

FRONTISPIECE. Slab of pumicell made from Oklahoma volcanic ash, showing cellular structure obtained by raising the temperature to $1,350^{\circ}\text{C}$. About $\times 2$.

OKLAHOMA GEOLOGICAL SURVEY

ROBERT H. DOTT, DIRECTOR

Circular No. 27

Cellular Products from Oklahoma Volcanic Ash

by

A. L. BURWELL

with a section on

GEOLOGY AND PETROLOGY

by

WILLIAM E. HAM

Norman

1949

OKLAHOMA STATE REGENTS FOR HIGHER EDUCATION

JOHN H. KANE, Chairman Bartlesville
W. D. LITTLE, Vice Chairman Ada
DIAL CURRIN, Secretary Shawnee
WHARTON MATHIES Clayton
FRANK BUTTRAM Oklahoma City
JOHN ROGERS Tulsa
CLEE O. DOGGETT Cherokee
GUY H. JAMES Oklahoma City
GUY M. HARRIS Ardmore

M. A. NASH, *Chancellor*

THOMAS G. SEXTON, *Administrative Assistant*

THE BOARD OF REGENTS

DON EMERY, President Bartlesville
JOE W. McBRIDE, Vice President Anadarko
NED SHEPLER Lawton
DR. OSCAR WHITE Oklahoma City
T. R. BENEDUM Norman
KENT W. SHARTEL Oklahoma City
DAVE J. MORGAN Blackwell

EMIL R. KRAETTLI, *Secretary*

GEORGE LYNN CROSS, Ph.D., *President*, University of Oklahoma

CONTENTS

	Page
Abstract	7
Chemical investigations	11
Introduction	11
Inorganic cellular and porous materials	12
Natural materials	12
Artificial inorganic cellular materials	13
Conversion of clays, shales, and slates	13
Conversion of volcanic glassy rocks	14
Manufactured glass	15
Nature of glass and glassy material	16
Experiments with Oklahoma volcanic ash	19
Definition of volcanic ash	19
Materials investigated	21
Susceptibility of Oklahoma volcanic ash to bloating	23
Small-scale experimentation	23
Laboratory procedure	23
Effects of temperature and time on bloating	23
Chemical composition and bloating properties	24
Cause of bloating	26
Larger-scale bloating	29
Physical tests of products	30
Effect of caustic soda as an additive	34
"Popping" of volcanic ash	34
Commercial application of products	39
Pumicell	39
Products from addition of caustic soda	40
Uses of popped volcanic ash	40
Volcanic ash deposits in Oklahoma	42

Geological and petrographic investigations	48
Introduction	48
Geology of volcanic ash	49
Physiographic and stratigraphic occurrence	49
Origin and deposition	51
Sites of deposition	52
Age	54
Particle Size	58
Laboratory procedure	58
Size analyses	60
Petrology	62
Mineral composition	62
Purpose and procedure	62
Petrography	72
Microscopic technique	72
Volcanic glass shards	74
Refractive indices	77
Quartz	78
Feldspar	78
Clay aggregates	80
Mica	80
Other minerals	81
Effect of mineral and textural composition on bloating	82

CELLULAR PRODUCTS FROM OKLAHOMA VOLCANIC ASH WITH A SECTION ON GEOLOGY AND PETROLOGY

ABSTRACT

Tests of Oklahoma volcanic ash show that when heated to relatively high temperatures the material will bloat or expand, offering possibilities for insulating and light-weight building materials. When heated alone at temperatures of 1,200° C. to 1,350° C. volcanic ash vitrifies and expands, producing a mass with cellular structure. This product has been named "pumicell." Addition of caustic soda, and heating to 850° C. produces a product with many interconnecting pores. Individual grains can be popped or expanded into cellular, bubble-like particles. Distinction is made between "cellular"—voids completely separated by impervious walls, as in bubbles; and "porous"—voids that are interconnected, as in a sponge.

Natural light-weight porous materials are fairly numerous, including travertine, tripoli, diatomaceous earth, and the like. Natural cellular materials are rare; pumice and scoria may be so classified, though commonly, even in these rocks, some of the voids are connected. Artificial cellular products are manufactured from clay, shale, slate, glassy volcanic rock (perlite), and manufactured glass, all of whose bloated products are glass, or contain a large proportion of glass.

Volcanic ash is the finest material blown into the air from explosive types of volcanoes; volcanic dust is a better term. It generally comes from an acidic or intermediate magma, which on crystallization would have produced a rhyolite or granite. The rapid cooling of the magma during violent eruption prevents the formation of minerals, and the result is volcanic glass.

In testing the susceptibility of Oklahoma volcanic ash to bloating, it was found that as the temperature is raised, the ash sinters, shrinks, and vitrifies, with a color change from gray to brick red. With further rise, the color becomes drab gray, and the mass gradually expands. The properties of this bloated product depend upon the temperature and length of time exposed to the temperature.

It is apparent that bloating is caused by the generation and expansion of gas or vapor within the mass itself, but the source of the gas or vapor is not so obvious. In clay, shale, and manufactured glass, authorities believe the bloating results from gases formed from sulfur, carbon or moisture. Chemical analyses indicate that Oklahoma volcanic ash does not contain sulfur or carbon, and moisture has been removed before the temperatures at which bloating

	Page
I. Composition range of raw materials used in producing light weight cellular and porous ceramic products	16
II. Chemical analyses of Oklahoma volcanic ash	22
III. Susceptibility of Oklahoma volcanic ash to bloating	following page 24
IV. Calculated composition of cellular products from Oklahoma volcanic ash	25
V. Physical properties of bloated products made from Dustin, Oklahoma, volcanic ash	32
VI. Physical properties of bloated volcanic ash compared with other structural materials	33
VII. Effect of popping on particle size of volcanic ash	37
VIII. Comparison of specific gravity of original and popped volcanic ash	38
IX. Volcanic ash deposits of Oklahoma	44
X. Size analyses of Oklahoma volcanic ash	following page 58
XI. Mineral composition of Oklahoma volcanic ash by size grades	63
XII. Summary of mineral composition of Oklahoma volcanic ash	76
XIII. Comparison of initial bloating temperatures to degree of alteration, relative purity, and texture of Oklahoma volcanic ash	84

ILLUSTRATIONS

Frontispiece—A slab of pumicell	
Plates	Page
I-V. Effect of temperature on expansion of volcanic ash	following page 24
VI. Effect of temperature and time	following page 24
VII. Photomicrographs of volcanic ash before and after "popping"	following page 40
VIII. Representative deposits of Oklahoma volcanic ash	following page 40
IX, X. Photomicrographs of volcanic ash shards	following page 72
Figures	
1. Mold used for larger-scale bloating	28
2. Burner assembly for "popping" volcanic ash	36
3. Map of Oklahoma showing distribution of volcanic materials	43
4. Curves showing texture of Oklahoma volcanic ash	61
5, 6. Mineral frequency diagrams of Oklahoma volcanic ash	69, 71
7. Relation of initial bloating temperature to incipient alteration, purity, and grain size	83

takes place. Release of oxygen through change of iron oxide from the ferric to the ferrous state seems adequate and plausible to account for bloating. Whatever the gas, gases, or vapor, and their source, they are generated within the material itself during the time, and at the temperature that causes the mass to be thermoplastic, and while it is sufficiently viscous to hold the gas in non-connecting voids. On cooling, the cellular structure is retained.

Physical tests prove that the laboratory products of bloated volcanic ash compare very favorably with light-weight products now in commercial production and use. Commercial application would be mainly as construction materials for insulation against heat, cold, sound, and electricity. Pumicell can be made in slabs, blocks, and other shapes. Products made with the addition of caustic soda should work well as acoustical insulation because of the large number of open pores. Popped volcanic ash would be a light-weight filler or aggregate for bricks, slabs, wall board, panel sheets, and plaster.

Geology. Volcanic ash occurs as widely scattered deposits in western, central, and east-central Oklahoma. All are thought to be of Pleistocene age except one in Woodward County that probably belongs in the Ogallala formation, of Pliocene age. Size of individual deposits has been estimated at 500 to 10,000,000 cubic yards.

The volcanic ash is believed to have come from a volcano in north-central New Mexico. Most deposits appear to be associated with high river terraces and show evidence of deposition in quiet water, suggesting they were formed as the ash settled from the air into lakes on the flood plains of rivers, with some additional concentration of ash by local run-off into lakes. The presence of tests of diatoms, and a fresh-water molluscan fauna found in associated clay in some localities, support the idea of lacustrine deposition.

Evidence of Pleistocene age of most of the Oklahoma volcanic ash is given by fossil vertebrates found in associated terrace deposits. The petrology of the volcanic ash shards and the molluscan fauna are the basis for correlating the Oklahoma deposits with the Pearlette ash of Kansas, which, in turn, has been correlated with deposits belonging to the Yarmouthian interglacial period of the Missouri Valley region. Volcanic ash of probable Pleistocene age on the surface of the High Plains probably represents deposits laid down in small ephemeral lakes similar to those that now form during rainy seasons in numerous undrained depressions.

All samples examined are fine-grained, and except for the one in Beaver County, are essentially similar in grain size distribution with at least 93 per cent of the particles being smaller than 0.246 mm and larger than 0.010 mm, and having an average median diameter of 0.0457 mm. In the exceptionally fine-grained Beaver County volcanic ash, 85 percent is finer than 0.030 mm and the sample has a median diameter of 0.0165 mm.

Mineral composition of the different samples ranges from 59.5 to 97.7 percent glass shards, 0.3 to 21.5 percent quartz, 0.7 to 5.3 percent orthoclase, and 0.7 to 13.2 percent clay aggregates. Some of the volcanic glass shards show incipient alteration to clay, the percentage of clay-altered shards ranging from a trace to 100 percent. In the sample from Woodward County that is thought to belong to the Ogallala formation of Pliocene age, all observed shards show pronounced incipient alteration.

The ash of highest purity, that is, with the greatest percentage of glass shards, is found in the western Oklahoma deposits, nearest the probable source. The greater impurity of the samples from central and eastern Oklahoma probably represents admixture of detrital material under local conditions of sedimentation.

In the samples of volcanic ash tested, purity and particle size have no consistent relation to initial bloating temperature (temperature at which cells $\frac{1}{4}$ mm in diameter first appear) in the production of pumicell. In general, however, the greater the percentage of clay-altered shards, the lower the initial bloating temperature.

CELLULAR PRODUCTS FROM OKLAHOMA
VOLCANIC ASH

CHEMICAL INVESTIGATIONS

by

A. L. BURWELL

INTRODUCTION

During the latter part of 1944 several new samples of volcanic ash were brought into the laboratory of the Oklahoma Geological Survey for examination and analysis. In the course of this work it was noted that when volcanic ash was subjected to temperatures in excess of those usually employed in determining loss on ignition the mass vitrified and expanded and that the expanded product on cooling possessed a cellular structure.

Because of this observation it was decided to undertake an investigation for the purpose of determining the susceptibility of representative samples from Oklahoma deposits to high-temperature treatment, the temperature or temperature range within which bloating or expansion takes place, the influence of time of heating, the effect of variation in composition, and the peculiarities of individual samples.

Acknowledgment is gratefully made of the encouragement and advice of Robert H. Dott, Director of the Oklahoma Geological Survey. W. E. Ham, Associate Geologist, has been of great help in matters involving petrography. A. C. Shead, Analytical Chemist, conducted many of the chemical analyses. To all, the author extends thanks.

INORGANIC CELLULAR AND POROUS MATERIALS

In order to clarify the subject it seems advisable to make certain observations in regard to differences in the meaning of words "cellular" and "porous." Porous structure is analogous to the sponge wherein the voids are connected. Cellular structure is analogous to foam wherein each void or cell is a separate unit and not connected to others. The two classifications are often used interchangeably, due probably to the common property of low bulk gravity (light weight), but they differ as regards transmission of heat and sound and as regards permeability to liquids and gases.

NATURAL MATERIALS

Natural occurrences of porous lightweight materials are fairly numerous. Some lightweight materials are thought to have been the result of the solvent action of circulating ground-water, as for example the conversion of chert and novaculite to tripoli and limy sandstone to porous sandstone. The lightweight material known as diatomaceous earth is the siliceous remains of the diatom after decomposition of organic matter. The light weight of travertine and the so-called sinters comes from the ingredients having been in solution in water and deposited unevenly, possibly with extraneous organic matter.

The occurrences of inorganic matter with a true cellular structure, however, are rare. The only large-scale occurrences in nature appear to be scoria and pumice, but even in these materials the percentage of interconnecting vesicles may be high, the cell wall more or less porous and pervious to liquids and gases. The physical condition of scoria and pumice has been explained as follows:

The lavas generally contain large amounts of gases when they are expelled from volcanoes. As they rise to the surface, the pressure on them is relieved and the gases expand. As a result the lavas often become porous and vesicular. On solidification

it makes froth-like rock, which is called pumice, or a rock with fewer and larger voids and called scoria.¹ Pumice is produced from acidic magma, whereas scoria is from basic magma.

ARTIFICIAL INORGANIC CELLULAR MATERIALS

Inorganic products with a more or less cellular structure have been made from clays, shales, slates, slags, volcanic glassy rock such as perlite, and from manufactured glass. The process has been described as "bloating", "expanding", and "popping" the designation depending upon the raw material and process used. In all instances the raw material is converted by means of heat into a plastic mass in which gas or vapor is generated by decomposition of inherent or added material, or is introduced from without the mass. If the raw material is not a glass, it is more or less converted into a glass phase in the course of the treatment it receives in the production of a cellular product. Therefore, these artificial inorganic cellular materials may be classified as glasses or as material in which the glass phase predominates.

The review of the literature may be separated for the sake of simplicity into three divisions based upon the raw material: (1) clays, shales, and slates, (2) volcanic glassy rock, and (3) manufactured glass.

Conversion of Clays, Shales, and Slates. The conditions under which clays and shales bloat successfully have been stated by Austin and others, as follows:

- (1) There must be a relatively large amount of glass phase formed.
- (2) There must be gas liberated within the mass while it is in a pyro-plastic condition. The thermal expansion of entrapped gas would not be sufficient to produce a vesicular structure.
- (3) The glass phase must be sufficiently viscous to maintain the vesicular structure.

Austin further states that the physical properties of the glass phase formed in burning clay affect the amount of bloating and the

¹ Emmons, W. H., Thiel, G. A., Stauffer, C. R., and Allison, I. S., "Geology: Principles and Processes": McGraw-Hill, pp. 311-12, 1929.

pore structure resulting therefrom. Glass phases of high viscosity tend to form smaller pores and allow a greater degree of bloating than those of low viscosity. A low viscosity will prevail if the clay contains relatively high percentages of lime and magnesia, but when lime and magnesia are low and the soda and potash are the principal fluxing agents a more viscous condition will be obtained, with smaller and more uniform pore structure in the product.² Conversely, high silica and high alumina are conducive to high viscosity.³ It is also interesting to note that Bigot makes the statement that "all kaolin and clays that swell above 1,000° C. contain free silica."⁴

Austin and his co-workers conclude that the gases responsible for the bloating of certain clays upon which they worked were water vapor and oxides of sulfur and carbon. They attribute the bloating primarily to sulfur whereas Conley thinks that graphitic carbon in the presence of ferric iron is responsible.⁵ In any event, the amount of gas needed to account for the pore space is extremely small, on the order of 0.06 to 0.08 percent of the weight of the product. The particle size of the clay influenced the temperature at which bloating occurred; the bloating was a function of the temperature and time; the rate of heating governed to a large extent the amount of any particular gas evolved, the amount varying inversely with the rate and directly with the air-flow over the material while heating; and a slightly reducing atmosphere was found preferable.⁶

Conversion of Volcanic glassy rocks. Gladney has devised a method for expanding consolidated volcanic ash, to which he assigns the name pumicite, and for further expanding pumice.⁸ Ralston has reviewed the literature on bloating or "popping" perlite, obsidian,

tuff, pumice, and other volcanic glassy rock and has come to the conclusion that "trapped moisture" is the agent responsible for the expansion.⁹ This is contrary to the findings of Hirito who made X-ray diffraction studies of Japanese material and concludes that water contained in glassy volcanic rock is not free but intimately bound in the molecular arrangement.¹⁰ Bigot contends that the swelling is due to volatilization of "mineral salts" which are released at the moment the material softens and vitrifies.¹¹ The translation as "mineral salts" probably might better have been "alkalies."

Manufactured glass. A product made from manufactured glass is known as foamglass. It has been defined as "cellular or foamy material consisting of a continuous network of walls which envelop completely isolated vesicles which may be filled with gases or vapor or may be partially or wholly evacuated".¹² Foamglass is cellular rather than porous, the cells are non-connecting, and the walls impervious to both water and vapor, "a property not available in any other known material except some organic cellular rubbers."¹³ Glassy materials with foamy structure have been produced by numerous methods, the majority of which fall conveniently into three groups: those produced from seedy glass, those produced from glass containing ingredients which generate gas while in the thermoplastic range, and those in which gas is introduced into the sintered or molten mass. Seedy glass when subjected to reduced pressure while at the proper temperature will expand into a lightweight foamy glass product. Glass that contains sulfur and carbon compounds, materials which oxidize readily to gaseous products, tends to become foamy when the glass is in the thermoplastic temperature range. Multivalent metal oxides such as iron, titanium, manganese, and chromium which may be constituents of glass, may dissociate at high temperatures and liberate oxygen. Such action would conform to the generalization that the lower valency com-

2. Austin, C. R., Nunes, J. L., and Sullivan, J. D., "Basic Factors Involved in Bloating Clays": discussed by J. E. Conley, *Trans. Am. Inst. Min. Eng.* Vol. 148, Industrial Minerals Division, p. 159, 1942.

3. Hodkin, E. A., and Cousen, A., "Text Book of Glass Technology": Constable & Co., 1925.

4. Bigot, A., "Action of Heat on Volume Variation of Clays, Kaolins and Bauxite": *Corriere Ceram.* Vol. 10, p. 349, 1929. Abstracted *Chem. Abst.* Vol. 25, pp. 3787-8.

5. Austin, C. R., Nunes, J. L., and Sullivan, J. D., "Basic Factors Involved in Bloating Clays": discussion by J. E. Conley: *Trans. Am. Inst. Min. Eng.* Vol. 148, Industrial Minerals Division, p. 160, 1942.

6. Sullivan, J. D., Austin, C. R., and Rogers, E. J., "Expanded Clay Products": *Trans. Am. Inst. Min. Eng.* Vol. 148, Industrial Minerals Division, pp. 139-148, 1942.

7. Moyer, Forrest T., "Lightweight Aggregate for Concrete": *U. S. Bur. Mines Inf. Cir.* 7195, 1942.

8. Gladney, Andrew, L., *U. S. Patent* 2,021,956, 1935.

9. Ralston, Oliver, C., "Perlite, Source of Synthetic Pumice": *U. S. Bur. Mines Inf. Cir.* 7364, 1946.

10. Hirito, Moriso, "X-ray Diffractions by Volcanic Glasses and Ashes": *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* Vol. 18, pp. 237-44, 1932. Abstracted *Chem. Abst.* Vol. 26, p. 5042.

11. Bigot, A., "Action of Heat on Volume Variation of Clays, Kaolins and Bauxite": *Corriere Ceram.* Vol. 10, p. 349, 1929. Abstracted *Chem. Abst.* Vol. 25, pp. 3787-8.

12. Kriedl, E. L., "Foamglass": *The Glass Industry*, Vol. 23, Nos. 7, 8, and 9, 1942.

13. Farquhar, Norman G., "Glass Cellulation Produces Lightweight Insulation": *Chem. Met. Eng.* Vol. 40, p. 98, Aug. 1943.

pounds of a multivalent element become increasingly more stable with increase in temperature. An illustration of the dissociation of an ordinarily stable oxide is the change of ferric oxide (Fe_2O_3) to magnetite (Fe_3O_4) with liberation of oxygen at $1,348^\circ\text{C}$. or thereabouts, under normal atmospheric oxygen pressure. The presence of impurities lowers the dissociation temperature. It should be noted, also, that the liberated oxygen is re-absorbed if the products are held in contact for some time at slightly lower temperature.¹⁴

TABLE I.

APPROXIMATE COMPOSITION RANGE OF THE THREE GENERAL TYPES OF RAW MATERIAL USED IN PRODUCING LIGHTWEIGHT CELLULAR AND POROUS CERAMIC PRODUCTS.

Oxide	Division 1. Clays, Shales, & Slates.	Division 2. Glassy Volcanic Rock.	Division 3. Soda-Lime Glass.
SiO_2	48 to 60	66 to 75	69 to 75
Al_2O_3	14 to 35	8 to 15	0 to 4
Fe_2O_3	1 to 7	1.5 to 3.8	0.1 to 2.5
CaO	0.1 to 7	0.3 to 2.7	5 to 14
MgO	0.3 to 1.5	tr to 0.9	0.5 to 4
$(\text{NaK})_2\text{O}$	1 to 4	5.7 to 9.1	13 to 17
Loss on Ign.	1 to 12	0.2 to 10.0	0

The introduction of gases into sintered or molten glass to produce a foamy product may be by blowing or by the addition of materials such as calcium carbonate and carbon black which yield gas under conditions encountered in the process. The existence of certain conditions is basically necessary in any method. During the production of gas within the mass or the introduction of gas into the mass, the mass must be sufficiently fluid to completely envelop the cells but not so fluid as to allow bubbles to rise to the surface, and the viscosity must be high enough to withstand the pressure from within the bubbles.

NATURE OF GLASS AND GLASSY MATERIAL

A recapitulation of the information on the three raw material divisions: clays, shales, and slates; volcanic glassy rocks; and manufactured glass, brings out the fact that irrespective of the raw material the bloated product is a glass or contains a large portion of glass. The composition range for the three divisions is given in Table I. from which the composition of the glass may be calculated

14. Ralston, Oliver C., "Iron Oxide Reduction Equilibrium": *U. S. Bur. Mines Bull.* 296, 1929.

approximately. The word glass as here used may be defined as a suitable mixture of oxides in mutual solution that was cooled so rapidly as to prevent crystallized-mineral formation. Such a mixture has the appearance and other properties commonly associated with the words glass and glassy. Because the products are glass or glassy we quote Hodkin and Cousen on the effect of composition of glass upon the viscosity and softening temperature:¹⁵

We possess little systematic knowledge of the effect of the individual glass-forming oxides upon the viscosity of glass, most of the data at present known being of the nature of qualitative comparisons. Feild using a modification of Margules' method, has determined the actual viscosity of blast furnace slags, which, whilst not resembling simple glasses, yet are composed of some of the oxides most commonly in glass—namely, silica, lime, alumina, and magnesia—and his results have given an invaluable indication of the effect of the oxides in question.

Silica: Other things being equal, increase of silica results in an increase in viscosity in all types of glass. The intensity of its effect depends upon the relative amounts of the other constituents of the batch. Generally speaking, highly siliceous glasses have a long viscosity range.

Lime: If lime is substituted for soda in batches, the silica being maintained constant, the viscosity of the glass produced increased with increase of lime content. Similarly, an increase in the rate of setting occurs. When however, the proportion of lime is increased relatively to those of silica and soda, beyond a certain limit a rapid decrease of viscosity takes place Increase of lime tends invariably to increase the rate of setting. It may be said that soda-lime glasses with a proportion of lime up to about 10 to 20 percent are quite viscous at temperatures below $1,300^\circ$, but are exceedingly fluid above $1,350^\circ$.

Boric acid: This substance causes a pronounced reduction of viscosity.

Sodium oxide: Addition of sodium oxide causes a reduction of viscosity, and produces a long viscosity range.

Potassium oxide: Potassium oxide is similar to sodium oxide in its action, but is less effective, weight for weight. An equimolecular mixture of soda and potash gives viscosity phenomena intermediate between those of the two oxides alone.

Alumina: Increase of alumina generally increases the viscosity of the glass more rapidly than increase of silica, but it also

15. Hodkin, E. A., and Cousen, A., "Text Book of Glass Technology": *Constable & Co.*, 1925.

increases the viscosity range. Small amounts of alumina added to a viscous lime-containing glass cause, however, a reduction of viscosity.

Magnesia: This oxide is somewhat similar in effect to lime, though in amounts up to 9 or 10 percent, it does not increase the viscosity to the same extent, whilst beyond this point no decrease in viscosity is obtained as in the case of lime. High magnesia glasses become cordy, ragged and stringy and appear to be very viscous on account of this. In general, it may be said that magnesia glasses do not become so fluid at high temperatures as lime glasses, whilst they set less quickly since they have a longer viscosity range. A small amount of magnesia added to a viscous lime glass causes a very pronounced reduction in viscosity.

Softening temperature: Although no definite melting point is obtained for glass, the range over which particular glasses soften is well defined. The following oxides lower the softening temperature: boric oxide, phosphoric oxide, lead oxide, baryta, soda, potash, iron oxide, and manganese oxide. On the other hand, the tendency of silica, lime, and magnesia is to give, in general, a higher softening point.

EXPERIMENTS WITH OKLAHOMA VOLCANIC ASH

Definition of Volcanic Ash. The term, volcanic ash is a source of much confusion due to the differences in the several definitions. To some persons anything that is ejected from an explosive-type volcano that falls to earth as solid matter is volcanic ash. To others only the finest air-born dust is volcanic ash. The fact that volcanic ash is sometimes called pumicite complicates the subject further. Quotations from several textbooks written by recognized authorities will serve to illustrate the need for clarification. Ladoo¹⁶ states:

Pumice is a highly vesicular or cellular, glassy volcanic lava, usually rhyolitic in composition. Its cellular structure is due to the expansion, during cooling, of steam and gases contained in the molten lava.

