

FUSED WOOD-ASH STONES: FAIRCHILDITE
(n.sp.) $K_2CO_3 \cdot CaCO_3$, BUELSCHLIITE (n.sp.)
 $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$ AND CALCITE, $CaCO_3$,
THEIR ESSENTIAL COMPONENTS

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ABSTRACT

Stones found in the trunks of standing partly burned forest trees are produced by fusion and ensuing crystallization of the ash of the wood. Freshly formed stones consist essentially of a new mineral fairchildite, anhydrous potassium calcium carbonate, $K_2CO_3 \cdot CaCO_3$. On wetting, or by atmospheric hydration, this is converted to buetschliite, a second new mineral, a hydrous potassium calcium carbonate, $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$, and calcite. On further leaching the buetschliite is decomposed to calcite with removal of the water-soluble potassium carbonate. The presence of the first three carbonates in wood-ash stones is established, and a general account of them with a review of pertinent literature is given. The artificial compounds corresponding to fairchildite and buetschliite were prepared and analyzed by Otto Buetschli in 1901-1905, but have not hitherto been reported in nature. Fairchildite is hexagonal, $\epsilon = 1.48$, $\omega = 1.530$, and buetschliite is probably also hexagonal, with $\epsilon = 1.455$ and $\omega = 1.595$.

OCCURRENCE

Stones of a peculiar type have been found within the trunks of standing partly burned trees at many localities in the forests of the western United States during the last twenty five years. These stones were obviously unlike those of the regional soil, and most of the finds gave rise to diverse conjectures as to their source. Although several investigators, as Englis and Day (1)† and Kienholz (2) had correctly described the essential nature and origin of the stones as early as 1929, few foresters appear to have been acquainted with their work, and as recently as 1938, there was a Sunday story in the *Oregon Journal* (October 2, 1938) by Louise E. Brogan, entitled "Do meteorites start fires in the forest?" (3). Moreover, correspondence in the writers' files seems to indicate that even some authorities on forestry have failed to understand the nature of these peculiar stones. It has therefore appeared desirable to assemble the recorded data, to discuss relevant studies in other fields, and to carry through such laboratory study as was necessary to make clear the natural history of wood-ash stones.

The number of localities where these stones have been obtained is fairly large, and doubtless, once the nature of the stones is generally

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† References cited in bibliography at end of paper.

known, many more occurrences will be noted. Some of the recorded occurrences with dates are:

- 1924 Clearwater National Forest, Idaho (2).
- 1925 Columbia National Forest, Washington (2), (in a score or more trees).
- 1926 Kaniksu National Forest, Idaho (2).
- 1927 Umatilla National Forest, Oregon (2), (noted in the forestry journal "Six Twenty Six" September 1927, with discussion of origin, November 1927).
- 1927 Cocur d'Alene National Forest, Idaho (2), (noted four years after fire).
- 1943 Grand Canyon National Park, Arizona (4).

Two of the occurrences listed above have been available for this study: The Kaniksu National Forest stone of the 1926 fire, and the Grand Canyon National Park stone of 1943. The chemical work on the former by Englis and Day (1) has been supplemented by microscopic and x-ray study, and the latter has been investigated chemically, optically, and by x-rays.

A letter (5) from Hugo Winkenwerder, Dean of the College of Forestry, University of Washington, states that "this stuff has been found rather often in our white fir and hemlock in this region of the country. . . ." On the other hand, there is no instance known to the writers where such stones have been found east of the Rocky Mountains. A letter addressed some years ago to the Chief of the Forest Service, Department of Agriculture, in Washington, D. C., regarding wood-ash stones, was referred to the Madison, Wisconsin, Forest Products Laboratory; but a reply from the Senior Chemist (6) of the Laboratory indicated that little if anything was known about them.

LITERATURE RELATING TO FUSED WOOD-ASH STONES

The first published description of these stones appears to have been in 1929, when D. T. Englis and W. N. Day, chemists at the University of Illinois, wrote a brief note in *Science* (1). Their interest was mainly in the chemical composition of the stones, or, as they termed them, clinkers. From analyses of three of these stones, and of sound wood (Analyses 1, 2, 3, and 4 of Table 2), they concluded that there was "no justification for the assumption that the clinkers were of meteoric origin" as had been supposed by some, but rather that "the peculiar rock-like character of the clinkers is probably due to the collection of a large quantity of ash in the hollow snag, followed by occasional wetting from rain and finally a fusion of the mass, during a later vigorous burning of the surrounding wood."

Later that year R. Kienholz (2) botanist at the University of Illinois, who had collected the specimens analyzed by Englis and Day, wrote a more detailed account, including many observations of especial interest.

