

ART. XI.—*Some Chemical Observations on the Volcanic Emanations and Incrustations in the Valley of 10,000 Smokes, Katmai, Alaska;* by J. W. SHIPLEY.¹

Contribution from the Chemical Laboratory, University of Manitoba,
Winnipeg.

The great volcanic explosion of June, 1912, in South-western Alaska which blew out the Katmai crater to a depth of over 3,700 feet, distributing more than two cubic miles of ash and pumice over the surrounding country, left on the Behring Sea slope of the Aleutian Peninsula in the Valley of 10,000 Smokes an excellent opportunity for studying the chemical nature of the gaseous emanations characteristic of the eruption. The volcanic gases have been pouring out continuously from vents distributed over an area of fifty square miles ever since the eruption and in the course of that time have built up large masses of incrustants around the vents. Extremely disintegrating in character, these gases have profoundly altered the chemical composition of the surface rock adjacent to the channels through which they find an exit. Igneous rock material has been decomposed and built up into altogether different chemical compounds by the action of the gaseous emanations in the presence of water.²

The floor of the valley through which the volcanic gases force their way is composed of volcanic detrital matter, pumice and ash, ejected by Novarupta volcano on the Behring Sea slope of the Aleutian peninsula. Novarupta, ten miles due west of Katmai, exploded before the latter and threw out much material locally. Falling hot on the snow-covered northern slopes and assisted by the heavy rainfall accompanying the eruption, much of this ejecta slid into the valleys and formed a vast mud flow.³ The flow continued down the main valley for over fifteen miles and, as it drained away, left a considerable residue adhering to the valley floor. The highest level attained by the flow of mud is marked on the valley walls frequently 300 feet above the present level. After coming to rest the mud was subjected to heat from below, dried, and caked and over a large part of the area was

¹ The author was attached to the 1917 Katmai Expedition of the National Geographic Society in the capacity of chemist.

² Shipley, *Science*, vol. 49, p. 589, June 20, 1919.

³ Described by Griggs, *Ohio Jour. of Science*, vol. 19, p. 117, 1918.

eventually baked. An examination of the baked mud showed it to be made up of angular pumice, tuff and volcanic ash having a specific gravity almost identical with that of building brick. The contracting, hardening mass split and cracked according to the strains and stresses set up by the irregularities of the valley floor beneath. The volcanic gases force their way upward through this superincumbent detrital material, using the existing cracks and fissures and dissolving out new channels where these were not available. The area covered by the mud flow is about fifty square miles and, by a strange coincidence, the limits of the mud flow are approximately the limits of the volcanic activity.

The distribution and superficial characteristics of the volcanic vents over this area have been excellently described by Griggs.⁴ The great volume of gases pour out from large well-defined vents, but in addition to these, the volcanic emanations exude from the surface of the mud flow over large areas not possessing any visible orifices whatsoever. The gases issue under considerable pressure at temperatures varying from atmospheric to well above 400°C. Unfortunately, the boiling point of mercury was the limit of our thermometry, but in 1918 Sayre and Hagelbarger with a thermo-electric pyrometer observed temperatures of 450°C. Our own observations indicated much higher temperatures than our thermometers would register.

The nature of the incrustations in the neighborhood of a vent was largely determined by the temperature of the issuing gases. Where the temperature was high the incrustations were anhydrous and baked and contained none of the more volatile sublimates or hydrated salts. Deposits of sulphur or orpiment were not found adjacent to a very hot vent and the deposition of ammonium chloride was in the throats of orifices little hotter than 100°C.

The Nature of the Gases.—The major part of the issuing gases consisted of water vapor. Many fumaroles emitted little else, but on the other hand, a few were almost anhydrous, scarcely any moisture condensing from samples drawn off. The latter were invariably strongly acid and in one particular contained large quantities of SO₃. Hydrochloric and hydrofluoric acids were common constituents of the vapors, the former being most mark-

⁴ *Nature*, vol. 101, p. 497, Aug. 22, 1918.

