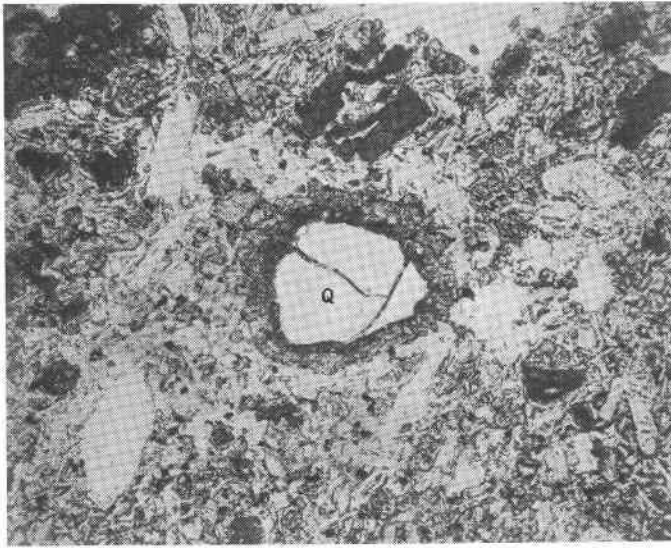


FIG. 1. Quartz phenocryst in a basalt from Valles Mountains, New Mexico, J. L. 23. Shows the characteristic corona of small augite rods. Enlarged 31 diameters.

thoroughly mixed and everything reworked but the quartz, after the inclusions were added and before eruption. The quartz must have been slow to go into solution. Quartz phenocrysts were found in no basalt that did not show quartz in the norm, and some of the quartz-olivine rocks have 6.9 per cent of quartz in the norm. Other rocks in the San Juan area that carry phenocrysts of olivine, but none of quartz, have as much as 12.7 per cent of quartz in the norm, and the groundmass alone may have as much as 17.4 per cent. Many olivine rocks have more than 8 per cent of quartz in the norm. Some of these rocks have determinable quartz and orthoclase in the groundmass. Properly most of these rocks should be called olivine or quartz-olivine andesites. Rocks with quartz pheno-

crysts not uncommonly have cristobalite in the gas cavities. When plotted on the variation diagram with the other rocks, the quartz basalts do not fit the variation diagram as well as do the other rocks, though some of them fit very well. A few are 2 per cent high in  $\text{SiO}_2$ , many are very low in  $\text{FeO}$ , and some are high in  $\text{MgO}$ . Table 1 gives some of the significant characters of six quartz basalts from the San Juan province.

TABLE 1.—PHENOCRYSTS AND NORMATIVE QUARTZ IN QUARTZ  
BASALTS FROM THE SAN JUAN PROVINCE  
(in percentages)

Rock	NM 421	J 117	NM 213	Up 23	Sc 1206	Up 24
Phenocrysts:						
Quartz.....	$\frac{1}{2}$	2	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Olivine.....	$\frac{1}{2}$	3	7	5	3	$\frac{1}{2}$
Diopside.....	$\frac{1}{2}$	...	1	$\frac{1}{2}$	2	1
Hypersthene.....	1	...	...	...	...	...
Plagioclase.....	$1\frac{1}{2}$	5	2	1	2	3
Sanidine.....	...	...	...	...	...	...
Quartz in norm of rock.	5.8	5.6	6.9	3.4	4.5	3.5
Quartz in norm of groundmass.....	6.1	5.7	7.8	5.3	5.4	...

NM 421. Lava from Hinsdale andesite dome called Cerro Aire, 4 miles east of No. Agua, N. Mex.

J 117. Lava from Santa Clara Canyon, 14 miles west of Espanola, N. Mex. The feldspar phenocrysts have a rounded, resorbed core of  $\text{An}_{46}$  and a sharply separated outer shell of  $\text{An}_{63}$ . The cores must be foreign to the magma. Small olivine crystals make up 5 per cent of the groundmass. An unusual rock.

NM 213. Lava of Ortez Peak, 3 miles south of Tres Piedras, N. Mex. A rather extreme type of quartz basalt.

Up 23. Hinsdale andesite-basalt from Cannibal Plateau, east of Lake City, Colo. The groundmass is 1.2 per cent low in  $\text{MgO}$ .

Sc 1206. Hinsdale andesite-basalt from area northeast of the mouth of Lost Trail Creek, near center of San Cristobal quadrangle, Colorado. Upper flow.

Up 24. Hinsdale andesite-basalt from Cannibal Plateau, east of Lake City, Colo. An unusual rock.

The olivine in the quartz basalts is about like the olivine in the rocks without quartz, and contains about 25 to 30 per cent of fayalite. (See the data on olivine, published later.) There is no reason to think that the quartz and olivine did not crystallize from the basaltic magma, except the experimental fact that in the simpler system,  $\text{MgO-FeO-SiO}_2$ , quartz and olivine are not in equilibrium.<sup>5</sup>

<sup>5</sup> Bowen, N. L., and Schairer, J. F., The system  $\text{MgO-FeO-SiO}_2$ ; *Am. Jour. Sci.*, 5th ser., vol. 29, pp. 151-217, especially pp. 214-215, 1935.

The equilibrium diagram of Bowen and Schairer for this system is of the utmost value to petrographers, and its usefulness will increase in years to come. However, I do not believe that we should draw too close an analogy between the crystallization of natural rocks and that shown in the equilibrium diagrams. The artificial system is much simpler than that of the natural basalts, which have at least nine essential components. Pressure also displaces the equilibrium. This complexity in the system reduces the temperature of crystallization of olivine—of the composition of the olivines in the quartz basalts—from a range between 1,500° and 1,600°C. in the system  $\text{MgO-FeO-SiO}_2$  to less than 900° in the quartz basalt. According to the equilibrium diagram, the olivines of basalts would be in equilibrium with a liquid that had just about enough  $\text{SiO}_2$  to form pyroxene. In the San Juan rocks olivine is found in rocks that contain as much as 12.7 per cent excess of  $\text{SiO}_2$  above saturation, and with rocks whose groundmass contains as much as 17.4 per cent excess of  $\text{SiO}_2$ . All the "quartz basalts" analyzed for us contained quartz in the norm, but some described by Iddings show a few per cent of olivine in the norm. On the diagram for  $\text{MgO-FeO-SiO}_2$  an excess of silica such as is common in quartz basalts would place the rock far from the olivine field and well in the field in which free silica would crystallize. I can see no justification for concluding from the equilibrium diagram that quartz in basalts must be foreign to the magma. The petrologic evidence points strongly to the conclusion that the quartz crystallized from the basalt magma as well as did the olivine. In fact, from analogy with the artificial system we might expect quartz but not olivine to crystallize from a magma of the composition of a quartz basalt.

