

ALTERATION OF THE LAVAS SURROUNDING THE  
HOT SPRINGS IN LASSEN VOLCANIC  
NATIONAL PARK

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INTRODUCTION

The general characters and many important details regarding the hot springs of the Lassen Volcanic National Park, California, have been presented by Day and Allen<sup>1</sup> in their admirable treatise. In this work, they devoted some discussion to the character of the rock decomposition produced by the hot springs, but indicated that further studies might profitably be made. Mr. R. H. Finch of the U. S. Geological Survey Volcanological Observatory, Mineral, California, also suggested the desirability of this work and to him the writer is indebted for many courtesies during the pursuit of the field work. It is a pleasure to acknowledge the helpful comments of Dr. E. T. Allen of the Geophysical Laboratory, Washington, D. C., regarding the character of the lava alterations.

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Dr. Howel Williams made some observations on the decomposition of the lavas while studying the geology of the region and has incorporated this information in his excellent report. For the location and geologic environment of the hot springs, the reader is referred to his map.<sup>2</sup>

Four main groups of hot springs were visited, Boiling Lake, Devil's Kitchen, Bumpass Hell, and Supan's Springs (Tophet Springs on the U. S. G. S. map). These lie southeast to southwest of Lassen Peak. Detailed maps of the first three areas showing the location of the various springs are to be found in the report of Day and Allen.<sup>3</sup>

ALTERATION OF THE LAVAS

SOURCE AND NATURE OF ACID. According to Day and Allen, the chief agent responsible for the alteration of the lavas is sulphuric

<sup>1</sup> Day, Arthur L., and Allen, E. T., The volcanic activity and hot springs of Lassen Peak: *Carnegie Inst. Wash. Publ.* 360, 1925.

<sup>2</sup> Williams, Howel, Geology of the Lassen Volcanic National Park, California: *Bull. Univ. of Calif. Publ., Dept. Geol. Sci.*, vol. 21, pp. 195-385, 1932.

<sup>3</sup> *Op. cit.*, pp. 92, 95 and 114.

acid. In their discussion of the origin of this acid, they concluded that it formed in part from the direct oxidation of hydrogen sulphide under the conditions prevailing in the hot spring basins. Also deposition of free sulphur and later oxidation in the moist warm air might form additional sulphuric acid.<sup>4</sup> According to them "none of the waters of these hot springs is far from neutrality. Of those analyzed six were practically neutral, four were alkaline and eight were acid. The acidity ranged from 19 mg. to 436 mg. H<sub>2</sub>SO<sub>4</sub> per liter, that is, from 0.002 to a trifle over 0.04 weight per cent."<sup>5</sup>

**FIELD APPEARANCE.** Several rock types have been affected by the action of the hot springs. These range from blue-black basalts at Boiling Lake, gray pyroxene andesites at Devil's Kitchen and Supan's Springs, to pale gray dacites at Bumpass Hell. Regardless of the initial character of the rock, they have been bleached and decomposed to glaring white, rarely to yellow brown and red products. Among these decomposed lavas lie clusters of fumaroles, hot springs and mud pots, containing sediments of decomposed lavas.

**MINERALOGICAL CHARACTER.** It is generally assumed that lavas attacked by sulphuric acid will alter to opal with the liberation of the alkalis, alkaline earths, iron, and aluminum as soluble sulphates. Although various soluble sulphates of these bases do occur around the hot springs, the insoluble residue does not in all cases consist of pure opal, for muds from the hot springs may be composed of nearly pure kaolin while others consist of opal and kaolin in varying ratios.

*Opal.* The opal is usually white and powdery; locally it may be compacted, and have waxy fracture surfaces. When examined under the microscope, it appears in honey yellow and dark gray grains, the latter evidently developing from the ferromagnesian minerals. The index of refraction is variable, chiefly ranging about  $1.450 \pm .005$ , but values as low as  $1.410 \pm .003$  were observed.

*Kaolin.* Frequently this mineral is so intimately associated with opal that no reliable value of the refractive indices can be obtained. Microcrystalline aggregates usually have an index of  $1.565 \pm .005$  but owing to the absence of large crystals, the inter-

<sup>4</sup> For the evidence pointing to this conclusion see Day and Allen, *op. cit.*, pp. 138-140.