⁵ *National Geog. Magazine*, vol. 33, Feb. 1918.

edly present in the lower part of the valley ten miles below Novarupta. The surface of the mud flow was impregnated with HCl condensing from the vapors passing over it. The presence of HF was not suspected until large deposits of amorphous SiO_2 were observed around vents from which issued strongly acid vapors. Later its presence was indicated by the etching of the gas-washing bottle into which the vapors were pumped and condensed and in the laboratory where fluorine was found in the majority of the incrustants examined.

Hydrogen sulphide and sulphur dioxide were common constituents of the evolved gases. In one instance, from a vent depositing flowers of sulphur SO_2 was strongly in evidence, while the lead acetate paper indicated the presence of sulphide. Possibly the gaseous reaction between the two gases was not complete or else a volatile sulphide other than H_2S was being emitted.

Volatile ammonium compounds were detected in almost all of the vapors examined. Some were very strongly impregnated and as already mentioned NH_4Cl was crystallizing in the throat of vents on the western rim of Novarupta. These were relatively cool, acid fumaroles from which the gases were issuing under low pressure. The salt collected in an annular mass on the walls of the vents a couple of feet within the orifices. Below the accumulation, the salt was no doubt dissociated into its gaseous constituents NH_3 and HCl. A 4-oz. bottle filled from one of these vents analyzed 98% NH_4Cl .

A rather interesting relationship between the growth of blue-green algæ and the presence of ammonium compounds in the emanations was established. Algæ were found growing up to the edge of vents where the thermometer indicated 100°C . No algæ grew where the vapors showed an absence of ammonium. This relationship held over the large areas where the gases were slowly exuding through the porous mud flow. Apparently, the evolution of ammonia compounds was quite general, for the afternoon sun disclosed the slopes surrounding Novarupta clothed in a coat of green provided by the growth of algæ.

Sulphur.—Sulphur deposits were not met with so frequently as might have been expected from the chemical conditions obtaining in the vapors. From the hotter vents the sulphur would escape into the atmosphere, but the most of the sulphur was fixed as sulphide, sulphates

or the free acids of sulphur. A series of vents on the rim of Novarupta had considerable quantities of flowers of sulphur depositing on the walls bathed by the escaping gases. It was here that SO_2 and H_2S apparently co-existed. These deposits were 99% pure containing iron as an impurity. Selenium or tellurium was not detected in any of the samples collected in the valley. Crystalline rhombic sulphur was frequently found associated in varying proportions with masses of amorphous SiO_2 . The two minerals had been deposited together with a little Fe_2O_3 as an impurity.

The most peculiar deposition of sulphur observed was in the form of rosettes around miniature orifices adjacent to the larger vents. The rosettes were composed of needle-like crystals of sulphur half an inch or more in length and apparently was sulphur in the monoclinic system. On attempting to collect the needles, however, they crumbled to pieces which on examination proved to be rhombic crystals of sulphur. The sulphur originally deposited as monoclinic had been transformed into rhombic crystals retaining the outward form of the monoclinic mass.

Arsenic.—Associated with sulphur as an incrustant over several of the fumarole cracks small deposits of sulphides of arsenic were discovered. The mass consisted of yellow crystals of orpiment containing some reddish crystals that may have been realgar or the β variety of orpiment which, according to Borodowsky,⁶ is red. On analysis the proportion of arsenic to fixed sulphur gave a ratio corresponding to the formula As_2S_5 but it may have been that the CS_2 extraction failed to remove all of the free sulphur.

Arsenic deposits.

Free S (soluble in CS_2)	52.0%
Fixed S	21.0%
As	19.6%
Residue (insol. in Na_2CO_3)	4.4%
Volatile at 80°	1.6%
not determined	1.4%
	100%

Fluorides.—The presence of fluorine was indicated by the etching of the glass gas-washing bottle through which

⁶ Chem. Abst., vol. 1, p. 1106, 1907.

samples of the volcanic gases had been pumped. The incrustants tested in the laboratory almost all reacted for fluorine. The amount present as fluoride varied from a fraction of a percent up to 7% and was most abundant in incrustants around the more acid fumaroles. No specific compound of fluorine was identified but calcium was usually present in more than sufficient amount to combine with it.