He listed five or six occurrences, all in the forests of the western United States. The trees in which the stones were found were mostly western hemlock (*tsuga heterophylla*), also Douglas fir (*pseudotsuga taxifolia*), and, occasionally, white fir (*abies grandis*), noble fir (*abies nobilis*), and, possibly, western white pine (*pinus monticola*). The stones only formed in rotten heartwood, usually in hemlocks affected by the Indian Paint fungus (*echinodontium tinctorum*) and in Douglas firs affected by the fungus (*trameles pini*). In localities where the Indian Paint fungus was not prevalent, no clinkers were observed following forest fires. Kienholz also mentions that similar clinkers had been observed with a different origin, namely in the fireboxes of boilers burning clean hemlock sawdust. The role of the fungus therefore in the formation of these stones is not an essential one, but merely to prepare the tree for the special mode of combustion, described below, that results in these stones. Kienholz cites various observers as having found the stones in deep cylindrical pockets from 2 to 40 feet deep, and from 4 to 40 feet above the ground, and always in trees a foot or more in diameter; younger trees had apparently not been subjected long enough to the action of the fungus, in producing the rotten heartwood. The stones varied in quantity in a single tree, from one to a hundred pounds or more; and a single chunk of 16 or 18 inches in diameter was found. The length of time that a tree burned could run into weeks or months, or even through an entire winter. No clinkers ever formed in logs burning on the ground, or in trees that burned upwards from a rotten butt. All of the stones slaked visibly on exposure. Kienholz remarked that "minerals probably do not crystallize out in the formation of the clinker, as has been held, but there is a fusion of the material brought about by the high temperature." This statement is not quite correct, for there are crystalline compounds—minerals—formed in the cooling of the fused mass.

In 1938 the *Portland Oregonian* (7) printed a news item as follows: "A meteorite, still white hot, was found buried in the smoking hole of a large white fir tree near La Pine, Oregon . . . the patrolmen found smoke issuing from a hole in the tree 60 feet from the ground. . . . They felled the tree . . . and found a glowing meteorite, described as of the size of a ten quart water pail. The metallic mass, resembling smelter slag, had penetrated the wood to a depth of 14 inches and was shattered by the impact" The stone was described as of light color and of light weight, and full of holes. The account was carried by the press services, and the story appeared in the Bend, Oregon, *Bulletin*, in *Time*, and in the *Christian Science Monitor*. J. Hugh Pruett in *Popular Astronomy* (8) the following year summarized the knowledge of this occurrence.

The interest of the writers in these stones dates from 1939 when Marcus

Goldman, geologist of the Geological Survey, kindly showed one of us (C. M.) a specimen of the Kaniksu stone described by Kienholz. This interest was renewed in 1944 when H. E. Gregory, geologist of the Geological Survey, referred to the Chemical Laboratory of the Geological Survey a stone from the Grand Canyon National Park, found 56 feet up in a white fir tree previously struck by lightning. In a letter to C. S. Ross, petrologist of the Geological Survey, Professor Gregory wrote: "Although it has been determined as fused limestone there is no way of explaining the presence of so large a piece of limestone in the top of a tree. . . . I am more inclined to consider the material as fused ashes."

In a brief popular account of these wood-ash stones by C. Milton (9) are photographs of a piece of the Kaniksu stone, and microphotographs of the Grand Canyon Stone referred to the Geological Survey by Gregory. There are also photographs of the tree from which the stones were taken made by the Forest Service ranger, William J. Kennedy.

Among the erroneous ideas that have been held concerning these stones, the following may be mentioned briefly: that they are meteorites, that they are fused limestone, that they are pathological growths in the living tree, that they are produced by excessive evaporation of sap, and that they are lightning-fused ash.

APPEARANCE AND MICROSTRUCTURE

The two specimens studied have somewhat different aspects, the Kaniksu stone being the more homogenous, and the Grand Canyon stone being markedly heterogenous. Both contain charcoal inclusions or blackened carbonaceous areas. The appearance of the stones is shown in Fig. 1. The Kaniksu stone is dense and stony, light-grayish in color, cracked by a few spall-like fissures along which it breaks in sharply angular fragments a centimeter or two across. There is some indication of flowage of the material during fusion, and a few deep rounded holes may be ascribed to escape of gases during fusion. After twenty years the stone shows little or no sign of disintegration or alteration. The Grand Canyon specimen varies from a hard internal bluish-gray stony mass to a crumbly white porcellanic crust; it appears to be disintegrating at a very slow rate. From the observations of others, recorded in letters to the writers, it seems that the other wood-ash stones are similar to these in their general character.