<sup>5</sup> *Op. cit.*, p. 113.

ference colors are hardly perceptible. Some isotropic aggregates gave very low values for the index of refraction ( $n=1.52 \pm .10$ ) suggesting halloysite. Four powder x-ray patterns of kaolin-rich sediment were prepared through the kindness of Mr. W. H. Dore, of the Division of Plant Nutrition, University of California, and these were examined by Professor Adolf Pabst of the department of geology of the same University. Owing to the contamination by alunite, quartz and tridymite, the several kaolin minerals could not be distinguished.

*Alunite.* Alunite ( $K_2O \cdot 3Al_2O_3 \cdot 4SO_4 \cdot 6H_2O$ ) is almost ubiquitous. This mineral is easily recognized because of its higher indices of refraction and greater birefringence compared to the common associates. It is present in isolated crystals and aggregates, the crystals seldom exceeding .03 mm. in dimension.

*Tridymite.* The tridymite may be residual in part, but is largely secondary. It occurs in radiating twinned crystals, .1 to .2 mm. in length, usually associated with opal or chalcedony. The optical properties are  $\alpha=1.474 \pm .002$ ;  $\gamma=1.478 \pm .002$ , parallel extinction with negative elongation,  $2V=30^\circ-40^\circ$  (estimate), positive. A thin section was treated with fuchsine dye after a 20 minute treatment with concentrated hydrochloric acid in order to eliminate the possibility that the tridymite might have been confused with a zeolite. The mineral remained unstained.

In addition to these minerals, quartz is occasionally found, residual in part. Pyrite is common in the sediments of the mud pots, though rarely found in the decomposed lavas surrounding the hot springs. Residual minerals include plagioclase, pyroxene, and to a minor extent, hornblende, biotite and magnetite. Zircon is present in many samples; and has probably been concentrated in some of the mud pots.

STAGES IN DECOMPOSITION. In many places it is possible to find fragments of lavas that have been partly altered so that a core of the original rock remains. At Devil's Kitchen and Bumpass Hell talus material is gradually brought to the hot springs, while at Supan's the hot springs occur in a caldera where the fragmental rocks suggest agglomerates and breccias infilling a vent.<sup>6</sup> Without exception, the soft, white, chalky exteriors are composed largely of opal with minor amounts of alunite. In a few specimens, tri-

<sup>6</sup> Williams, *op. cit.*, p. 244.

dymite was found, and, to judge from chemical analyses and staining with fuchsine dye, kaolin is also present in minor amounts.

Williams<sup>7</sup> has suggested that decomposition commences with the porphyritic pyroxenes, for specimens studied by him from the western end of Bumpass Hell and from Diamond Peak showing incipient alteration are characterized by chlorite, calcite, (?) sericite and talc pseudomorphs of the ferromagnesian minerals. However, among the specimens studied by the writer in which blocks of lava with a decomposed exterior grade to a fresh core, this selective decomposition is not apparent. In some specimens there may be limited selection of the feldspar phenocrysts while in others the groundmass has suffered more alteration. Locally the boundary between fresh and decomposed rock is quite sharp, but elsewhere it is feathery. Again, a hard bleached zone an inch or more in width separated the two. But no early decomposition of the ferromagnesian minerals is discernible and in some partially altered lavas, fresh pyroxene is imbedded in opal. The cause of these conflicting observations may be that the specimens studied by the writer represent fragments of lavas that are being altered at the present time, while the specimens studied by Williams are now removed from active solfataric action and may be the result of decomposition when the solfataric action was of a different character.

Frequently there is a retention of the original texture even after complete alteration. In thin section the outline of the phenocrysts and microlites will be well preserved and the original ferromagnesian minerals will be marked by opal colored with dark dust. But when the polarizer is inserted, the field appears black owing to the isotropic opal with the exception of occasional tridymite and almost ubiquitous alunite crystals. The latter mineral may be found concentrated near the fresh rock replacing the plagioclase or scattered evenly throughout the altered rock. A surprising feature is the presence of original magnetite crystals in some of these intensely decomposed lavas; evidently the magnetite is not appreciably attacked by the sulphuric acid.