Apart from the importance of HF in the gases as a disintegrating agent the presence of fluorine was very significant as to the origin of the gases. Clarke⁷ states that fluorine compounds "are especially characteristic of the deep-seated or plutonic rocks where the gaseous exhalations have been retained under pressure, and are commonly regarded as of pneumatolytic origin."

Corundum.—Several of the incrustants after decomposition with sodium carbonate left a residue of small crystals which on examination proved to be corundum. The presence of these crystals is rather interesting in view of Hautefeuille's⁸ synthesis of corundum by the action of HF on alumina and by Bruhns⁹ in the wet way on heating NH_4F with alumina to a temperature above 300° . The conditions under which Bruhns synthesized corundum obtain naturally in the Valley of 10,000 Smokes.

Silica.—The most characteristic deposit of the fumarole activity consists of amorphous silica. Many fumaroles have built up deposits of almost pure SiO_2 several feet high choking up the vents and causing the gases to force their way out through secondary orifices in the accumulated, baked, mass. Sulphur was frequently associated with these deposits and all samples tested in the laboratory showed the presence of fluorine. These deposits of SiO_2 although most marked around the hotter, acid, vents nevertheless were common over the whole valley. Three of the purest samples analyzed as follows:

Analysis of Silica deposits.

Sample No.	SiO_2 %	Free S %	Fe_2O_3 %	Undetermined. %
I	93.5	3.4	3.0	0.1
II	95.8	3.9	0.2	0.1
III	96.7	3.1	0.2

⁷ Data of Geochemistry, page 336.

⁸ Ann. Chim. phys., vol. 4, p. 153, 1865.

⁹ Neues Jahrb., vol. 2, p. 62, 1884.

The deposition of SiO_2 probably results from the decomposition of SiF_4 in the volcanic gases by the action of the water contained in the gases. Many of the fumaroles have temperatures, a few feet within the orifice, above the critical temperature of water, 375°C . Decomposition of the SiF_4 would only take place after the issuing gases had cooled off sufficiently to permit the formation of water. The decomposition of the silicates constituting the mud flow is quite marked over practically all areas of activity and, immediately surrounding the more active vents, the ash and pumice have been completely disintegrated. According to Moissan¹⁰ SiO_2 begins to volatilize at about 1200°C while Day and Shepherd¹¹ found it to sublime readily at 1755°C . There is no indication of temperatures approaching these in the fumaroles of the valley.

Boron.—Qualitative tests gave no indication of the presence of borates in the incrustants of the valley.

Gypsum and Apatite.—Nodular concretionary depositions of mixed crystals with well-developed pure crystals of selenite, halite and alum attached to the main mass were frequently found covering the orifices of active areas. Next to the deposits of SiO_2 these nodular masses were the most common type of incrustation. The nodular mass on analysis proved to contain calcium, fluorine, chlorine, phosphate (PO_4) and sulphate—the latter two acid radicals predominating. Over the hotter vents the principal constituent of the nodular mass was anhydrite. Apatite was not definitely identified but was presumably the form of phosphate present because of the association with chlorine and fluorine. Thin layers of Fe_2O_3 were observed buried in these nodular masses.

Alum.—Potassium alum in lichen-like incrustations was forming in all active areas in the valley. After a few hours without rain the accumulations became very apparent only to disappear, wherever exposed, as soon as the rain began again. The less soluble sulphates and phosphates of calcium preserved a lichen-like structure on which the crystals of alum reformed when weather conditions permitted. A small pond fed by surface drainage over the mud flow was so impregnated with alum as to be altogether unfit for drinking.

Iron.—Compounds of iron were omnipresent, the beau-

¹⁰ Compt. Rend., vol. 138, p. 243, 1904.

¹¹ Science, N. S., vol. 23, p. 670, 1906.

tiful coloring of the incrustants being largely due to the salts, oxides and hydroxides of iron. Chlorides of iron were recognized but due to the deliquescence of the crystals were not identified. Ferrous and ferric sulphates were collected, but the compounds were not identified.

