VOLCANIC ASH AS A SOURCE OF SILICA FOR THE SILICIFICATION OF WOOD.*

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ABSTRACT. The chemical and physical properties of volcanic ash make it a rich source of readily available silica for geochemical processes. In recent years, more and more sedimentary formations are being recognized as containing volcanic ash or its decomposition products. The common association of silicified wood with volcanic ash is viewed as the result of a genetic relationship arising from the alterability of the ash. Silicified wood may serve as an indicator for volcanic material in sedimentary deposits.

INTRODUCTION.

THE demonstration by Hewett[1] and by Wherry[2] in 1917 that bentonite is a decomposition product of water-laid volcanic ash stimulated geological explorations which have revealed bentonite and other materials of volcanic origin in Paleozoic, Mesozoic, and Tertiary sediments in widely scattered regions of North America. Many formations, like those of the Upper Cretaceous series of the Gulf Coastal Plain, have been shown through systematic study to be unexpectedly rich in volcanic ash and its decomposition products.[3,4] The Mowry shale of Wyoming and its western equivalent, Aspen, are believed by Rubey[5] to have formed through submarine decomposition of a highly siliceous volcanic ash. Extensive beds of zeolitic minerals that originated through the alteration of volcanic ash have been described by Ross,[6] Bradley,[7] and Bramlette and Posnjak.[8] Not only have beds of pure volcanic materials been located, but also pyroclastics diluted with varying amounts of sand and shale have been recognized in many for-

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[1] Hewett, D. F.: Jour. Washington Acad. Sci. 7, 196, 1917.

[2] Wherry, E. T.: idem 7, 576, 1917.

[3] Ross, C. S., Miser, H. D., and Stephenson, L. W.: U. S. Geological Survey Prof. Paper 154-F, 1929.

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[8] Bramlette, M. N., and Posnjak, E.: Am. Mineralogist 18, 167, 1933.

mations. Volcanic ash, therefore, occurs rather commonly in sedimentary formations, and is also a fertile source of various minerals that originate through its decomposition and alteration.

THE ALTERATION OF VOLCANIC ASH.

The chemistry of the alteration of volcanic ash is still little understood. However, the liberation of large amounts of silica has become recognized as an important feature of this alteration. Free silica is often found in weathered volcanic ash. Pirsson[9] in discussing the microscopic characters of volcanic tuffs states:

> "One of the earliest indications of a change in tuffs, when examined in section, is the deposition in them of some form of hydrated silica, opal, chalcedony, etc."

Chert layers and nodules at the base of Ordovician bentonite beds have been noted by Nelson[10] and by Rosenkrans,[11] and the latter has interpreted the silica of the chert as having come from the parent volcanic ash. The hardening of shales that immediately underlie Upper Cretaceous bentonite beds of Wyoming was shown by Rubey[12] to be correlated with an excessive amount of silica, which may have been derived from the parent ash beds. Heathman[13] recently published an excellent photograph of such a hardened shale.

Occasionally a bed of volcanic ash is found that is fresh at one place and altered to bentonite at another. If it can be shown that the bed was uniform originally, such an occurrence makes it possible to compare the composition of the initial and final products of alteration and throws light on the chemical changes involved. Ross, Miser, and Stephenson[14] and Bramlette[15] have made such studies. The percentage of silica and alumina in the parent igneous materials and in the bentonites derived from them, as reported by these authors, is given in the fol-

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[9] Pirsson, L. V.: This Journal 40, 205, 1915.

[10] Nelson, W. A.: Bull. Geol. Soc. Am. 33, 605, 1922.

[11] Rosenkrans, R. R.: This Journal 27, 113, 1934.

[12] Rubey, W. W.: op. cit., p. 155, 1929.

[13] Heathman, J. H.: Geol. Survey Wyoming Bull. 28, 6, 1939.

[14] Ross, C. S., Miser, H. D., and Stephenson, L. W.: op. cit., p. 186.

[15] Bramlette, M. N.: The analyses are given in U. S. Geol. Survey Bull. 878 by R. C. Wells, pp. 13 and 66, 1937. They are discussed by Bramlette in an unpublished paper on the Monterey shale of California.

lowing table. For the complete analyses, the reader should consult the original works:

	1	2	3	4
SiO_2	62.97	45.12	65.66	50.03
Al_2O_3	19.00	28.24	12.71	16.75
SiO_2: Al_2O_3	5.6:1	2.7:1	8.8:1	5.1:1

1. Trachyte, Howard County, Arkansas.
2. Bentonitic mineral concentrated from bentonite derived from trachytic pumice, Howard County, Arkansas.
   Analyses 1 and 2 from Ross, Miser, and Stephenson.
3. Volcanic ash from the Santa Monica Mountains, Los Angeles County, Calif.
4. Bentonite resulting from the decomposition of 3.
   Analyses 3 and 4 from Bramlette.