Quartz phenocrysts are rare in the olivine-free andesites and where present they show the resorption and augite coronas characteristic of the quartz phenocrysts of the basalts.

Quartz phenocrysts are more common in the quartz latites than in any of the other rocks, but probably less than half even of the quartz latites carry such phenocrysts. They are never present in excess of 5 per cent of the rock. The great flows and tuffs of Alboroto quartz latite characteristically carry quartz phenocrysts, as do most of the quartz latites of the Piedra, but they are never present in the Treasure Mountain quartz latites, although these three quartz latites cover the same range in composition and show no appreciable difference in bulk composition. All the quartz latites carry phenocrysts of biotite and plagioclase; those with quartz phenocrysts carry in addition phenocrysts of orthoclase, hornblende, and titanite, with or without augite, whereas those without quartz phenocrysts carry only augite phenocrysts in addition to those of biotite and plagioclase. In the Alboroto rocks, which contain quartz

and orthoclase, the plagioclase is more sodic than in the Treasure Mountain rocks, which lack these phenocrysts, but in the Piedra rocks the plagioclase phenocrysts are about like those of the Treasure Mountain rocks. The simplest explanation for this condition would be that crystallization had proceeded farther in the rocks with quartz and orthoclase phenocrysts than in those that lack these phenocrysts, but a comparison of the groundmasses of the two types shows that in both types the groundmass varies considerably in composition and over the same range. We are forced to the conclusion that some of the "intangibles," such as pressure or mineralizers, determine the intratelluric crystallization of the quartz, orthoclase, hornblende, and titanite in the one group and augite in the other. In confirmation of this conclusion, the quartz, orthoclase, and hornblende all show more or less resorption, which suggests that crystallization at greater depth favors their formation.

Quartz phenocrysts are less common in the rhyolites than in the quartz latites. They are present to the extent of a few per cent in the Hinsdale rhyolite, but this rhyolite is of small extent and thickness. They are present in amounts up to 15 per cent in the Sunshine Peak rhyolite, a local body of rhyolite in the northwestern part of the San Cristobal quadrangle. They are rare in the extensive rhyolites of the Potosi series but are found in some small dikes and other intrusive rocks of Potosi age.

Quartz is the chief silica mineral in the groundmass of the andesites and andesite-latites. It commonly occurs in a very fine spongelike intergrowth with alkali feldspar, which extinguishes in relatively large areas and contains minute tablets of plagioclase and grains of iron ore. As this intergrowth increases in coarseness it becomes a typical micrographic intergrowth. In the groundmass of the rhyolites and quartz latites quartz is less common than tridymite and cristobalite. These groundmasses nearly all tend to be fine fibrous intergrowths, either in spherulites or in less regular forms. Quartz is only occasionally the silica mineral in these growths. An interesting form of quartz in the rhyolites from the Creede area has been described and figured by Emmons and Larsen.<sup>6</sup> The rock is fluidal, and much of it is reddish brown and dense, with nearly white, porous streaks, roughly ellipsoidal in shape and of the order of magnitude of 200 by 20 by 2 millimeters. Under the microscope the dense part is holocrystalline but so finely crystalline that it might be mistaken for glass, whereas the light porous parts are rather coarsely crystalline and are made up of quartz and alkali feldspar. The feldspar is in good crystals and is concentrated near the borders, but the quartz

<sup>6</sup> Emmons, W. H., and Larsen, E. S., *Geology and ore deposits of the Creede district, Colo.: U. S. Geol. Survey, Bull. 718*, pp. 18-24 and pls. 5, 6, 7, 1923.



is concentrated near the more porous central parts. These streaks grade into less regular streaks. They clearly represent rounded patches or bubbles, rich in mineralizers, which formed just before the last movement of the rock and have been drawn out by flow; they are probably the last part of the rock to crystallize. They might be considered as analogous to the pegmatitic patches in granite.

A groundmass made up of microgranular quartz and feldspar is very rare in the San Juan lavas.

#### TRIDYMITE

Tridymite is less common than cristobalite in the basalts, but in a few basalts a friable material that partly fills the gas cavities is made up

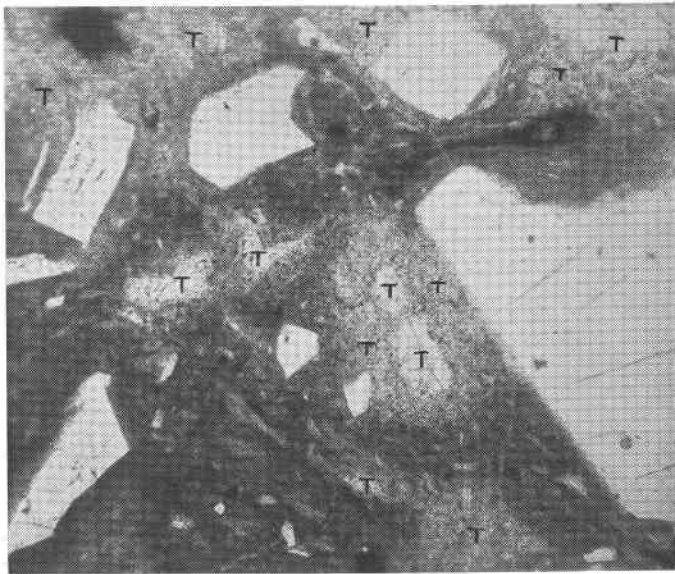


FIG. 2. Thin section in ordinary light of tridymite latite from Piedra flow of Bulldog Mountain, west of Creede, Colo. (Lag. 48). Relatively coarsely crystalline feldspar and tridymite (T) in the porous parts of the rock, and submicroscopic feldspar and cristobalite (?) in the dense parts. Enlarged 31 diameters.

chiefly of tridymite together with some albite and pale biotite, and rarely needles of hornblende and prisms of zircon.