Magnetite and amorphous Fe_2O_3 were met with everywhere. Considerable deposits of "Venetian Red," Fe_2O_3 , were forming around cracks in the side of a gully from which the volcanic gases were slowly seeping.

Vivianite ($\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$).—Several acres of the mud flow are covered with a hot blue mud, six inches deep, resting upon the surface of volcanic ash. The blue mud is saturated with water and on cool days vapors could be seen rising from the surface. A brown crust of oxide of iron covers the surface and a chemical examination of the mud showed it to be impregnated with magnetite and vivianite ($\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$). This is one of the most interesting volcanic formations in the district.

Pyrite.—Well-developed isometric crystals of FeS_2 imbedded in a gangue composed of the phosphate and sulphate of calcium together with silica were found in the wall of an inactive vent. The deposit had been exposed by the water erosion of a surface stream flowing across a line of activity in the upper valley. The deposit had formed about ten feet beneath the surface of the ash and was the only one of pyrite observed in the valley.

Manganese.— Na_2CO_3 fusions indicated the presence of manganese in many of the incrustants, at times in considerable quantities. None of its compounds, however, were identified. A small deposit of a brilliant, orange-yellow, highly hygroscopic, incrustant was collected along the cooler marge of a small orifice. It was almost entirely water soluble and on analysis, yielded the following percentages: Mn 17.3, Al 17.5, Fe 6.9, Ca 1.1, Cl 15.5 and F 7.0. I should not care to venture even a guess as to what this incrustant might be.

Tar.—A most interesting organic deposit resembling coal tar in odor and appearance was observed saturating the ash around fumaroles on the western slope of Novarupta volcano and in the immediate neighborhood of the NH_4Cl fumaroles. One fumarole in this same area was emitting nitrous acid. The gases from fumaroles in this area possessed a similar tarry odor and emitted much H_2S . On analysis of the impregnated ash the deposit proved to be of a very complex character. A 20-gram

sample was extracted successively with the following solvents until no further extract from each was obtained. The solvents in the order used were: ether, petroleum ether, carbon disulphide, benzene, carbon tetra-chloride, ethyl alcohol and glacial acetic acid. Each of the solvents extracted organic matter varying in amount from half a gram to a centigram, CS_2 and $(\text{C}_2\text{H}_5)_2\text{O}$ being the most effective. Several of the solvents extracted considerable quantities of free sulphur. On evaporation, a brownish-black resinous mass was left by each solvent. None of the extracts belonged to the aliphatic series, none contained nitrogen and none were unsaturated.

Steam distillation carried over the organic matter together with the free sulphur, and the first portion of the distillate gave an unmistakable odor of *naphthalene*.

The occurrence of this deposit of aromatic hydrocarbons may have some significance in the theory of volcanic origin for such compounds. The deposit lies close to the most active area of the district and is associated with NH_4Cl and sulphur, while H_2S is unusually concentrated in the escaping gases. On the other hand they might equally well be attributed to steam distillation from the sedimentary rocks with subsequent condensation in the ash on the surface. The Jurassic sandstones meet the igneous intrusion in the immediate neighborhood.

Surface Temperatures.—The normal temperature for the volcanic ash in the month of July was between 10° and 12°C at a depth of four inches. Owing to there being considerable areas over which the activity seemed to be general rather than confined to a narrow vent or fissure, the temperature of the mud flow was taken at numerous places. Temperatures above 10° - 12° were abnormal and indicated hot gases permeating the mass of the flow. The temperatures recorded varied from 10° to 100°C ., higher temperatures than 100° only being found in the open vents or cracks but hot vents and fissures were frequently surrounded by areas covered with blue mud the temperature of which approximated 100° . This blue mud was a mixed layer of ash and the phosphate of iron already described, saturated with water to a depth of four to eight inches. Such an area of hot vents and viscous blue mud covering at least five acres occurs about five miles down the valley from Novarupta volcano. This area is quite fluid beneath the brown crust covering the mud.