BUMPASS HELL. A sample of dacite from Bumpass Hell (spring 14) was selected for analysis of the core, bleached hard transition zone, and the soft powdery exterior (Table I, nos. 1, 2, 3). Some alteration of the core has taken place judging from the rather high

<sup>7</sup> *Op. cit.*, p. 263.

content of water, although no perceptible alteration is visible in thin section. The progressive leaching of the bases outward from the core with marked increase in the silica content is quite pronounced. In the transition zone, a striking feature is the relatively high amount of sulphate. Assuming that the  $K_2O$  and  $Na_2O$  are combined in alunite, there should be 9 per cent of alunite in this zone, with only 1 per cent in the altered exterior. The analysis indicates that the altered material is largely opal, and this is easily confirmed under the microscope. In addition scattered residual quartz phenocrysts from the original dacite add to the content of silica. Tridymite is present in minute wedge-twinned crystals, in part associated with chalcedony. From the analysis, it is seen that only a fraction of the alumina is present in alunite, and assuming that all of it is combined to form kaolin there would be  $2\frac{1}{2}$  per cent of this mineral in the altered exterior. Upon staining a slide with

TABLE I

	1	2	3	4	5	6
SiO <sub>2</sub>	63.80	75.70	92.20	57.25	47.51	54.97
TiO <sub>2</sub>	0.55	0.65	1.25	0.42	0.65	0.83
Al <sub>2</sub> O <sub>3</sub>	17.55	8.53	1.02	18.25	34.08	27.72
Fe <sub>2</sub> O <sub>3</sub>	1.28	1.85	nil	1.44	1.17	0.88
FeO	2.44	1.40	0.40	4.73	0.52	0.32
MgO	2.02	0.05	nil	4.57	0.28	0.20
CaO	2.60	0.50	0.35	8.12	0.08	0.39
Na <sub>2</sub> O	2.70	0.12	tr	2.85	0.21	0.41
K <sub>2</sub> O	1.82	0.89	tr	0.99	0.11	0.46
H <sub>2</sub> O+	2.80	3.42	1.65	0.65	11.60	9.93
H <sub>2</sub> O-	1.85	2.40	2.80	0.31	1.89	2.54
CO <sub>2</sub>	nil	nil	nil	—	—	—
ZrO <sub>2</sub>	—	—	—	0.01	0.09	0.03
P <sub>2</sub> O <sub>5</sub>	tr	tr	nil	0.18	0.81	0.11
MnO	tr	nil	nil	0.11	tr	—
S		0.05	0.03	—	0.63	1.11
SO <sub>3</sub>	0.48	4.58	0.35	—	—	—
BaO				0.05	0.05	0.03
SrO				0.08		
	99.89	100.14	100.05	100.01	99.68	99.93

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| 1. Fresh core dacite block, Bumpass Hell | } Analyses by W. H. Herdsman.                     |
| 2. Bleached transition zone              |   |
| 3. White powdery exterior                |   |
| 4. Basalt from Boiling Lake              | } Quoted from Williams, <i>op. cit.</i> , p. 285. |
| 5. Mud from Boiling Lake                 |   |
| 6. Mud from Devil's Kitchen              |   |
- Analyst, Wheeler.

fuchsine dye, and assuming that the finely divided material that absorbed the dye is kaolin,<sup>8</sup> it appears that the mineral is largely developed in some of the phenocrysts and microlites of feldspar, in intimate association with opal. This mixture is sensibly isotropic and no reliable value of the index of refraction can be obtained.

Some tridymite is present in the glassy groundmass of the unaltered core and may be original similar to the occurrences reported by Kuno.<sup>9</sup> But much tridymite is associated with veinlets of pyrite and chalcedony, and must therefore be of secondary origin. Also it is usually concentrated in the completely altered exterior, so that it appears to be forming now. This is of interest because the temperatures of this spring are recorded by Day and Allen<sup>10</sup> as ranging from 90°C. to 94.1°C. the latter being above boiling point at that elevation. Daubrée<sup>11</sup> has reported the formation of tridymite at temperatures as low as 73°C. at Plombières, France, where Roman bricks have been altered by hot spring action to a zeolitic mass containing opal and tridymite.