In the rhyolites and quartz latites tridymite is the chief silica mineral. It is confined to the groundmass and is especially common in the more porous, coarsely crystalline parts of the groundmass that were richer in mineralizers and that crystallized last. Figures 2 and 3 show thin sections of typical tridymite rhyolite and latite, and Fig. 4 shows a thin

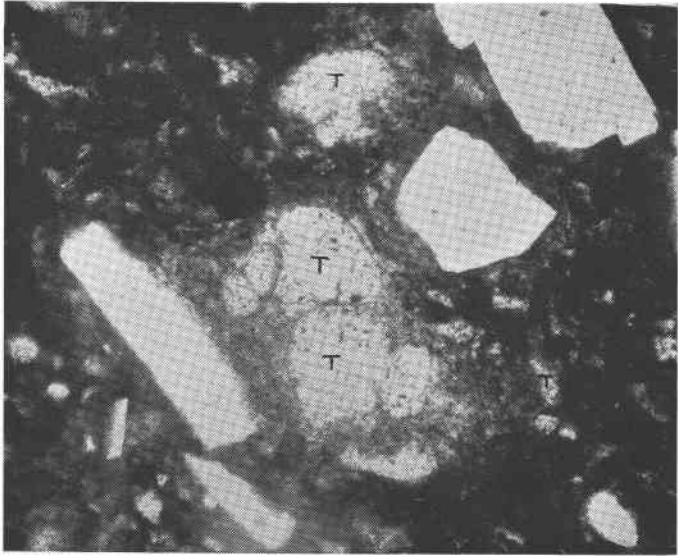


FIG. 3. Thin section in ordinary light of tridymite rhyolite from the Alboroto flow of Pine Creek Mesa, along road 3 miles S. 30° W. of Sapinero, Colo. (Up. 3027). Tridymite (T) concentrated in the coarser, more porous parts of the groundmass. Enlarged 31 diameters.

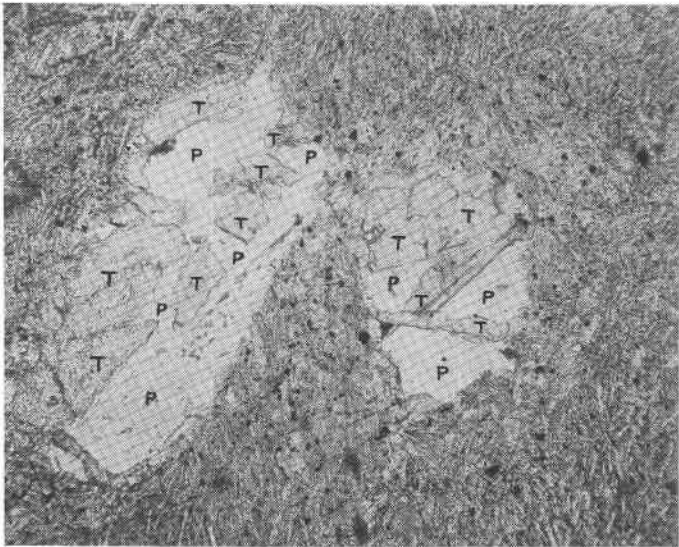


FIG. 4. Thin section in ordinary light showing coarse tridymite (T) in the porous (P) layers of a latite of pre-Potosi age (*D.N. g.*). From Red Rock Creek, 2½ miles above valley in northeastern part of Del Norte quadrangle, Colorado. Enlarged 31 diameters.

section of a latite with unusually coarse tridymite plates that can be easily seen in the hand specimen. Many rocks contain 25 per cent of tridymite. In the andesites tridymite is rather uncommon.

Tridymite is an abundant mineral in some of the rhyolitic tuffs, where it in part forms the binder for the tuff and was formed after the tuff was deposited. Such tuffs were no doubt deposited while they were still hot and contained abundant mineralizers. Some of these tuffs have much the appearance of lava flows, and they grade into eutaxitic rhyolites.

Rhyolites with quartz phenocrysts carry much tridymite in the groundmass as commonly as do those without such phenocrysts. I have never seen the slightest tendency for the quartz to be inverted to tridymite or replaced by it.

#### CRISTOBALITE

Cristobalite was microscopically identified in the San Juan lavas only as rounded spherulites or crystals perched on the walls of the larger gas

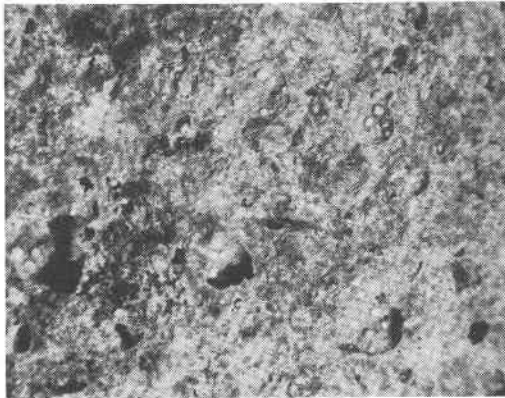


FIG. 5. Cristobalite spherulites (white) on the walls of vesicles in an andesite from the ridge west of the mouth of Hot Spring Creek, Jemez quadrangle, New Mexico. Photograph of part of a hand specimen. Enlarged 2 diameters.

cavities. In most specimens they are sparsely scattered on the cavity walls, but in some they are closely spaced. They are commonly less than a millimeter across, but in some lavas they reach a diameter of a little more than a millimeter. They are less well formed but are otherwise very similar to crystals of cristobalite deposited by steam on the surface of tubes of silica glass and described and figured by Greig, Merwin, and Shepherd.<sup>7</sup>

<sup>7</sup> Greig, J. W., Merwin, H. E., and Shepherd, E. S., Notes on the volatile transport of silica: *Am. Jour. Sci.*, 5th ser., vol. 25, pp. 61-73, 1933.

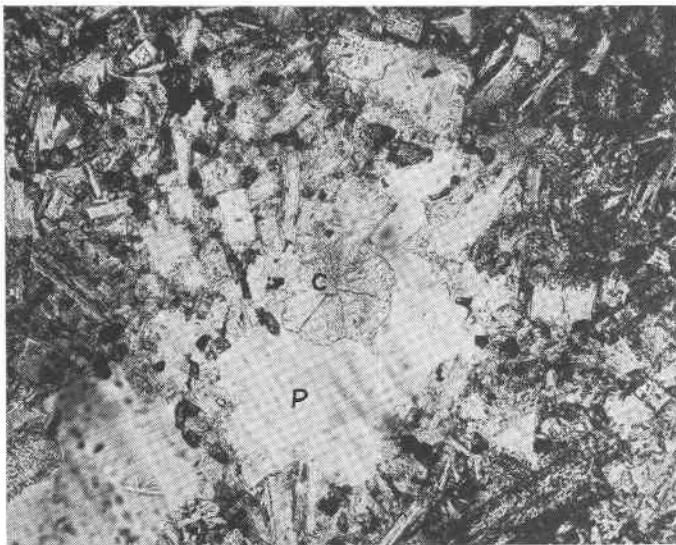


FIG. 6. Thin section in ordinary light of cristobalite (C) in the vesicles (P) of an andesite from Antone Peak, New Mexico. Enlarged 62 diameters.