A series of surface temperatures was taken at ten-yard intervals at a depth of four inches across a relatively inactive area in the upper valley. The series extends from the base of Mount Cerberus to a point 1160 yards to the northward approximately half way across the mud flow.

The accompanying curve contains the temperatures plotted against the distance. There are only two intervals where the temperatures approximate normal, namely the 170 to 300 yard interval and the 590 to 730 yard interval. Both these areas are covered with water-deposited ash freshly lain after every heavy rainfall. Sub-surface temperatures at a depth of twelve inches ran from 7 degrees to 10 degrees higher. It follows, therefore, that the whole surface of the mud flow over which this series extends has an abnormally high temperature and is being supplied with heat from below.

As the active vents are approached, the surface temperature rises and remains relatively high until the activity diminishes. It is over these areas that the hot volcanic emanations are percolating through the porous mass of the mud flow. The mud flow is either in intimate contact with a heated mass of the earth's crust or the outlets for the gaseous emanations from the magma are well distributed beneath the flow.

Common origin of Novarupta Lava Plug and the Mud Flow.—In order to establish any relationship of common origin in the ejecta of the district, the silica, iron and alumina in representative samples of the lava plug of Novarupta, the Great Mud Flow, the Katmai Red Mud Flow and the pre-eruptive (1912) volcanics as represented in the rocks of Falling Mountain were determined. The results follow:

<i>Rock</i>	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %
Lava plug	75.2	14.2	3.2
Great Mud Flow.....	73.7	13.8	3.8
Red Mud Flow.....	63.6	18.4	7.8
Pre-eruptive volcanics...	69.2	17.9	6.3

It is rather interesting to note that the Katmai ejecta and the old volcanics are of similar composition while the lava plug of Novarupta and the Great Mud Flow are much alike. The two latter apparently are of common magmatic origin and differ markedly from the Katmai

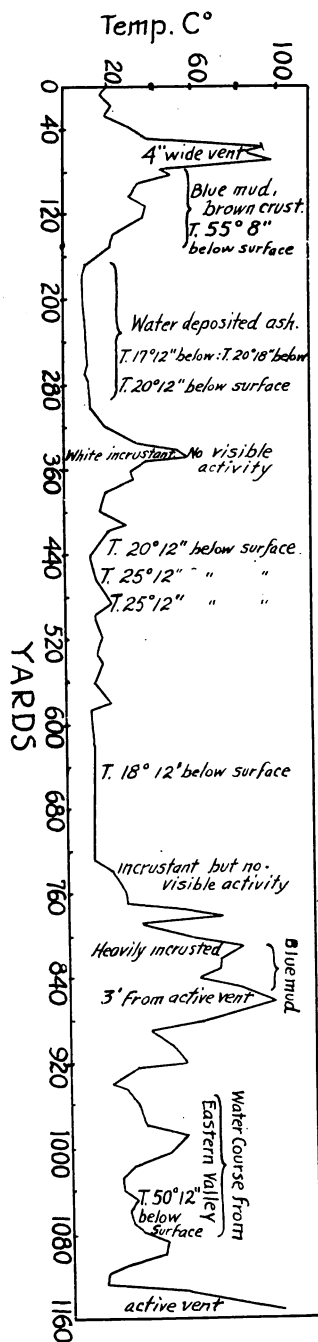


FIG. 1.—Surface temperature of mud flow at a depth of four inches.

ash which because of its location on the peninsula axis was largely composed of pre-eruptive material blown to powder.

Metamorphic action of the Volcanic Gases.—The country rock (volcanic ash and pumice) in the neighborhood of an active vent was subjected to the chemical action of permeating gases and solutions. The porous character of the rock permitted easy, intimate, contact and also offered the maximum of surface so that chemical action was speedy and effective. Adjacent to the hot acid vents the ash was completely disintegrated. As the distance from the vents increased the metamorphism diminished until the unaffected ash was reached. The decomposition resulted in the formation of more or less soluble salts of the bases present in the ash combined with the acids free in the volcanic vapors or dissolved in the percolating waters. These salts were deposited at or near the surface on the evaporation of the water or within the vent itself if the temperature was above the boiling point of water. In the latter case the salts were anhydrous.