TABLE II  
Partial Analyses

	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	93.6	58.2	60.5	60.1	98.3	63.7	70.5	71.9	90.5	94.79
Al <sub>2</sub> O <sub>3</sub>	3.0	26.2	23.3	28.7	1.5	20.4	17.8	20.2	1.6	1.18
Loss on ignition	3.7	16.0	15.2	11.2	0.6	15.9	11.5	8.1	8.3	3.05*

\* Reported as H<sub>2</sub>O.

1. Specimen immersed in hot water, Devil's Kitchen.
2. White sediment from hot spring fifty feet above Warner Creek, Devil's Kitchen.
3. Mud from mud pot above Warner Creek, Devil's Kitchen.
4. Sediment from mud pot near water level of Warner Creek, Devil's Kitchen.
5. Dense white altered lava, not near present activity, Supan's Spring.
6. Sediment from mud pot, north of highway, Supan's Spring.
7. Sediment from mud pot, Bumpass Hell.
8. White altered lava along road cut, Little Hot Spring Valley.
9. Near No. 8.
10. Sample from surface of hill, Bumpass Hell. Quoted from Day and Allen, *op. cit.*, p. 142.

<sup>8</sup> Holmes, Arthur, *Petrographic methods and calculations*, p. 275, 1931.

<sup>9</sup> Kuno, Hisashi, On silica minerals occurring in the groundmass of common Japanese volcanic rocks: *Bull. Earthquake Research Inst., Tokyo Imp. Univ.*, vol. 11, pp. 382-390, 1933.

<sup>10</sup> *Op. cit.*, p. 107.

<sup>11</sup> Daubrée, M., Sur la présence de la Tridymite dans les briques zéolithique de Plombières: *Bull. Geol. Soc. France*, 3rd ser., vol. 4, pp. 523-524, 1876.

DEVIL'S KITCHEN. The soft powdery exterior of a block of andesite partly submerged in the hot water of spring 1, Devil's Kitchen, was partially analyzed (Table II, No. 1) and is practically identical with the analyzed material from Bumpass Hell, except for a higher content of alumina. If all of this alumina is present in kaolin, there would be over 7 per cent of this mineral in the decomposed lava, but actually the amount is less due to the presence of alunite. Staining with fuchsin dye revealed that the clay is limited to original feldspar microlites, and as in the specimen described from Bumpass Hell the clay is intimately admixed with opal. Tridymite is also present in wedge-shaped twins. A veinlet of opal containing crystals of alunite indicates that this mineral may be deposited from solution.

Two samples of andesite were studied from Devil's Kitchen where only steam now has access to the rocks; here the alteration products were dry and powdery and of only limited development. In one specimen sulphur crystals were being deposited on the surface. The dry powder from the exterior consisted of opal, sulphur and unaltered plagioclase and hypersthene crystals. In thin section, it was noted that the plagioclase phenocrysts may be partly replaced by opal and sulphur while fresh feldspars and pyroxene might be traversed by minute veinlets of sulphur. There was a suggestion that sulphur partly replaced the groundmass. In the other specimen, the dry altered lava consisted of opal accompanied by crystals of alunite and tridymite.

LITTLE HOT SPRING VALLEY. In the above cases, transitions to fresh rock are always found, but in road cuts between Supan's Springs and Bumpass Hell (above Little Hot Spring Valley), lavas are exposed that have been completely altered leaving no trace of the original rock and there has been a cessation of thermal activity. Two specimens collected a short distance apart and identical in appearance from a macroscopic examination were partially analyzed (Table II, Nos. 8 and 9) and the differences are quite striking. Assuming that all the alumina is present in the form of kaolin there would be 51 per cent in No. 8 and only 4 per cent in No. 9.

HOT SPRING MUDS. As revealed by microscopic examination, the muds from the hot spring basins consist largely of opal and kaolin accompanied by variable quantities of alunite, tridymite, and residual minerals such as feldspar, pyroxene and zircon with fragments of lava in all stages of decomposition. Some of the

muds, e.g., from Devil's Kitchen (Table I, No. 7, Table II, No. 2) may contain considerable quantities of kaolin, while certain of those in Bumpass Hell are colored yellow by much precipitated sulphur. A sample from spring 4, Bumpass Hell, studied by Day and Allen<sup>12</sup> contained 64 per cent sulphur, 17.6 per cent opal, 15 per cent kaolin, 3.3 per cent alunite and a trace of pyrite.