Pumicite, or volcanic ash, is a more or less finely divided powder or dust made up of small, sharp, angular grains of volcanic glass of about the same composition as pumice. It is formed by the violent and explosive eruption of volcanoes, which throw out the dust in great clouds. Ultimately, the dust settles, often many hundreds or thousands of miles from its original source, and forms beds of pumicite.

In discussing the eruption of volcanoes, Johannsen¹⁷ says:

If this is quiet, the lava flows out as a stream or sheet; if it is explosive, on account of included gases, the material is blown out in fragmental or dustlike form. The material from these explosive eruptions may be derived from the solid volcanic material filling the vent, or it may be produced from the blowing into fragments of the still liquid material. The coarser blocks . . . are called *bombs*. . . . smaller fragments are known as *lapilli*, while the finest material is called *volcanic sand*, "*ashes*," or *dust*.

Pirsson and Schuchert¹⁸ use the term volcanic ashes in a different sense as shown in their discussion of fragmental products from volcanoes:

These are the volcanic projectiles, the material blown into the air by the sudden liberation of gases. They may be derived from the crust, or plug, of hardened lava left in the upper part

16. Ladoo, Raymond B., "Non-Metallic Minerals": McGraw-Hill, p. 455, 1925.

17. Johannsen, Albert, "Petrography of Igneous Rocks, Vol. 1": Univ. Chicago Press, p. 7, 1929.

18. Pirsson, Louis V., and Schuchert, Charles, "A Textbook of Geology": John Wiley & Son, 3rd. Edit., p. 247, 1929.

of the conduit after a previous eruption, from rock material torn from its walls, or from lava ejected from the upper part of the liquid column by the violent escape of gases from the magma. Although the lava may start on its aerial flight in a liquid condition, it generally hardens in its passage and falls in solid form. The pieces of rock and the particles of magma driven upward and solidified are of all dimensions: from dust so fine it may float in the atmosphere for several years, to large masses of several tons in weight. According to size, they are roughly classified as follows: pieces the size of an apple, or larger, are called *blocks* if ejected as solid fragments and *bombs* if ejected as particles of still-fluid magma; those the size of a nut are termed *lapilli* (meaning little stones); those the size of a pea are volcanic *ashes*, while the finest is volcanic dust. The ashes and lapilli are frequently spoken of as *volcanic cinders*, and the cones made of them as cinder cones.

Apparently, Grout¹⁹ holds a similar conception as indicated by his statement: "Volcanic dust (and possibly ash up to the size of a pea) when cemented form tuffs."

The so-called volcanic ash of Oklahoma conforms very well to Ladoo's definition, but we concur with Johannsen when he defines volcanic ash as "The finest material blown out by volcanic explosions. *Volcanic dust* is a better term."²⁰ The Oklahoma deposits are generally grey in color, unconsolidated, finely divided material in beds of varying thickness. More or less extraneous matter has been picked up during air transport, during secondary transport by air or water, and during and after deposition. Alteration in various degrees commonly has taken place.

It is generally accepted that volcanic ash and pumice are derived from acidic or intermediate magma the viscous properties of which are conducive of explosive eruptions. This is in contrast to the basic magma which being less viscous and more fluid exudes rather than erupts, yielding rock of the basalt type. Naturally, the violently ejected material is more quickly subjected to atmospheric cooling, and because of rapid cooling the different elements contained in the magma do not have the opportunity to group themselves into molecules that form definite minerals but rather are present as oxides in mutual solution, the product being vitreous or glassy.

MATERIALS INVESTIGATED

For the purpose of this investigation thirteen samples of volcanic ash were selected as representing the several types and classes found in Oklahoma. Included also was a single sample of volcanic tuff from McCurtain County because of similarity of origin and composition. Also, two samples of bentonitic clay were included because such material is recognized as an alteration product of volcanic ash. Chemical analyses made in the laboratory of the Oklahoma Geological Survey during this investigation by A. C. Shead and A. L. Burwell, and several other analyses of volcanic ash from the records of the Oklahoma Geological Survey for the purposes of comparison, are given in Table II. In addition, analyses are given on three clays which were used by Austin, Nunes, and Sullivan in their report on the basic factors involved in the bloating of clay.²¹

19. Grout, Frank F., "Petrography and Petrology": McGraw-Hill, p. 116, 1932.

20. Johannsen, Albert, *op. cit.*, p. 242, 1939.

21. Austin, C. R., Nunes, J. L., and Sullivan, J. D., "Basic Factors Involved in Bloating Clays": discussed by J. E. Conley, *Trans. Am. Inst. Min. Eng.* Vol. 148, Industrial Minerals Division, 1942.

TABLE II.
ANALYSES OF OKLAHOMA VOLCANIC ASH AND CERTAIN CLAYS FOR COMPARISON

Sample No.	County	Sec. T. R.	Lab. No.	SiO ₂	R ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LOI @ 1,000°C	H ₂ O @ 105°C	S	TiO ₂	Notes
1 ^b	Beaver	8 5N 28ECM	4698	72.65	14.39	12.47	1.82	1.78	0.53	—	—	4.76	0.72	0.01	—	Volcanic ash
2 ^b	Blaine	4 18N 12W	4670	67.99	17.46	16.70	1.77	0.62	0.27	—	—	6.96	1.56	0.01	—	Volcanic ash, bentonitic clay
3 ^a	Garvin	20 4N 3E	4813	76.05	13.30	10.54	2.76	0.61	0.41	3.35	2.04	4.40	1.29	—	—	Volcanic ash, some clay
4 ^a	Haskell	17 9N 21E	1660	72.11	14.58	12.19	2.39	0.68	0.38	4.07	2.55	5.85	1.30	—	—	Volcanic ash, clay and sand
5 ^a	Haskell	17 9N 21E	1665	69.65	16.13	13.13	3.00	0.71	0.47	3.25	2.28	7.58	2.16	0.01	—	Volcanic ash with clay
6 ^a	Hughes	4 9N 12E	4326	72.06	14.42	12.41	2.01	0.78	0.35	3.98	2.41	6.01	0.89	—	—	Volcanic ash
7 ^a	Hughes	4 9N 12E	4327	73.69	13.64	11.43	2.21	0.74	0.32	3.52	2.41	5.90	0.96	—	—	Volcanic ash
8 ^b	Kiowa	28 6N 18W	9571	72.03	15.05	11.53	2.52	1.74	0.27	—	—	4.89	0.24	0.01	—	Volcanic ash
9 ^b	McCurtain	21 5S 22E	9591	75.72	16.42	14.00	2.42	0.91	0.56	—	—	1.74	0.16	—	—	Volcanic tuff
10 ^a	Oktuskee	19 10N 10E	6860	72.74	13.47	11.55	1.92	0.64	0.17	4.84	2.93	5.46	0.81	0.01	—	Volcanic ash
11 ^a	Oktuskee	19 10N 10E	6861	73.16	14.05	12.25	1.80	0.68	0.23	4.89	2.57	5.27	0.89	0.01	—	Volcanic ash
12 ^b	Wagoner	20 16N 18E	3245	73.58	14.37	13.22	1.15	1.35	0.21	—	—	3.60	0.29	—	—	Volcanic ash
13 ^b	Wagoner	19 16N 18E	9592	72.55	15.73	14.01	1.72	1.14	0.37	—	—	4.22	0.47	0.01	—	Volcanic ash
14 ^b	Woodward	13 23N 22W	9425	66.64	15.00	13.34	1.66	1.93	1.35	—	—	11.23	4.18	0.01	—	Volcanic ash, bentonitic clay
15 ^b	Woodward	13 23N 22W	9426	50.83	18.49	15.93	2.56	3.23	4.32	—	—	24.08	15.63	—	—	Bentonitic clay
16 ^b	Dewey	21 19N 19W	9430	56.42	16.36	14.48	1.88	2.58	3.79	—	—	20.73	13.14	—	—	Bentonitic clay
	Beaver ^a	8 5N 28ECM		72.96	14.65	12.91	1.60	0.37	tr	4.40	2.96	4.33	0.41	—	—	0.14
	Blaine ^a	4 18N 12W		70.44	16.12	—	—	0.58	—	—	—	6.17	—	—	—	—
	Custer ^a	15 14N 16W		70.12	15.80	—	—	0.53	0.23	3.20	4.42	6.43	—	—	—	—
	Harpers ^a	10 28N 26W		72.50	13.70	12.08	1.50	1.08	nll	5.67	2.91	3.75	0.62	—	—	0.12
	Woods ^a	—		79.52	11.56	—	—	1.08	—	total alkali	3.06	—	—	—	—	—
Clay A ^d				60.0	—	18.0	7.1	0.5	2.0	—	3.1	7.3	0.6	0.22	—	—
Clay B ^d				58.6	—	16.3	5.6	5.1	2.0	—	2.3	8.0	0.4	0.16	—	—
Clay C ^d				58.0	—	18.6	5.7	0.8	1.4	—	4.8	6.1	1.4	0.3	—	—

^a analysis by A. C. Sheard. ^b analysis by A. L. Burwell. ^c analyses from O.G.S. records. ^d clays used by Austin, Nunes, and Sullit

SUSCEPTIBILITY OF OKLAHOMA VOLCANIC ASH TO BLOATING SMALL-SCALE EXPERIMENTATION

Laboratory Procedure. Samples were air dried and put through a 40 mesh sieve to remove extraneous matter. The bulk density of each sample was determined approximately by weighing a measured volume of the loose powder. Eight grams of a sample were placed in a Coors low-form porcelain crucible and shaken lightly to level the contents. The crucible with contents was placed in a cold furnace and the temperature brought up to 1,090° C. over a period of 4 hours and held at this temperature for an additional 2 hours. The crucible with contents was then transferred to a small platinum-heating-element electric furnace maintained at a specified higher temperature, where it was held for a definite length of time, then removed and allowed to cool under atmospheric conditions. Sixteen samples were investigated in this manner. The time of exposure to the higher temperature was 15 minutes for one series, and 1 hour for a second series.

The effect of the treatment—the degree of expansion and development of cellular structure—is shown in Plates I-V, inclusive. The photographs give a direct comparison between the original volcanic ash in the crucible, the material after bloating at 1,090° C., and after being subjected to bloating temperatures of 1,200°, 1,250°, 1,300°, and 1,350° C. for 15 minutes. Plate VI compares specimens bloated at 1,200°, 1,350°, and 1,300° C. for 15 minutes with specimens of identical material bloated at the same temperatures for 1 hour. The crucibles were embedded in plaster of paris and cut with a diamond saw.

EFFECTS OF TIME AND TEMPERATURE ON BLOATING

It may be said that in general as the temperature is raised the volcanic ash sinters, shrinks, and vitrifies with the color changing from gray to brick red of one shade or another, then with further rise the color becomes drab gray which is followed by gradual expansion of the mass as it becomes plastic. The initial bloating occurs on all samples within the temperature range of 1,175° to 1,225° C., a total difference of only 50° C. As the temperature is increased the amount of glass phase increases and the expansion

becomes more pronounced. In more than half the samples a heavy viscous condition existed at the top temperature of these tests ($1,350^{\circ}\text{C}$). A lower viscosity allows an increase in cell size up to the point where the viscosity is insufficient to withstand the pressure within the cells and where the cell walls collapse. Only the bentonitic clays became so fluid as to permit escape of the gases which produced the bloat, and this situation is evident in samples containing appreciable bentonitic clay. These samples also show more rapid progress in bloating but not necessarily an earlier initial bloating temperature, because the shrinking and vitrification of the clay requires a higher temperature than the volcanic ash. As a result the most apparent effect of the presence of bentonitic clay is to shorten the bloating range. A sample of volcanic tuff reacted similarly to impure volcanic ash.

The length of time that the sample is exposed to the bloating temperature of $1,200^{\circ}\text{C}$. appears to have had little influence on the degree of expansion. The influence of increase of time from 15 minutes to 1 hour at $1,250^{\circ}$ and $1,300^{\circ}\text{C}$. is evident in the photographs, which indicate that 15 minutes at $1,300^{\circ}\text{C}$. is equivalent approximately to 1 hour at $1,250^{\circ}\text{C}$. It is noted, however, that there are differences among the samples in their reaction to extension of the time of heating. Also, from these and other experiments it appears, in some cases at least, that prolonged heating at temperatures which lower the viscosity of the mass has a tendency to cause coalescence or merging of the voids or cells with the creation of larger ones having heavier walls. Of course, if the viscosity is lowered to the point where the gases escape the product no longer will qualify as cellular. Table III is a tabulation of the results of these experiments.

CHEMICAL COMPOSITION AND BLOATING PROPERTIES

The calculated composition of the solid material of the products, based upon the analyses of the raw material from which they were made, are shown in Table IV.

It is evident that in order for a volcanic ash to qualify as potential raw material for the production of cellular ceramic products it must conform to certain limits in composition. These limits can not be established without comprehensive study and experimental-

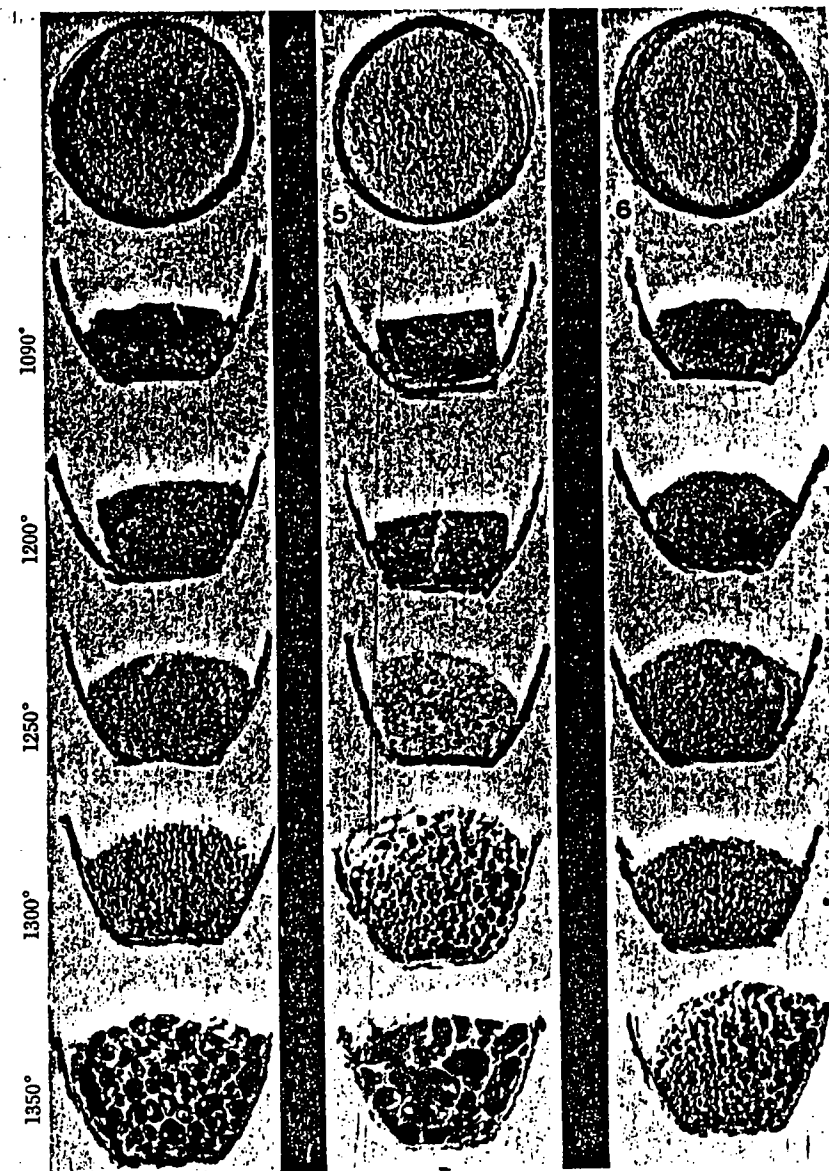


PLATE II. Expansion of volcanic ash and development of cellular structure after igniting at $1,090^{\circ}\text{C}$., and after being subjected to bloating temperatures of $1,200^{\circ}$, $1,250^{\circ}$, $1,300^{\circ}$, and $1,350^{\circ}\text{C}$. for 15 minutes. Samples 4-6.

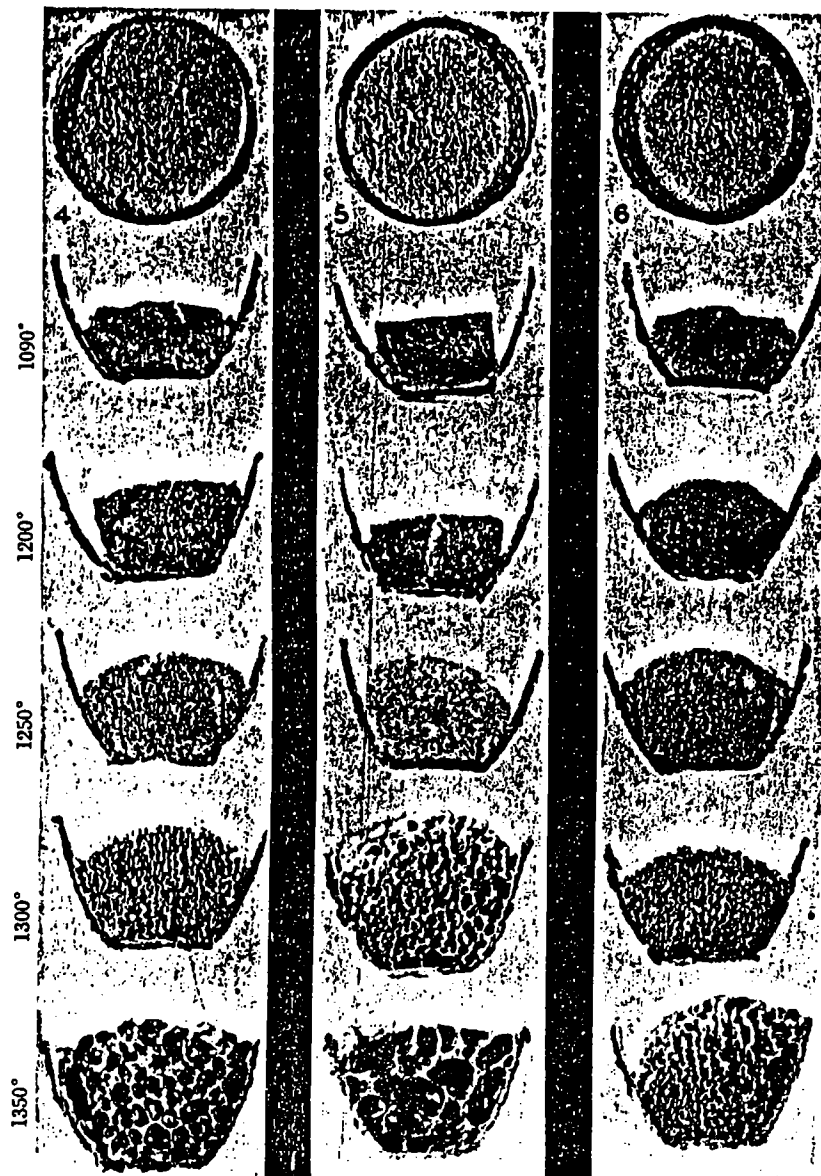


PLATE II. Expansion of volcanic ash and development of cellular structure after igniting at 1,090° C., and after being subjected to bloating temperatures of 1,200°, 1,250°, 1,300°, and 1,350° C. for 15 minutes. Samples 4-6.

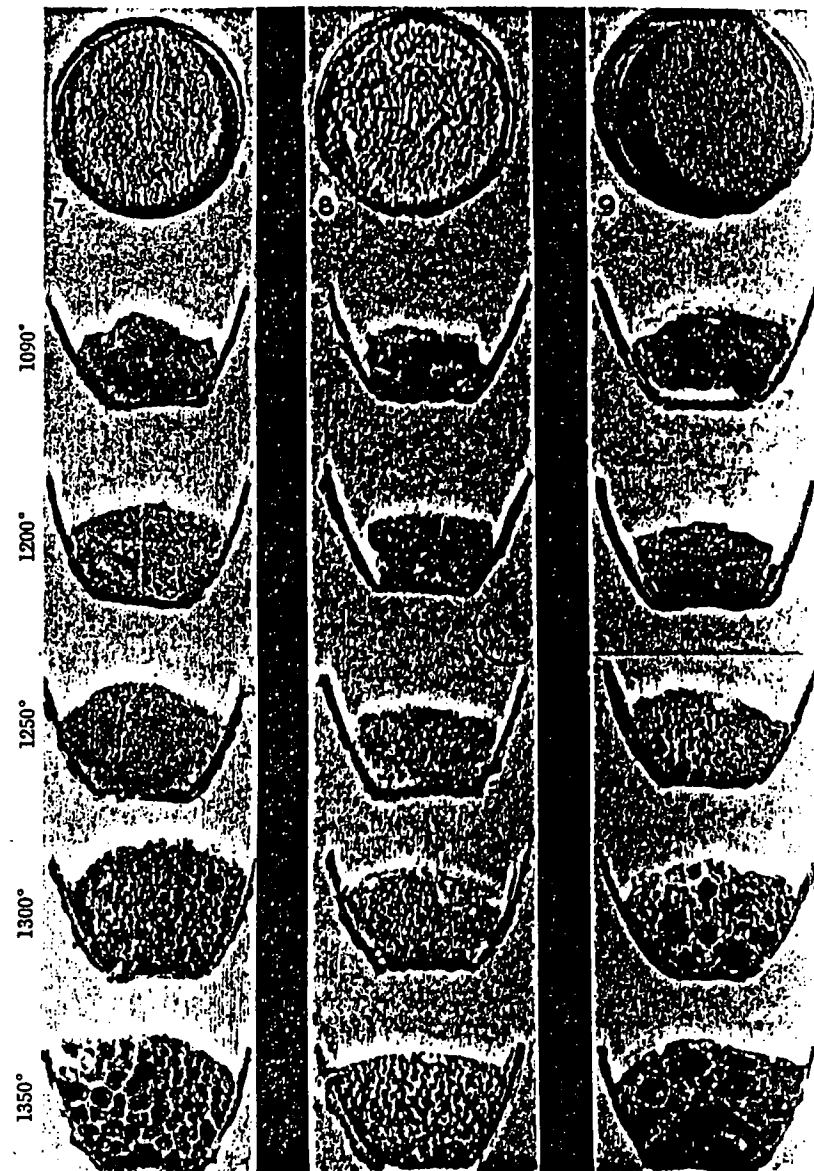


PLATE III. Expansion of volcanic ash and development of cellular structure after igniting at 1,090° C., and after being subjected to bloating temperatures at 1,200°, 1,250°, 1,300°, and 1,350° C. for 15 minutes. Samples 7-9.

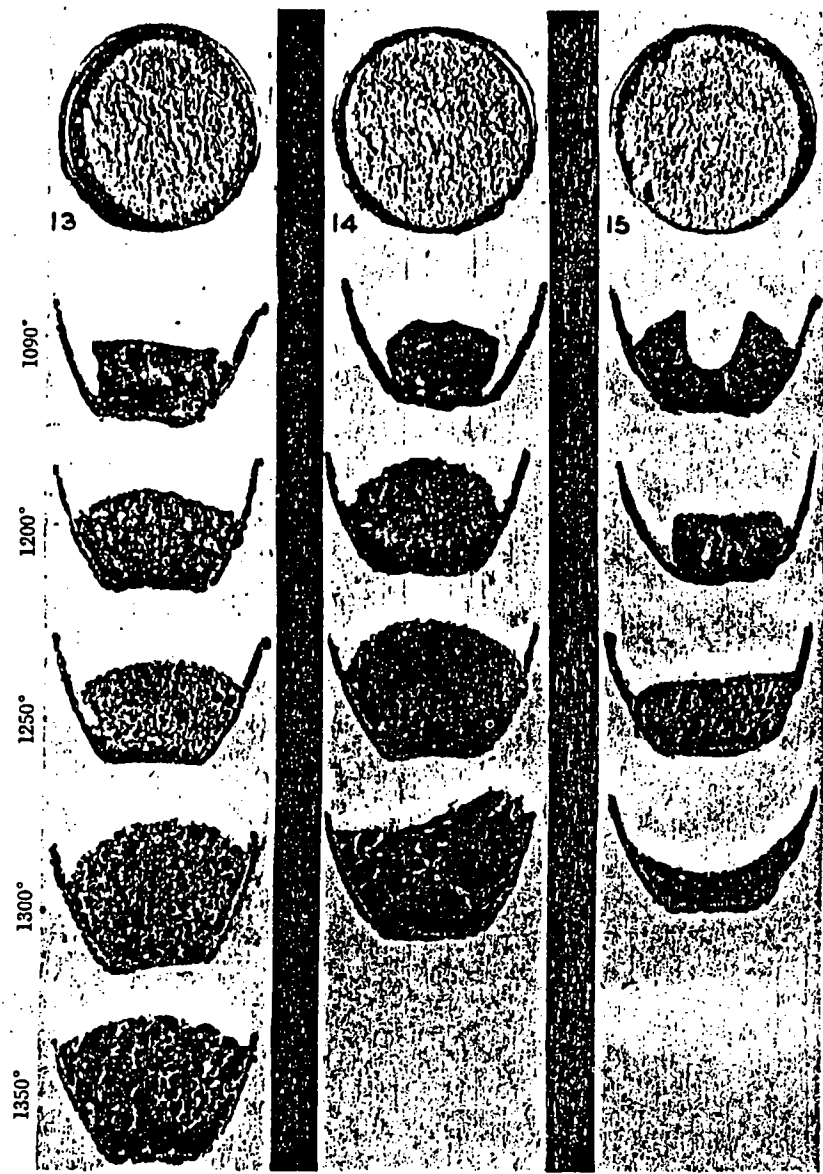


PLATE V. Expansion of volcanic ash and development of cellular structure after igniting at 1,090° C., and after being subjected to bloating temperatures at 1,200°, 1,250°, 1,300°, and 1,350° C. for 15 minutes. Samples 13-15.