The preparation of thin-sections of these stones for microscopic study is rather difficult. The more friable ones require a preliminary cementation with Canada Balsam or other hard embedding medium. Water decomposes the stones, therefore kerosene or other inert liquid must be employed in grinding the sections. Because of the hydrous character of

much of the crystalline material of the stones, they cannot be heated too much. With these precautions observed, however, fairly satisfactory thin sections can be made. The illustrations, Figs. 2, 3, 4, and 5, show the microstructure of wood-ash stones. The first impression one obtains in studying these thin sections is that of a disorderly array of a badly crys-

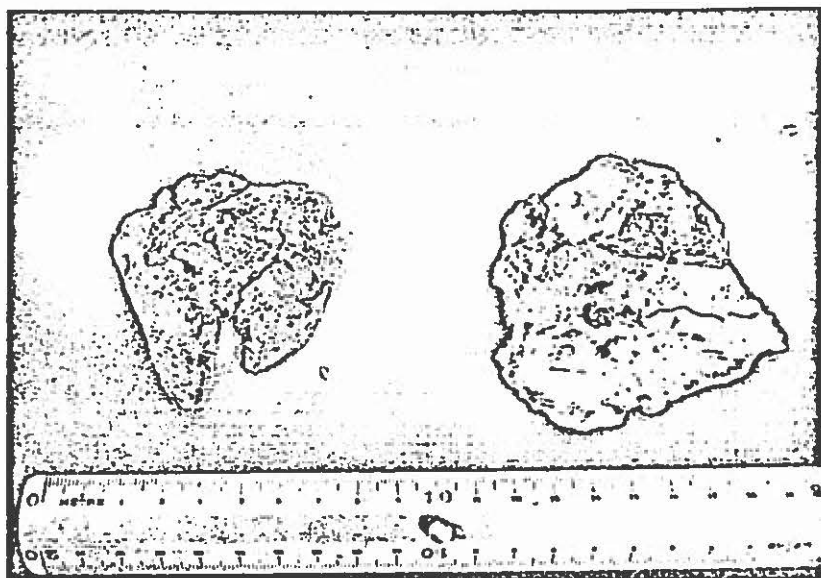


FIG. 1. *Left:* Stone from Kaniksu National Forest, Coolin, Idaho. Black embedded fragments are charcoal. *Right:* Stone from Grand Canyon National Park, Arizona. Shows striated surface caused by molding of fused ash against charcoal, which was temporarily preserved from combustion by lack of oxygen.

tallized aggregate, but this largely resolves itself on study. The most striking feature is the long blades of moderately birefringent clear colorless fairchildite, $K_2CO_3 \cdot CaCO_3$, showing very little relief against the Canada Balsam (Fig. 2). Most of the fairchildite however has altered to buetschliite, $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$, which is usually difficult to distinguish in thin-section from calcite.

At places, however, the abundant calcite in these stones can be recognized by its characteristic rhombohedra, and by the "twinkle" effect (difference in relief observed on rotating the section) observable when using the lower nicol only. Much of the thin-section however remains at best difficultly decipherable, and looks like a heterogenous, carbonaceous, extremely fine grained crystalline aggregate. In fact, without the help of



FIG. 2. Fused wood-ash stone, Kaniksu National Forest, Idaho. Shows slightly altered lath-shaped cross-sections of fairchildite in a fine groundmass containing buetschliite and calcite. This thin-section shows rather more and better fairchildite than usually seen. $\times 30$ ordinary light.

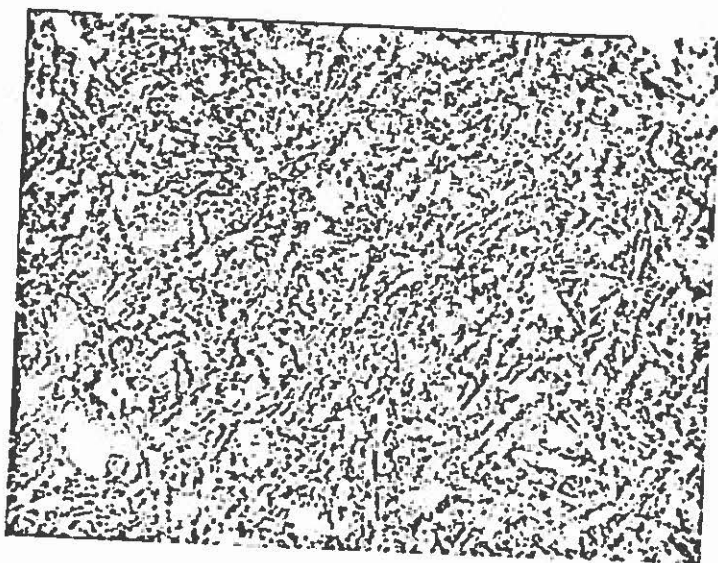


FIG. 3. Fused wood-ash stone, Grand Canyon National Park, Arizona. Shows fairchildite largely replaced by buetschliite and calcite, which retain the form of the original fairchildite. $\times 30$ ordinary light.



FIG. 4. Fused wood-ash stone Grand Canyon National Park, Arizona. This section was ground with water instead of oil; under these conditions decomposition of the fairchildite has produced buetschliite and calcite. The buetschliite has crystallized in characteristic stubby barrel-shaped crystals. $\times 30$ ordinary light.