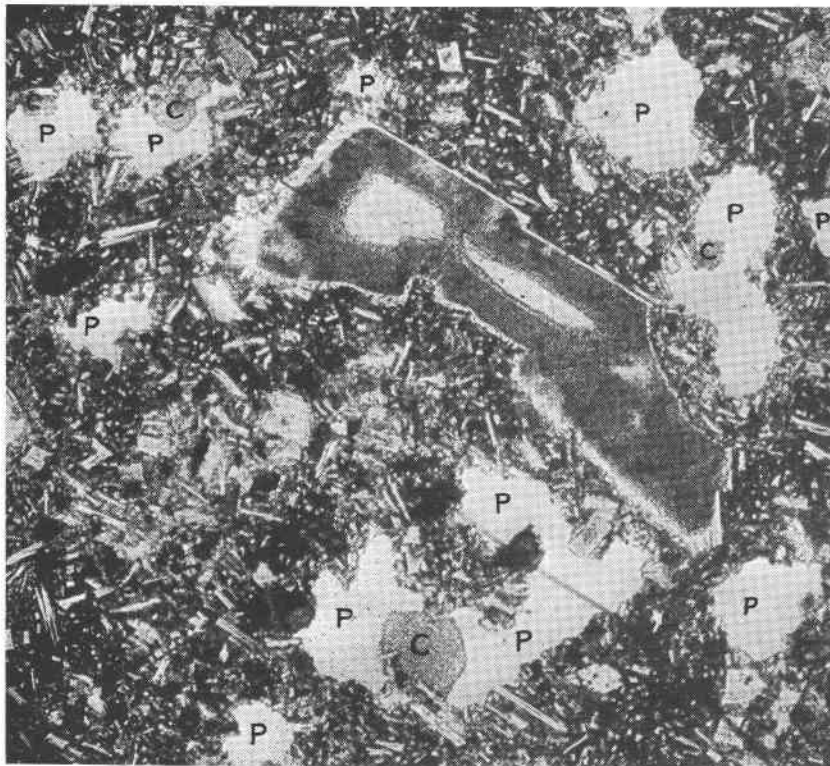


FIG. 7. Same as Fig. 6. Enlarged 30 diameters. The cristobalite spherulite near the upper left corner is enlarged in Fig. 6.

Cristobalite is the most common silica mineral in the gas cavities of basaltic lavas, and is present in about a fourth of the basaltic lavas examined. It is less common in the andesites. It is very rare in gas cavities of the rhyolitic rocks, and in these rocks was found only on the walls of the cavities of large spherulites, especially where these spherulites are embedded in obsidian. Typical cristobalite spherulites are shown in hand specimen in Fig. 5 and in thin section in Figs. 6 and 7. Rogers found cristobalite to be the common silica mineral of spherulites, and *x*-ray studies by Dr. C. S. Hurlbut have confirmed this determination.<sup>8</sup> Hurlbut found that the silica mineral of spherulites and similar submicroscopic intergrowths in the groundmasses of rhyolites from the San Juan region is cristobalite. In some of these spherulites the cristobalite is more or less concentrated in concentric rings or in rounded areas.

#### CONDITIONS OF FORMATION OF THE SILICA MINERALS

Quartz is the only silica mineral found in phenocrysts and in the granular rocks, where it must have crystallized slowly and under conditions favorable for equilibrium. We are therefore justified in believing that the quartz crystallized as a stable form and hence below the quartz-tridymite inversion temperature, which is 870°C. at a pressure of one atmosphere.<sup>9</sup> At a pressure of 1,000 atmospheres, corresponding to a depth of nearly 2½ miles, this inversion temperature is estimated to be increased to about 970°.<sup>10</sup>

It is very probable that the quartz phenocrysts, even of the quartz basalts, were the stable form at the time the lava flows were extruded, because the liquid (groundmass) in which the quartz was embedded should have served as a flux to hasten equilibrium, as it contained several per cent of free silica and must have been a solvent for silica. This is also shown by the resorption of the quartz. The conclusion seems justified that the San Juan lavas were extruded at temperatures below about 900°C.

Both quartz and tridymite formed in the mineralizer-enriched parts of the groundmasses. No clue was found as to why quartz crystallized in the porous groundmass in one rock and tridymite in another, but tridymite is much the commoner of the two. Cristobalite is the characteristic mineral of the dense, submicroscopic parts of the groundmasses,

<sup>8</sup> Rogers, A. F., Natural history of the silica minerals: *Am. Mineral.*, vol. 13, p. 82, 1928. Hurlbut, C. S., personal communication.

<sup>9</sup> Fenner, C. N., The stability relations of the silica minerals: *Am. Jour. Sci.*, 4th ser., vol. 36, p. 383, 1913.

<sup>10</sup> Bowen, N. L., Geologic thermometry, from Fairbank's Laboratory investigation of ores, p. 181, McGraw-Hill Book Co., 1928.

including the spherulites, and is confined to such groundmasses. Cristobalite is the chief silica mineral of the larger gas cavities, though tridymite and quartz are both found in such cavities. Tridymite clearly developed as an unstable form owing to rapid crystallization in the presence of mineralizers. Cristobalite developed as an unstable form during the relatively rapid crystallization of the viscous cotectic groundmass. Where crystallization is more free, quartz forms in the groundmass.

Rogers<sup>11</sup> states: "I doubt whether tridymite is ever even a late magmatic mineral . . . The tridymite-bearing streaks I would interpret as having been formed by pneumatolytic metamorphism." And again, "In my opinion tridymite is not a magmatic mineral, but a metamorphic one." I cannot agree with Rogers. In the San Juan area, and in many other places as well, tridymite is found in the freshest rocks and is in no way associated with altered rocks or with areas in which the rocks are altered. It is not confined to red or brown rocks, although most of the rhyolites and quartz latites are red, but is found as well in white or gray rocks. A red or brown color in lavas is not evidence of alteration but is commonly the color of the fresh rock and was formed during the crystallization of the rock. This is especially true of rhyolitic rocks.