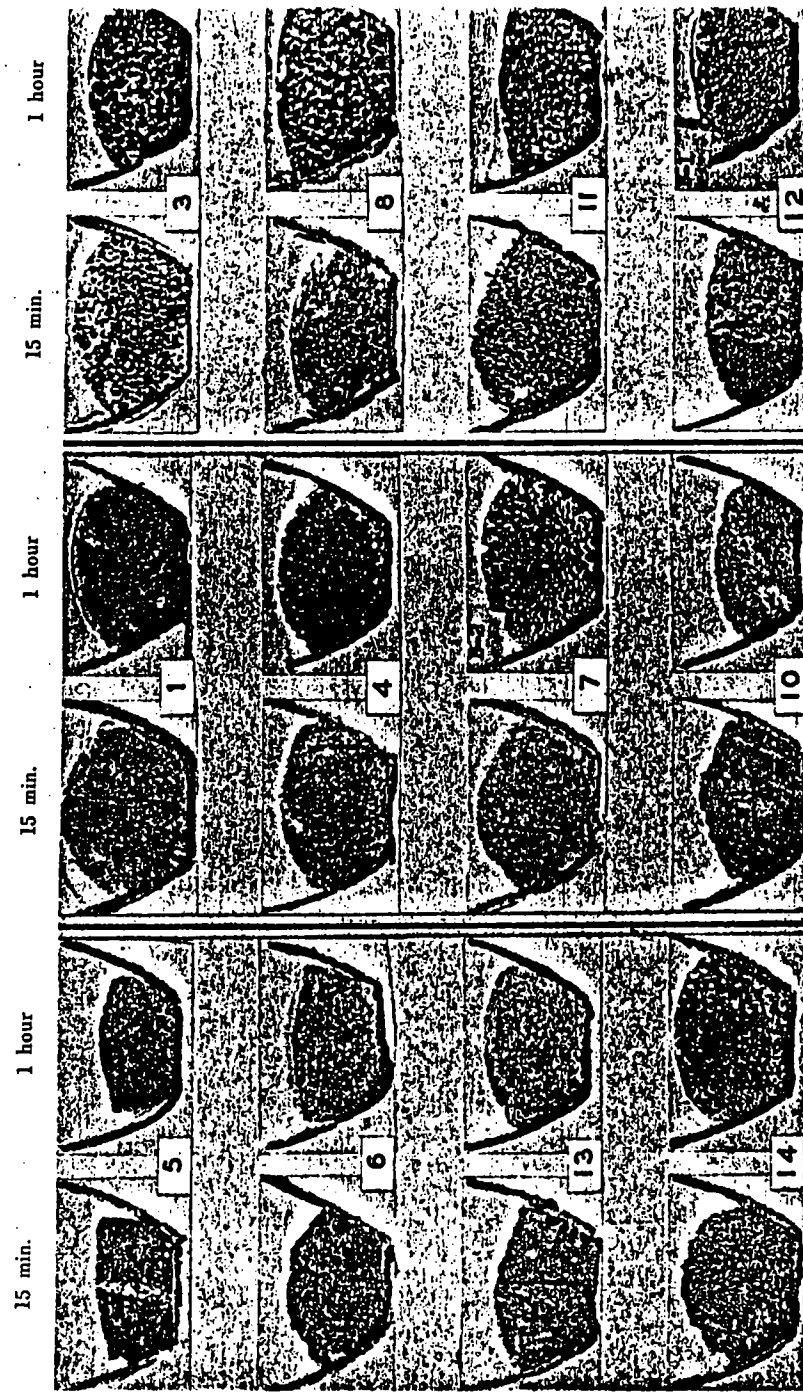


PLATE VI. Effects of temperature and time. Comparison of cell structure of specimens bloated at 1,200°, 1,250°, 1,300°, and 1,350° C. for 15 minutes, with identical material bloated at the same temperatures for 1 hour.

TABLE III
SUSCEPTIBILITY OF OKLAHOMA VOLCANIC ASH TO BLOATING
TABULATION OF EXPERIMENTAL RESULTS

Sample Number	1	2	3	4
County	BEAVER	BLAINE	GARVIN	HASKELL
Laboratory Number	4698-4679	5428	4913	1669
Bulk sp. gr.	0.6	0.6	0.5	0.5
Color	cream white	smoky gray	cinnamon	pale olive buff
After ign. at 1,090°C for 2 hrs.				
apparent sp.gr.	2.0	1.1	1.2	1.4
color	brick red	orange red	brick red	brick red
condition	vitreous	fine sinter	fine sinter	vitreous
Followed by 15 min. at 1,200°C				
apparent sp.gr.	1.4	2.1	1.7	1.1
color	light gray	gray	gray	reddish gray
condition	vitreous	vitreous	vitreous	v. sl. cell.
or				
Followed by 15 min. at 1,250°C				
apparent sp.gr.	y 1.1	1.7	1.3	y 0.9
color	light gray	light gray	light gray	light gray
condition	v. sm. cells	v. sm. cells	¼-½ mm. cells	¼ mm. cells
or				
Followed by 15 min. at 1,300°C				
apparent sp.gr.	0.6	0.6	0.8	0.7
color	light gray	gray, glassy	light gray	light gray, glassy
condition	sm. cells	½ mm. cells	1 mm. cells	1 mm. cells
or				
Followed by 15 min. at 1,350°C				
apparent sp.gr.	<0.6	<0.6	0.7	<0.6
color	light gray	gray, glassy	gray, glassy	gray, glassy
condition	1 mm. cells	3-4 mm. cells	2-3 mm. cells	3-5 mm. cells
or				
Followed by 1 hr. at 1,200°C				
apparent sp.gr.
color				
condition				
or				
Followed by 1 hr. at 1,250°C				
apparent sp.gr.	y 0.7	y 0.8
color	gray			gray
condition	sm. cells			½ mm. cells
or				
Followed by 1 hr. at 1,300°C				
apparent sp.gr.	z 0.8
color			gray, glassy	
condition			3-7 mm. cells	

References: 1 Volcanic tuff
2 Metabentonite
Series x; effect of time at 1,200°C
Series y; effect of time at 1,250°C
Series z; effect of time at 1,300°C
sm. cells—small cells
v. sm. cells—very small cells
v. sl. cell.—very slightly cellular
by. walls—heavy walls

TABLE IV
COMPOSITION OF CELLULAR PRODUCTS FROM OKLAHOMA VOLCANIC ASH
CALCULATED FROM ANALYSES OF RAW MATERIALS AND IGNITION LOSS AT 1,090°C.

Sample No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	(K ₂ O.Na ₂ O)	Remarks re. product
1	76.28	13.09	1.91	1.87	0.56	6.29	small uniform cells
2	73.08	16.89	1.90	0.67	0.29	7.19	uniform cells above 1,300°C, very little expansion below
3	79.42	11.01	2.88	0.64	0.43	5.63	uniform cells above 1,200°C, no expansion below
4	76.41	12.92	2.53	0.72	0.40	7.01	viscosity probably too low above 1,350°C
5	75.32	14.20	3.24	0.77	0.51	5.98	viscosity rather low at 1,350°C
6	76.66	13.20	2.14	0.83	0.37	6.80	uniform cells
7	78.13	12.15	2.34	0.78	0.34	6.29	viscosity probably too low above 1,350°C
8	75.73	12.12	2.65	1.83	0.28	7.38	small uniform cells
9	77.06	14.25	2.46	0.93	0.57	4.73	irregular cell size above 1,250°C
10	76.74	12.18	2.03	0.96	0.59	8.20	small uniform cells
11	76.54	12.82	1.88	0.71	0.24	7.80	little expansion at 1,250°C, uniform cells above
12	76.33	13.71	1.19	1.40	0.22	7.15	no expansion at 1,200°C, small uniform cells above
13	75.75	14.63	1.80	1.19	0.39	6.36	uniform cells; low viscosity at 1,350°C
14	75.07	15.03	1.87	2.17	1.52	5.46	uniform at 1,200 and 1,250°C; viscosity too low above
15	66.12	20.72	3.33	4.21	5.62	0.00	fluid at 1,300°C; not suitable material
16	71.17	18.27	2.37	3.25	4.78	0.15	fluid at 1,300°C; not suitable material
A	64.72	19.42	7.66	0.54	2.16	3.34	"satisfactory product"
B	63.70	17.72	6.00	5.54	2.17	2.50	"unsatisfactory product"
C	61.77	19.81	6.07	0.85	1.49	5.11	"satisfactory product"

* Austin, C. R., Nunes, J. L., and Sullivan, J. D., *op. cit.*

tion. However, from the work done it appears that the ratio of silica to alumina and to alkali and alkaline earth fluxing agents is of primary importance. The samples with relatively low alkaline earth and relatively high alkali content yield satisfactory bloated products whereas samples with reverse alkaline earth-alkali ratio did not. The effect of variation in iron content is not apparent from these experiments.

Cause of bloating. The source and cause of the production of gas and vapor which brings about the bloating of volcanic ash has not been determined but is worthy of some speculation. It does not appear that oxides of carbon or sulfur are responsible as Austin and Conley contend is the case with clays, shales, and slates, because the means for their generation are not present in more than trace amounts. It is improbable that either combined or trapped water—that is water in solution in the mineral—can supply sufficient vapor, even if present in the original volcanic ash, after the prolonged ignition to which the material is subjected before exposure to the bloating temperature. However, water in solution in some minerals is difficult to remove entirely and as much as 0.02 and 0.03 percent may remain in some cases after prolonged ignition at 1,400° C. Probably such retention is exceptional. Nevertheless, Ralston, Wilson, and others²² contend that trapped water is essential to the bloating of perlite, obsidian, pumice, and other volcanic glasses and that the higher the “loss on ignition” as determined by analysis the better the bloating (popping) properties of the material. Obviously, the “popping” of perlite where the material is subjected suddenly to high temperature is distinctly different from the process we have used in testing volcanic ash and also different from the procedure of Austin and others^{23 24} in bloating clays and shales.

Analysis of gases coming off during the bloating would not give positive proof of what the bloating agent is because the gases that actually cause the bloat are retained within the cells and do not pass off. The presence of sulfur dioxide in the cells of some

22. Ralston, Oliver C., “Perlite, Source of Synthetic Pumice”: *U. S. Bur. Mines Inf. Cir.* 7364, 1946.

23. Austin, C. R., Nunes, J. L., and Sullivan, J. D., “Basic Factors Involved in Bloating Clays”: discussed by J. E. Conley, *Trans. Am. Inst. Min. Eng. Vol. 148, Industrial Minerals Division*, 1942.

24. Sullivan, J. D., Austin, C. R., and Rogers, E. J., “Expanded Clay Products” *Trans. Am. Inst. Min. Eng. Vol. 148, Industrial Minerals Division*, 1942.

bloated clay, and also in some cellular glass, can readily be detected by breaking a specimen. Sulfur was not found in the volcanic ash used in these experiments.

It has been suggested that oxygen liberated during dissociation of ferric oxide causes the bloat, but this would be difficult or impossible to prove directly by analysis of the gas, for it is quite possible that the liberated oxygen, if any, has been re-absorbed. There is considerable merit in the idea, however. First, there is the change in color from brick red to drab gray, suggesting change from ferric to ferrous iron. Second, there are numerous references in the literature on glass and other ceramics that indicate the hypothesis is entirely reasonable. Kinnison studied the temperature at which reduction takes place, using a mixture of kaolin, silica, and ferric oxide. As reported by Ries,²⁵ Kinnison states that “. . . the smaller the $Al_2O_3:SiO_2$ ratio the lower the temperature of formation of ferrous silicates. . .” and “. . . in mixtures with large amounts of fluxes, the reduction is associated with solution, and the dissociation temperature is about 1,210-20° C.” These data are pertinent to volcanic ash, for the analyses show the presence of a considerable percent of fluxing material in the form of alkali, alkaline earth, and iron oxide; also, bloating commenced in the 1,200° to 1,250° range. Nevertheless, positive proof of what gas causes the bloating and its source is lacking.

The experimental results do indicate that there are certain conditions necessary for the production of a satisfactory cellular product from volcanic ash. These conditions may be summarized as follows: the volcanic ash must be of such composition (1) that gas, gases, or vapor will be generated from and within itself when heated to temperatures that cause the mass to be thermoplastic, and (2) that the mass will be sufficiently viscous while in the thermoplastic stage that it will hold the gas, gases, or vapor in non-connecting voids, and on cooling the mass will retain the form and cellular structure caused by the expanded gas during the thermoplastic stage. It is also apparent from the experiments that these products from volcanic ash resemble foamglass more than those products from clay or shale, or those known as “popped” perlite.

25. Ries, Heinrich, *Clays, their occurrences, properties, and uses*. John Wiley & Sons, p. 123, 1927.

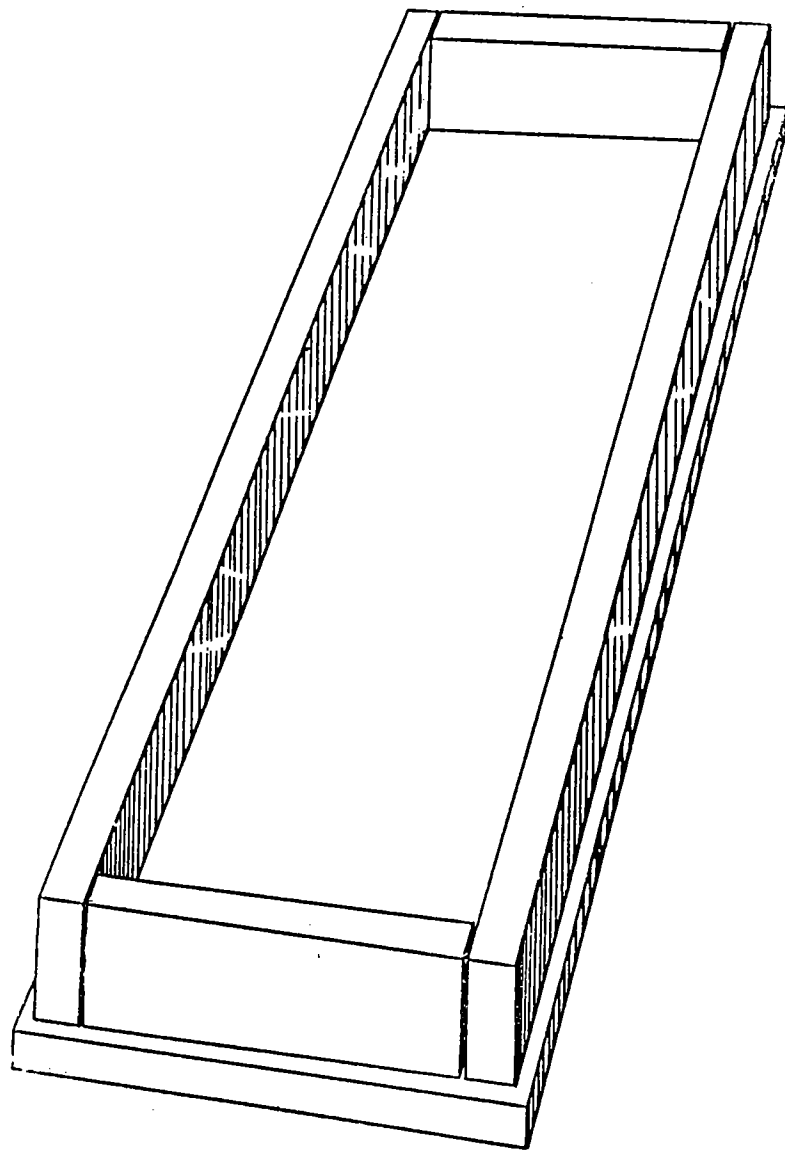


FIGURE 1. Mold used for larger-scale experiments, made of refractory slabs $\frac{3}{4}$ inch thick, with base 8 by 18 inches, and with sides and ends of several heights ranging from $\frac{3}{4}$ inch to 3 inches. Molds were moistened and dusted with a "parting compound" consisting of silica dust and fire clay, filled with volcanic ash, and placed in a Glo-bar furnace.

LARGER-SCALE BLOATING

In order to obtain a better idea of the bloating properties of Oklahoma volcanic ash and to obtain products suitable for testing, series of experiments were carried out in a Glo-bar electric furnace which has a hearth area 9 inches wide by 19 inches deep. It will accommodate a refractory mold with a base 18 by 8 inches. The molds were made up of separate parts to serve as base, sides, and ends, and were cast from Hi-Cast #30 (Denver Fire Clay Co.). All parts were $\frac{3}{4}$ inch in thickness. The side pieces were 18 inches and the end pieces 6 inches in length and were of several heights: $\frac{3}{4}$, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, and 3 inches. Prior to use the mold parts were moistened and dusted with a "parting compound" composed of silica dust and fire clay, and then assembled, using cotton twine to hold the parts in place. Figure 1 is a sketch of the assembled mold. The mold thus prepared was filled with volcanic ash and placed in the furnace. Small pieces of refractory "furniture" were used to prevent the sides and ends from being dislodged during the processing.

The furnace temperature was raised to $1,090^{\circ}$ C. at the rate of 275° per hour, this rate having been shown by preliminary tests to yield satisfactory but not necessarily the best results. It was used because it enabled a test to be completed in a 24 hour period. A small amount of air was admitted to the furnace during the heating to assure oxidizing conditions. After reaching $1,090^{\circ}$ the temperature was maintained for 2 hours and then raised at the rate of 275° per hour to that desired for bloating. Bloating temperatures of $1,250$, $1,300$, $1,325$, $1,350$, and $1,375^{\circ}$ C. were employed. The time of exposure to the bloating temperature was varied, using 15 minutes, 30 minutes, 1 hour, and 2 hours durations. At the end of the bloating period the heat was shut off and the furnace and contents allowed to cool, opening the several port-holes to hasten the process. If the test was started at 8 a.m. the temperature had fallen to about 300° by the same hour the following morning. The mold and contents were then removed. In order to prevent too rapid fall to room temperature, which might have caused cracking or checking, the mold and contents were covered until cool enough to handle.

The products obtained were of various shades of drab gray, and the upper surface glassy and relatively smooth. The sides and ends were somewhat rough and coated more or less with the "parting compound." The cell size increased with temperature but the cell size at any one temperature was not the same for all samples of ash. Volcanic ash from the western and northwestern districts of the state gave products with cell size relatively smaller than cells in pieces made from volcanic ash from other districts.

When the sides and end pieces of the mold were over 2 inches in height the product generally showed a tendency for the top-center to fall or collapse, especially when the higher temperatures were used for bloating. In some instances expansion had been enough to cause overflow, and yet the top-center would fall before the mass cooled sufficiently to solidify. A more uniform temperature throughout the mass might be attained through the use of other refractory material for the molds having greater heat conductivity. With wall height of 2 inches and less the tendency for the "cake to fall" was usually negligible.

These experiments confirmed the earlier observation that in the higher bloating range prolongation of the bloating period did not yield greater bulk volume but did yield larger cells and correspondingly thicker cell walls. It appears that differences in the way the several volcanic ash samples respond to heating procedure was more pronounced in these larger-scale tests than in the small-scale tests, but not unduly so.

Physical Tests of Products. Several products made during these experiments have been subjected to a series of tests designed to indicate their adaptability to industrial uses. Tests were made to determine the apparent specific gravity, the volume of open pores and the volume of closed cells.²⁶ Thermal conductivity and specific heat were determined on one specimen only. Specimens heated at 870° C. for 24 hours were apparently unchanged except for color which became dark bronzy brown.

As was to be expected, the least bloated material showed the greatest resistance to crushing. The pressure required to crush

the several specimens ranged from 250 pounds per square inch to over 5,000 pounds per square inch. Generally less pressure was needed to crush when applied vertically than when applied horizontally, due probably to a tendency of the cell axes to elongate horizontally. The cell size in any specimen appears to be fairly uniform with the maximum cell size being not over twice the average size. The average cell size ranged from 0.02 to 0.30 millimeters.

Although the information given here is limited to a few specimens it does serve as an indication of what may be expected from products derived from different Oklahoma volcanic ash deposits when processed under several variations in procedure. Some physical properties of bloated products are shown in Table V and others in Table VI where comparisons are made with other structural materials. The Frontispiece pictures a piece sawed from a slab of bloated volcanic ash.

²⁶ Andrews, A. I., "Ceramic Tests and Calculations": John Wiley & Sons, 1928.

TABLE V
PHYSICAL PROPERTIES OF BLOATED PRODUCTS MADE FROM DUSTIN, OKLAHOMA, VOLCANIC ASH ^a

Product Number	1	2	3	4	5	6 ^b
Rate of temp. increase	275°C per hr.	275°C per hr.	275°C per hr.	275°C per hr.	275°C per hr.	275°C per hr.
Time held at 1,090°C	-----	2 hrs.	2 hrs.	2 hrs.	2 hrs.	-----
Bloating temperature	1,090°C	1,300°C	1,350°C	1,350°C	1,350°C	850°C
Time at bloating temp.	2 hrs.	1 hr.	15 min.	1 hr.	2 hrs.	3 hrs.
Average cell diameter	-----	0.02 mm.	0.07 mm.	0.10 mm.	0.30 mm.	0.05 mm.
Max. cell diameter	-----	-----	0.10 mm.	0.20 mm.	0.60 mm.	-----
Sp. Gr. of solids	2.37	2.34	2.34	2.34	2.34	2.48
Apparent Sp. Gr. ^c	2.05	1.18	1.05	0.86	0.92	0.54
Absorption by weight ^c	3.61%	1.16%	2.68%	7.56%	11.19%	1.28%
Apparent porosity ^c	7.40%	1.37%	2.81%	6.49%	10.32%	69.4 %
Closed cells by vol. ^c	4.97%	50.82%	52.33%	56.77%	50.25%	8.74%

^a Sec. 4, T. 9 N., R. 12 E., Hughes County.

^b All products were made from natural volcanic ash without additions except No. 6 which was made from a mixture of 87.5% volcanic ash and 12.5% commercial caustic soda by weight.

^c Tests and calculations made according to Andrews, A. I., "Ceramic Tests and Calculations", John Wiley & Sons, pp. 37-8. 1928.

TABLE VI
PHYSICAL PROPERTIES OF BLOATED VOLCANIC ASH COMPARED WITH OTHER STRUCTURAL MATERIALS

Material	Bulk Sp. Gr. lbs/cu.ft.	Thermal conductivity Btu/hrs/sq.ft./°F/inch	Crushing strength lbs/sq.inch	Specific heat Btu/lbs/°F
Pumicell	45 to 90	-----	250 to 5000	-----
Pumicell Specimen Dustin ash	53-54	1.13 at 75°F	893 horizontal 447 verticle	0.163
P. C. Foamglas	10 to 11(1)	0.45 at 75°F(1)	150(1)	0.16 to 0.19(1)
Pumice stone	23 to 56(2) avg. 40	1.68 at 70°F(2)	-----	-----
Pumice concrete	60 to 90(3) 71(6)	-----	up to 2500(3) 1156 (6)	-----
Cinder concrete	90 to 106(2) avg. 100	2.40(2) 2 to 3(4)	-----	0.186(2)
Gypsum plaster, molded and dry	78(2)	3.00 at 68°F(2)	-----	0.259(2)
Brick, common	100 to 144(2)	3 to 6 at 75°F(2)	3000 to 6500(4)	0.2(about) (2)
Stone concrete	130 to 150(2) avg. 144(4)	6.48(2) 6 to 9 (4)	2000 to 6000(5) 800 to 3800(4)	0.156 (2)

- References: (1) Chem. & Met. Eng., Aug. 1943. p. 100.
 (2) Chemical Engineers Handbook; McGraw-Hill Book Co., 2nd. Edit.
 (3) Pumice Producers Assoc. advertisement: Rock Products, Dec. 1948, p. 203.
 (4) Handbook of Chemistry & Physics; Chemical Rubber Publ. Co., 23rd. Edit.
 (5) Rock Products; Dec. 1948, p. 130.
 (6) Pumice concrete brick purchased and tested in O.G.S. laboratory.

EFFECT OF CAUSTIC SODA AS AN ADDITIVE

Patents have been granted to Kaloustian²⁷ and Nevins²⁸ on high-porosity acoustical material made from volcanic ash and caustic soda by heating the mixture. Small scale experiments conducted in our laboratory show that such mixtures will bloat at lower temperatures than volcanic ash alone, and that the products will be different physically as well as chemically.