If the assumption is made that no change in the amount of alumina occurred during the alteration, the loss of silica was 52 and 42 per cent of the original amount in the Arkansas and California materials respectively. That a similar liberation of silica takes place during the katamorphism of igneous rocks in general has been known for many years. However, the porous and finely divided condition and the highly unstable nature of glassy volcanic ash allow a far more rapid alteration of ash than of a massive, crystalline rock. It is not necessary to consider in this paper the fate of the soluble alkalies and alkaline earths and other aspects of the alteration.

Recently, Hauser and Reynolds[16] described hydrothermal experiments in which montmorillonite, the most common clay mineral of bentonites, was obtained from a synthetic glass and from an obsidian of Yellowstone Park, in acid, neutral, and alkaline media at 300° C. in 150 hours. Concerning the removal of excess silica from the obsidian during alteration they state,

> "The silica is presumably transported either as a solution or in the form of a silicic acid sol."

The results of their study agree with those of related experiments by Noll[17] in many respects, one being that within limits the composition of the initial mixture with regard to silica and alumina has little influence on the formation of montmorillonite.

The common association of large deposits of diatomite and volcanic ash in both marine and fresh-water formations throughout the world has been discussed by Taliaferro,[18] and

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[16] Hauser, E. A., and Reynolds, H. H.: Am. Mineralogist 24, 590, 1939.

[17] Noll, W.: Min. petr. Mitt. 48, 210, 1936.

[18] Taliaferro, N. L.: Univ. Calif. Bull. Dept. Geol. Sci. 23, 1-56, 1933.

he has concluded that the volcanic ash was the rich source of silica which allowed a rapid and continued growth of diatoms. This genetic relationship between the siliceous tests of diatoms and volcanic ash would indicate that at least the initial alteration of ash and liberation of silica were rapid relative to the deposition of normal sediments, which would otherwise bury the ash and make its silica unavailable to the diatoms.

The evidence briefly outlined above suggests that volcanic ash is a rich source of readily available silica. Therefore it seems reasonable to believe that the chance for woody materials to become silicified would be greatly enhanced if they were buried, under conditions of minimum decay, in volcanic ash or in sediments rich in volcanic ash. Actually, a great many occurrences of silicified wood in volcanic ash are known. Silicification by percolating waters is also conceivable in a porous stratum, like a coarse sandstone, that is under- or overlain by a deposit of volcanic ash.

THE OCCURRENCE OF SILICIFIED WOOD.

Wieland[19] has classified the rocks that yield silicified wood into two types, the eruptives and the sedimentaries. When petrified logs are found embedded in undoubted volcanic ash or lava, few would deny that the silica in the fossils was derived from them. But, in recent years, more and more formations, which were believed to be normal sedimentary sands and shales, have been found contaminated with volcanic ash or its decomposition products. Therefore the number of occurrences involving products of volcanism is increasing relative to the number in normal sedimentary materials, and the importance of volcanic materials in the silicification of wood is becoming more generally recognized.

The petrifaction of wood by silica-charged magmatic waters migrating upward in intruded and faulted areas has been emphasized by some writers.[20, 21] This may have been the mode of formation of the logs reported from Broken Hills Range, Nevada, by Palmer,[22] which contain appreciable amounts of

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[19] Wieland, G. R.: The Cerro Cuadrado Petrified Forest, Carnegie Inst. Washington Pub. 449, p. 54, 1935.

[20] Randolph, G. C., and Dake, H. C.: Mineralogist 3, No. 4, p. 5, 1935.

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[22] Palmer, W. S.: Mining and Metallurgy 16, 335, 1935. See also Gianella, V. P., and Wheeler, H. E.: Geol. Soc. Amer. Proc. for 1936 (1937).

gold. Merwin[23] has found that wood immersed in the siliceous hot springs of Yellowstone Park becomes partly impregnated with silica in a few months. His observations are of interest not only in the study of some occurrences of silicified wood that may have originated through the agency of such hot springs, but also in the general problem of the mechanism of silicification, irrespective of the kind of water involved.

Some formations such as the Eugene of Oregon and the Triassic Otterdale sandstone of Virginia contain silicified wood and are also intruded by sills and dikes, but unfortunately no field study of the silicifying activity of the intrusives has been made. The evidence for extensive silicification of wood by magmatic waters is still meager. For the details of current theories on silicification, the reader is referred to Stromer, Kraut, and Storz,[24] to St. John,[25] and to Wieland.[26]

A list of occurrences of silicified wood in the United States has been compiled from the literature and from unpublished information in the hands of the members of the Geological Survey. The literature on silicified wood is difficult to examine because it is very scattered and fragmentary. No claim is made for completeness, but the list nevertheless gives a rough idea of the distribution of silicified wood in this country. Most of the references cited in the footnotes to the following table just briefly note the presence of silicified wood in a given area and formation. Where collection and study of the wood were made, the names of the genera recognized are given in the table.