Two partially metamorphosed samples of the volcanic ash, after extraction with water, were analyzed. The results show a loss of silica, sodium and potassium with a relative concentration of the iron and alumina. These samples were from areas where hydrofluoric acid was present in the vapors and consequently the loss of the SiO_2 would be expected, in fact, deposits of amorphous SiO_2 occurred around the vents at the surface.

Analysis of partially metamorphosed volcanic ash (percentages).

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	F
I.—	50.6	21.1	14.8	0.3	5.0	4.8	3.4	0.8	1.0
II.—	60.6	21.6	5.7	—	5.5	5.9	—	—	1.1

Sample No. II was more decomposed than No. I having lost much of its iron.

Pneumatohydatogenesis.—The above term was applied by Bunsen to the combined action of gases and water solutions in the formation of salts. The salts and compounds found in the Valley of 10,000 Smokes have their origin in such combined action. Hydatogenesis in the valley is confined largely to the surface layers for, as already mentioned, the temperature of many fumaroles is above that of the critical temperature of water and consequently,

water as such does not occur. That the disintegration of the ash in the mud flow was modified at considerable depth was evidenced by a cave-in exposing a subterranean, horizontal tunnel, twelve feet in diameter and seventy-five feet below the surface. The walls were composed of the characteristic mud flow material baked a deep brick red, apparently unattacked and containing no incrustants. Tunnels closer to the surface were heavily incrustated due to the cooling down of the vapors and sublimates and the possibility of salt formation and transportation in the presence of water.

Stream erosion across several active areas exposed cross sections of some of these tunnels, giving an excellent opportunity for studying the disintegration and deposition of material in the surface layers of the mud flow. Directly above the tunnel the ash was almost completely disintegrated and replaced by a deposit of SiO_2 , while laterally the decomposition fell off and the ash was impregnated with deposits of oxides, sulphates, phosphates and chlorides together with amorphous SiO_2 . The affected area extended from the tunnel fan-wise to the surface with the greatest accumulation of salts near the surface.

Conclusion.—It is quite impossible to differentiate the primary and secondary volcanic compounds in this region. The majority of the incrustants examined were secondary products arising from the decomposition of the ash by the volcanic gases, but, on the other hand, the great volume of escaping vapors has a magmatic origin. Gautier¹² and other investigators have shown that most of the gaseous products and sublimates observed in volcanic emanations can arise from the interaction of water, carbon dioxide, and the solid constituents of the lava. In the Valley of 10,000 Smokes, water vapor is the major constituent of the emanations. Its origin is debatable, but according to Gautier, one cubic kilometer of granite can provide 30,700,000 metric tons of water from its water of combination and oxidizable hydrogen. Consequently, should a portion of the earth's crystallized crust come in contact with the heated magma, sufficient water could be freed to give rise to the phenomena observed in the Valley of 10,000 Smokes.

Much of the surface drainage enters the porous mud flow and adds its quota to the saturation of the ash. Sur-

¹² *Compt. Rend.*, vol. 142, p. 1465, 1906.

face drainage in flood time has poured into open vents, the evidence of the ensuing struggle between inflowing water and issuing gases being found in the form of mounds of ash and pumice six to eight feet high, spewed out around the vents. To what extent surface infiltration provides water for the mud flow will remain problematical but the source of the heat necessary to account for the high temperatures prevailing must be considered magmatic.

The temperature a short distance within the hotted vents was several degrees lower than that at the orifice, and vacuum tubes filled with the hot gases on being sealed after cooling, sometimes blew out the glass capillary. Evidently the issuing gases were not in equilibrium and chemical action continued after their collection, resulting in an increase in the volume. The higher temperature at the orifice would indicate an oxidation of the volcanic gases on contact with the air.

A thorough study of the mineralization going on in this valley would provide valuable data concerning the formation of a number of economically important chemical compounds. A study of the physico-chemical relations existing within the vents where salts are being deposited would be equally interesting. The Valley of 10,000 Smokes is but one of Nature's huge chemical laboratories thrown open for inspection by the eruption of 1912.

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