Larger scale experiments made on the same scale as previously carried out on volcanic ash without addition seem to indicate that the processing of the mixture will be more difficult to control. Some products were much more glassy than others, and the degree of bloating differed greatly for the several samples of volcanic ash. A number of products were brittle and cracked badly on cooling. However, a very satisfactory porous product was made from the Dustin, Hughes County volcanic ash by the following procedure:

The dry volcanic ash was mixed thoroughly with a solution prepared by dissolving caustic soda in water in the proportions of 12.5 percent caustic soda and 25 percent water calculated on the weight of the volcanic ash. The damp mixture was dried on a steam-heated table and the dried mass pulverized in a disk grinding mill. The pulverized material was placed in a refractory mold assembled from separate base, sides, and end pieces that had been coated with a suitable "parting compound." The mold and contents were placed in the furnace, the heat increased at the rate of 275° C. per hour up to 850° C., held at 850° C. for 3 hours, and then allowed to cool to room temperature in the furnace. Slabs were prepared in this manner with thickness of 1 inch and 2 inches. Physical properties of the product are shown in Table V.

The product is light bluish gray in color, is readily cut and shaped with the carborundum saw, contains a high percentage of open pores, weighs less than 35 pounds per cubic foot, and resisted crushing up to approximately 1,080 pounds per square inch.

"POPPING" VOLCANIC ASH

Attempts to "pop" the fine powdery unconsolidated volcanic ash by the methods advocated for perlite, obsidian, and other con-

solidated volcanic glassy rock have not been successful. Processing of volcanic ash in a rotary kiln generally results in agglutination of the particles and adhesion to the kiln walls in a slag-like mass. Because the composition of volcanic ash conforms to the specifications for mineral materials that respond to the popping procedure²⁹ it offers the provocative problem of finding means whereby the material can be subjected to the necessary sudden high temperature to make it thermoplastic and generate water vapor within the plastic particle at one and the same time, but without causing adhesion of particles to each other and to the surroundings.

From previous work it is known that the viscosity of volcanic ash in the thermoplastic stage is sufficiently high to retain the gases evolved, and that when retained the pressure exerted will cause bloating. It is known also that the temperature of the flame when natural gas is burned in high-efficiency burners is usually high enough to cause volcanic ash to become thermoplastic. It is further known that volcanic ash contains a relatively high water content. These facts suggested that if the volcanic ash could be introduced into the gas and air mixture prior to ignition it would be subjected to conditions conducive to popping when the mixture was ignited. The duration of the contact with the high temperature would depend upon the length of the flame, which in turn depends upon the shape, size, and capacity of the burner, and upon the pressure of the gas. The desired conditions might be attained by introducing a stream of volcanic ash into the air-intake of an inspirator-type gas burner, so that the air and volcanic ash would be injected together into the venturi tube of the gas coming through the orifice under relatively high pressure. Figure 2 is a sketch of such an assembly.

It was found by experiment that under these conditions the individual particles of volcanic ash would expand or "pop", and retain this physical state when ejected from the flame into the air. The particles of the original volcanic ash as seen under the microscope are very small dense glassy flakes or shards. After passing through the flame the particles appear as glassy beads of irregular shape and each bead containing one or more bubbles. Most of the beads were found to float indefinitely on water in contrast to the

27. Kaloustian, George, U. S. Patent 2,209,163, 1940.

28. Nevins, Howard S., and Kaloustian, George, U. S. Patent 2,209,170, 1940.

29. Ralston, Oliver C., "Pelite, Source of Synthetic Pumice": U. S. Bur. Mines Inf. Cir. 7364, 1946.

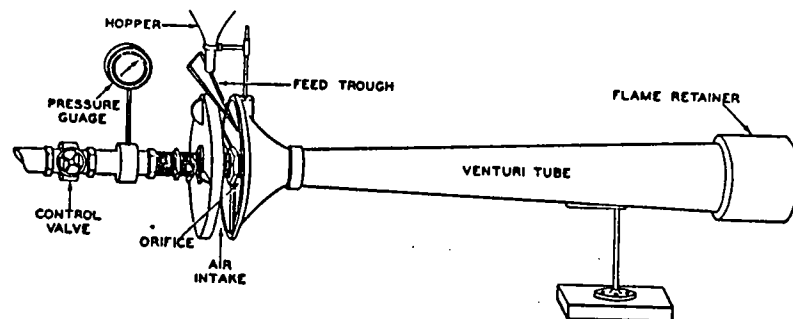


FIGURE 2. Burner assembly used in experimental "popping" of volcanic ash. The ash is introduced through a hopper into the air intake of an inspirator-type gas burner, so that the air and volcanic ash are injected into the venturi tube by the gas coming through the orifice under relatively high pressure, and the ash passes into the flame with a high percentage of the volcanic ash particles being subjected suddenly to the flame temperature. The particles become thermoplastic and simultaneously expand from the pressure of vaporization of the contained water. Instantaneous cooling of the particles after they leave the flame results in retention of the bubble-like form. (See Plate VII).

original particles and unchanged particles which sink promptly. The expanded particles are very light in weight. Their separation from the air and the gaseous products of combustion should be attained by some one of the conventional methods used in dust removal and collection. Plate VII shows microphotographs of original and popped volcanic ash.

In experimenting, inspirator-type gas burners manufactured by the Denver Fire Clay Co. were used. Burner No. 782 B-N furnished with a No. 31 orifice and a flame retainer was found satisfactory for volcanic ash of the particle size commonly occurring in Oklahoma although the smaller burner No. 781 may prove to be better on the finer materials. The burner was connected to a natural gas line carrying pressure upward of 25 pounds per square inch. A pressure gauge was installed close to the orifice and between the orifice and a control valve. Products were produced using pressure at the orifice in the range from 2 to 15 pounds per square inch.

A product was produced with this equipment, feeding the volcanic ash in an even stream into the air intake at the rate of 33 pounds per hour while maintaining 5 pounds per square inch pressure at the orifice. At this pressure the capacity of the burner is approximately 256 cubic feet of 1,000 Btu gas per hour. Assuming

TABLE VII
EFFECT OF POPPING ON PARTICLE SIZE OF REPRESENTATIVE SAMPLES OF OKLAHOMA VOLCANIC ASH
Percent by weight

SIZE IN MICRONS.	over 351	351-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	less than 10
Composite of Lab. No. 4698-99-4700 Beaver County											
Original	-----	0.3	0.6	1.4	1.4	3.6	(1.1	6.1	23.7	37.4	24.1)
Popped	5.1	7.0	8.3	8.4	12.6	13.1	(45.6)
Lab. No. 9592 Wagoner County											
Original	-----	1.6	3.6	9.2	9.0	24.8	(9.7	14.6	13.8	8.4	4.7)
Popped	2.1	17.0	17.8	17.8	16.6	11.2	(17.4)

the gas to cost 15 cents per thousand cubic feet, the fuel expense for popping would be \$2.32 per ton of volcanic ash.

The present recovery of volcanic ash in the form of popped product will depend upon the efficiency of the collecting system but a shrinkage in weight obviously will be had. The probable shrinkage in weight can be estimated by the difference in LOI (loss on ignition at 1,000° C.) between the volcanic ash and the popped product made from it. A representative sample of volcanic ash with a LOI of 4.2 percent on processing gave a popped product with a LOI of 2.5 percent, which means a processing loss of 1.7 percent is to be expected. Therefore, the fuel expense is computed at \$2.36 per ton of popped material.

TABLE VIII
SPECIFIC GRAVITY COMPARISON
Original Volcanic Ash vs Popped Volcanic Ash

	True Sp.Gr.	Apparent Sp.Gr.	Bulk Sp. Gr.
Beaver County, original	2.34	0.69
popped	0.55	0.22
Wagoner County, original	2.36	0.89
popped	0.32	0.095
Okfuskee County, original	2.39	0.81
popped	0.30	0.088

Lacking dust collecting equipment for the experiments a small sheet-metal building was utilized as a substitute. The building size was approximately 8 feet by 10 feet, by 8 feet in height and had a small louvre ventilator. Products of the flame were passed into the building through a hole 8 inches in diameter cut in the side. In the building most of the heat was dissipated and a large portion, but not all of the popped product settled out. Considerable material was lost through the ventilator which would have been saved by a more efficient collector.

The bulk specific gravity (weight per unit volume of loose material) of the popped volcanic ash depends upon the conditions under which the popping takes place and also upon the particle size of the original volcanic ash. In the section on Particle Size, W. E. Ham shows the particle size distribution for the samples under investigation (Table X, fig. 4). Differences between the several

samples should be noted. Corresponding differences have been found in the popped products. Particle size distribution of popped and unpopped material for two samples is shown in Table VII. The true specific gravity and the bulk specific gravity of three volcanic ash samples, and the apparent specific gravity of the particles and their bulk specific gravity after popping are given in Table VIII.

Popped volcanic ash was subjected to thermal shock by heating and quickly chilling in the air. Application of temperatures up to 800° C. followed by chilling did not cause appreciable change in the material. Cracked or fractured particles attributable to thermal shock were not detected. Heating at 850° C. for 1 hour caused a very slight color change from light gray to light tan and also a very small shrinkage in volume. Heating at 1,090° C. for periods of 1 hour and 15 hours gave shrinkage in bulk volume of about 85 percent and 95 percent respectively. The 1 hour treatment sintered the material and caused the color to change from light gray to dark tan. The individual particles were observed to be shrunken but the bubbles could still be seen. The 15 hours treatment partially vitrified the material and changed the color to dark brown, the particles now appearing as nearly round solid glass pellets, cemented to each other at points of contact. The effect of heat on the popped material is quite similar to that on the original volcanic ash when subjected to the same treatment. This is evidence to support the contention that *bloating after ignition* is a distinctly different operation from *popping* and that the gases which cause expansion probably are derived from different types of reaction.

COMMERCIAL APPLICATIONS OF PRODUCTS.

PUMICELL

The name Pumicell has been coined to designate the cellular products which we have made from volcanic ash, the derivation being from the word pumicite, a synonym for volcanic ash, and the word cellular which describes the character of many of the products.

Cellular and porous lightweight products made from clays, shales, and slates, and from slags, perlite, and other consolidated glassy rocks have been used mainly in compositions, concretes being the largest consumer, whereas foamglass is used principally in shapes obtained during the processing. Because the bloated products

obtained from high-temperature treatment of volcanic ash resemble foamglass quite closely it seems likely that their commercial application might be along similar lines, that is, insulation. Any advantage that foamglass may possess due to its lighter weight may be offset by the greater strength of pumicell.

PRODUCTS FROM ADDITION OF CAUSTIC SODA

Products produced from volcanic ash and fluxing additives should exhibit acoustical properties due to the high porosity. This property suggests use as tile and panels for sound-proof partitions.

USES OF POPPED VOLCANIC ASH

Interesting lightweight concrete products were made by mixing the popped volcanic ash with Portland cement and water. Similar mixtures of popped material with gypsum plaster and with dolomitic lime (finishing plaster) also gave products that suggested commercial usefulness. To illustrate the possibilities, a mixture was made in the following proportions:

	by volume	by weight
Popped volcanic ash	68%	26.5%
Portland cement	17%	41.0%
Water	15%	32.5%

These proportions produce a damp mixture which was pressed into bricks firm enough to handle. The bricks were air-dried, water cured for a short time, and re-dried, after which they were subjected to tests from which the following information was obtained:

Bulk Specific gravity	0.76
Apparent specific gravity	1.66
Water absorption by weight	76.3%
Apparent porosity by volume	55.9%
Volume of closed cells	16.8%
Crushing strength	375 to 400 psi

Variation in the mixture should yield products having very different physical properties, possibly with great differences in usefulness.

Compositions containing popped volcanic ash should exhibit both cellular and porous structure, both of which properties can be modified or controlled, to satisfy the specifications determined by its ultimate use. It might be suggested that light weight, sound

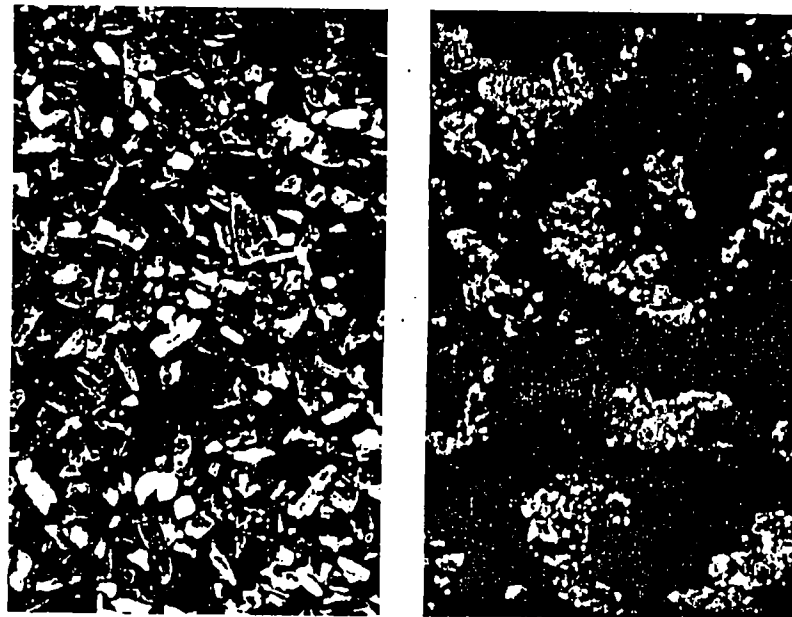


PLATE VII. Photomicrographs of volcanic ash shards showing expansion by "popping." Untreated volcanic glass shards at left; "popped" particles at right. X28.



PLATE VIII. Representative deposits of Oklahoma volcanic ash.
A. Deposit near Gate, northeastern Beaver County.
B. Deposit near Tullahassee, southern Wagoner County.

absorption, thermal conductivity, and dielectric properties indicate that compositions will find use as insulation against heat, cold, sound, and electricity. Emphasis should be placed on possibilities of consumer commodities in forms and shapes, such as blocks, bricks, slabs, wall board, panel sheets, and the like, but monolithic construction, especially for covering lath, is a definite possibility. Products can be made that are impervious and non-absorbent and others that will permit passage of liquids and gases. The products will be relatively inert, fire-proof and vermin proof, and readily cut, machined and fashioned with suitable tools. The culls, rejects and scrap may be crushed and used as lightweight aggregate.

With three avenues of approach, that is (1) by heating the volcanic ash without any addition to relatively high temperatures under controlled conditions to yield strong, lightweight cellular material, (2) by heating volcanic ash that has previously been treated with a fluxing agent to relatively medium temperatures, and (3) by popping the individual volcanic ash particles, and with the definite knowledge that the products possess desirable characteristics from a commercial standpoint, it seems reasonable to expect industrial utilization of Oklahoma volcanic ash.

U. S. Patent 2,466,001, dated April 5, 1949, entitled "Method of Making Cellular Products from Volcanic Ash" has been issued to A. L. Burwell and is owned jointly by the University of Oklahoma Research Institute and the Research Corporation of New York. This method falls under the first classification above.

The so-called Cobrecite patents, U. S. 2,209,163 and 2,209,170, issued in 1940 to George Kaloustian and Howard S. Nevin are on processes which fall under the second classification.

The method for popping the individual volcanic ash particles as given in the preceding pages is currently the subject of application for patent.

VOLCANIC ASH DEPOSITS IN OKLAHOMA

Volcanic ash deposits have been reported in 25 counties in Oklahoma. Estimates on the size of individual deposits range from as little as 500 cubic yards for the smaller ones to as much as 10,000,000 cubic yards for the larger ones. The thickness of the deposits range from 1 foot to 70 feet and the overburden from nothing to 30 feet and possibly more in a few instances. Figure 3 shows the approximate location of deposits. Table IX shows the section, township, and range, the thickness and overburden, and estimates of the amount of material in the deposits. Included in the tabulation are notes relative to the type of material, impurities observed, etc. Views of two representative deposits—near Gate, in Beaver County, and near Tullahassee, in Wagoner County—are shown in Plate VIII.

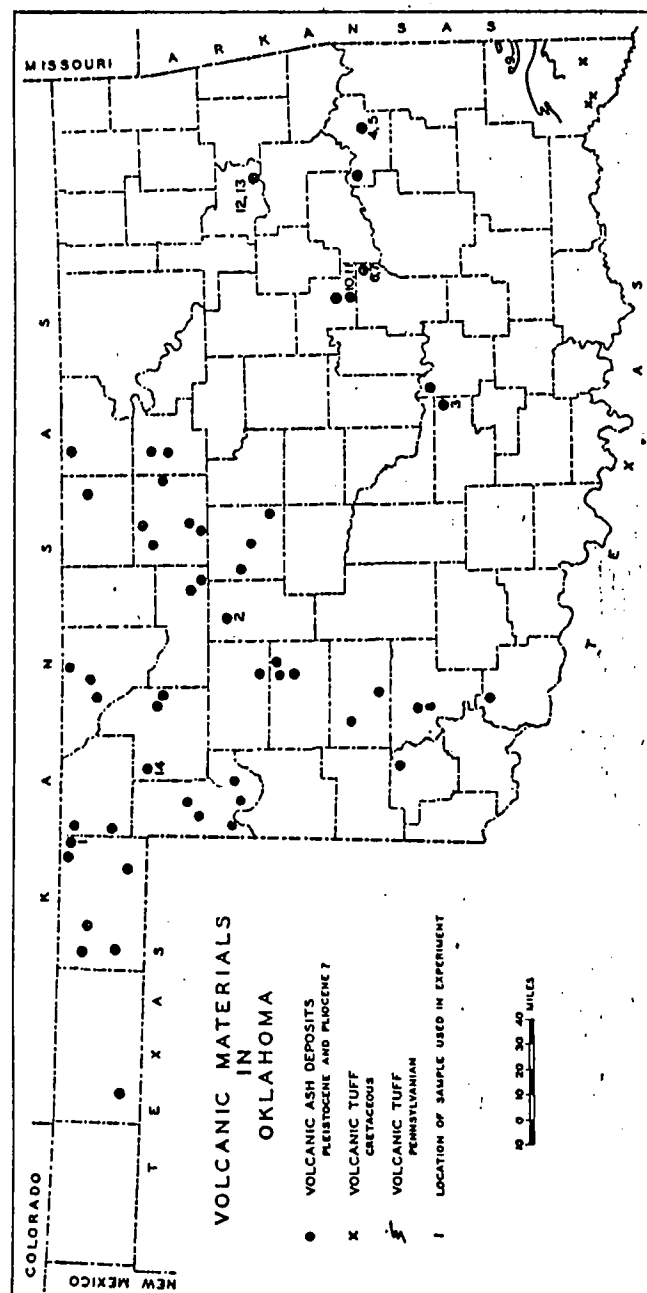


FIGURE 3. Map of Oklahoma showing distribution of known deposits of volcanic materials. Numbers refer to deposits represented by samples used in experiments.

TABLE IX
VOLCANIC ASH DEPOSITS OF OKLAHOMA

No.	Sec.	Location T.	R.	Thickness ft.	Overburden ft.	Estimated No. cu. yds.	Remarks: Identification and grade
BEAVER COUNTY							
(1)	2	4N	21 ECM	15	2	120,000	Volcanic ash
(2)	25	2N	26 ECM	2 to 6	2 to 6	15,000	Volcanic ash
(3)	20	4N	23 ECM	4 to 5	-----	-----	-----
(4)	1	5N	27 ECM	12	-----	-----	-----
(5)	3, 10	5N	28 ECM	7	3	-----	Volcanic ash, lake deposit, few diatoms, quartz, etc.
(6)	5, 8	5N	28 ECM	35 to 70	4 to 25	500,000	Volcanic ash
(7)	2	4N	21 ECM	2	1 to 8	-----	*Volcanic ash, active quarry Volcanic ash
BLAINE COUNTY							
(8)	4	18N	12W	3 to 5	4 to 8	250,000	*Volcanic ash, some metabentonite; swells to twice its volume in water.
CUSTER COUNTY							
(9)	14	14N	16W	3 to 15	2 to 4	11,000	Volcanic ash, some carbonate
(10)	15	14N	16W	12	3 to 8	-----	Volcanic ash, abandoned quarry: easy access.
(11)	6	15N	15W	10 to 15	-----	-----	Volcanic ash
(12)	27, 34	15N	16W	-----	-----	-----	Volcanic ash reported; no sample.
DEWEY COUNTY							
(13)	13	16N	16W	4 to 5	4	500	Volcanic ash
(14)	25	16N	16W	1 to 3	1 to 4	1,500	Volcanic ash
ELLIS COUNTY							
(15)	11, 12	16N	24W	2 to 4	1 to 7	35,000	Volcanic ash mixed with low-grade metabentonite.
(16)	35	18N	23W	3	4 to 8	5,000	Volcanic ash reported; no sample
(17)	23	18N	26W	-----	-----	-----	Deposit reported; no sample
(18)	3	20N	25W	5	1 to 2	-----	Volcanic ash
(19)	28	21N	24W	-----	-----	-----	Deposit reported; no sample

* Sample used in experiments.

TABLE IX
VOLCANIC ASH DEPOSITS OF OKLAHOMA

No.	Sec.	Location T.	R.	Thickness ft.	Overburden ft.	Estimated No. cu. yds.	Remarks: Identification and grade
GARFIELD COUNTY							
(20)	7	20N	6W	1 to 12	1 to 6	1,000,000	Reported as mixture volcanic ash and sand
(21)	33	20N	7W	6	1 to 5	20,000	Sandy volcanic ash
(22)	36	20N	7W	2 to 10	1 to 2	400,000	Sand and volcanic ash
(23)	8	22N	3W	-----	-----	-----	Volcanic ash reported
(24)	5	23N	7W	4 to 6	2 to 6	10,000	Volcanic ash, no sample
(25)	25	24N	6W	1	-----	-----	Small amount volcanic ash reported overlying shale bed.
GARVIN COUNTY							
(26)	20	4N	3E	3	3	180,000	*Volcanic ash
(27)	NW, NE 29,	4N	3E	3	3	3,000	Volcanic ash
(28)	NE, NE 29,	4N	3E	2½	6	32,000	Volcanic ash
(29)	29, 32	4N	3E	2½	3	8,000	Volcanic ash
GRANT COUNTY							
(30)	3	27N	4W	3 to 4	2 to 6	40,000	Volcanic ash
GREER COUNTY							
(31)	5	7N	22W	7	10	-----	Mostly volcanic ash, slight iron stain on some grains. A few anisotropic grains. Few feldspar grains, trace carbonate.
HARPER COUNTY							
(32)	10	28N	26W	1 to 15	3 to 8	25 acres	Volcanic ash with trace carbonate; some anisotropic and feldspar grains.
(33)	28, 33	26N	26W	1 to 5 or more	1 to 2	10,000	Volcanic ash

* Sample used in experiments.

TABLE IX
VOLCANIC ASH DEPOSITS OF OKLAHOMA

No.	Sec.	Location T. R.	Thickness ft.	Overburden ft.	Estimated No. cu. yds.	Remarks: Identification and grade
HASKELL COUNTY						
(34)	3, 4	9N 18E				
(35)	33, 34	10N 18E	1½ to 2	½ to 2½	2,000	Impure volcanic ash, with clay, metabentonite, sand.
(36)	7	9N 21E	½ to 5	2 to 10	-----	Volcanic ash with various impurities.
	17	9N 21E	1 to 5 or more	1 to 14	75,000	*Volcanic ash interbedded with mixtures of sand and volcanic ash; contains metabentonite in places.
HUGHES COUNTY						
(37)	3, 4, 9	9N 12E	10 to 20	2 to 10	4,000,000	*Volcanic ash, trace of carbonate; has been quarried.
KAY COUNTY						
(38)	2	28N 1W	4 to 6	3	-----	Volcanic ash, small deposit
KINGFISHER COUNTY						
(39)	1, 2	15N 5W	1 to 4	2 to 3	-----	Volcanic ash; reported thicker in nearby wells.
(40)	27	17N 9W	2	4 to 6	-----	Volcanic ash, mostly
(41)	6	16N 7W	1½	30	-----	Volcanic ash: sample from well.
MCOWA COUNTY						
(42)	28	6N 18W	6	0 to 10	-----	*Volcanic ash. Quarried during 1943-4.
MAJOR COUNTY						
(43)	6	20N 10W	1 to 10	0 to 7	76,000	Volcanic ash
(44)	28	20N 10W	-----	-----	-----	Volcanic ash
MCCURTAIN COUNTY						
(45)	25, 26, 36	2S 25E	40	0	-----	*Volcanic tuff, hard, consolidated. Outcrops total more than 200 lineal miles; 90 feet thick in places. These localities are representative of many occurrences.
	16, 34	4S 22E				
	14, 28	4S 23E				
	10, 16, 21	5S 22E				
* Sample used in experiments.						
NOBLE COUNTY						
(46)	14	23N 1W	6	6	-----	Volcanic ash
(47)	15	22N 1W	-----	-----	-----	Volcanic ash
OKFUSKEE COUNTY						
(48)	19, 20	10N 10E	9	2 to 3	10,000,000	*Volcanic ash, trace carbonate.
(49)	34	11N 10E	2	1 to 3	10,000	Volcanic ash
PONTOTOC COUNTY						
(50)	35	5N 4E	-----	6 to 8	-----	Volcanic ash interbedded with sand and clay.
TEXAS COUNTY						
(51)	26	2N 11 ECM	1 to 3	1 to 3	-----	Volcanic ash reported.
TILLMAN COUNTY						
(52)	19	1N 17W	-----	2 to ?	-----	Volcanic ash and bentonitic ash interbedded. Thin beds.
WAGONER COUNTY						
(53)	19, 20	16N 18E	1 to 30	1 to 20	1,000,000	*Volcanic ash. Sandy and bentonitic ash in places. Thin clay beds. Has been quarried.
WASHITA COUNTY						
(54)	15	8N 17W	2 to 3	1 to 3	4,000	Volcanic ash, some carbonate.
(55)	16	8N 17W	1 to 5	1 to 8	10,000	Volcanic ash, several deposits.
(56)	4	10N 19W	1 to 4	1 to 5	-----	Volcanic ash
WOODS COUNTY						
(57)	3	27N 16W	½ to 1	20 to 30	-----	Thin irregular bed, also present in other sections.
(58)	19, 30	27N 17W	-----	-----	-----	Volcanic ash in small deposits. Carbonate present.
(59)	20	27N 17W	1 to 9	1 to 3	3,000	Small deposit volcanic ash, some carbonates.
(60)	23	27N 17W	1 to 5	0 to 3	3,600	Volcanic ash
(61)	27	27N 17W	1 to 4	0	400	Small deposit volcanic ash
(62)	35	27N 17W	3 to 7	1 to 10	500	Volcanic ash
(63)	32	29N 15W	5	10 to 15	6,000	Volcanic ash, few anisotropic grains. Trace carbonate.
WOODWARD COUNTY						
(64)	32	23N 17W	3 to 5	5 to 10	12,000	Bentonitic volcanic ash, some carbonate.
(65)	23	23N 18W	3 to 4	3 to 5	5,000	Bentonitic volcanic ash
(66)	13, 14, 25	23N 22W	-----	-----	large quantity	*Bentonitic volcanic ash, some sand.