The occurrences have been classified into two groups, (I) those in formations that contain various amounts of volcanic material, and (II) those in formations not reported to contain volcanic material.

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Occurrences of Silicified Wood in the United States.

I. In formations that contain various amounts of volcanic material.

Age	Formation	Location	Fossil species	Reference
Pliocene	Ricardo	Mohave Desert, Calif.	Robinia, Palmoxylon	1, 2
Pliocene	Sonoma andesite	Sonoma & Napa Cos., California	Sequoia and others	3
Pleistocene and Pliocene	Gila conglomerate	Graham Co., Arizona	Sassafras (?)	4
Pliocene	Upper Cedarville	Washoe Co., Nevada	Silicified wood	5
Pliocene	Hagerman lake beds	Snake R. Plain, Idaho	Silicified wood	6
Pliocene		Bruneau R. Basin, Idaho	Silicified wood	7
Miocene	Payette	Snake R. Valley, Idaho	Silicified stumps	8
Miocene	Yakima basalt	Central Washington	Ginkgo and others	9
Miocene	Trout Creek	S. E. Oregon	Silicified stumps	10
Miocene		Florissant, Colorado	Sequoia stumps	11
Miocene	Esmeralda	Nevada	Cupressus	12, 13, 14
Miocene	Virgin Valley beds	Humbolt Co., Nevada	Silicified logs	15, 16
Miocene (?)	Catahoula	Gulf Coast states	Palmoxylon	17 page 726
Oligocene and Miocene	John Day	Central Oregon	Silicified wood	18, 19x
Miocene or Oligocene	Challis volcanics	Central Idaho	Sequoia (?)	20
Oligocene or Miocene	Eagle Creek	Columbia R. Gorge, Oregon & Washington	Silicified wood	21
Oligocene	Mehama volcanics	Near Mehama, Oregon	Silicified wood	22
Oligocene	Eugene	Oregon	Silicified wood	23
Oligocene	Weaverville	Trinity Co., Calif.	Silicified wood	24
Oligocene (?)		Yellowstone Park, Wyo.	Conifers and dicotyledons	25, 26, 27
Oligocene	White River	S. Dakota & Nebraska	Silicified wood	28, 29, 30x, 31x
Oligocene (?)	Wiggins	Absaroka Range, Wyo.	Silicified wood	32
Upper Eocene	Tepee Trail	Absaroka Range, Wyo.	Petrified stumps	32
Eocene	Green River	Wyoming	Silicified wood	33, 34x
Eocene	Torrejon	San Juan Co., N. M.	Silicified wood	35, 36
Eocene	Auriferous gravels	Nevada Co., Calif.	Silicified wood	37, 38x

Age	Formation	Location	Fossil species	Reference
Eocene	Jackson	Southern Texas, La.	Silicified wood	17 page 690, 39, 40, 41, 42
Eocene	Yegua	Texas	Palmoxylon, Cupressinoxylon	42, 17 page 671
Eocene	Rockdale	Texas	Silicified wood	17 page 593
Eocene (?)	Calapooya	S. W. Oregon	Platanus, Populus	43
Paleocene and Upper Cretaceous	Animas	San Juan Basin, Colo. & N. M.	Silicified wood	44 page 56
Tertiary	lava flow	Wasatch Mts. near Provo, Utah	Silicified wood	45
Tertiary	lava flow	Eureka Co., Nev.	Silicified wood	46
Tertiary		Nye Co., Nev.	Sequoia	47, 48x
Paleocene and Upper Cretaceous	Ft. Union and Lance	Mont., N. Dakota, Wyoming	Cupressinoxylon	49–56x
Tertiary or Upper Cretaceous		Artillery Peak dist., Mohave Co., Ariz.	Palmoxylon and others	57
Upper Cretaceous	Eutaw	Mississippi	Silicified wood	58
Upper Cretaceous	Tornillo clay	Texas	Silicified wood	17 page 509
Upper Cretaceous	McDermott	San Juan Basin, N. M. & Colo.	Silicified wood	44 pp. 24-26 and page 57
Upper Cretaceous	Frontier	Wyoming	Coniferous wood	59
Upper Cretaceous	Aspen and Wayan	Wyoming & Idaho	Tempskya	60, 61x
Upper Cretaceous	Meeteetse	Park Co., Wyo.	Silicified logs and roots	62
Upper Cretaceous	Judith River	Ingomar anticline, Montana	Silicified wood	63
Lower Cretaceous	Ringbone shale	Little Hatchet Mts., New Mexico	Silicified logs	64
Jurassic	Morrison	Wyoming & Colorado	Cycadeoids, Araucarioxylon	65, 66, 66x
Triassic	Chinle	Arizona, Utah, and Nevada	Araucarioxylon, Woodworthia	67–72x
Middle and Upper (?) Devonian	Arkansas novaculite	Arkansas	Callixylon	73, 74x