FIG. 4a same as Fig. 4 under higher magnification. $\times 120$ ordinary light.

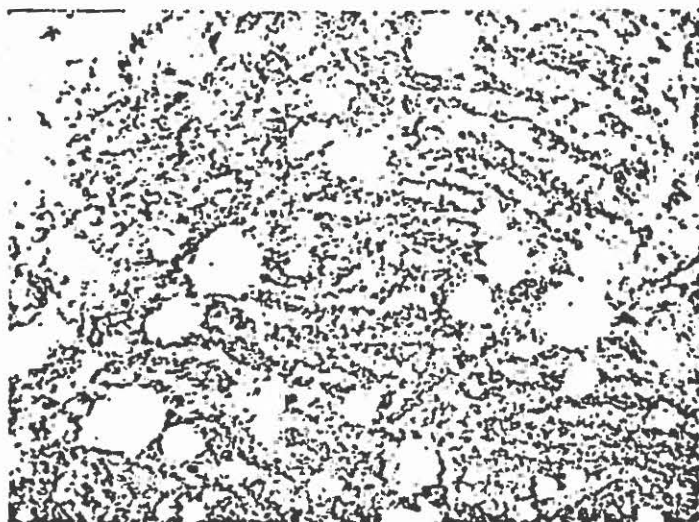


FIG. 5. Fused wood-ash stone, Grand Canyon National Park, Arizona. Shows buetschliite-calcite aggregate replacing fairchildite. The dark streaks are carbonaceous particles, segregated during crystallization of the fairchildite. The rounded clear areas are holes, caused by formation of carbon dioxide (and monoxide) from combustion of wood or charcoal during fusion of the ash; or, perhaps, by formation of carbon dioxide produced in the thermal decomposition of fairchildite at very high temperatures. $\times 30$ ordinary light.

x-ray study, the interpretation of the petrographic evidence would remain a most difficult and uncertain matter.

X-RAY STUDY

Figure 6 shows X-ray powder patterns obtained from the various substances under consideration.

From the x-ray study it appears that on wetting, or on slow hydration, in air, fairchildite ($K_2CO_3 \cdot CaCO_3$) forms buetschliite ($3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$). Leaching decomposes buetschliite, leaving residue of calcite. When the natural wood-ash stones are remelted in the laboratory fairchildite forms again, insofar as the stone has not previously been leached of its potassium carbonate content; the calcite present in the remelted stone is to some extent a measure of the degree of previous leaching. Presumably therefore, wood-ash stones originally consisted of the anhydrous fairchildite, subsequently hydrated to buetschliite. As buetschliite, both the natural and the synthetic material are firm and coherent; but on leaching, with formation of calcite, the synthetic material crumbles to powder and the natural mineral probably does also. As long as the wood-ash stones retain their stony character they contain con-