* Sample used in experiments.

GEOLOGICAL AND PETROGRAPHIC INVESTIGATIONS

BY

WILLIAM E. HAM

Introduction

Volcanic materials in Oklahoma occur as thick beds of consolidated volcanic tuff of Pennsylvanian and Cretaceous age, and as widely scattered deposits of unconsolidated volcanic ash or pumice, mostly of Pleistocene age.

The consolidated volcanic tuffs of pre-Tertiary age crop out in southeastern Oklahoma, chiefly in McCurtain County, and consist mostly of crystal and lithic fragments of igneous rocks together with a small amount of volcanic glass that is now completely devitrified. In some places these deposits are contaminated with quartz sand, clay, sedimentary rock fragments, and glauconite.

The older of the tuffs is in the lower part of the Stanley shale of Lower Pennsylvanian age and is approximately 100 feet thick.³⁰ It crops out in the Ouachita Mountains where the rocks are complexly folded, producing an intricate zig-zag outcrop pattern which gives the tuff a linear extent of more than 200 miles. A sample of this material was bloated successfully in the series of tests described in the first part of this report.

The tuff of Cretaceous age is in the Woodbine formation, which crops out on the Gulf Coastal Plain just south of the Ouachita Mountains. In Oklahoma the tuffaceous part of the Woodbine formation is at least 100 feet thick in places and consists of fragmental phonolite admixed with quartz, glauconite, and other sedimentary material.³¹ No samples of Woodbine tuff were tested for bloating properties.

In their lithic and crystal composition, their consolidation, bedded character, and association with marine strata, the Pennsylvanian and Cretaceous tuffs differ from the surficial fresh-water

30. Honess, C. W., "Geology of the Southern Ouachita Mountains of Oklahoma": *Okla. Geol. Survey Bull.* 32, Part I, pp. 144-150, 1923.

31. Ross, C. S., Miser, Hugh D., and Stephenson, L. W., "Water-Laid Volcanic Rocks of Early Upper Cretaceous Age in Southwestern Arkansas, Southeastern Oklahoma, and Northeastern Texas" in "Shorter Contributions to General Geology": *U. S. Geol. Survey Prof. Paper* 154, pp. 178-180 and 194, 1929, also published as *Prof. Paper* 154-F.

deposits of unconsolidated volcanic ash, which form the principal subject of the present investigation.

Geology of Volcanic Ash

The unconsolidated volcanic ash of Oklahoma occurs in surficial deposits of late Tertiary and Pleistocene age, associated with similarly unconsolidated sediments such as clay and sand. The known outcrops occur widely scattered in 25 counties, chiefly in western, central, and east-central Oklahoma. Individual deposits are small and lenticular, and many are associated with terrace deposits of major streams.

The maximum observed thickness in Oklahoma volcanic ash deposits is 70 feet, but ranges downward to only a few feet and most deposits are less than 20 feet (Table IX). So far as known all deposits are less than 1 square mile in areal extent, and the greatest estimated volume at a single locality is 10,000,000 cubic yards (Table IX). Some deposits are nearly pure unaltered volcanic ash; some are interbedded with sand and clay; and in other deposits the glass shards themselves are altered to montmorillonite so that the ash beds grade into bentonitic clays. A few volcanic ash deposits are cemented by calcium carbonate or contain concretions of it. A fresh-water snail fauna is found in some localities and all have yielded the opal tests of aquatic diatoms.

The samples of Oklahoma volcanic ash studied in the laboratory are without exception of fine grain size, the largest particles being approximately 0.25 mm in diameter and the average median diameter being 0.0457 mm. In mineral composition the samples show a considerable range in percentage of volcanic glass shards, the purest sample containing 97.7 percent and the most contaminated only 59.5 percent.

PHYSIOGRAPHIC AND STRATIGRAPHIC OCCURRENCE.

Despite an incomplete knowledge of geologic details at most of the known volcanic ash deposits, three general types of occurrences have been noted as follows: (a) deposits on high terraces of major streams, probably of Pleistocene age, representing the most widespread and common type; (b) deposits on the surface of the High Plains in the Oklahoma Panhandle, probably of Pleis-

tocene age; and (c) deposits included within the Ogallala formation of Pliocene age.

Volcanic ash in the Ogallala formation of Pliocene age is least known of all. Only the deposit west of Woodward (laboratory number 9425) is assigned to this formation, the assignment being made on petrographic similarities with ash of known Pliocene age from other areas, as discussed on following pages. Its Pliocene age seems probable in spite of the fact that the Geologic Map of Oklahoma³² shows it to be in an area of Quaternary terrace deposits, about 10 miles from the nearest outcrops of the Ogallala formation.

Deposits on the surface of the High Plains in the Oklahoma Panhandle are likewise incompletely known. None of the volcanic ash deposits of Beaver and Texas Counties appear to belong to the Ogallala formation, yet neither are they as clearly associated with terraces of major drainage systems as those farther east. Those north of Gate, northeastern Beaver County, may well have been deposited on a former flood plain of the Cimarron River, now a greatly dissected high-level terrace. Other deposits on the High Plains surface, between major valleys, are probably related to the so-called "buffalo wallows"—the depressions that are so characteristic of High Plains topography.³³

Most volcanic ash deposits in Oklahoma are known or strongly suspected of being associated with stream terraces. The evidence is clear that the deposits in Wagoner, Haskell, and Pontotoc Counties lie on high river terraces, the one in Wagoner County being on a terrace associated with the Arkansas River, and those in Haskell and Pontotoc Counties being associated with the Gerty terrace sand, which represents a former level of the Canadian River.³⁴ The

³² Miser, H. D., "Geologic Map of Oklahoma": *U. S. Geol. Survey*, 1926.

³³ Schoff, S. L., "Geology and Ground Water Resources of Texas County, Oklahoma": *Okla. Geol. Survey Bull.* 59, pp. 22-23, 1939.

³⁴ Taff, J. A., "Geologic Atlas of the United States": *U. S. Geol. Survey, Coalgate Folio* (No. 74), p. 4, 1901.

Taff, J. A., *U. S. Geol. Survey, 19th Ann. Rept.*, Pt. 3, p. 439, 1899.

Morgan, G. D., "Geology of the Stonewall Quadrangle, Oklahoma": *Bureau of Geology Bull.* 2, pp. 142-145, 1924.

Hendricks, T. A., "Geology and Fuel Resources of the Southern Part of the Oklahoma Coal Fields"; Part 1, "McAlester District"; *U. S. Geol. Survey Bull.* 874-A, pp. 26-33, 1937.

Oakes, M. C., and Knechtel, M. M., "Geology and Coal Resources of Haskell County, Oklahoma": *Okla. Geol. Survey Bull.* 67, p. 63, 1949.

Garvin County deposits probably are related to the Gerty sand, and those in Hughes and Okfuskee Counties appear to rest on terraces related to the North Canadian River.

Less detailed information is available on the other deposits, but all volcanic ash localities reported from Ellis, Harper, Kay, Major, Tillman, and Woodward Counties, and some from Garfield County, either coincide with or are immediately adjacent to areas of Quaternary terrace deposits shown on the Geologic Map of Oklahoma. Permian bed rock is shown on the Geologic Map at the other localities in Garfield County, as well as at localities of volcanic ash reported from Blaine, Custer, Dewey, Grant, Greer, Kingfisher, Kiowa, Noble, Washita, and Woods Counties. It is suspected that when these areas are investigated in detail, the volcanic ash will be found in association with terrace materials rather than resting directly on Permian red beds; and that, excepting the deposit west of Woodward, all volcanic ash east of the Panhandle will prove to be related to Quaternary terrace deposits.

Origin and deposition. From the purely volcanic character of the glass shards, which predominate in all samples examined, it is clear that the materials in the Oklahoma deposits were derived chiefly from a volcanic source. The glass shards together with other volcanic materials such as orthoclase and biotite were explosively ejected from a volcano or group of volcanoes and carried by wind to or near the sites of the present deposits.

The location of such volcanoes is not known with assurance, although they certainly were not in Oklahoma. The nearest volcanoes that were active in Pleistocene time are in northeastern New Mexico, and the Capulin group in that region was suggested by Landes³⁵ to be the source of volcanic ash deposits in Kansas. Swineford³⁶ suggests an alternative source in the Valle Grande region, part of the Jemez Mountains, Sandoval County, about 30 miles west of Santa Fe, New Mexico:

. . . the cones (of the Capulin group) are comparatively small and the lavas . . . consist of basalts, andesites, trachytes, soda trachytes, and phonolites . . .

³⁵ Landes, K. K., "Volcanic Ash Resources of Kansas": *State Geol. Survey of Kansas Bull.* 14, p. 19, 1928.

³⁶ Swineford, Ada, "Source Area of Great Plains Pleistocene Volcanic Ash": *Jour. Geol.* Vol. 57, pp. 307-12, 1949.

Valle Grande is judged to be a probable source of the Pearlette volcanic ash for the following reasons: (1) Only an extremely large caldera, emitting highly acid lavas, such as Valle Grande, could supply ash which is as extensive as the Pearlette. (2) The volcano is situated to the southwest of the known Pearlette lentils. (3) The petrographic character and chemical composition of the glassy part of some of the tuff and pumice are similar to those in the Pearlette. (4) The tuffs are said to be of early Pleistocene age.

The glassy fragments are the product of a highly siliceous magma whose crystallized equivalent would be a rhyolite or granite. The purest samples of Oklahoma volcanic ash show on chemical analysis a silica content of 72 percent, and the glass shards in more contaminated deposits show by their index of refraction (Table XII) that the silica content probably exceeds 70 percent for all samples.³⁷

Sites of deposition. The relatively pure parts of most volcanic ash deposits in Oklahoma are massive, lacking stratification or other bedding characters from which the probable site of deposition could be interpreted. Other evidences, however, plainly indicate that the wind-blown volcanic ash now preserved in scattered deposits was laid down mostly in fresh-water lakes, where the glassy fragments were brought to rest and admixed with variable amounts of locally derived non-volcanic materials. Any alteration to bentonitic clay likewise took place after deposition in lake waters.

Probably the most convincing evidence of lacustrine deposition consists of the random distribution of the ash bodies and the occurrence of freshwater snails, which have been found near the base of two deposits in Oklahoma as well as many in Kansas, Nebraska, and Texas. It is also true that the tests of aquatic diatoms have been found in every sample of Oklahoma volcanic ash examined for this report, leading to the conclusion that all deposits probably are water-laid. Deposition in lakes seems more probable than in rivers because the deposits so far known are randomly scattered rather than having an alignment suggesting the linear or sinuous form of stream-channel deposits. Some volcanic ash in eastern Oklahoma that is much contaminated by sand and clay may be stream-deposited along with other terrace ma-

³⁷ George, W. O., "The Relation of the Physical Properties of Natural Glasses to their Chemical Composition": *Jour. Geol.*, Vol. 32, p. 365, 1924.

terials, but the majority of relatively pure volcanic ash deposits are believed to have been laid down in lakes. Gardner in 1923 suggested such a site of deposition for the volcanic ash in Okfuskee County.³⁸

In further support of lacustrine deposition it is noted that certain volcanic ash deposits elsewhere show water-laid characteristics very plainly and have been interpreted as deposits in lakes. One extensive deposit in Scotts Bluff County, Nebraska, is

... composed of nearly equal amounts of silt and pumicite, together with a liberal sprinkling of diatom frustules and spicules of one-rayed sponges . . . [Some beds] . . . are so distinctly laminated that they are obviously water deposits. The pumiceous dust was dropped into lakelets of that time and on settling was stratified and laminated after the manner of water deposits. In such beds one finds occasional fresh water snails, which, in one instance at least, were very abundant.³⁹

In the Oklahoma deposits diatoms are ubiquitous but relatively scarce and are concentrated in the size grades smaller than 40 microns (Table XI, Sample 14). The opal tests or frustules, showing well preserved delicately sculptured ornamentation and minute perforations, are boat-shaped, biconvex, spherical, or rod-shaped. The elongate tests range in length from about 15 to 35 microns (0.015 to 0.035 mm) and in width from about 7 to 18 microns. The spherical diatoms are 10 to 20 microns in diameter, and fragments of others indicate the occurrence of larger forms.

The volcanic glass fragments were not necessarily deposited in a lake directly from the air, although this could have happened locally and resulted in a relatively thin and pure ash deposit. Rather it is believed that volcanic dust from one or more eruptions was wind-transported into Oklahoma and deposited as a blanket covering areas of wide extent.^{39a} Reworking of this blanket by wind, rainfall, and tributaries to lakes concentrated the ash in relatively thick deposits in lake basins. Inevitably there would be mixing of the volcanic glass and associated pyroclastic materials with non-

³⁸ Gardner, J. A., "Volcanic Ash in North Canadian Valley": *Bull. Amer. Assoc. Petrol. Geol.*, Vol. 7, p. 578, 1923.

³⁹ Barbour, E. H., "Nebraska Pumicite": *Nebraska Geol. Survey, Publications*, Vol. 4, Pt. 27, pp. 361-362, 1916.

^{39a} Buttram, Frank, "Volcanic Dust in Oklahoma": *Oklahoma Geol. Survey Bull.* 13, p. 49, 1914.

pyroclastic minerals derived from local bedrock and surficial deposits. The degree of mixing is a function chiefly of the thickness of the wind-deposited ash blanket and the rapidity with which the underlying bedrock or soil is exposed.

The deposits in western Oklahoma, being closer to the probable volcanic source, apparently accumulated from thicker blankets of ash and thus are less likely to contain contaminating materials. The samples studied from Beaver, Blaine, Kiowa, and Woodward Counties represent large deposits, and without exception are more nearly pure than any from central or eastern Oklahoma, having an average glass shard content of 96.5 percent by weight. Records in the files of the Oklahoma Geological Survey, however, show other, smaller deposits in the northwestern part of the state which contain much sand, so that a generalization on the relation of purity to proximity of source must be applied with due caution.

Volcanic ash deposits in central and eastern Oklahoma, locally accumulated from thinner blankets deposited much farther from the parent volcanoes, are more contaminated by non-volcanic materials and have an average shard content of 85.9 percent.

In summary, it appears probable that most volcanic ash deposits in Oklahoma were laid down in lakes, or exceptionally in stream channels, where diatoms and snails were living, and into which the glassy volcanic materials settled from the air or were washed in by run-off water. Contaminating non-volcanic materials were introduced in the same way. Lakes in the Panhandle of Oklahoma probably occupied shallow depressions similar to the numerous wet weather lakes that characterize the High Plains today, whereas the volcanic ash preserved eastward from the Panhandle most likely was deposited in lakes filling depressions on the alluvium of stream terraces.

AGE

Several lines of evidence suggest the Pleistocene age of most of the Oklahoma ash deposits, particularly those on old river terraces. Morgan⁴⁰ reports vertebrate remains of Pleistocene age in the Gerty

40. Morgan, G. D., "Geology of the Stonewall Quadrangle, Oklahoma": *Bureau of Geology Bull.* 2, p. 144-145, 1924.

sand of Pontotoc County. Great numbers of Pleistocene vertebrate remains—teeth, tusks, and bones—have been found in gravel and sand pits worked in terrace deposits throughout the state.⁴¹ Similarity of position of terraces along the valleys of all major rivers in Oklahoma points strongly to their essential contemporaneity, thus furnishing a guide to the age of the associated volcanic ash deposits.

Evidence from southwestern Kansas, gained through detailed studies by the State Geological Survey of Kansas, adds pertinent information regarding the age of the Oklahoma volcanic ash deposits.

Prior to the last decade and a half, the surficial mantle of western Kansas was generally considered to belong largely to the Ogallala (Pliocene) formation. Recent detailed studies have resulted in the placement within the Pleistocene of a large percentage of these deposits, and, further, in the subdivision of the Pleistocene strata in different parts of the state into named stratigraphic units. The most extensive ash horizon of southwestern Kansas, the Pearlette ash, occurs within the Meade formation, and Hibbard has collected vertebrate fossils of definite Pleistocene age from below this ash at many localities.⁴²

Hibbard⁴³ named the faunal assemblage from below the Pearlette ash the "Cudahy fauna", and interpreted it to be, in part at least, a glacial fauna. Previously⁴⁴ he described another fauna from above the Pearlette ash, found in a single locality in Meade County, Kansas. This he called the "Borchers fauna", and interpreted it as having lived in a warm climate, belonging to an interglacial stage of the Pleistocene. Recently,⁴⁵ Hibbard proposes to revise the Meade formation by splitting off upper beds and assigning them to what he proposes to call the Crooked Creek formation. The Pearlette ash and the Cudahy and Borchers fauna would fall into this unit.

41. Stovall, J. W., Personal Communication.

42. Swineford, Ada, and Frye, John C., "Petrographic Comparison of Pliocene and Pleistocene Volcanic Ash from Western Kansas": *State Geol. Survey of Kans. Bull.* 64, pp. 3, 4, 1946.

43. Hibbard, Claude W., "Stratigraphy and Vertebrate Paleontology of Pleistocene Deposits of Southwestern Kansas": *Bull. Geol. Soc. of America*, Vol. 55, pp. 718, 741-743, 1944.

44. Hibbard, Claude W., "The Borchers Fauna, a New Pleistocene Interglacial Fauna from Meade County, Kansas": *State Geol. Survey of Kans. Bull.* 38, pp. 197-220, 1941.

45. Hibbard, Claude W., "Pleistocene Stratigraphy and Paleontology of Meade County, Kansas": *Contrib. Mus. Pal. Univ. Michigan*, Vol. VII, pp. 63-90, 1949.

Volcanic ash also occurs in Kansas within the Ogallala formation of the Pliocene age, and a petrographic study was undertaken by Miss Swineford to determine differences between ash of the two ages. The samples studied were from deposits whose age relations had been determined either from stratigraphic or paleontologic evidence. The fossils include a fauna of fresh water snails, found immediately beneath the Pearlette ash in many localities, and vertebrate fossils found in associated strata.

"Several petrographic characteristics are common to all Pleistocene samples, which serve to differentiate them from all Pliocene samples."⁴⁶ Among the samples examined, and determined petrographically to be of Pleistocene age, was one from near Gate, Beaver County, Oklahoma. (No. 1, Table IX, this report). This deposit also yielded a snail collection.

The following information is contained in a communication from Frye, giving results of a field conference by a group of Pleistocene geologists, covering parts of Illinois, Iowa, South Dakota, and Nebraska; and field trips into Kansas, Oklahoma, and northern Texas, by members of the staff of the State Geological Survey of Kansas:

It seems now as though we have been able to establish a datum in the glaciated area definitely tied into the till sheets of western Iowa and southeastern South Dakota and to carry that datum across Nebraska, diagonally across Kansas, the western corner of Oklahoma, to northwest Texas. We spent a total of six days in western Oklahoma, and checked the localities around Woodward, near Hobart, Thomas, and Canton. At only two localities did we manage to get a good snail collection and that was east of Woodward and north of Hobart. The petrology seems to be checking out splendidly in all instances, and fits nicely with the faunal correlation based on snails. It looks now as if the only major changes that will have to be made in correlation is in southwest Kansas, but that may have some minor effect in Oklahoma. . . .⁴⁷

In a subsequent letter, Frye stated:

... I wrote you of the Oklahoma localities we had visited, and our tentative conclusions concerning correlations at each locality. The only one we visited that we thought might be Pliocene in age was the one just west of Woodward where the ash

has many characteristics that are in common with the ash at Hemphill, Texas. We have found that particular type of ash nowhere else in the Ogallala and so would not want to make any definite statements about this particular correlation. The two Ogallala (Pliocene) ash falls that we get farther north in Kansas and in Nebraska have different characteristics from the Hemphill material.⁴⁸

Results of these studies are summarized in the following abstract:

Correlation of Pleistocene deposits of the Great Plains with the glacial succession of the upper Mississippi Valley presents a major problem in Great Plains stratigraphy. The presence of lenticular deposits of volcanic ash and commonly associated fossil mollusks interstratified with both the glacial and associated deposits of the Missouri Valley and the non-glacial deposits to the west and southwest affords a new and independent method of attacking this problem. These ash deposits collectively are known as the Pearlette ash and represent a single fall that can be differentiated unmistakably by petrographic characters from other late Cenozoic ash deposits of the Plains region. Pearlette ash is represented in 48 localities studied, distributed from southeastern South Dakota to west-central Texas. The associated molluscan fauna presents an unforeseen degree of uniformity throughout this entire region, and the presence of restricted species, extinctions, and first appearances confirms the contemporaneity of the several volcanic ash deposits. The Pearlette ash and closely associated fossil-bearing beds occur within the Loveland formation of Iowa (below the Loveland loess), the Upland formation of Nebraska, the McPherson formation of central Kansas, the Meade formation of Southwestern Kansas and Northwestern Oklahoma, and the Tule formation of northwestern Texas. In the Missouri Valley area the Pearlette zone is contained in beds unconformably overlying Kansas till and below Loveland loess and Iowa till. It is judged, therefore, that the age of these severally named formations is latest Kansan and Yarmouthian.⁴⁹

The most recent and most comprehensive discussion on the age of the volcanic ash deposits of the central Great Plains is a recent paper by Frye, Swineford, and Leonard.⁵⁰

46. Frye, John C., Letter to R. H. Dott, Nov. 20, 1947.

48. Frye, John C., Swineford, Ada, and Leonard, A. Byron, "Correlation of the Pearlette Volcanic Ash from the Glaciated Region into the Southern High Plains" (abstract): *Bull. Geol. Soc. of America*, Vol. 58, p. 1182, 1947.

49. Frye, John C., Swineford, Ada, and Leonard, A. Byron, "Correlation of Pleistocene Deposits of the Central Great Plains with the Glacial Section": *Jour. Geol.*, Vol. 56, pp. 501-525, 1948.

50. Swineford, Ada, and Frye, John C., *op. cit.*, p. 29.

47. Frye, John C., Letter to R. H. Dott, Oct. 8, 1947.

Particle Size of Volcanic Ash

Laboratory Procedure. The samples of volcanic ash studied for this report were very loosely consolidated and needed to be disaggregated only by gentle crushing between the fingers. Each sample thus crushed was passed through a 40-mesh screen, after which it was ready for size analysis.

The size determinations were made by screening the disaggregated sample in a nest of suitably chosen sieves and by sedimenting the remaining fine particles in a column of water. The size distribution of each of the 12 samples analyzed is shown as a cumulative frequency curve constructed on semi-logarithmic paper from ten control points.

Fifty grams of disaggregated sample, weighed to one decimal, was placed in a nest of 6 Tyler screens of 60, 80, 115, 170, 250, and 325 meshes per inch, and with openings respectively of 0.246, 0.177, 0.124, 0.088, 0.062, and 0.043 mm. The sample was sieved for 15 minutes on a Ro-Tap mechanical shaker. The material retained on each screen was weighed to one decimal and the weight-percentage of each separated fraction calculated. The sieve loss by screening is represented in Table X as the difference between 100 percent and the highest value of the cumulative percent.

Constructing a cumulative frequency curve from the results reveals on most samples that an abnormally high percentage is retained on the 170 mesh screen, and microscopic examination shows that this abnormality results from the presence of aggregates. It is possible to reduce such aggregates to discrete particles by additional crushing but in so doing the brittle volcanic ash shards are unduly fragmented and the error introduced probably would be greater than is the error of leaving the particles as aggregates. A similar abnormal concentration on the 170 mesh screen is apparent in certain samples of volcanic ash from Kansas, as can be seen on curves constructed from data presented by Swineford and Frye.⁵¹

Volcanic ash, passing the 325-mesh screen, with grain diameters less than 43 microns, was dispersed and sized according to settling

⁵¹ Swineford, Ada, and Frye, John C., "Petrographic Comparison of Pliocene and Pleistocene Volcanic Ash from Western Kansas": *State Geol. Survey of Kans. Bull.* 64, Table 3, pp. 27-28, 1946.