The distribution of tridymite in the rocks and the study of the thin sections in no way suggests a secondary origin, although such evidence is not conclusive. Tridymite is characteristic of certain lava flows, many of which can be followed for tens of miles in the walls of canyons. In any particular flow both the quantity and distribution of the tridymite are uniform, so that a specimen or thin section of a flow taken at one locality is almost identical with others from the same flow 10 miles or more distant. Indeed, the particular rock to which Rogers refers in the first statement quoted from him came from a flow, or possibly a group of related flows, near Creede, Colo., that are nearly flat and a few hundred feet thick and that lie at a definite stratigraphic horizon in the section over an area nearly 30 miles across. Specimens from this horizon from any part of this area are all rich in tridymite and nearly identical in character. In this area some of the overlying and underlying layers may or may not have tridymite—some are tuffs, some are glassy, and some have quartz in the groundmass. The rocks are generally fresh, but locally, as near some of the mineralization near Creede, they are altered and quartz has replaced much of the rock.

In a series of superimposed flows one flow may have tridymite and a groundmass of a particular habit, another tridymite and a groundmass of a different habit, and still another may have a groundmass that con-

<sup>11</sup> Rogers, A. F., Natural history of the silica minerals: *Am. Mineral.*, vol. 13, pp. 80-81, 1928.

tains quartz. Many of the flows have a thin layer of fresh obsidian at the base throughout their extent and, rather sharply separated from this layer, a main part in which the groundmass is crystalline and carries as much as 20 to even 30 per cent of tridymite.

There seems little room for doubt that the tridymite crystallized after the lavas had practically ceased to flow, but during their original cooling and as a part of the crystallization of the groundmass of the rock. The tridymite tended to concentrate, as did the quartz, in the last residual, mineralizer-rich part of the magma. To a very small extent, tridymite was deposited in gas cavities during the cooling of the rock, but after the crystallization of the groundmass.

On hydrothermal or any other metamorphism the unstable form tridymite should be changed to the stable form quartz, unless the temperature was above the quartz-tridymite inversion temperature, a very rare condition under metamorphism. On the recrystallization of a glass or introduction of silica by steam or other gases, the unstable form might be deposited, as it might be less soluble than the silica of the glass or might be brought in from an environment—such as higher temperature—in which silica was more soluble.

Tridymite has been found in the gas cavities of a few basalts, where it clearly crystallized from a gas phase, but cristobalite is the common form in the large gas cavities. The two forms were rarely found in the same gas cavity. The tridymite fills a much greater part of the cavities, than does the cristobalite. The cristobalite, and probably the tridymite in these cavities probably formed by transport of silica by steam.<sup>12</sup>

Quartz may be found as phenocrysts in a rock and tridymite or cristobalite in the gas cavities or in the groundmass, but rarely have two forms been found to have crystallized together. In some rocks quartz is present as phenocrysts, tridymite in the porous parts of the groundmass, and cristobalite in the dense, submicroscopic parts of the groundmass.

To sum up the conditions under which the three forms of silica were crystallized in the San Juan area:

1. Quartz alone forms as phenocrysts in the granular rocks, in the intrusive rocks, or wherever crystallization was slow enough for equilibrium to be reached.

2. Tridymite, less commonly quartz, forms during the crystallization of the porous parts of the groundmass, the tridymite as an unstable form owing to rapid crystallization.

3. Cristobalite forms in the dense parts of the groundmass when crystallization is rapid or retarded and is not "lubricated" by mineralizers.

<sup>12</sup> Greig, J. W., Merwin, H. E., and Shepherd, E. S., *op. cit.*

4. Cristobalite, rarely tridymite or quartz, forms in the larger gas cavities by gas transfer after solidification of the groundmass, especially in the andesites and basalts.

#### INVERSIONS OF SILICA MINERALS

In the San Juan rocks the tridymite and cristobalite, though of Miocene age, show no trace of a change to quartz except in a very few places where they have been recrystallized by hydrothermal solutions that altered the whole rock. Moehlman<sup>13</sup> has described paramorphs of quartz after both tridymite and cristobalite in altered rocks from the vicinity of Ouray, Colo., in the western part of the San Juan region. The freshness of the tridymite and cristobalite in the fresh rocks indicates that these minerals may persist indefinitely under favorable conditions. However, I have seen neither of them in rocks older than Tertiary. It is not surprising that these forms of silica, which are unstable under most conditions under which the rocks we see were formed, are not found in older rocks, for they would probably be replaced by quartz during even a very low degree of metamorphism or recrystallization. It will be interesting to record any finds of tridymite or cristobalite in older rocks. A similar observation in regard to old volcanic glasses would be interesting. True glass should be distinguished from material with submicroscopic crystallization. In my experience, true glass is definitely vitreous in appearance and not felsitic.

#### 3. PYROXENES

BY ESPER S. LARSEN AND JOHN IRVING

##### GENERAL FEATURES

The pyroxenes are the most abundant mafic minerals of the San Juan extrusive rocks as a whole. They are associated with olivine in the basalts, are the only mafic silicates in most of the low-silica andesites, are present with biotite, with or without hornblende, in more than half of the quartz latites, and are present in small amount in some of the rhyolites. Monoclinic pyroxene, which probably approaches pigeonite in composition, is the only pyroxene in most of the basalts. In the andesites both hypersthene and diopside are commonly present, with diopside usually predominating. In the more siliceous rocks the pyroxene is nearly all diopside.

Hypersthene is rarely found in the same rock with olivine, except in the olivine andesites, and it is rare in rocks that contain less than 54 per cent of SiO<sub>2</sub>. It is present in most rocks that contain from 57 to 59

<sup>13</sup> Moehlman, R. S., Quartz paramorphs after tridymite and cristobalite: *Am. Mineral.*, vol. 20, pp. 808-810, 1935.



per cent of SiO<sub>2</sub>; with higher content of SiO<sub>2</sub> it is less common; and in rocks that contain more than 65 per cent of SiO<sub>2</sub> it is rare and present in very small amount.

In the basalts the clinopyroxene is mostly interstitial to the feldspar, or in the groundmass, and is rarely present as phenocrysts. In the andesites it is chiefly present as early phenocrysts but partly as small crystals in the groundmass. In the quartz latites and rhyolites it occurs almost exclusively as phenocrysts.

The hypersthene usually occurs in better-formed crystals than the augite. Hypersthene is to a large extent altered to bastite, whereas the clinopyroxene is commonly fresh. The pyroxenes in some of the rocks are irregularly colored reddish brown, probably from partial oxidation of the iron by gases. Diopside grows around hypersthene and probably partly replaces it in a few specimens.