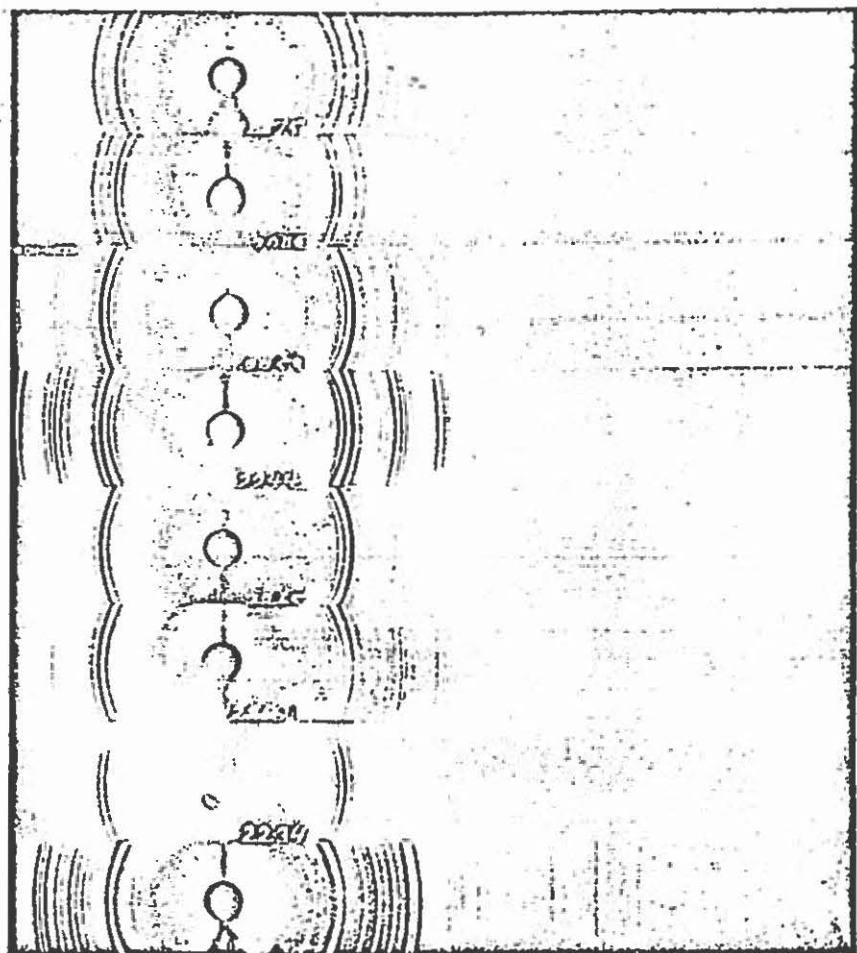


FIG. 6-A. Synthetic fairchildite made by fusion of components (film 2275). 6-B. Remelted (in laboratory) stone from Grand Canyon National Park, Arizona. It is a mixture of fairchildite and calcite, with an unidentified substance, and a little buetschliite (presumably formed by atmospheric hydration from fairchildite) (film 2243). 6-C. Synthetic buetschliite prepared from oyster shell according to Buetschli's method described in the text (film 2253). 6-D. Synthetic fairchildite, after five months' exposure in the laboratory, giving the buetschliite pattern, without observable calcite lines (film 2244). 6-E. Stone from Kaniksu National Forest, Coolin, Idaho, after fifteen years' exposure in the laboratory. A hole was drilled through the outer portion, and the interior material x-rayed. The pattern is almost entirely that of buetschliite, with no observable fairchildite lines (film 2265). 6-F. Stone from the Grand Canyon National Park. A sample from the interior gives the same pattern as the Kaniksu stone (film 2266). 6-G. Wetted synthetic fairchildite. Patterns from buetschliite, a little calcite, and undecomposed fairchildite are seen (film 2234). 6-H. Completely leached synthetic fairchildite; only calcite remains (film 2240).

siderable potassium carbonate in chemical combination, either as fairchildite or as buetschliite.

Measurements of the powder patterns of fairchildite (film 2275) and of buetschliite (film 2244) are given in Table 1.

TABLE 1. MEASUREMENTS OF X-RAY PATTERNS

Fairchildite $K_2CO_3 \cdot CaCO_3$		Buetschliite $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$					
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
6.64	m	4.97	vw	1.455	vw	.905	w
4.59	w	4.52	w	1.420	vw	.896	w
4.31	vw	4.15	vw	1.380	vw	.882	w
3.53	vvw	3.25	w	1.345	m	.863	vw
3.33	vw	3.16	vw	1.263	m	.853	w
3.19	vs	3.03	s	1.246	m	.844	vw
2.689	w	2.860	vvs	1.230	w	.837	vw
2.641	s	2.688	s	1.217	m	.827	vw
2.283	vw	2.306	w	1.205	vw	.822	vw
2.211	m	2.251	ms	1.130	vw	.813	vw
2.154	m	2.070	s	1.118	vw	.790	vw
2.027	w	2.012	m	1.108	vw	.777	vw
1.880	m	1.960	ms	1.101	w		
1.749	vvw	1.751	m	1.052	w		
1.710	vvw	1.690	s	1.042	m		
1.696	w	1.642	vw	1.024	m		
1.663	vvw	1.612	ms	1.016	w		
1.607	vw	1.583	m	.951	vw		
1.522	w	1.553	w	.933	w		
1.405	vw	1.508	w	.919	w		
1.319	vw						
1.277	vw						
1.215	vw						
.....							

The first two analyses, of stones from a single occurrence, show the similarity to be expected; the most noticeable difference being in the content of Na_2O . Also to be expected is the similarity of these two analyses to that of a stone from the same kind of tree, though from a different locality (3). Further, the relation of these three analyses, to the fourth, of ash from wood of the same kind of tree, burned in the laboratory, is evident. The fifth analysis, of a stone from another type of tree, from a different part of the country, does not differ greatly, the variation being chiefly in $R_2O_3 \cdot P_2O_5$ content. On the whole, the stones analyzed consist

of about two-thirds by weight of calcium and potassium carbonates. It may be here remarked that for the minor constituents, such as P_2O_5 , $Al_2O_3 \cdot Fe_2O_3$, and Mn_2O_4 , no crystalline compound of them has been recognized in wood-ash stones. As for MgO and Na_2O , it is probable that they can enter isomorphously the double carbonates present, but such isomorphous replacement would not be shown by the methods employed in this study.