II. In formations not reported to contain volcanic material.

Age	Formation	Location	Fossil species	Reference
Pliocene or Pleistocene		Flora, Miss.	Silicified logs	75, 76
Pliocene	Wildcat	Humbolt Co., Calif.	Sequoia, Pseudotsuga	3
Oligocene	Forest Hill sand	Mississippi	Silicified wood	58
Eocene	Wilcox	Gulf Coast states	Cupressinoxylon, Laurinoxylon	77, 78
Cretaceous and Tertiary (?)	Overton fangl.	S. E. Nevada	Tempskya	60, 79
Upper Cretaceous	Parkman ss.	Sheridan Co., Wyo.	Silicified wood	80
Upper Cretaceous	Dakota (?)	Southern Utah	Silicified wood	68 page 95
Upper Cretaceous	Ojo Alamo ss.	San Juan Basin, N. M. & Colo.	Silicified logs	44 pp. 29 and 57
Upper Cretaceous	Kirtland and Fruitland	San Juan Basin, N. M. & Colo.	Silicified wood	44 pp. 21–22
Upper Cretaceous	Mesaverde	Chuska Mt. region, N. M.	Cycadeoidea, Dicotyledonous wood	81
Upper Cretaceous	Vermejo	Colorado	Silicified wood	82
Upper Cretaceous	McNairy sand member of Ripley formation	Mississippi	Silicified wood	58
Lower Cretaceous	Horsetown	Shasta Co., Calif.	Silicified logs	83
Lower Cretaceous	Trinity group	Texas	Cycadeoidea, Silicified wood	84
Lower Cretaceous	Playas Peak	Little Hatchet Mts., New Mexico	Silicified wood	64
Lower Cretaceous	Kootenai	Near Geyser, Mont.	Silicified wood	85
Lower Cretaceous	Lakota	Black Hills, S. Dak.	Cycadeoidea, Silicified logs	66
Lower Cretaceous	Potomac group	Maryland & Virginia	Cyacadeoidea, Cupressinoxylon	86, 66
Triassic	Dockum group	Texas & N. Mex.	Silicified wood	87, 88
Triassic		Sonoma Range, Nev.	Araucarioxylon	89
Triassic	Shinarump congl.	Arizona, Utah & Nevada	Araucarioxylon	90
Triassic	Otterdale ss.	Richmond basin, Va.	Araucarioxylon	91
Pennsylvanian	Eldora ss.	Hardin Co., Iowa	Dadoxylon	92
Pennsylvanian	Mahoning ss. member of Conemaugh formation	Ohio & Kentucky	Psaronius	93
Devonian (?)	Woodford chert	Oklahoma	Callixylon	94
Devonian	New Albany shale	Scott Co., Indiana	Callixylon	95

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The widely occurring association of silicified wood with products of volcanism in the West and the South is apparent from group I of the table. The fact that abundant bentonite has been found in the Chinle formation,[27] which is the source of the logs in the well known Fossil Forest of Arizona, is especially striking. The well preserved fern *Tempskya* in the Aspen shale of Wyoming and Idaho and the *Palmoxylon* in the Yegua and the Catahoula formations of the Gulf Coastal states are other noteworthy examples of silicified wood in sedimentary formations that contain volcanic material.

Group II is interesting because it may contain examples of silicified wood whose silica came from sources other than volcanic ash, or the formations involved will be found in the future to contain volcanic material. Some of these formations merge into or are otherwise stratigraphically equivalent to others in which volcanic material has been recognized. Examples of these are the Ojo Alamo with respect to the Animas, a part of the Mesaverde with respect to the Mancos, and the Shinarump conglomerate with respect to the lower part of the Chinle formation.

Future geological studies may very well show that some of the formations now considered as ordinary sandstones and shales do contain volcanic products, if not as beds of pure ash or bentonite then as materials interspersed among the normal clastics, as in the Fort Union and Lance formations of Montana.[28] The physical basis for the association of silicified wood and volcanic material is believed to lie in the rapid alterability of the ash, as was discussed in the first part of this note. The evidence at hand justifies a search for volcanic material in all formations that commonly contain silicified wood.

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During the summer of 1931, Roland W. Brown and the writer noted many occurrences of silicified wood in these formations.

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