Three analyses of diopsides from rocks of different composition and one of hypersthene have been made by F. A. Gonyer and are given, together with other data, in Table 2. None of the pyroxene of the basalts was suitable for analysis. All four pyroxenes show a deficiency of SiO<sub>2</sub> of 4 to 6 per cent for a metasilicate formula. The diopsides have about enough silica to form the maximum amount of acmite, diopside, and clinohypersthene, leaving little or none to be allotted to the Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. The diopsides have only moderate amounts of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, but the hypersthene has a large amount of Fe<sub>2</sub>O<sub>3</sub>. The diopsides from the

TABLE 2. ANALYSES AND OPTICAL PROPERTIES OF PYROXENES FROM THE SAN JUAN LAVAS

	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub> .....	51.05	51.45	50.74	51.58					
TiO <sub>2</sub> .....	0.36	0.36	0.95	0.45					
Al <sub>2</sub> O <sub>3</sub> .....	1.80	1.50	2.98	1.70					
Fe <sub>2</sub> O <sub>3</sub> .....	2.03	3.15	2.37	3.15					
FeO.....	6.56	6.45	10.04	18.11					
MnO.....	1.22	0.53	0.17	0.39					
MgO.....	13.82	14.11	14.24	22.01					
CaO.....	22.06	21.69	17.88	1.82					
Na <sub>2</sub> O.....	0.38	0.32							
K <sub>2</sub> O.....	0.08	None	0.67						
H <sub>2</sub> O—.....	0.04	None	0.03						
H <sub>2</sub> O+.....	0.17	0.16	0.17	0.40					
P <sub>2</sub> O <sub>5</sub> .....	0.46	0.48							
F.....	Trace								
	100.03	100.20	100.24	99.61					

WEIGHT PER CENT OF CONVENTIONAL MOLECULES<sup>1</sup>

NaFeSi <sub>2</sub> O <sub>6</sub> ...	3.2	2.3	5.1	...					
CaMgSi <sub>2</sub> O <sub>6</sub> ...	75.2	76.3	69.1	7.1					
CaFeSi <sub>2</sub> O <sub>6</sub> ...	5.5	3.7	...	...					
CaMnSi <sub>2</sub> O <sub>6</sub> ...	4.3	2.0	...	...					
MgSiO <sub>3</sub> .....	...	...	3.6	51.8					
FeSiO <sub>3</sub> .....	9.3	9.8	18.7	33.7					
Fe <sub>2</sub> Si <sub>3</sub> O <sub>9</sub> .....	...	1.6	...	2.5					
Fe <sub>2</sub> O <sub>3</sub> .....	1.0	1.6	.6	1.9					
Al <sub>2</sub> O <sub>3</sub> .....	1.8	1.5	3.0	1.7					
Deficiency of SiO <sub>2</sub> for metasilicate	5.1	4.2	6.2	2.7					
MgO(mol.)	2.56	2.60	2.04	1.84					
2Fe <sub>2</sub> O <sub>3</sub> +FeO									
$\alpha$ .....	1.684	1.686	1.695	1.702	1.692	1.696	1.690	1.688	1.690
$\beta$ .....	1.691	1.693	1.701	1.707		1.703	1.694	1.693	
$\gamma$ .....	1.712	1.713	1.719	1.712	1.723	1.730	1.721	1.701	1.720
2V.....	60+	64	55		Rather small	Rather small	Medium		
$\gamma/\epsilon$ .....	41	40	41						
Specific gravity....	3.370	3.37	3.405	3.481					

<sup>1</sup> Small amount of MnSiO<sub>3</sub> included in FeSiO<sub>3</sub>.

1. Diopside from phenocrysts of Treasure Mountain quartz latite (DN 3006) about 5 miles southeast of Del Norte, Colorado, north fork of Gulch between Lime and Raton Gulches, one-fourth mile below upper contact of Treasure Mountain formation. Powder analyzed contained about 1 per cent apatite and less feldspar.

2. Diopside from phenocrysts of Los Pinos andesite-latite (Con A) from northern part of Conejos quadrangle, Colorado, north of Green Ridge and just east of Goat Ranch. Powder analyzed contained about 1 per cent apatite and less feldspar.

3. Diopside from phenocrysts of pyroxene andesite of Sheep Mountain andesite (Sv 9), from southern part of Summitville quadrangle, Colorado. Analyzed sample contained 2 per cent each of hypersthene and groundmass. Analysis corrected for this material. Indices of refraction vary  $\pm 0.01$  from the values given, which are the average.

4. Hypersthene phenocrysts from same specimen as diopside 3 (Sv 9). Pleochroism  $\alpha$ =pink,  $\beta$ =yellow,  $\gamma$ =green. Indices of refraction vary  $\pm 0.01$ . Powder analyzed contained about 3 per cent augite, and the analysis is corrected for this material. Indices vary  $\pm 0.01$ .

5. Diopside approaching pigeonite from San Antone basalt from Buffalo Butte, New Mexico, (NM 78). Indices vary  $\pm 0.01$ .

6. Diopside approaching pigeonite from Hinsdale basalt, railroad cut near Servilleta Plaza, N. Mex. (NM 3004). Indices vary  $\pm 0.01$ .

7. Diopside, Piedra rhyolite-latite glass (SC xx). Eastern part of San Cristobal quadrangle, Colorado, along road on north side of Rio Grande, north of mouth of Spring Creek. (SC xx glass of rock analyzed.)

8. Hypersthene Piedra rhyolite-latite, same specimen as 7 (SC xx).

9. Diopside from Hinsdale rhyolite (SC 906) from northeastern part of San Cristobal quadrangle, Colorado. Along road between Creede and Lake City at head of Big Spring Gulch.

quartz latite (1) and from the latite-andesite (2) are much alike; and they show some clinohypersthene in solid solution. The diopside from the pyroxene andesite (3), which is from the same rock as the hypersthene (4), has more clinohypersthene in solid solution than the other diopsides.