TABLE 2. ANALYSES. CHEMICAL COMPOSITION OF WOOD-ASH STONES, FAIRCHILDITE, AND BUETSCHLIITE

	1	2	3	4	5	6	7
SiO_2	0.32	0.38	0.41	—	—		
P_2O_5	6.96	6.58	5.47	10.5			
$Al_2O_3 \cdot Fe_2O_3$	1.68	.99	.34	4.4	1.0		
SO_2	tr.	tr.	.67	—	.7		
Cl	tr.	tr.	tr.	—	—		
CaO	22.02	21.90	21.79	20.1	18.5	23.5	15.4
MgO	6.28	4.48	4.06	10.4	2.3		
Mn_2O_4	1.21	1.32	7.17	11.7	—		
K_2O	25.01	24.54	30.42	34.9	23.6	39.5	39.1
Na_2O	5.31	2.06	4.20	8.0	10.7		
CO_2	19.76	25.47				37.0	30.6
H_2O			25.47				
C, etc. (diff.)	11.65	12.28	(by diff.)		43.2 (calc.)		14.9
	100.00	100.00	100.00	100.0	100.0	100.0	100.0

1, 2. Fused wood-ash stone, Kaniksu National Forest, Coolin, Idaho (*tsuga heterophylla*, western hemlock). R. KIENHOLZ, analyst (2).

3. Fused wood-ash stone, Wind River Country, southern Washington (*tsuga heterophylla*, western hemlock). R. KIENHOLZ, analyst (2).

4. Ash of sound wood, Wind River Country, southern Washington (*tsuga heterophylla*, western hemlock). R. KIENHOLZ, analyst (2).

5. Fused wood-ash stone, Grand Canyon National Park, Arizona (*abies concolor*, white fir). C. MILTON, analyst.

6. Theoretical composition of fairchildite, $K_2CO_3 \cdot CaCO_3$.

7. Theoretical composition of buetschliite, $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$.

ASH CONTENT OF WOOD IN RELATION TO STONE FORMATION

The quantity of ash that a given weight of dry wood will yield on burning is shown in Table 3.

The deciduous trees apparently give a higher ash content than the conifers. Further analyses of wood ashes may be found in Hagglund's treatise; here it need only be noted that all show predominant potash and lime.

As to the quantity of wood-ash stone that a single tree may yield, Kienholz (2) mentions "a hundred pounds or more." This is not excessive, as the following computation shows. Assuming 0.20% as the ratio of ash to wood, and 0.75 as an average for the density of the wood, a tree four feet in diameter and eighty feet high would yield a hundred pounds of ash. In considering Kienholz's figure, it should be mentioned that wood-ash stone differs from the true ash in containing a considerable quantity of combined carbon dioxide, water, and also perhaps charcoal; and furthermore, that a tree that is struck by lightning (which may have started

TABLE 3. PERCENTAGE OF ASH OBTAINED FROM DRY WOOD

Western hemlock	.215	Kienholz (2)
European larch (splint)	.22	Hagglund (10)
European larch (heart)	.12	Hagglund (10)
European pine (splint)	.19	Hagglund (10)
European pine (heart)	.15	Hagglund (10)
European fir (splint)	.26	Hagglund (10)
European fir (heart)	.20	Hagglund (10)
European oak (splint)	.42	Hagglund (10)
European oak (heart)	.16	Hagglund (10)
European beech (splint)	.47	Hagglund (10)
European beech (heart)	.40	Hagglund (10)

the fire in the tree) is likely to be among the tallest trees in its neighborhood. There is therefore no question of the adequacy of the quantity of ash available to produce such wood-ash stones as have been found.

CHEMISTRY OF THE SYSTEM K_2CO_3 - $CaCO_3$ - H_2O

Since wood-ash stones are composed mainly of these three compounds in various combination, the chemistry of their reactions with one another will be briefly discussed.

In 1894 H. Le Chatelier (11) had prepared in the dry way the anhydrous double carbonate of potassium and calcium. He described a series of compounds all apparently isomorphous, uniaxial negative, with excellent basal cleavage, and having the general formula $R_2O \cdot RO \cdot 2CO_2$, the univalent metals being sodium and potassium (but not lithium) and the bivalent metals being calcium, strontium, and barium. The various compounds were easily produced by fusion of the components. In his account

he refers to still earlier syntheses of these compounds by Berthelot.

The system K_2CO_3 - $CaCO_3$ was first studied by P. Niggli (12) in 1916. The double salt melts at $815^\circ C.$ and forms a eutectic with K_2CO_3 at $455^\circ C.$, or more precisely, with mixed crystals of K_2CO_3 containing up to a little over 12% of $CaCO_3$. Above $815^\circ C.$, $CaCO_3$ decomposes and it is therefore necessary to maintain an atmosphere of CO_2 under pressure to prevent decomposition at temperatures higher than this. To synthesize the anhydrous double carbonate, however, the elaborate apparatus employed by Niggli and later workers is not needed, since, as shown by Le Chatelier, it is easily prepared by simple fusion of the two components in correct proportions, in an ordinary covered platinum crucible over a Meeker burner. In this way coarsely crystallized masses of a pinkish-gray color, showing excellent cleavages a centimeter or two across, are obtained. The compound is described as hexagonal, forming basal plates or masses with excellent basal cleavage, and having refractive indices $\epsilon = 1.48$ and $\omega = 1.530$. Skalijs (13) and later Eitel and Skalijs (14) give the Laue x-ray pattern of the anhydrous double carbonate; the powder x-ray pattern, and measurements of the principal lines, are given in Table 1 and Fig. 6 of this paper.