TABLE X.

SIZE ANALYSES OF OKLAHOMA VOLCANIC ASH

Sample number and location						Weight percent (p) and cumulative percent (c) for specified particle diameters										Quartile diameters (in mm) from cumulative curves			Specific gravity of <.043 mm fraction		
Sample number	County	Sec.	Twp.	Range	Laboratory number	Diameter (mm)	Analysis by sieving						Analysis by sedimentation					Q ₁		Median	Q ₃
							0.246	.246-.177	.177-.124	.124-.088	.088-.062	.062-.043	.043-.040	.040-.030	.030-.020	.020-.010	<.010				
1	Beaver	8	5N	28ECM	4698 4699 4700	p c	0.2 0.2	0.4 0.6	0.6 1.2	1.4 2.6	1.4 4.0	3.6* 7.6	1.1 8.7	6.1 14.8	23.7 38.5	37.4 75.9	24.1 100.0	.025	.0165	.0103	2.34
2	Blaine	4	18N	12W	5428	p c	1.2 1.2	3.0 4.2	7.8 12.0	15.6 27.6	12.8 40.4	26.4 66.8	3.1 69.9	7.0 76.9	8.7 85.6	7.1 92.7	6.4 99.1	.090	.055	.034	2.40
3	Garvin	20	4N	3E	4813	p c	0.4 0.4	1.6 2.0	5.8 7.8	13.8 21.6	12.6 34.2	32.4 66.6	11.7 78.3	8.2 86.5	6.1 92.6	4.0 96.6	2.6 99.2	.074	.050	.040	2.49
4	Haskell	17	9N	21E	1660	p c	0.4 0.4	0.8 1.2	2.0 3.2	6.2 9.4	7.0 16.4	24.2 40.6	11.2 51.8	18.5 70.3	16.4 86.7	10.1 96.8	3.0 99.8	.050	.040	.028	2.40
5	Haskell	17	9N	21E	1665	p c	2.2 2.2	2.8 5.0	5.6 10.6	11.8 22.4	10.6 33.0	28.4 61.4	12.0 73.4	9.2 82.6	8.4 91.0	4.9 95.9	3.8 99.7	.077	.048	.038	2.40
6	Hughes	4	9N	12E	4326	p c	1.4 1.4	3.0 4.4	6.6 11.0	13.2 24.2	11.6 35.8	26.0 61.8	7.4 69.2	10.4 79.6	9.8 89.4	6.8 96.2	3.1 99.3	.080	.051	.034	2.38
7	Hughes	4	9N	12E	4327	p c	0.8 0.8	3.0 3.8	6.6 10.4	11.2 21.6	8.6 30.2	22.8 53.0	8.6 61.6	13.3 74.9	12.4 87.3	8.2 95.5	4.1 99.6	.074	.046	.030	2.36
8	Kiowa	28	6N	18W	9571	p c	0.2 0.2	0.8 1.0	2.6 3.6	6.4 10.0	6.4 16.4	17.4 33.8	10.5 44.3	17.6 61.9	19.0 80.9	15.3 96.2	3.4 99.6	.050	.036	.023	2.35
10	Okfuskee	19	10N	10E	6860	p c	0.2 0.2	0.8 1.0	4.6 5.6	13.4 19.0	12.8 31.8	31.4 63.2	8.2 71.4	14.6 86.0	7.2 93.2	4.9 98.1	1.5 99.6	.071	.050	.039	2.39
12	Wagoner	20	16N	18E	3245	p c	0.2 0.2	1.0 1.2	3.6 4.8	7.2 12.0	5.8 17.8	17.2 35.0	4.0 39.0	22.0 61.0	27.9 88.9	9.2 98.1	1.2 99.3	.052	.034	.026	2.38
13	Wagoner	19	16N	18E	9592	p c	0.6 0.6	1.0 1.6	3.6 5.2	9.2 14.4	9.0 23.4	24.8 48.2	9.7 57.9	14.6 72.5	13.8 86.3	8.4 94.7	4.7 99.4	.060	.043	.029	2.36
14	Woodward	13	23N	22W	9425	p c	3.6 3.6	4.0 7.6	6.8 14.4	12.0 26.4	8.8 35.2	22.8 58.0	7.6 65.6	12.1 77.7	10.4 88.1	5.6 93.7	5.1 98.8	.087	.050	.033	2.31

* Dispersed, wet sieved, and sieved dry.

velocities calculated from the equation of Stokes' law. The general pipetting procedure outlined by Krumbein and Pettijohn⁵² was adopted. A weighed amount, 10 to 20 grams, of dry material was introduced into a liter graduated cylinder filled exactly to 1,000 ml with N/100 NH₄OH in distilled water. The ammonia acts as a dispersing or peptizing agent, but to promote dispersion the sample was allowed to soak approximately 1 hour, during which time the suspension was agitated intermittently with a stirring rod of the type figured by Krumbein and Pettijohn.⁵³ After dispersion was complete and settling velocities for the desired sizes calculated, the suspension was sampled by pipetting 20 ml into tared 50 ml beakers, evaporated to dryness, and weighed. All weighings were carried out to 4 decimals on a Chainomatic analytical balance. Data were obtained for the 43-40 micron, 40-30 micron, 30-20 micron, and 20-10 micron fractions, the first two of which were sampled at settling depths of 20 cm and the last two at 10 cm.

Settling velocities for specified particle sizes were calculated from the formula of Stokes' law,

$$v = \frac{2(d_1 - d_2)g r^2}{9 n}$$

where v is the velocity in cm per second; r the particle radius measured in cm; and g the acceleration due to gravity, a constant of 980 cm per second per second. The variables to be determined in the laboratory are n , the viscosity of water measured in poises, the value of which for any laboratory temperature may be obtained in handbooks; d_1 , the specific gravity of the material put into suspension; and d_2 , the specific gravity of the fluid medium, which is a constant of 1.00 if distilled water is used and the analysis is conducted at a temperature at or below 32° C.

52. Krumbein, W. C., and Pettijohn, F. J., "Manual of Sedimentary Petrology": *Appleton Century*, pp. 166-172, 1938.

53. *Idem.*, p. 167.

The determination of specific gravity of the material to be sized by sedimentation was done according to the pycnometer method, which is subject to serious errors unless adequate precautions are taken against them.

The following description tells the procedure used for the volcanic ash samples studied in this report. Weigh about 4 grams of -43 micron ash in a tared 50 ml pycnometer and add about 20 ml of freshly boiled distilled water. Heat in an oven at 110° C. for 1 hour and then boil carefully about 5 minutes under reduced pressure in a suction filter jar. Allow approximately 1 hour additional in the jar to enable the vacuum to remove as much as possible of any remaining entrapped air. Fill pycnometer with water and insert the thermometer in the ground glass joint, which has been covered with a thin film of vaseline to prevent evaporation, as advocated by Hillebrand.⁵⁴ Weigh to four decimals and record temperature to nearest tenth of a degree. Final calculation of specific gravity can be made after weighing the same pycnometer filled with distilled water and at exactly the same temperature as the previous weighing.

The inherent errors in size determinations of fine particles by pipette analysis, using an application of Stokes' law, have been examined and found to be so small that the results are highly practical.⁵⁵ Good results may be expected if the operator is sufficiently skilled in laboratory technique and normal precautions are exercised. The fact that a smooth cumulative frequency curve could be constructed for each sample from the combined results of screening and from pipetting, indicates the reliability of the sedimentation method as here performed. Furthermore, enough measurements of grains in the pipetted fractions were made by ocular micrometer of the petrographic microscope to demonstrate that the calculated size closely approximates actual size.

SIZE ANALYSES

The results of the size determinations are shown in Table X, and the data therein are summarized in the form of cumulative

⁵⁴ Hillebrand, W. F., "The Analysis of Silicate and Carbonate Rocks": U. S. Geol. Survey Bull. 700, pp. 54-56, 1919.

⁵⁵ Krumbein, W. C., and Pettijohn, F. J., *op. cit.*, pp. 95-102.

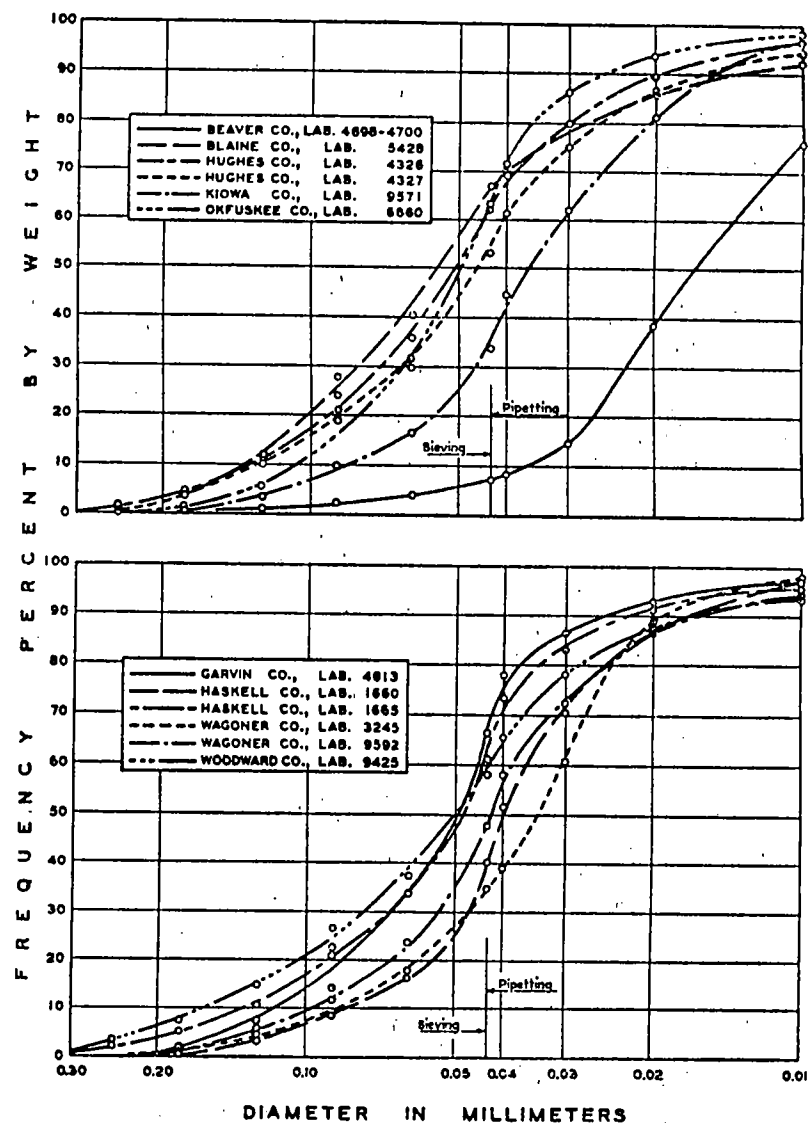


FIGURE 4. Cumulative frequency curves showing texture of volcanic ash from Oklahoma deposits.

"frequency curves in figure 4. It will be noted from the similarity in shape and position of the curves that all samples except that from Beaver County are essentially similar in grain size distribution and degree of sorting. In these samples, representing deposits in western, central, and eastern Oklahoma, 93 percent or more of the particles are smaller than 60 mesh (0.246 mm) and larger than 0.010 mm (10 microns). The rather high degree of sorting is indicated by the large average percentage (69.3) of grains with diameters between 0.10 and 0.025 mm.

Textural differences among the 11 samples exclusive of Beaver County are expressed in part by the quartile diameters Q_3 , M_d , and Q_1 ,⁵⁸ shown in Table X. The median diameter M_d ranges between 0.055 and 0.034 mm and averages 0.0457 mm. Samples with the greatest percentage of coarse particles, i. e., with the highest value of Q_3 , are those from Blaine County, Haskell County (lab. 1665), Hughes County (lab. 4326); and Woodward County. Samples with the greatest percentage of fine particles, and therefore with the lowest values of Q_1 , are from Haskell County (lab. 1660), Hughes County (lab. 4327), Kiowa County, and Wagoner County (lab. 3245 and 9592).

The sample from Beaver County is unlike any of the others analyzed. It is clearly the finest-grained of the lot, containing only 10.6 percent by weight of grains coarser than the 325 mesh screen (0.043 mm or 43 microns) and 85 percent finer than 30 microns. Its median diameter is 0.0165 mm.

PETROLOGY

MINERAL COMPOSITION

Purpose and Procedure. The discovery that volcanic ash from different deposits may have considerably different bloating properties led to the investigation of the mineral composition of the ash in the hope that its behavior under heating might be explained by differences in mineral impurities. The investigation conducted for

⁵⁸ Quartile diameters are read directly from the cumulative curve. Q_3 , the third quartile, is that diameter in millimeters obtained by the intersection of the curve with the 25-percent line, 25 percent of the grains being coarser than this diameter and 75 percent being finer. Q_1 is the first quartile and is the diameter on the curve that intersects the 75-percent line. M_d , the median diameter, is determined by the intersection of the curve and the 50-percent line.

TABLE XI
MINERAL COMPOSITION OF OKLAHOMA VOLCANIC ASH, BY SIZE GRADES

1. Beaver County, Lab. Nos. 4698, 4699, 4700															
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative		
Size grade percent by weight of total sample ¹		0.2	0.4	0.6	1.4	1.4	3.6	1.1	6.1	23.7	37.4	24.1	mineral percent		
Volcanic glass shards	Size grade ² total sample ³	(99.2) 0.20	(99.2) 0.40	(99.2) 0.60	(99.2) 1.39	(99.2) 1.39	(99.2) 3.57	(98.1) 1.08	(97.9) 5.97	(97.1) 23.01	(97.5) 36.47	(98.4) 23.71	97.79	97.81*	
Orthoclase	size grade				0.1	(0.1)	0.2	(0.8)	(1.0)	1.3	(1.1)	0.6			
	total sample				0.00	0.00	0.01	0.01	0.06	0.31	0.41	0.14	0.94	0.94	
Quartz	size grade				0.7	(0.6)	0.3	(0.4)	(0.4)	0.4	(0.3)	0.2			
	total sample				0.01	0.01	0.01	0.00	0.02	0.09	0.11	0.05	0.30	0.30	
Clay aggregates	size grade				0.00	(0.1)	0.2	(0.7)	(0.8)	1.2	(1.1)	0.8			
	total sample				0.00	0.00	0.01	0.01	0.05	0.28	0.41	0.19	0.95	0.95	
2. Blaine County, Lab. No. 5428															
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative		
Size grade percent by weight of total sample		1.2	3.0	7.8	15.6	12.8	26.4	3.1	7.0	8.7	7.1	6.4	mineral percent		
Volcanic glass shards	Size grade total sample	(98.0) 1.18	(96.8) 2.90	(96.1) 7.50	(95.4) 14.88	(94.2) 12.06	(94.2) 24.87	(95.6) 2.96	(95.9) 6.71	(96.3) 8.38	(96.2) 6.83	(95.7) 6.12	94.39	95.22*	
Orthoclase	size grade	(0.2)	0.6	(0.9)	1.3	(2.0)	2.8	(2.2)	(2.1)	1.9	(1.5)	0.4			
	total sample	0.0	0.02	0.07	0.20	0.26	0.74	0.07	0.15	0.17	0.11	0.03	1.82	1.84	
Quartz	size grade	(0.0)	0.7	(1.7)	2.3	(2.0)	1.0	(1.0)	(1.0)	1.1	(0.9)	0.8			
	total sample	0.0	0.02	0.13	0.36	0.26	0.26	0.03	0.07	0.10	0.06	0.05	1.34	1.35	
Clay aggregates	size grade	(1.8)	1.9	(1.4)	1.0	(1.7)	2.0	(1.3)	(1.1)	0.7	(1.4)	3.1			
	total sample	0.02	0.06	0.11	0.16	0.22	0.53	0.04	0.08	0.06	0.10	0.20	1.58	1.59	
													99.13	100.00	

¹ Percent obtained by sieving and sedimentation; data from Table X.

² Mineral percent by volume obtained by grain counts of specified size grades; figures in parentheses interpolated from curves.

³ Mineral percent per size grade contributed to the total sample, calculated as the product of 1 and 2 divided by 100.

* Cumulative mineral percent corrected to 100.

3. Garvin County, Lab. No. 4813

Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative	
Size grade percent by weight of total sample		0.4	1.6	5.8	13.8	12.6	32.4	11.7	8.2	6.1	4.0	2.6	mineral percent	
Volcanic glass shards	size grade	(97.0)	89.8	(84.0)	76.9	(68.5)	57.8	(51.0)	(49.5)	47.4	(48.0)	50.6	percent of	
	total sample	0.39	1.44	4.87	10.61	8.63	18.73	5.97	4.06	2.89	1.92	1.32		
Quartz	size grade		1.5	(3.0)	6.1	(12.5)	25.0	(28.0)	(28.0)	27.6	(25.0)	18.4		
	total sample		0.02	0.17	0.84	1.58	8.10	3.28	2.30	1.68	1.00	0.48		
Orthoclase	size grade		0.2	(1.0)	1.8	(4.0)	8.3	(6.0)	(5.5)	3.5	(2.5)	0.9		
	total sample		0.0	0.06	0.25	0.50	2.69	0.70	0.45	0.21	0.10	0.02		
Clay aggregates	size grade	(3.0)	8.5	(12.5)	14.9	(13.8)	8.7	(14.0)	(15.5)	20.1	(22.3)	26.4		
	total sample	0.01	0.14	0.73	2.06	1.74	2.82	1.64	1.27	1.23	0.89	0.69		
Mica	size grade				0.3			(0.3)	(0.5)	1.4	(2.0)	3.8		
	total sample				0.04			0.04	0.04	0.09	0.08	0.10		
													0.39	0.39
													98.87	100.00

4. Haskell County, Lab. No. 1660

Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative	
Size grade percent by weight of total sample		0.4	0.8	2.0	6.2	7.0	24.2	11.2	18.5	16.4	10.1	3.0	mineral percent	
Volcanic glass shards	size grade	(100.0)	(100.0)	(100.0)	100.0	(100.0)	96.5	(83.5)	(79.5)	74.6	(75.0)	80.2	percent of	
	total sample	0.4	0.8	2.0	6.2	7.0	23.35	9.35	14.71	12.23	7.58	2.41		
Quartz	size grade						2.2	(11.0)	(13.5)	17.3	(17.1)	14.3		
	total sample						0.53	1.23	2.50	2.84	1.73	0.43		
Orthoclase	size grade						0.5	(2.2)	(2.5)	2.9	(2.2)	1.0		
	total sample						0.12	0.25	0.46	0.48	0.22	0.03		
Clay aggregates	size grade						0.8	(3.1)	(3.4)	3.9	(3.6)	3.0		
	total sample						0.19	0.35	0.63	0.64	0.36	0.09		
Mica	size grade							(0.7)	(0.8)	1.3	(1.4)	1.5		
	total sample							0.08	0.15	0.21	0.14	0.05		
													0.63	0.63
													99.76	100.00

TABLE XI (Continued)
MINERAL COMPOSITION OF OKLAHOMA VOLCANIC ASH, BY SIZE GRADES

5. Haskell County, Lab. No. 1665

Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative	
Size grade percent by weight of total sample		2.2	2.8	5.6	11.8	10.6	28.6	12.0	9.2	8.4	4.9	3.8	mineral percent	
Volcanic glass shards	size grade	(87.5)	92.0	(94.7)	97.5	(97.4)	93.2	(84.0)	(82.0)	76.8	(72.2)	64.9	percent of	
	total sample	1.93	2.58	5.30	11.51	10.32	26.66	10.08	7.54	6.45	3.54	2.47		
Quartz	size grade	(0.4)	0.5	(0.4)	0.2	(0.6)	2.8	(6.0)	(7.0)	10.4	(7.3)	1.2		
	total sample	0.09	0.01	0.02	0.02	0.06	0.80	0.72	0.64	0.87	0.36	0.05		
Orthoclase	size grade	(0.0)	0.0	(0.1)	0.1	(0.5)	1.9	(2.6)	(2.9)	3.8	(3.4)	0.4		
	total sample	0.0	0.0	0.01	0.01	0.05	0.54	0.31	0.27	0.32	0.17	0.02		
Clay aggregates	size grade	(11.3)	7.4	(4.5)	2.3	(0.8)	2.0	(4.2)	(5.0)	7.8	(12.5)	30.3		
	total sample	0.25	0.21	0.25	0.27	0.08	0.57	0.50	0.46	0.66	0.61	1.15		
Mica	size grade	(0.1)	0.1	(0.0)	0.0	(0.0)	0.1	(0.3)	(0.5)	1.1	(1.7)	3.2		
	total sample	0.00	0.00	0.00	0.0	0.00	0.03	0.04	0.05	0.09	0.08	0.12		
													0.41	0.41
													99.14	100.00

6. Hughes County, Lab. No. 4326

Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative	
Size grade percent by weight of total sample		1.4	3.0	6.6	13.2	11.6	26.0	7.4	10.4	9.8	6.8	3.1	mineral percent	
Volcanic glass shards	size grade	(8.8)	90.1	(91.0)	93.7	(94.0)	92.3	(92.0)	(91.9)	91.8	(91.0)	89.9	percent of	
	total sample	1.23	2.70	6.01	12.37	10.90	24.00	6.81	9.56	9.00	6.19	2.79		
Quartz	size grade	(3.8)	3.8	(3.8)	3.9	(3.8)	3.8	(3.5)	(3.3)	2.9	(2.6)	1.8		
	total sample	0.05	0.11	0.25	0.51	0.44	0.99	0.26	0.34	0.28	0.18	0.06		
Orthoclase	size grade	(0.8)	0.9	(0.8)	0.7	(1.3)	2.8	(2.5)	(2.4)	1.9	(1.7)	1.1		
	total sample	0.01	0.03	0.05	0.09	0.15	0.73	0.19	0.25	0.19	0.12	0.03		
Clay aggregates	size grade	(6.3)	4.1	(3.0)	1.7	(1.0)	0.8	(1.2)	(1.3)	2.1	(2.9)	5.1		
	total sample	0.09	0.12	0.20	0.22	0.12	0.21	0.09	0.14	0.21	0.20	0.16		
Mica	size grade	(0.2)	0.3	(0.1)	0.0	(0.1)	0.2	(0.7)	(0.8)	0.9	(1.1)	1.5		
	total sample	0.00	0.01	0.01	0.00	0.01	0.05	0.05	0.08	0.09	0.07	0.05		
Diatoms	size grade									0.3	(0.4)	0.6		
	total sample									0.03	0.03	0.02		
													0.08	0.08
													99.13	100.00

TABLE XI (Continued)
MINERAL COMPOSITION OF OKLAHOMA VOLCANIC ASH, BY SIZE GRADES

7. Hughes County, Lab. No. 4327																
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative mineral percent			
Size grade percent by weight of total sample		0.8	3.0	6.6	11.2	8.6	22.8	8.6	13.3	12.4	8.2	4.1				
Volcanic glass shards	percent of	size grade total sample	(71.6) 0.57	74.4 2.23	(77.4) 5.11	81.5 9.13	(88.3) 7.59	94.8 21.61	(92.5) 8.00	(92.2) 12.26	91.7 11.37	(92.4) 7.58	96.8 3.97	89.42	89.94*	
Quartz		size grade total sample	(16.3) 0.13	15.6 0.47	(13.0) 0.86	11.2 1.25	(8.0) 0.69	3.7 0.84	(4.2) 0.36	(4.2) 0.56	4.5 0.56	(3.7) 0.30	1.2 0.05	6.07	6.11	
Orthoclase		size grade total sample	(2.5) 0.02	3.3 0.10	(4.0) 0.26	5.0 0.56	(2.8) 0.24	1.5 0.34	(1.7) 0.15	(1.8) 0.24	1.8 0.22	(1.5) 0.12	0.3 0.01	2.26	2.27	
Clay Aggregates		size grade total sample	(9.0) 0.07	6.8 0.20	(5.0) 0.33	2.4 0.27	(1.0) 0.09	0.0 0.0	(1.0) 0.09	(1.2) 0.16	1.5 0.19	(1.3) 0.11	1.0 0.04	1.55	1.56	
Biotite		size grade total sample									0.5 0.06	(0.5) 0.04	0.4 0.02	0.12	0.12 99.42 100.00	
8. Kiowa County, Lab. No. 9571																
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative mineral percent			
Size grade percent by weight of total sample		0.2	0.8	2.6	6.4	6.4	17.4	10.5	17.6	19.0	15.3	3.4				
Volcanic glass shards		percent of	size grade total sample	(87.0) 0.17	91.4 0.73	(95.0) 2.47	97.9 6.27	(96.8) 6.20	96.0 16.70	(96.4) 10.12	(96.5) 16.98	96.8 18.39	(96.7) 14.80	96.5 3.28	96.11	96.47*
Quartz			size grade total sample	(0.5) 0.0	0.4 0.00	(0.3) 0.31	0.1 0.01	(0.4) 0.03	0.9 0.16	(0.8) 0.08	(0.8) 0.14	0.7 0.13	(0.7) 0.11	0.8 0.03	0.70	0.70
Orthoclase	size grade total sample		(0.0) 0.00	0.0 0.00	(0.2) 0.00	0.5 0.03	(1.3) 0.08	1.8 0.31	(1.8) 0.19	(1.8) 0.32	1.8 0.34	(1.4) 0.21	0.6 0.02	1.50	1.51	
Clay aggregates	size grade total sample		(5.2) 0.01	3.2 0.02	(2.0) 0.05	1.1 0.07	(1.0) 0.06	0.9 0.16	(0.8) 0.08	(0.8) 0.14	0.7 0.13	(0.9) 0.14	1.6 0.05	0.91	0.91	
Biotite	size grade total sample		(0.0) 0.00	0.0 0.00	(0.0) 0.0	0.0 0.00	(0.0) 0.00	0.0 0.00	(0.0) 0.00	(0.0) 0.00	0.1 0.02	(0.2) 0.03	0.5 0.02	0.07	0.07	
Calcite	size grade total sample		(8.0) 0.02	5.0 0.04	(2.6) 0.07	0.5 0.03	(0.5) 0.03	0.5 0.09	(0.3) 0.03	(0.2) 0.03	0.0 0.00	(0.0) 0.0	0.0 0.0	0.34	0.34 99.63 100.00	