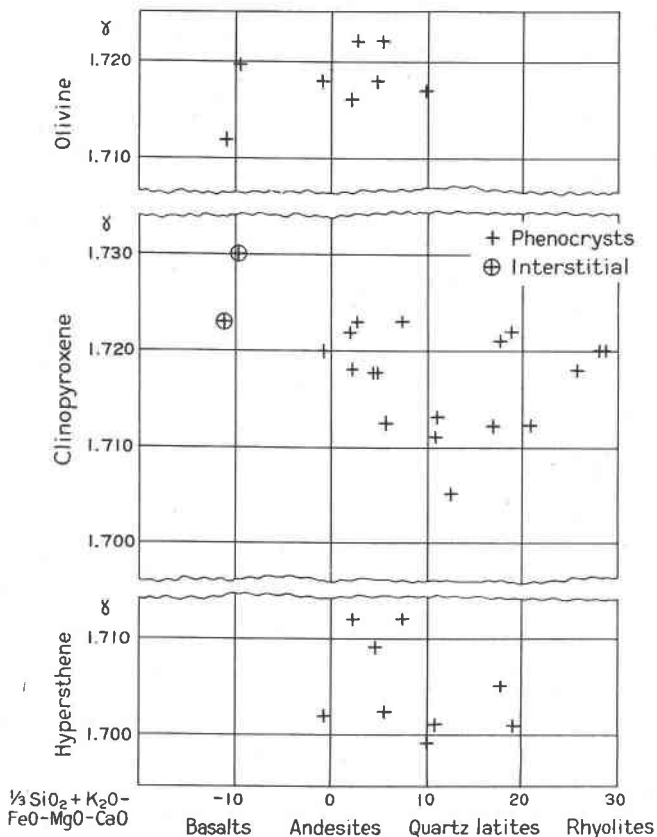


FIG. 8. The  $\gamma$  index of refraction of the olivines, clinopyroxenes, and hypersthene of the San Juan lavas plotted against their position between basalt and rhyolite.

The optical data indicate that the pyroxenes in the basalts have still more clinohypersthene and that they approach pigeonite in composition. MnO is higher in the pyroxenes from the quartz latites than in those from the andesites.

Optical data are given in the table for a number of pyroxenes from some of the San Juan lavas. Other unanalyzed pyroxenes were measured and the  $\gamma$  indices are plotted in Fig 8. The pyroxene phenocrysts show only a moderate variation in composition—from 22 to 31 per cent of

$\text{FeSiO}_3$  for the hypersthene, and nearly the same variation as that shown in the analyses of Table 2, for the diopsides. The pigeonites of the basalts differ more and are higher in iron and in clinohypersthene. The iron content of the pyroxenes is lower in the quartz latites than in the andesites or rhyolites, but the variation is not very regular. Without exception the values of  $\gamma$  for diopside phenocrysts and olivine in the same rock differ from each other by less than 0.003, and the value for the olivine tends to be lower by only 0.001. In the basalts the interstitial pyroxene has a value for  $\gamma$  about 0.010 greater than that of the olivine in the same rock. The  $\gamma$  for hypersthene shows less similarity to that of diopside and is from 0.007 to 0.021 lower, averaging about 0.014 lower;  $\beta$  averages about the same for the two pyroxenes.

These data indicate that the iron is distributed systematically between the olivine and the diopside and that the ratio  $\text{MgO}/\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MnO}$  is higher in olivines than in the diopsides that accompany them. The hypersthene is less systematic in its iron content, but in general it has about the same  $\text{Mg}/\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MnO}$  ratio as the diopside that accompanies it.

The tendency for the pyroxene phenocrysts in the pyroxene andesites to have more iron than those of the quartz latites and rhyolites is not in accordance with what we would expect from the physical chemistry of the pyroxene systems<sup>14</sup> nor does it agree with the data of Tsuboi for Japanese rocks. Tsuboi found that the pyroxene phenocrysts have higher indices of refraction as the feldspar becomes poorer in lime.

For the White Mountain magma series, a group of mildly alkaline rocks, Chapman and Williams found "a great increase in iron relative to magnesia in going from the basic to the siliceous end of the series."<sup>15</sup>

Barth<sup>16</sup> found that in basalts the clinopyroxene phenocrysts as com-

<sup>14</sup> Vogt, J. H. L., The physical chemistry of the magmatic differentiation of igneous rocks, Part 1: *Vidensk. Skr.*, **1**, *Mat. Naturv. Klasse*, no. 15, pp. 100–118, Kristiania, 1924.

Fenner, C. N., The crystallization of basalt: *Am. Jour. Sci.*, 5th ser., vol. **18**, pp. 225–253, 1929.

Bowen, N. L., *The evolution of the igneous rocks*, pp. 79–81, Princeton Univ. Press, 1928.

Bowen, N. L., and Schairer, J. F., The system  $\text{MgO}-\text{FeO}-\text{SiO}_2$ : *Am. Jour. Sci.*, 5th ser., vol. **29**, pp. 159–160, 1935.

Tsuboi, S., On the course of crystallization of pyroxenes from rock-magmas: *Japanese Jour. Geol. and Geog.*, vol. **10**, pp. 67–82, 1932. (See Fig. 4; the text, p. 74, makes the reverse statement.)

<sup>15</sup> Chapman, R. W., and Williams, C. R., Evolution of the White Mountain magma series: *Am. Mineral.*, vol. **20**, p. 514, 1935.

<sup>16</sup> Barth, T. F. W., Crystallization of pyroxenes from basalts: *Am. Mineral.*, vol. **16**, pp. 195–208, 1935.

Powers, H. A., Differentiation of Hawaiian lavas: *Am. Jour. Sci.*, 5th Ser., vol. **30**, pp. 57–71, 1935.

pared with those of the groundmass are poorer in iron as well as in clinohypersthene. Kuno and Sawatari<sup>17</sup> found the pyroxene phenocrysts of two basalts from Japan to be zoned diopside with the borders richer in iron than the cores, and Kuno has shown that this holds for both the augites and olivines from the Alaid volcano.<sup>18</sup>

This decrease in the ratio total Fe as FeO/MgO from the pyroxene of the basalts to those of the rhyolites in the San Juan rocks is in contrast to the increase in this ratio in the rocks themselves, from  $1\frac{1}{2}$  in the average of the San Juan basalts to 7 in the average of the rhyolites with about 75 per cent SiO<sub>2</sub>. In the rhyolites the iron is mostly in the form of oxides, magnetite, hematite, and ilmenite.

The apparent inconsistency is not easily explained—that the pyroxenes which crystallized later in any single rock are richer in iron than those that crystallized earlier, although in a differentiation series the pyroxenes of the late, low-temperature members (rhyolitic rocks) have a lower Fe/Mg ratio than those of the earlier members (basaltic rocks), and even though in the rocks as a whole the Fe/Mg ratio is greater in the late rocks.