However, Otto Buetschli, employing altogether different methods, had already in 1901 synthesized and identified the same compound. He observed that by treating calcareous sponge spicules with 35% KOH solution, hexagonal tablets crystallized. In his first published account of this work, in 1898 (15) he considered the possibility that they might be calcium carbonate; but later (16) showed that the crystals were decomposed by water, with formation of calcium carbonate. Therefore, he reasoned the tablets themselves could not be calcium carbonate, but had to be a double carbonate of potassium and calcium. His conclusions, however, were not accepted and several authorities raised objections.

The first to question Buetschli's findings was W. Biedermann (17). In 1901 he published his own observations, made independently of Buetschli. He too had observed the formation of hexagonal plates on treating calcareous mollusc shells with potash lye, and that these plates were decomposed by water, with formation of rhombohedral crystals. However, he misinterpreted the phenomena he observed, for he took the hexagonal plates to be calcium phosphate, which water caused to "recrystallize" into a rhombohedral form. In fact he believed that he had thus discovered a reaction for detecting minimal quantities of calcium phosphate.

That same year Buetschli reviewed Biedermann's work, pointed out his errors, and reiterated that a double carbonate of potassium and calcium was the compound in question (16).

In 1902 Biedermann found that the crystals were formed in the ab-

sence of any phosphate, by treating gaylussite (sodium calcium carbonate) with potash lye, or, calcium chloride or sulphate, with potash lye. He therefore withdrew his previous identification of the compound as calcium phosphate; but, without reference to Buetschli's work, observed that these crystals were to be classed as a potassium-calcium compound, whose composition was yet to be established.

Notwithstanding the clarity of Buetschli's published work, with its evident corroboration by Biedermann, O. Maas (18) in 1904 declared Buetschli's results altogether erroneous. According to him, 35% KOH had no effect at all, either on calcite or on freshly precipitated calcium carbonate. The sole effect on sponge spicules, he asserted, was to break up a single crystal spicule into an aggregate of smaller and diversely oriented calcite crystals; and the way this was done, was by the KOH dissolving a certain organic cement whose existence Buetschli had overlooked. The only new crystals that might be formed were those of potassium carbonate (by absorption of carbon dioxide from the air).

Buetschli considered all of Maas' statements and refuted them in a lengthy paper which appeared in 1905 (19). In it he presented analytical data from which he correctly deduced the composition not only of the anhydrous double carbonate (fairchildite) but also of a hydrous double carbonate (buetschliite). He gave a wealth of detail concerning the conditions of their formation, the form of their crystals, and further gave an extended discussion of related compounds, such as gaylussite and other hydrous sodium calcium carbonates, calcium phosphate, and hydrous calcium carbonate. He pointed out that Liebig, as far back as 1832, had shown that hot caustic potash attacks chalk, giving a soluble carbonate. In presenting his analyses, Buetschli modestly deprecated his ability as a chemist, observing that he had been unable to secure the help of an expert analyst, and therefore had to perform the analyses himself. However, his analyses, presented with most detailed explanation of all the analytical procedures employed, appear to be satisfactory in all respects; and his analysis giving the formula for the double hydrous carbonate (buetschliite) is accepted by the writers as correct.

Even while this paper of Buetschli's, which should have put an end to the controversy, was in the hands of the printer, there appeared, to his astonishment and dismay, a denial of the validity of its contents by no less an authority than Ernst Weinschenk (20). Weinschenk was Professor of Petrography at the University of Munich Mineralogical Institute, and an outstanding figure in mineralogy. He affirmed all of Maas' erroneous work and explicitly condemned that of Buetschli. More in sorrow than in anger, Buetschli took on this adversary, and in

the same journal that had published Weinschenk's attack, wrote a brief reply (21). To his still unpublished 1905 paper he added a long appendix, pointing out the errors and fallacies of Weinschenk's pronouncement. One sentence of Buetschli's may be quoted, as showing the spirit in which the controversy was carried on both sides. "Among other things, he derides me, because (he says) no such double salt as I have described is known, notwithstanding that potassium carbonate and calcium carbonate are substances that have been so completely investigated." On the other hand, Weinschenk claimed that the crystals which he himself (and Maas) had observed to form were simply anhydrous potassium carbonate, to which Buetschli dryly remarked that such a compound was not known to form in the wet way either; and then, by careful analysis, proved that the crystals produced in the course of Weinschenk's (and Maas') experiments, could not be other than $2K_2CO_3 \cdot 3H_2O$. In 1944 this was fully verified by Ervin, George, and McCarthy (22) who show that this hydrate is the only stable phase crystallizing from solution at all ordinary temperatures.