MUD POTS. The mud pots are essentially hot springs with a limited supply of water so that there is no visible outlet, and the basin contains thick pasty mud constantly agitated by escaping gas. Partial analyses of four air-dried muds (Table II, Nos. 3, 4, 6, 7) indicate that kaolin is the chief constituent, an assumption easily verified by the microscope. Finely divided opal is always present, frequently in intimate association with the kaolin. A similar association of these minerals has been reported from the Yellowstone mud pots by Allen.<sup>13</sup> Alunite was observed in 14 out of 18 of the Lassen samples. The mud pots frequently contain many of the residual minerals, such as unaltered plagioclase and pyroxenes, and the apparent concentration of zircon in some sediments is quite striking.

In addition to the minerals, the tests of diatoms were noted in three mud pots, one at Devil's Kitchen and two from Supan's Springs, while a questionable diatom was noted from Bumpass Hell. Diatoms comprising 10 per cent of the sediment have been reported from mud pots near Beowawe, Nevada,<sup>14</sup> but in the Lassen sediments, the diatoms constitute less than one per cent. Dr. G. D. Hanna of the California Academy of Sciences has kindly examined the samples from the mud pots and has reported the following species:

*Caloneis bacillum* (Grunow). Most common form.

*Caloneis latiuscula* Kutzing.

*Neidium iridis* (Ehrenberg).

*Pinnularia microstauron* (Ehrenberg).

*Rhopalodia gibbia* (Ehrenberg).

According to Dr. Hanna, these diatoms may very well have lived in the cooler moist portions of the mud pots rather than in the hot mud itself which frequently attains a temperature close to 90°C.

<sup>12</sup> *Op. cit.*, p. 120.

<sup>13</sup> Allen, E. T., Hot springs of Yellowstone Park: *16th International Geological Congress*, Guidebook 24, pp. 16 and 23, 1933.

<sup>14</sup> Nolan, T. B., and Anderson, G. H., The geyser area near Beowawe, Eureka County, Nevada: *Am. Jour. Sci.*, 5th ser., vol. 27, pp. 226-227, 1934.



**BOILING LAKE.** The sediment from Boiling Lake is also composed largely of kaolin (Table I, No. 5). This lake is an oval basin of hot water about 200 yards in largest diameter. Gas bubbles rise occasionally to various points on the surface while the lake is encircled by a chain of hot springs and mud pots, most of which are near the boiling temperature. The temperature of the water in the lake averages about 50°C. The floor of the lake consists of a cream colored mud while the basalt surrounding the basin has been decomposed to reddish and white alteration products.

In addition to the kaolin, which comprises the major portion of every sample examined, small amounts of opal, alunite, pyrite, and, occasionally, iron oxide, may be present. Angular quartz grains were found in some of the samples, and as quartz does not appear in the basalt surrounding the lake, it appears reasonable to assume that it developed as a result of alteration.

**FORMATION OF QUARTZ.** At Supan's Springs, some altered material is composed largely of microcrystalline quartz (Table II, No. 5). These specimens are usually harder and more flint-like in appearance than products from the other hot spring areas. In thin section relic porphyritic textures may be recognized but upon inserting the analyzer the rock is resolved into a microcrystalline aggregate of quartz accompanied by minor quantities of alunite and opal. Thin sections of similar character from other areas in the park (Warner Creek, one to two miles below Drakesbad, and at base of Pilot Pinnacle) were loaned to the writer by Dr. Williams. His specimens and those from Supan's Springs are all removed from areas of present active hot springs indicating that the decomposition took place when activity was more widespread and that sufficient time has elapsed for the opal to change to microcrystalline quartz.

However, minor quantities of quartz associated with opal were observed replacing the groundmass of some of the lavas from Devil's Kitchen, and angular quartz fragments were noted in sediments from mud pots and hot springs derived from quartz-free andesites. Several examples of the replacement of tridymite by microgranular quartz were observed. Possibly, therefore, some quartz forms directly. Day and Allen<sup>15</sup> report the presence in two springs of well faceted, double terminated quartz crystals which may have formed during decomposition.