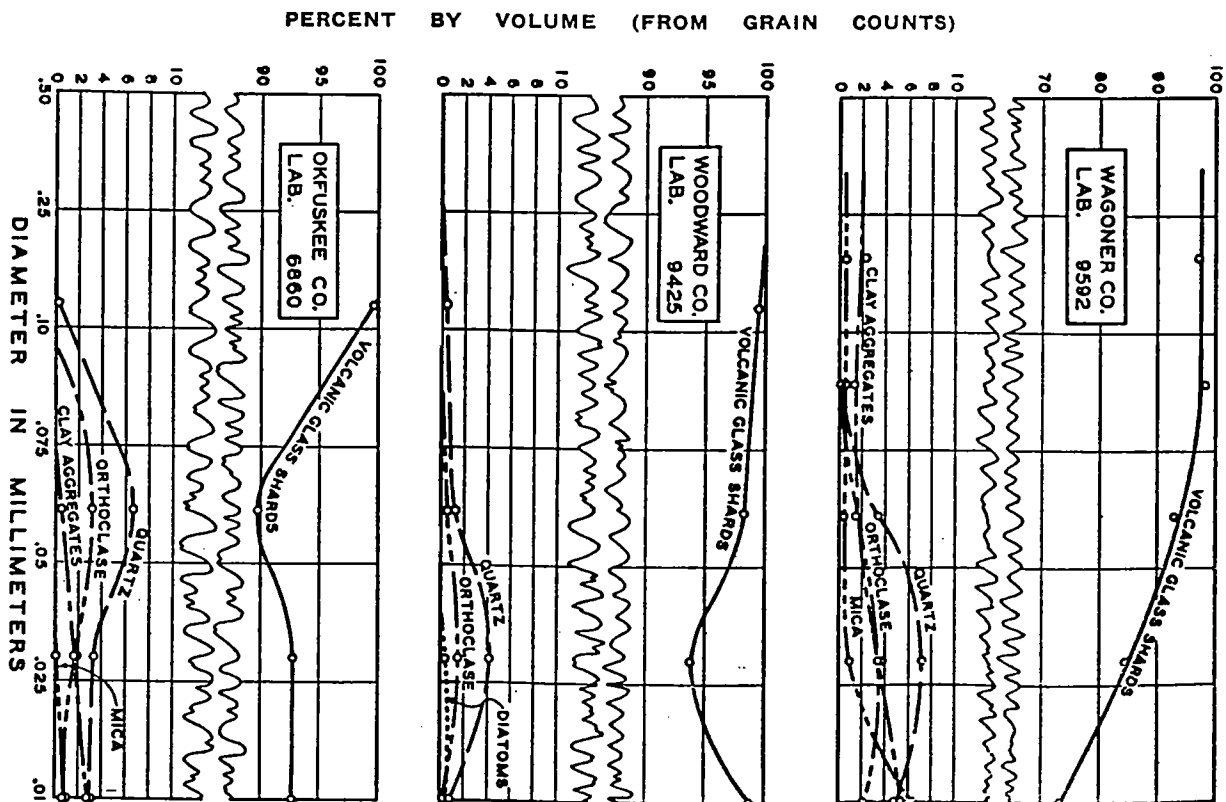
10. Okfuskee County, Lab. No. 6860													
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative
Size grade percent by weight of total sample		0.2	0.8	4.6	13.4	12.8	31.4	8.2	14.6	7.2	4.9	1.5	mineral percent
Volcanic glass shards	size grade	(100.0)	(100.0)	(100.0)	99.8	(95.5)	89.7	(91.6)	(92.1)	92.8	(92.8)	92.6	92.94 93.26*
Quartz	total sample	0.20	0.80	4.60	13.37	12.22	28.17	7.51	13.45	6.68	4.55	1.39	
Orthoclase	size grade				0.2	(3.1)	6.7	(4.9)	(4.5)	3.3	(3.1)	3.0	4.03 4.04
	total sample				0.03	0.40	2.10	0.40	0.66	0.24	0.15	0.05	
Clay Aggregates	size grade				(1.4)	3.1	(2.6)	(2.5)	1.7	(1.2)	0.9	1.92 1.93	
	total sample				0.18	0.97	0.21	0.37	0.12	0.06	0.01		
Biotite	size grade				(0.0)	0.5	(1.2)	(1.3)	1.9	(2.0)	2.8	0.73 0.73	
	total sample				0.0	0.16	0.10	0.19	0.14	0.10	0.04		
	size grade					0.0	(0.0)	(0.0)	0.2	(0.4)	0.7	0.04 0.04	
	total sample					0.0	0.0	0.0	0.01	0.02	0.01		
99.66 100.00													
12. Wagoner County, Lab. No. 3245													
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative
Size grade percent by weight of total sample		0.2	1.0	3.6	7.2	5.8	17.2	4.0	22.0	27.9	9.2	1.2	mineral percent
Volcanic glass shards	size grade	(100.0)	99.0	(97.9)	96.7	(95.7)	93.7	(91.8)	(91.0)	90.2	(90.0)	89.9	91.56 92.21*
Quartz	total sample	0.2	0.99	3.52	6.96	5.55	16.12	3.67	20.02	25.17	8.28	1.08	
Orthoclase	size grade		0.0	(0.6)	0.9	(1.5)	2.5	(4.4)	(5.3)	6.3	(6.3)	6.3	4.38 4.41
	total sample			0.03	0.06	0.09	0.43	0.18	1.17	1.76	0.58	0.08	
Clay aggregates	size grade				0.6	(0.7)	0.9	(1.5)	(1.7)	1.8	(1.6)	1.1	1.32 1.33
	total sample				0.04	0.04	0.15	0.06	0.37	0.50	0.15	0.01	
Biotite	size grade	1.0	(1.5)	1.7	(2.2)	2.9	(2.3)	(2.1)	1.7	(1.4)	1.1	1.97 1.99	
	total sample	0.01	0.05	0.12	0.13	0.50	0.09	0.46	0.47	0.13	0.01		
	size grade									(0.4)	1.7	0.06 0.06	
	total sample									0.04	0.02		
99.29 100.00													

TABLE XI (Continued)
MINERAL COMPOSITION OF OKLAHOMA VOLCANIC ASH, BY SIZE GRADES

13. Wagoner County, Lab. No. 9592													
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative
Size grade percent by weight of total sample		0.6	1.0	3.6	9.2	9.0	24.8	9.7	14.6	13.8	8.4	4.7	mineral percent
Volcanic glass shards	size grade	(98.0)	(98.0)	97.0	(98.0)	98.3	93.1	(89.0)	(88.0)	84.4	(81.0)	73.2	
	total sample	0.59	0.98	3.49	9.02	8.85	29.09	8.63	12.85	11.65	6.80	3.44	89.39 89.97*
Quartz	size grade					0.1	3.4	(6.5)	(6.8)	7.1	(7.0)	4.9	
	total sample					0.01	0.84	0.63	1.00	0.98	0.59	0.23	4.28 4.31
Orthoclase	size grade					0.1	1.5	(2.8)	(3.0)	3.4	(3.2)	2.1	
	total sample					0.01	0.37	0.27	0.44	0.47	0.27	0.10	1.93 1.94
Clay aggregates	size grade	(2.0)	(2.0)	2.2	(1.6)	1.2	1.4	(2.5)	(2.8)	3.7	(4.0)	5.3	
	total sample	0.01	0.02	0.08	0.15	0.11	0.35	0.24	0.41	0.51	0.34	0.25	2.47 2.49
Mica	size grade	(0.5)	(0.5)	0.7	(0.5)	0.2	0.5	(0.5)	(0.5)	1.0	(2.0)	6.5	
	total sample	0.00	0.00	0.02	0.05	0.02	0.12	0.05	0.07	0.14	0.16	0.31	0.94 0.95
Diatoms	size grade											7.2	
	total sample											0.34	0.34 0.34
													99.32 100.00

14. Woodward County, Lab. No. 9425													
Size grade diameters in microns		351-246	246-177	177-124	124-88	88-62	62-43	43-40	40-30	30-20	20-10	<10	Cumulative
Size grade percent by weight of total sample		3.6	4.0	6.8	12.0	8.8	22.8	7.6	12.1	10.4	5.6	5.1	mineral percent
Volcanic glass shards	size grade	(100.0)	(100.0)	(100.0)	99.4	(99.0)	98.2	(95.6)	(95.0)	93.8	(94.6)	98.7	
	total sample	3.60	4.00	6.80	11.93	8.71	22.39	7.27	11.50	9.76	5.30	5.03	96.29 97.43*
Quartz	size grade				0.5	(0.8)	1.1	(3.5)	(3.8)	4.2	(3.7)	0.8	
	total sample				0.06	0.07	0.25	0.27	0.46	0.44	0.21	0.04	1.80 1.82
Orthoclase	size grade				0.1	(0.2)	0.6	(1.1)	(1.2)	1.5	(1.3)	0.0	
	total sample				0.01	0.02	0.14	0.08	0.15	0.16	0.07	0.0	0.63 0.64
Diatoms	size grade									0.5	(0.5)	0.5	
	total sample									0.05	0.03	0.03	0.11 0.11
													98.83 100.00

Figure 5. Mineral frequency diagrams of volcanic ash from Wagoner, Woodward, and Okfuskee Counties.



this purpose consisted of a mineralogical examination of unconsolidated volcanic ash under the petrographic microscope, together with grain counts by which quantitative estimates of mineral constituents could be made.

Owing to differences in mineral composition and mineral ratios in different sizes of the volcanic ash, it is necessary to determine percentages of the several constituents throughout the range of particle size. In this investigation grain counts were made as a general rule on five size fractions, which were so distributed through the size range that interpolation could be made between them to give a rather accurate estimate of the mineral composition of the bulk sample. The fractions generally examined were: 0.246 to 0.177 mm (60 to 80 mesh), 0.124 to 0.088 mm (115 to 170 mesh), 0.062 to 0.043 mm (250 to 325 mesh), 0.030 to 0.020 mm, and the fraction less than 0.01 mm.

When the mineral composition of selected sizes had been determined, the percentage of a particular mineral, such as orthoclase, was plotted as a point for each size counted and these points connected by a smooth curve. From this curve the percentage in the uncounted sizes may be read directly. Like the cumulative frequency curves showing texture (figure 4), the mineral frequency curves show continuous distribution of all mineral constituents through the size range of the sample.

The mineral frequency curves for five samples of volcanic ash, selected to show the wide range in character of mineral distribution, are given in Figures 5 and 6; and the data for all samples are given in Table XI.

Bulk composition of each sample of volcanic ash was calculated from the data obtained by size analysis, grain counts, and interpolation from the mineral frequency curves. The calculations are illustrated by the following example: In a sample from Hughes County, laboratory number 4327, volcanic glass shards constitute 94.8 percent of the constituents present in the 0.062-0.043 mm size grade, and this size grade is 22.8 percent of the total sample, so that the volcanic glass shards in this size grade is 21.61 percent of the total sample. The sum of the calculations for all the size grades

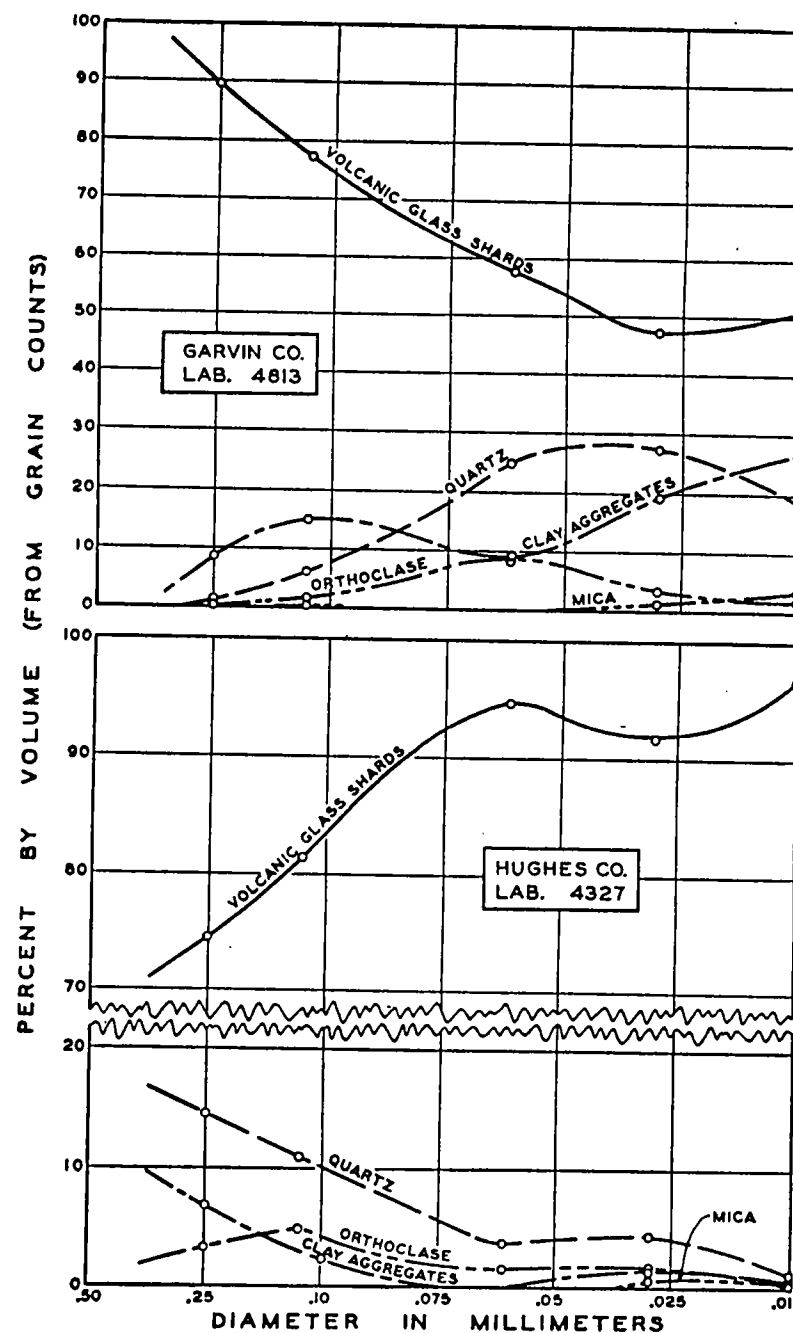


FIGURE 6. Mineral frequency diagrams of volcanic ash from Garvin and Hughes Counties

represents the percentage of shards in the total sample. The percentages of other prominent minerals are calculated in the same manner. In the next to last column of Table XI the calculated mineral composition for each sample is tabulated as the cumulative mineral percent.

As determined by grain counts, each mineral constituent is expressed in volume-percentage, because all grains in a sized fraction have the same average diameter and will have the same volume if particle shape is the same. A source of error is introduced where particle shape is different for different constituents. Platy fragments such as micas and flat volcanic glass shards have considerably less volume than sub-spherical quartz or feldspar grains of the same diameter. Appreciable errors resulting from differences in shape, however, are introduced only in the coarser size fractions of a few Oklahoma volcanic ash samples which have abundant platy glass shards, but even in these the total error is small because most samples contain a low percentage of constituents other than glass shards and furthermore the coarse fractions constitute only a very small percentage of the entire sample.

Owing to a mechanical loss in sieving the sample, the total weight-percent of the size grades is less than 100.0 percent, resulting in a corresponding departure from 100.0 percent in the mineral composition calculations. As this loss probably is distributed uniformly among the different mineral constituents, a correction to 100.0 percent was made for each sample. (Last column Table XI)

A final correction was made for specific gravity differences so that weight-percent of the minerals could be compared directly with the chemical analyses. This was done by multiplying the volume-percentages of the mineral constituents by their respective specific gravities, using 2.4 as the gravity of the glass shards, and reducing the total to 100.0 to give percentage weights of each. The final results are given in summary form in Table XII.

PETROGRAPHY

Microscopic technique. The examination of mineral and volcanic glass particles from Oklahoma volcanic ash was facilitated by use of the petrographic microscope. A Bausch and Lomb research



PLATE IX. Photomicrographs of volcanic ash shards in reflected light. About X150.

- A. Shards in 250-325 mesh (0.061-0.043 mm) size grade, from Woodward County (lab. 9425), with incipient alteration to clay mineral, probably montmorillonite. Fragments most altered appear light gray.
- B. Shards in 115-170 mesh (0.124-0.088 mm) size grade, from Kiowa County (lab. 9571), showing angular character and abundance of highly vesicular glass fragments (light gray).

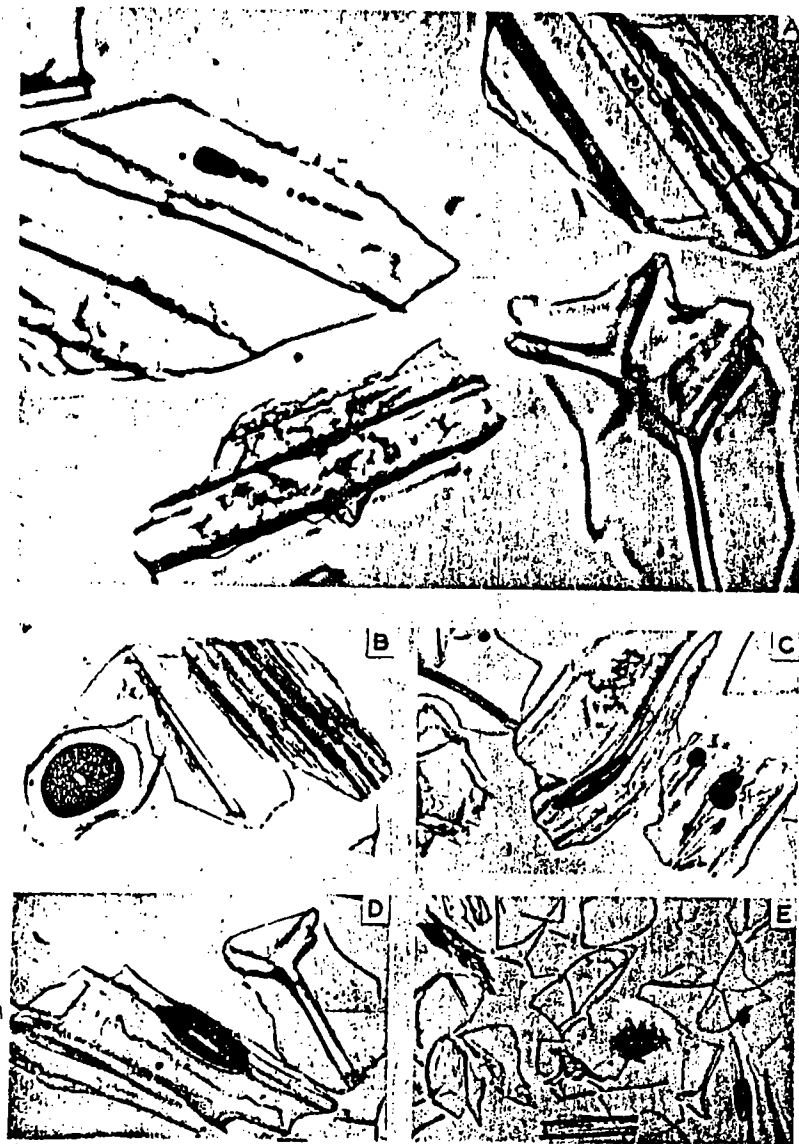


PLATE X. Photomicrographs of volcanic ash in transmitted light, embedded in oil of 1.54 refractive index. About X150, except A, which is about X300.

A, B, C, and D. Shards in 115-170 mesh size grade from Kiowa County, illustrating common shard types found in Oklahoma volcanic ash deposits. Note "fluted" or "ribbed" shards in A; bogen structure in D; bubble inclusions (dark areas) in B, C, and D; and elongate vesicles in B, upper right. E. Shards in 250-325 mesh size grade from Beaver County. Unaltered glass fragments with variety of shard types.

microscope with magnifications ranging up to 970 diameters permitted observation of optical properties and identification of fragments as small as about 2 microns in diameter; and by use of a mechanical stage it was possible to complete the large number of grain counts with considerable accuracy and minimum effort. The completed examination of the twelve samples involved identification and counting of about 68,000 grains.

The procedure adopted for this investigation consisted of embedding on a glass slide the loose mineral fragments in an immersion oil of 1.54 refractive index, covering the mount with a cover glass, and clamping the slide in a mechanical stage. Grain counts were made by traversing the slide by means of the mechanical stage, identifying and counting each grain that passed under the cross-hairs of the microscope ocular. For most slides at least 1,000 grains were counted.

A magnification of 100 diameters gave satisfactory results in size fractions larger than 0.043 mm, but higher magnifications were used for smaller sizes as follows: particles 0.030-0.020 mm, magnification 321 diameters; particles less than 0.01 mm, magnification 430 diameters. Minerals of doubtful identity in the smaller sizes were examined at a magnification of 970 diameters with oil immersion objective.

Extensive use of the accessory gypsum plate gave valuable assistance in making grain counts. Particularly in the smaller sizes is it difficult to make rapid distinction of glass shards from quartz and feldspar, but between crossed nicols and with gypsum plate inserted the separation is made easy by the red color of the isotropic shards, which contrast sharply with the yellow and blue interference colors of anisotropic quartz and feldspar. In slides consisting predominantly of glass shards the gypsum plate is removed only when necessary to ascertain, by Becke line determination of refractive index, whether an isotropic grain is orthoclase or quartz.

An added advantage of this method is the prominence into which it brings fine-grained alteration products that occur inside or coating volcanic glass shards. The low-order interference color of montmorillonite fibers or aggregates is accentuated by use of the

gypsum plate, bringing the montmorillonite into sharp outline and permitting rapid count of clay-altered and unaltered grains.

VOLCANIC GLASS SHARDS

The most abundant component in all samples studied is volcanic glass, which occurs as angular fragments or shards that have been shattered into small particles by the explosive force of an erupting volcano. The glass itself is similar to other natural volcanic glasses like obsidian, perlite, and pumice, but differs from them in its fragmental character and its transportation from the original volcanic source to the region in which it was later concentrated by wind or water.

A sample of nearly pure volcanic ash from typical Oklahoma deposits is light gray in color, so soft that it can be readily crumbled between the fingers, and has a characteristic gritty feel that results from the sharp edges and corners of the glass shards. The luster is dull and earthy in material that is extremely fine-grained or has been at least partly altered to clay minerals, and is vitreous or glassy in volcanic ash that is mostly unaltered or contains conspicuously large, flat shards. In the unaltered varieties light is reflected as tiny pin-points from many individual flat surfaces, giving the sample a sparkling appearance.

Glass shards are so abundant in most samples that the occurrence and percentage of other mineral constituents is difficult to determine without microscopic examination, but in general it is possible to distinguish grains of quartz, feldspar, and mica in the hand specimen with a hand lens of ten power magnification.

Those samples containing highest percentages of volcanic glass, as determined by grain counts, are located without exception in western Oklahoma, in localities nearest the probable source of the ash (north-central New Mexico). The shard content in samples from western Oklahoma counties—Beaver, Blaine, Kiowa, and Woodward—ranges approximately between 95 and 98 percent. In samples from localities in central and eastern Oklahoma, more remote from the probable source, glass shards constitute approximately 60 to 93 percent, the differences resulting from the amount

of admixed detrital constituents contributed under local sedimentational conditions.

Under the petrographic microscope several kinds of glass shards may be distinguished (Plates IX and X). A common type consists of slightly curved plates of uniform thickness or wedge-shaped in cross-section, with irregular, angular outline and sharp corners. A few are curved so slightly as to appear practically flat. They are the remains of thin walls that surrounded relatively large gas bubbles in the highly viscous, frothy magma at the time it was blown from the volcano.

Some of the thin-walled shards are otherwise unmodified, but many of them have on their outer, convex side one or more low ridges that represent parts of the walls of adjoining bubbles. The characteristic bogen structure is developed where three ridges are joined at a somewhat thickened point, two of the ridges being connected and sharply bent into a parabolic curve like a bow and the third projecting forward from it like an arrow (Plate X-D). The bow-like curved ridge is part of the wall of an elongated ellipsoidal bubble.

Such shards generally are so thin that they contain no inclusions or flow lines and show no vesicular structure; and as a rule they are unaltered even though other types of shards in the same sample are incipiently altered to clay minerals. The sample from Woodward County, laboratory number 9425, is a notable exception in which nearly all shards are both platy and conspicuously altered (Plate IX-A).