Finally in 1907 Buetschli (23) published his last work on these double carbonates. Most of the paper deals with gaylussite ($Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$) and a (new) dehydration product $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$ but in his first paragraph he once more affirms that $K_2CO_3 \cdot CaCO_3$ and $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$ crystallize when calcium carbonate reacts with a strong K_2CO_3 -KOH solution.

Some years later Barre (24) also synthesized $K_2CO_3 \cdot CaCO_3$, obtaining acicular crystals by digesting precipitated $CaCO_3$ in strong K_2CO_3 solution. Water or solutions of potassium carbonate containing less than 59.25% K_2CO_3 at 19° C. or 61.78% at 98° C. decompose the compound. Apparently Barre was unaware of Buetschli's prior work.

In 1913 Datta and Mukherjea (25) described the preparation of a compound reported to be $3K_2CO_3 \cdot CaCO_3$, but their account is not very convincing. They precipitated a jelly-like mass by adding concentrated calcium chloride solution to a saturated potassium carbonate solution; on standing this jelly formed crystals which were dried by suction without washing. Under these conditions it is difficult to see how adherence of potassium carbonate could be avoided. The composition of the crystals was determined solely by determination of the CaO content. The authors state that no water of crystallization was found, but this must be considered doubtful. Probably they were dealing with a mixture containing the hydrous double carbonate as well as potassium carbonate sesquihydrate.

The compounds in the system K_2CO_3 - $CaCO_3$ - H_2O which need be con-

sidered with reference to wood-ash stones are listed in the following table:

TABLE 4. COMPOUNDS OF K_2CO_3 - $CaCO_3$ - H_2O IN RELATION TO WOOD-ASH STONES

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- A. Compounds identified in wood-ash stones
- $K_2CO_3 \cdot CaCO_3$, Fairchildite; hexagonal, in basal plates with excellent basal cleavage. $\epsilon = 1.48$; $\omega = 1.530$ (-). Formed by fusion below $815^\circ C$. and also from concentrated aqueous solutions.
- $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$, Buetschliite; hexagonal (probably) in stubby barrel-shaped crystals. $\epsilon = 1.455$; $\omega = 1.595$ (-). Formed by hydration of fairchildite, or by crystallization from less concentrated solutions.
- $CaCO_3$, Calcite; hexagonal. $\epsilon = 1.491$; $\omega = 1.658$ (-). Formed by decomposition of buetschliite by water, and also in the hydration of fairchildite.
- B. Compounds which may have a transient existence in wood-ash stones, but by their extreme solubility or unstable chemical character, are not likely to be recognized or present.
- K_2CO_3 , monoclinic; $\alpha = 1.426$; $\beta = 1.531$; $\gamma = 1.541$ (-). $2V = 35^\circ$, lamellar twinning, oblique extinction. Made by fusion of hydrates; not known as a mineral.
- $2K_2CO_3 \cdot 3H_2O$, monoclinic; $\alpha = 1.474$; $\beta = 1.483$; $\gamma = 1.510$ (+). $2V = 66^\circ$, extinction $15^\circ - 20^\circ$. This is the stable phase crystallizing from aqueous solutions at ordinary temperatures.
- CaO , Lime; cubic; $n = 1.837$; perfect cubic cleavage. Hydrates rapidly in air.
- $Ca(OH)_2$, Portlandite; hexagonal; $\epsilon = 1.545$; $\omega = 1.574$ (-); basal cleavage. Made by hydration of lime out of contact with CO_2 (or air).
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NEW MINERAL NAMES: FAIRCHILDITE AND BUETSCHLIITE

The names chosen to designate these naturally occurring double carbonates are in honor of our co-worker, John G. Fairchild, chemist of the Geological Survey, United States Department of the Interior, and of Otto Buetschli (1848-1920), professor of zoology at the University of Heidelberg from 1878 to 1919. John G. Fairchild has for over thirty years devoted his analytical skill to the study of geochemical problems. Otto Buetschli, although a zoologist, and not a chemist, was the first to synthesize, and to correctly understand the relations of both fairchildite and the compound now named after him. His findings were sharply challenged during his lifetime, but the present study must be regarded as completely vindicating his work. It is also worth a moment's reflection, to recall that it was the work of an investigator in Germany, primarily concerned with the morphology of sponge skeletons, that was to be the key to the understanding of puzzling stones found after forest fires in western American forests. It is but another illustration, if such were needed, that no one may prescribe the results or possible applications of free scientific inquiry.

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