<sup>15</sup> *Op. cit.*, p. 119.

## CONCLUSION

In summary it may be stated that opal is the chief product in the altered exteriors of all lava fragments collected where active decomposition is taking place, accompanied by minor amounts of kaolin and alunite. The muds from the hot spring basins may be somewhat similar in composition except that they usually contain more kaolin. The mud pots and the sediments from Boiling Lake all consist largely of this mineral.

Day and Allen suggested that two types of lava decomposition appear to be in progress:

"the one producing *kaolin* and some *silica without aluminum sulphate*, the other producing *silica with aluminum sulphate*. In the fact that kaolin is decomposed by strong sulphuric acid into silica and aluminum sulphate, the key to the difference is doubtless to be found. If the acid forms in a place where sufficient water is percolating, its concentration is kept down to such a value that the decomposition of feldspars, volcanic glass, and possibly other minerals is incomplete. The intermediate, and comparatively stable compound *kaolin* results, and this, as we have seen generally occurs in the springs, together with very dilute acid. It would not be surprising if the fine sticky mud of the low and wetter portions of the Devil's Kitchen and Bumpass Hell should also prove to contain kaolin, but observations have not been extended to these points.

"On the other hand, if sulphuric acid forms in nearly dry ground it will accumulate by progressive oxidation of the sulphur gases and the concentration may reach comparatively high values—probably in the form of sirupy films. It is under such conditions that this more complete type of rock decomposition occurs, as field observations indicate."<sup>16</sup>

There is considerable evidence in support of their conclusion, namely the high alumina content of the sediments from Boiling Lake where one might expect the greatest dilution of sulphuric acid. Also the mud from Devil's Kitchen near Warner Creek (Table II, No. 4) is from the wetter portions referred to in the above quotation. Moreover, opal is being formed from lavas that are being attacked by steam where the acid may be more concentrated.

But the occurrence in the hot springs of decomposed lava fragments consisting of opal (Table II, No. 1) requires some explanation, if the above conclusion is acceptable. Needless to say, these fragments, if altered in another environment could be transported only a very short distance because of their incoherent character. However, if the rocks above the water level of the springs were

<sup>16</sup> *Op. cit.*, p. 144.

attacked by acid developed by condensation of the water vapor and oxidation of the hydrogen sulphide, and this acid were to become concentrated by progressive oxidation, pure opal might form, and lavas so altered might drop a very short distance into the water without loss of form. According to Dr. E. T. Allen<sup>17</sup> this acid formed above the water level of springs at the Geysers, California, may exceed 30 per cent concentration while the strongest sulphuric acid in spring water that he has found (Yellowstone) had a concentration of only 0.4 per cent. This would indicate that rocks attacked by spring water would be subjected to a weak acid while rocks immediately above the water line would be attacked by acid many times the concentration, and would explain why the sediments in the mud pots and springs are richer in clay compared to the rocks above the water level of the springs. The point might be raised that the springs would in time have their outlets lowered owing to the soft character of the altered lavas, and rocks rich in kaolin might then be attacked by more concentrated acid, altering them to alunite and opal, as suggested in the above quotation. However, no specimens were found where there is any suggestion of this although it might be difficult to recognize a relic kaolin-rich stage.

Another explanation was offered by Day and Allen for the concentration of the kaolin in the mud pots. "Where the springs have an outlet much of the finest material is naturally carried away by flowing water, but where the conditions favor its retention, as they do in the mud pots, the chief constituent of the sediment is kaolin."<sup>18</sup> However, in attempting to separate the kaolin from the opal and alunite, Dr. F. A. Johnson, of the University of California, treated a sample in a centrifuge, and even after prolonged rotation, the kaolin did not separate, and the fact that muds from hot springs with outlets may also contain a large portion of kaolin casts some doubt upon this suggestion. It appears that the high content of this mineral is probably related to conditions of formation rather than to mechanical separation.

Another suggestion for the high concentration of kaolin in the mud pots and hot spring basins might be offered. When one examines the chemical composition of the gases evolved from these

<sup>17</sup> Personal communication.