Thick-walled shards of several modifications make up a substantial part of the volcanic glass. One type that is common in most samples consists of rather thick plates with parallel closely spaced ridges, either straight or curved, which represent walls of small elongated bubbles. These "fluted" or "ribbed" shards, being relatively thick, not uncommonly contain inclusions of small spherical bubbles and elongated vesicles. They are more likely to show incipient alteration to clay minerals than shards of the thin-walled, flat type.

other minerals, all analyses are not reliable indications of the chemical composition of the glass shards themselves. The two purest samples, from Beaver and Kiowa Counties, show respectively a silica content of 72.65 and 72.03 percent. Analyses of these two samples probably give the closest approximation to the chemical character of the normal volcanic glass found in the Oklahoma deposits herein discussed. The highly siliceous volcanic glass corresponds chemically with rhyolites and granites.

QUARTZ

The most abundant accessory mineral in most Oklahoma volcanic ash deposits is quartz. It constitutes 0.3 to 2.0 percent of the four samples from western Oklahoma, and 3.5 to 21.4 percent of those from central and eastern Oklahoma.

The quartz is of two types, pyroclastic and detrital. Pyroclastic quartz, derived from the fragmentation of quartz crystals that were present in the magma before its explosive ejection, is recognized by its angular shape and clear, fresh appearance. It was transported by wind along with the glass shards. Detrital quartz was introduced and mixed with the wind-transported ash mostly through the action of running water, which obtained the quartz grains from local sands of stream valleys and sandstones of Pennsylvanian and Permian age. The characteristic features of detrital quartz are sub-rounded outline, a result of abrasion during transportation, and pitting, secondary crystal enlargements, or clay coatings. Rounded grains of chert are associated with detrital quartz in a few samples, being most abundant in the very sandy ash from Garvin County.

Detrital quartz is much more abundant than pyroclastic quartz in all samples studied except that from Beaver County, in which all quartz observed is clear and angular and presumably is of pyroclastic derivation.

FELDSPAR

Like quartz, the feldspars in Oklahoma volcanic ash are of pyroclastic and detrital origin. The most common feldspar is orthoclase. It is the only feldspar which is definitely pyroclastic and is so recognized when it occurs as angular, very clear, colorless

fragments, lacking Carlsbad or other twinning and showing no cleavage lines. This feldspar is sanidine or the high temperature potassium feldspar characteristic of volcanic rocks, as shown by its small axial angle $2V$. Its dispersion is distinct, $\rho > v$. Pyroclastic orthoclase predominates over detrital orthoclase in samples from Kiowa, Beaver, and Blaine Counties, in a ratio of about 10 to 1, but this relation is reversed in samples from other localities in the State. Detrital orthoclase is sub-rounded to sub-rectangular, very commonly turbid as a result of incipient alteration, and shows well-developed cleavage lines. A considerable percentage of the larger grains appear light pink in color under the microscope. Undoubtedly they were derived from the disintegration of granites or gneisses, in which the typical color is flesh-red.

Next in abundance to orthoclase is microcline, which invariably is a detrital constituent of the ash deposits. It is recognized by the characteristic cross-hatched twinning lamellae under crossed nicols of the petrographic microscope. Microcline is not to be expected as a pyroclastic mineral because it does not occur in glassy extrusive rocks, but in addition clear evidence of clastic origin is found in the sub-rounded shape and partly altered condition of the fragments themselves. Their ultimate sources are granites, pegmatites, and gneisses, which have contributed to the formation of arkosic deposits, and these in turn have been disintegrated, transported, and mixed with the volcanic shards.

Microcline occurs only in volcanic ashes that are high in detrital quartz and orthoclase, such as those from Wagoner, Hughes, Haskell, Garvin, and Okfuskee Counties; and it is lacking or extremely rare in deposits from Kiowa, Beaver, Blaine, and Woodward Counties.

The plagioclase feldspars, albite and oligoclase, recognized by the characteristic albite twinning bands, occur as rare constituents in a few deposits of volcanic ash where they have been introduced as clastic, sub-rounded fragments.

In the mineral composition tables (Table No. XI) all feldspars, regardless of pyroclastic or detrital origin, are included under the name orthoclase, which, in the samples studied, constitutes 95-100 percent of the total feldspar.

TABLE XII.
SUMMARY OF MINERAL COMPOSITION OF OKLAHOMA VOLCANIC ASH DEPOSITS

Sample number	Sample County	Laboratory Number	Volcanic glass shards	Calculated mineral constituents, weight percent				Mica	Diatoms	Percent of glass shards that are clay-altered, 0.062-0.043 mm
				N _d	Quartz	Orthoclase	Clay aggregates			
1	Beaver	4698	97.7	1.499	0.3	1.0	1.0	P	P	Trace
2	Blaine	4899	94.9	1.501	1.5	2.0	1.6	P	P	3.9
3	Garvin	5428	59.5	1.498	21.5	5.3	13.2	0.5	P	4.3
4	Haskell	4813	84.9	1.500	10.3	1.7	2.3	0.8	P	31.9
5	Haskell	1660	88.4	1.503	4.1	1.9	5.1	0.5	P	48.3
6	Hughes	1665	92.4	1.500	3.5	1.9	1.8	0.4	0.1	51.7
7	Hughes	4326	89.0	1.498	6.8	2.5	1.6	0.1	P	38.4
8	Kiowa	9571	96.2	1.501	0.8	1.6	0.9	0.1	P	0.8
10	Oktuskee	6860	92.6	1.498	4.5	2.1	0.7	0.1	P	11.7
12	Wagoner	3245	91.5	1.497	4.9	1.4	2.0	0.1	P	6.2
13	Wagoner	9592	89.2	1.496	4.8	2.1	2.5	1.2	0.3	41.6
14	Woodward	9425	97.2	Indefinite	2.0	0.7	—	P	0.1	100.00

P—present
N_d—refractive index for sodium light

Another type is represented by shards of tetrahedral shape, which are formed of a relatively large mass of glass at the common junction of four adjoining bubbles.

Present in all samples but less abundant than other types are fragments of finely vesicular pumice. They are characterized by highly irregular shape, by the presence ordinarily of many small bubbles, elongated vesicles, and flow lines, and have formed from that part of the volcanic glass in which large bubbles were not generated or preserved.

Refractive indices. Refractive indices of glass shards from samples examined for this report are given in Table XII. All samples except that from Woodward County contained abundant unaltered shards on which refractive index could be determined precisely. The Woodward County material is so thoroughly altered that its index is indefinite. Refractive index determinations were made by the immersion method under the petrographic microscope, using monochromatic light from a sodium lamp which gives the index for the D line (n_d). Recently standardized Shillaber's index liquids in intervals of 0.002 were used, so that the probable range of error is considerably less than ± 0.002 . In every sample some shards are present which deviate as much as 0.003 from the recorded value, but the refractive index here recorded is that of the majority of shards in the sample.

The range in indices is from 1.496 to 1.503, both extremes being found in east-central Oklahoma. Eight of the eleven samples for which an index is recorded lie within the range 1.495 to 1.501, which is remarkably constant when it is considered that the known range of natural glass is from 1.48 to 1.62.⁵⁷ It is thus probable that the volcanic glass in all these samples was derived from a single source area and in all likelihood belongs to one period of eruption. This period, however, may have included several falls of ash.

Chemical analyses of bulk samples of volcanic ash from Oklahoma as given in Table II (tuffs and bentonitic clays excepted) show a range in silica from 67.99 percent to 76.05 percent. But, because some samples are contaminated with detrital quartz and

57. George, W. O., "The Relation of the Physical Properties of Natural Glasses to their Chemical Composition": *Jour. Geol.*, Vol. 32, p. 365, 1924.

Orthoclase ranges between 0.7 and 5.2 percent, and in most samples it is about 2 percent. Orthoclase predominates over all other accessory minerals in the ash deposits of Beaver, Blaine, and Kiowa Counties, which are composed almost exclusively of pyroclastic materials. The predominance of orthoclase in the ash indicates that phenocrysts of this mineral were more abundant than phenocrysts of other minerals in the molten glass before its ejection, this being the normal petrologic occurrence.⁵⁸

CLAY AGGREGATES

The term clay aggregates as here used includes rock or mineral particles of diverse origin and mineral composition whose identity could not be established with certainty. The particles consist chiefly of fine-grained clay fibers aggregated in random orientation and generally with aggregate polarization. Sub-rounded grains of this general type occurring in volcanic ash samples with a large percent of detrital admixture are probably indurated shale fragments. A few fragments that show parallel, straight lines, probably representing cleavage, may be completely altered grains of detrital feldspar.

In relatively pure volcanic ash such particles not uncommonly show the remains of bubble-like inclusions and curved flow lines, indicating a derivation from volcanic glass shards. The resulting clay mineral probably belongs to the montmorillonite group. There is a wide range in percentage of clay aggregates in different samples of Oklahoma volcanic ash, as well as in the relative proportions of clay aggregates, quartz, and orthoclase. Clay aggregates range between 0 and 13.4 percent in the samples examined, being least abundant in western Oklahoma where the deposits are relatively pure volcanic ash.

MICA

Biotite and muscovite are present in all samples in amounts ranging from less than 0.1 to 1.2 percent, and the highest concentration is in the finer sizes of the ash. In general it is difficult to assign to them an unquestionable pyroclastic origin, although the large flakes that are quite clear and free from alteration, and which

occur in the western Oklahoma deposits, probably were borne directly by wind with the glass shards. In other deposits there is no reliable criterion by which their origin may be determined, except that in the grade size less than 10 microns a considerable part of the mica occurs in the form of sericitic shreds that appear to have been derived from shales.

Biotite is more abundant than muscovite. Under the microscope it appears as thin flakes with pale green, golden-brown, or dark brownish-green color in which 2V is nearly zero. Muscovite flakes are colorless and have a moderate axial angle.

OTHER MINERALS

Oklahoma volcanic ash contains in different localities very small quantities of the common heavy accessory minerals such as zircon, tourmaline, rutile, hornblende, garnet, magnetite, hematite, limonite, ilmenite, and leucoxene. Part of the hornblende probably is pyroclastic but the other minerals mostly are rounded by attrition and undoubtedly are clastic. They are relatively most abundant in samples with highest percentage contamination of detrital quartz and feldspar.

A small amount of calcite in the form of interstitial cement was found in the sample from Kiowa County. It is lacking in the other samples and apparently it has not formed as an alteration product of volcanic glass shards.

Opal in the form of minute diatom tests was observed in every sample studied. The opal tests form only a small part of each sample, but their occurrence is peculiarly significant in a consideration of the origin of the deposits.

⁵⁸ Grout, Frank F., "Petrography and Petrology": McGraw-Hill, p. 114, 1932.

EFFECT OF MINERAL AND TEXTURAL COMPOSITION ON BLOATING PROPERTIES

All true volcanic ashes tested in this investigation yielded a bloated product on application of sufficient heat. These several products were similar in general properties, but showed the most notable differences in the temperature at which they began to bloat. Very fine cells, too small to measure, developed at temperatures as low as 1,090° C. in some samples. For purpose of comparison, "initial bloating" is here considered the temperature at which cells 0.25 mm minimum diameter first appeared, which, for the samples studied, ranged from 1,200° to 1,350° C. The studies of grain size and mineral composition of crude volcanic ash, whose results are given on earlier pages, were made in an attempt to explain some of these differences.

Inspection of Table XIII and figure 7 suggests as a general trend that the higher the degree of purity of the volcanic ash, the higher the initial bloating temperature. Samples 1, 2, 8, 10, and 12, with shard content exceeding 91 percent, begin to bloat at 1,300° C., or higher. Samples 3, 4, 7, and 13, with shard content ranging between 59.5 and 89.2 percent, begin to bloat at 1,250° C. Such a condition results evidently from the fluxing action of the alkalis in the feldspar and clay aggregates of the more impure ash deposits.

There is, however, no fixed relation of volcanic ash purity, based on percentage of volcanic glass shards, to initial bloating temperature. Sample no. 1 (Beaver County) has nearly the same shard percentage as no. 14 (Woodward County) yet they begin to bloat at 1,350° C., and 1,200° C. respectively, these temperatures representing extremes of the initial bloating range. Furthermore a sample highly contaminated with quartz, feldspar, and clay aggregates like no. 3 (Garvin County), and containing only 59.5 percent shards, begins to bloat at the same temperature (1,250° C.) as sample no. 6 which contains 92.4 percent shards.

Similar difficulty is experienced in trying to analyze the influence of volcanic ash texture. Ordinarily the finest-grained material would be expected to become glassy and bloat at a lower temperature than coarse-grained material, yet the two finest-grained

volcanic ashes (numbers 1 and 12, Table XIII and figure 7) begin to bloat at the highest temperature, 1,350° C. Samples 3, 10, and 14, moreover, of identical median diameter, begin to bloat at 1,250°, 1,300°, and 1,200° C. respectively. From these observations it appears that texture has the least influence of all factors on initial bloating temperature.

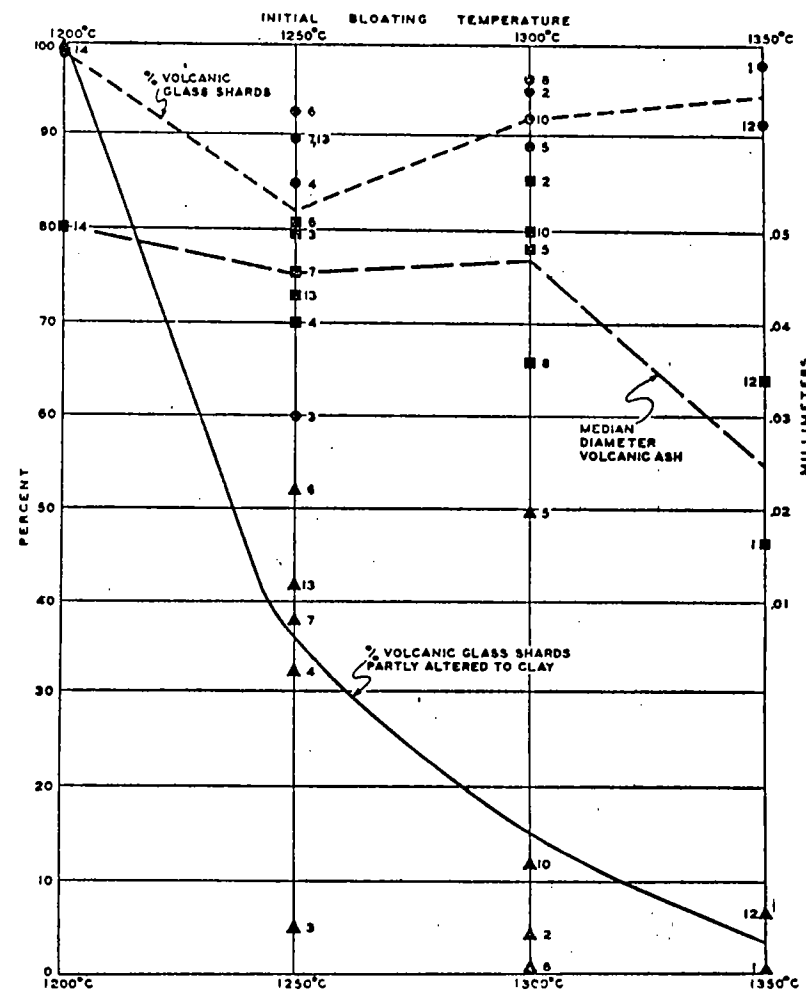


FIGURE 7. Relation of initial bloating temperatures of Oklahoma volcanic ash to degree of incipient alteration, purity, and grain size. Numbers refer to sample numbers (See Table II).

TABLE XIII

COMPARISON OF INITIAL BLOATING TEMPERATURE TO DEGREE OF ALTERATION, RELATIVE PURITY, AND TEXTURE OF OKLAHOMA VOLCANIC ASH.

Sample number	County	Initial bloating temperature ¹	Degree of alteration ² (percent)	Relative purity ³ (percent)	Texture median diameter (mm)
1	Beaver	1350° C.	trace	97.7	0.0165
2	Blaine	1300° C.	3.9	94.9	0.055
3	Garvin	1250° C.	4.3	59.5	0.050
4	Haskell	1250° C.	31.9	84.9	0.040
5	Haskell	1300° C.	48.3	88.4	0.048
6	Hughes	1250° C.	51.7	92.4	0.051
7	Hughes	1250° C.	38.4	89.0	0.046
8	Kiowa	1300° C.	0.8	96.2	0.036
10	Okfuskee	1300° C.	11.7	92.6	0.050
12	Wagoner	1350° C.	6.2	91.5	0.034
13	Wagoner	1250° C.	41.6	89.2	0.043
14	Woodward	1200° C.	100.0	97.2	0.050

¹ Temperature at which cells 0.25 mm minimum diameter first appeared.² Percent of glass shards partly altered to clay in 0.062-0.043 mm size grade.³ Percent of volcanic glass shards in total sample.

Probably more influential than texture and relative purity on the bloating characters of volcanic ash is the alteration of the volcanic glass shards themselves. The samples examined in this investigation show in general that the greater the percentage of glass shards incipiently altered to clay minerals, the lower the initial bloating temperature (Table XIII and figure 7). The most conspicuous example is sample no. 14 from Woodward County. It contains 97.2 percent glass shards but each shard is partly altered to montmorillonite clay, and the sample begins to bloat at 1,200° C. Other samples of high purity such as 1, 2, 8, and 12 contain mostly unaltered shards and their initial bloating temperature is 1,300°—1,350° C. Two samples from the same deposit in Wagoner County, numbers 12 and 13, have 6.2 and 41.6 percent shard alteration respectively and they begin to bloat at 1,350° and 1,250° C. respectively; although as shown in Table XII and figure 7 their percentage mineral composition is nearly the same. The alteration products appear to play a dominant role, but the explanation of their relation to bloating temperature is not apparent from the present investigation.

INDEX

INDEX

A

Abstract	7
Accessory minerals in volcanic ash	78-81
Acid, boric, effect on viscosity	17
Age of Oklahoma volcanic ash	49, 54, 55, 56, 57
Alkali, effect on bloating	26
Alkaline earth, effect on bloating	26
Alumina, effect on viscosity	14, 17
Applications, commercial	
Popped volcanic ash	40
Products from addition of caustic soda	40
Pumicell	39
Artificial inorganic cellular materials	13
Ash, volcanic—see Volcanic ash	

B

Barbour, E. H., quoted on deposition	53
Bloating, cause of	26
Bloating, gases during	26
Bloating, larger-scale	29
Bloating or "popping" obsidian	14
Bloating or "popping" perlite	14
Bloating or "popping" pumice	15
Bloating or "popping" tuff	15
Bloating period, effect of time	30
Bloating properties of volcanic ash	
Affected by chemical composition	24
Effect of mineral composition	82
Effect of purity	84
Effect of textural composition	82
Bloating temperatures	29
Blocks, volcanic	20
Bombs, volcanic	19
Boric acid, effect on viscosity	17

C

Calcium carbonate in volcanic ash deposits	49
Carbon compounds, producing foamy structure	15
Cause of bloating	26
Caustic soda addition, commercial application of products	40
Caustic soda, effect of	34
Cell size	31
Cellular materials, artificial inorganic	13
Cellular product, conditions necessary for	27
Cellular structure, definition	12
Cellular structure in nature	12
Chemical composition and bloating properties	24
Cinders, volcanic	20
Clay aggregates in volcanic ash	80
Clays, cellular products from	13
Commercial applications	
Popped volcanic ash	40
Products from addition of caustic soda	40
Pumicell	39

Composition and bloating properties	
Alteration of volcanic glass shards	84
Chemical	24
Mineral	82
Purity of	84
Textural	82
Compounds, carbon, producing foamy structure	15
Compounds, sulfur, producing foamy structure	15
Conditions necessary for bloated product	27
Conductivity, thermal, of products	30
Conversion of volcanic glassy rocks	14
Cousen and Hodkin, quoted on glass composition effect	17
Crushing strength	30

D

Definition of volcanic ash	19
Deposition and origin of volcanic ash	51
Deposition sites of volcanic ash	52
Deposits, volcanic ash, in Oklahoma	42-47
Determination of specific gravity of volcanic ash	60
Diatoms	49, 52, 53, 81
Dioxide, sulfur, as bloating agent	26
Dust, volcanic	19, 21

E

Effect of alkali on bloating	26
Effect of alkaline earth on bloating	26
Effect of alteration of volcanic glass shards on bloating	84
Effect of caustic soda	34
Effect of mineral composition on bloating properties	82
Effect of textural composition on bloating properties	82
Effect of viscosity on bloating	14, 24

F

Fauna, molluscan	57
Fauna, snail	49, 53, 56
Feldspar, as accessory mineral	78, 80
Ferric oxide as bloating agent	27
Ferric oxide, oxygen liberated	27
Ferric oxide, source of gas	16
Foamglass	15
Foamy structure in glass, causes	15
Fossil evidence for age of volcanic ash	49, 54, 55, 56, 57
Frye, John C., quoted on age of volcanic ash	57

G

Gases, during bloating	26
Gases responsible for bloating certain clays	14
Glass and glassy material, nature of	16
Glass, manufactured, conversion of	15
Grain size, volcanic ash	49
Gravity, specific, of products	30

H

Heat, specific, of products	30
Hodkin and Cousen, quoted on glass composition effect	17

J

Johannsen, quoted on eruption of volcanoes	19
--	----

L

Ladoo, quoted on volcanic ash	19
Lapilli	19, 20
Larger-scale bloating	29
Lime, effect on viscosity and setting	14, 17

M

Magnesia, effect on viscosity	14, 18
Manufactured glass, conversion of	15
Materials, porous, natural	12
Metal oxides, multivalent	15
Mica, as accessory mineral	80
Mineral composition, differences in	70
Mineral composition, effect on bloating properties	82
Mineral composition of volcanic ash	62-72
Minerals, accessory	78-81
Molluscan fauna	57
Multivalent metal oxides	15

N

Natural porous materials	12
Nature of glass and glassy material	16

O

Obsidian, bloating or "popping"	14
Origin and deposition of volcanic ash	51
Oxide, ferric, as bloating agent	27
Oxide, ferric, oxygen liberated	27
Oxide, potassium—see Potash	
Oxide, sodium—see Soda	

P

Particle size of volcanic ash	58-62
Perlite, bloating or "popping"	14, 26
Petrography of volcanic ash	72
Physical properties of products	30, 33
Physical properties of pumice	12
Physical properties of scoria	12
Pirsson and Schuchert, quoted on volcanic ashes	19
Potassium oxide—see Potash	
"Popping" perlite	26
Popped volcanic ash, uses	40
Porous materials, natural	12
Potash, effect on viscosity	14, 17
Properties, physical, of products	30, 33
Pumice	19
Bloating or "popping"	15
Physical properties	12
Pumicell, commercial applications	39
Pumicite	19
Purity, effect on bloating volcanic ash	84

Q

Quartz, as accessory mineral	78
------------------------------------	----

R

Refractive indices of glass shards	77
--	----

S

Sand, volcanic	19
Schuchert and Pirsson, quoted on volcanic ashes	19
Scoria, physical properties	12
Shales, cellular products from	13
Silica, high viscosity	14, 17
Silica range in volcanic ash	77
Size, cell	31
Size of volcanic ash particles	58-62
Slates, cellular products from	13
Snail fauna	49, 53, 56
Soda, caustic, effect of	34
Soda, effect on viscosity	14, 17
Sodium oxide—see Soda	
Softening temperature of glass	18
Specific heat of products	30
Specific gravity of products	30
Specific gravity of volcanic ash, determination of	60
Strength, crushing	30
Structure, cellular, definition	12
Structure, cellular in nature	12
Structure, porous, definition	12
Sulfur compounds, producing foamy structure	15
Sulfur dioxide as bloating agent	26
Swineford, quoted on source	51

T

Temperature, softening of glass	18
Temperature, time, effects on bloating	23, 24
Temperatures, bloating	29
Textural composition, effect on bloating properties	82
Thermal conductivity of products	30
Time, effect on bloating	30
Time, temperature, effects on bloating	23, 24
"Trapped moisture" responsible for expansion	15
Tuff, bloating or "popping"	15
Tuff, volcanic, bloating	24

U

Uses of popped volcanic ash	40
Uses of products from addition of caustic soda	40
Uses of pumicell	39

V

Viscosity, effect of	14
Viscosity, effect on bloating	24
Volcanic ash, accessory materials	78-81

Volcanic ash

Age	49, 54-57
Clay aggregates in	80
Definition	19
Differences in mineral composition	70
Geology	49
Grain size	49
In Ogallala formation	50
Mica as accessory mineral	80
Mineral composition	62-72
On High Plains	50
Origin and deposition	51
Particle size	58-62
Petrography	72
"Popping"	34-39
Range in silica	77
Sites of deposition	52
With stream terraces	50

Volcanic ash deposits

Calcium carbonate in	49
In Oklahoma	42-47
Source	51
Thickness	49
Types	49

Volcanic ashes	19, 20
Volcanic blocks	20
Volcanic bombs	19
Volcanic cinders	20
Volcanic dust	19, 20
Volcanic glass, refractive indices	77
Volcanic glass shards, alteration of	84
Volcanic glass shards, kinds	75, 77
Volcanic glass shards, percentages in samples studied	74
Volcanic glassy rocks, conversion of	14
Volcanic sand	19
Volcanic tuff, bloating	24