The crystallization of the pyroxenes in a given rock, as shown by zoning, gives more directly the course of crystallization of the pyroxenes, and it conforms to the data on the melting phenomenon of the pyroxenes. The decrease in iron content in the pyroxenes from basalt to rhyolite is due to the fact that the iron goes into the hornblende and biotite, which are high in iron, and into the iron ore, leaving little for the pyroxenes.

#### CONDITIONS OF FORMATION OF PIGEONITE

In the San Juan lavas pyroxenes approaching pigeonite are confined to the basalts; these rocks contain olivine but no hypersthene. Pigeonite rarely or never occurs as good phenocrysts but is interstitial to the feldspar. In the pyroxene andesites both augite (with 22 per cent of clinohypersthene in analysis 3) and hypersthene are present, whereas in the quartz latites and rhyolites the augites contain about 10 per cent of clinohypersthene in solid solution (analyses 1 and 2). These facts indicate that a high concentration of clinohypersthene in clinopyroxenes takes place in the high-temperature rocks and decreases as the temperature of crystallization falls. At the temperature of crystallization from a basalt magma the clinopyroxene may carry all the hypersthene molecule of

<sup>17</sup> Kuno, H., and Sawatari, M., On the augite from Wadaki, Idu, and Yoneyama, Etigo, Japan: *Japanese Jour. Geol. and Geog.*, vol. 11, pp. 328–343, 1934.

<sup>18</sup> Kuno, H., Petrology of Alaid Volcano, North Kurile: *Japanese Jour. Geol. and Geog.* vol. 12, pp. 161–162, 1935.

the magma in solid solution; at the temperature for pyroxene andesite the clinopyroxene can carry only 24 per cent of hypersthene in solid solution; and at the temperature of crystallization of quartz latite and rhyolite the clinopyroxene can carry only 10 per cent of hypersthene in solid solution.

The above conclusion does not entirely conform to the data of Barth<sup>19</sup> and others, who found the phenocrysts in basalt to be a diopside with less than 10 per cent excess of clinohypersthene, and the groundmass pyroxene to be an ordinary pigeonite. So far as we are aware, pigeonite is almost entirely confined to the groundmass or interstitial pyroxene. Does pigeonite form only during rapid crystallization and as an unstable form? Barth<sup>20</sup> has offered a similar explanation. Bowen and Andersen<sup>21</sup> have shown that at the temperature of crystallization of melts of the pyroxenes, diopside and clinoenstatite are miscible in all proportions, but it does not follow that they are miscible in all proportions at the temperatures of crystallization of basaltic and andesitic rocks. In fact, the common association in pyroxene andesites, gabbros, and other rocks of diopside, with some clinoenstatite in solid solution, and hypersthene would seem to show that under the conditions of crystallization of a basaltic magma clinohypersthene has a limited miscibility in diopside and that the amount that can be carried in solid solution decreases with temperature. This conclusion is strengthened by the fact that in coarsely crystalline gabbros of the same composition as the diabases and basalts, pigeonite has never been described, and diopside is commonly associated with hypersthene. This indicates that when the crystallization is slow enough to allow the stable forms to crystallize, hypersthene and augite crystallize and not pigeonite.

#### 4. OLIVINE

BY ESPER S. LARSEN AND JOHN IRVING

Olivine forms the chief or only phenocrysts in the basalts. It decreases in amount as the silica content of the rock increases and was not found in those with more than 56 per cent SiO<sub>2</sub>. In the quartz basalts it is

<sup>19</sup> Barth, T. F. W., Crystallization of pyroxene from basalts: *Am. Mineral.*, vol. 16, pp. 195-208, 1931.

Kuno, H., and Sawatari, M., On the augite from Wadaki, Idu, and Yoneyama, Etigo, Japan: *Japanese Jour. Geol. and Geog.*, vol. 11, pp. 328-343, 1934.

<sup>20</sup> Barth, T. F. W., Mineralogical petrography of the Pacific lavas: *Am. Jour. Sci.*, 5th ser., vol. 21, pp. 390-391, 1931.

Kuno, H., Preliminary note on the occurrence of pigeonite as phenocrysts in some pyroxene-andesite from Hakona Volcano: *Jour. Geol. Soc. Japan*, vol. 42, pp. 39-44, 1935.

<sup>21</sup> Bowen, N. L., and Andersen, O., The binary system MgO-SiO<sub>2</sub>: *Am. Jour. Sci.*, 4th ser., vol. 37, pp. 487-500, 1914.

associated with quartz phenocrysts, and it is commonly present as phenocrysts in lavas that contain either cristobalite or tridymite in the gas cavities. It is also found in lavas in which there is quartz in the groundmass, or in which there is as much as 12 per cent of quartz in the norm of the rock, or 17 per cent of quartz in the norm of the groundmass.

Without exception the olivine phenocrysts show much magmatic resorption, and almost without exception they are partly altered to iddingsite. In some rocks the olivine is completely replaced by iddingsite or iron oxide. Very rarely it is altered to serpentine. In the granular intrusive rocks the alteration to iddingsite was not found, but that to serpentine is common.

The olivines vary only moderately in their optical properties. An analysis and the optical properties of a fresh olivine from the basalt of Buffalo Buttes (belonging to the Hinsdale andesite), in New Mexico, about 16 miles south of Antonito, is given in Table 3. The optical properties of the olivine from the widespread Hinsdale basalt flows of New Mexico, just south of the San Luis Valley, indicate an olivine with about 21 mol. per cent of fayalite. The  $\gamma$  index of refraction of eight olivines from the San Juan lavas is plotted in Fig. 8 against the composition of the lava in which the olivine occurs. The content of forsterite ranges only between 21 and 30 per cent; in general the forsterite content is higher in the less siliceous rocks.

TABLE 3. OLIVINE FROM BASALT OF BUFFALO BUTTES.

SiO <sub>3</sub> . . . . .	39.31	$\alpha = 1.675$	Opt. —, 2V near 90°
TiO <sub>2</sub> . . . . .	0.06	$\beta = 1.694$	$r > v$ perceptible
Al <sub>2</sub> O <sub>3</sub> . . . . .	1.68	$\gamma = 1.712$	
Fe <sub>2</sub> O <sub>3</sub> . . . . .	None		
FeO . . . . .	19.84		23 mol. per cent fayalite
MnO . . . . .	0.17		
MgO . . . . .	37.74		
CaO . . . . .	<u>0.87</u>		
	99.67		