<sup>18</sup> Day and Allen, *op. cit.*, p. 119.

hot springs<sup>19</sup> it is seen that CO<sub>2</sub> is the chief constituent. It ranges in amount from 89.80 per cent (spring 24, Devil's Kitchen) to 96.40 per cent (spring 16, Bumpass Hell). On the other hand, the percentage of hydrogen sulphide may range from nothing to 2 per cent, and with most of the gases analyzed, it is less than 1 per cent. There has been no uniformity of opinion regarding the origin of kaolin, some investigators suggesting atmospheric weathering, others pneumatolytic action and others thermal waters. Any of these processes may be operative, but Stremme<sup>20</sup> has ascribed their action in all cases to the chemical activity of carbonic acid. Clarke summarizes the situation by saying, "In short, kaolin, like many other substances, may be formed by any one of several processes, in all of which, water, hot or cold, and carbonic acid take part."<sup>21</sup>

Considering that carbon dioxide is the chief gas in these thermal waters, it might be expected that the carbonic acid would attack the rocks in its upward movement and that kaolin would be produced from the feldspars and glass of the lavas forming soluble carbonates and soluble silica. However, soluble carbonates were only reported in three of the spring waters,<sup>22</sup> described as alkaline springs, but if sulphuric acid were formed at the surface, the carbonates would react with the acid to form sulphates with escape of CO<sub>2</sub> into the atmosphere. The soluble sulphates are "those of the *common rock bases, with the exception of alumina*, which, in four-fifths of the samples, varies from 0 to 0.2 mg. per 100 cc., the amount used in analysis. In other words, four-fifths of the waters examined were virtually free from alumina. The more acid waters contain more alumina."<sup>23</sup> However, Dr. Allen<sup>24</sup> explains this by the fact that iron and aluminum are similar in some ways, in that both are held in solution when the sulphuric acid is strong enough, but are precipitated where it is weak. In the case of the alumina, it possibly unites with silica to form kaolin. Dr. Allen has informed the writer that in the Yellowstone Park area, rock is altering to clay in a very few alkaline springs, but the cores of two

<sup>19</sup> Day and Allen, *op. cit.*, pp. 131-133.

<sup>20</sup> Stremme, H., Über Kaolinbildung: *Zeit. für prakt. geol.*, vol. 16, p. 128, 1908.

<sup>21</sup> Clarke, F. W., The data of geochemistry: *U. S. Geol. Surv.*, Bull. 770, p. 495, 1924.

<sup>22</sup> Day and Allen, *op. cit.*, p. 111.

<sup>23</sup> Day and Allen, *op. cit.*, p. 110.

<sup>24</sup> Personal communication.

drill holes from the geyser basins studied by Fenner yielded no clay down to depths of 400 feet. The studies of the gases in the alkaline areas showed that most of the free carbonic acid had been combined to form bicarbonates at depths beyond the present range of exploration.

In a recent paper, Allen<sup>25</sup> has suggested that in these alkaline springs of Yellowstone the water supply is large, penetrating to considerable depths so that carbon dioxide is fixed below ground by chemical reaction with the surrounding rocks. But in the sulphate areas, a small water supply limits the depth of penetration of the water, so that atmospheric oxidation of the hydrogen sulphide forms sulphuric acid which attacks the rocks. In alkaline springs, the hydrogen sulphide passes directly into alkali sulphate, instead of sulphuric acid. Presumably in the sulphate springs with a limited downward extension of water, the time element might be a factor in the opportunity of the carbonic acid to react with the rocks, particularly as near the surface, it escapes readily in the atmosphere owing to the heated character of the water.

In summary, it appears that the various types of alteration products are related to the concentration of the sulphuric acid; where the acid is strong, comparatively pure opal will form, as in areas attacked by steam and above the water level of the springs. In the springs and mud pots, as well as Boiling Lake, where the acid concentration is low, kaolin is the important constituent. That the carbonic acid is an effective agent in the formation of the kaolin appears questionable in the light of the results so far obtained from Yellowstone and so kindly reported to the writer by Dr. Allen.

<sup>25</sup> Allen, E. T., Neglected factors in the development of thermal springs: *Proc. Nat'l. Acad. Sci.*, vol. 20, pp. 345-349, 1934.