24. *Gases and Deposits from Fumaroles on the New Dome "Showa-Shinzan", Volcano Usu, Hokkaido, Japan.*

By Hiromichi TSUYA and Toshiaki SHIRAI,

Earthquake Research Institute.

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After a period of quiescence of thirty-three years since 1910, Volcano Usu, Hokkaido. Japan, became active with forerunning local earthquakes at the end of December, 1943, and in the following two years gave birth to a new composite dome "Showa-Shinzan", about 405 m in height above the sea, on the northeastern flank near its base. The new dome is double in structure as well as in form, consisting of two parts—the first dome ("roof-mountain"), about 200 m in relative height and 1000 m in diameter, accompanied with terrace-like fore-hills and formed virtually by upheaval of the old ground, and the second superincumbent dome, about 150 m in height above the top of the first dome and 300 m in diameter at its base, formed by protrusion of a column of juvenile viscous lava (acidic hypersthene-andesite).

Since its birth in November, 1944, the second dome has been active in belching up a large quantity of vapors from a number of fumaroles on the fissures, with which it is cut in various directions throughout its height. According to their physical and chemical properties, these fumaroles are to be classified into two different types, high-temperature and low-temperature fumaroles. The high-temperature fumaroles, which are very hot and dry, are found for the most part on the fissures in the newly protruded lava exposed on the south and southwest sides of the second dome (Fig. 1), while a few are found on the opposite sides, where they occur in grottos, boring deep in the ash and debris-covered ground and glowing inside. The low-temperature fumaroles, which are wet and 100° or lower in temperature, are developed not only on all sides of the second dome but also on the ground surrounding it (Fig. 2).

The high-temperature fumaroles are mostly inaccessible on account of their heat and dense stimulative gases, but some of them, together with the low-temperature fumaroles, are accessible for the observation of the exhalations. The present report summarizes the results of chemical study of gases and deposits collected by the writers in 1948 from some of the fumaroles.

High-temperature fumaroles. In 1948, when the writers visited the volcano, one of the high-temperature fumaroles, about 20 cm in diameter at the orifice, was glowing inside with a red-hot rock (700°C ca.) exposed on the floor at a depth of about 20 cm. Gases, about 650°C at the orifice and 100°C in the air 40 cm above it, were being exhaled with hissing noises and with such a high pressure as to blow off a pebble thrown into them. At the orifice, the escaping gases were hardly visible owing to the high temperature. Thus, although superheated steam occupied the main part of the gases, it was disappearing into the air without condensing to visible fume.

The gases from the high-temperature fumaroles consist of hydrogen and some other acidic gases such as hydrogen fluoride, hydrogen chloride and boric acid, besides water vapor and inert gas, as shown in Table I.

Table I. Composition of gases from the high-temperature fumaroles.

	(Vol. %)
Water vapor	96.9
Acidic gases, HCl, HF, H_3BO_3	2.1
Hydrogen sulphide, H_2S	0.7
Hydrogen, H_2	0.3
Inert gas.	0.1

(T. SHIRAI, analyst)

Close to their orifice, the high-temperature fumaroles were virtually devoid of sublimates, although their wall-rocks were found to have been subjected more or less to some thermal and chemical changes. Thus, for example, the rocks around the orifice of most of the high-temperature fumaroles were found to have become black as if they had been smoked. Our experiment has shown that the black color was due to ferric oxide (Fe_2O_3) contained in the rocks and heated by the gases to a temperature above several hundred degrees. Ferric oxide has a character to turn black at such a high temperature. Moreover, at several places where the high-temperature fumaroles were exhaling gases from openings in a sandy

Table II. Fe^{++}/Fe ratio of the sand on the ground about one of the high-temperature fumaroles.

	Total Fe content (Wt. %)	Fe^{++} (Wt. %)	$(Fe^{++}/Fe)\times 100$
Sand, very close to the fumarole	5.3	1.0	19
Sand, 1 m apart from the fumarole	5.3	0.7	13

in a sandy ground, the sand near the openings was found to have been subjected to a reducing process, probably by the hydrogen gas, as shown by Fe^{++}/Fe ratio of the sand (Table II).

At places where hot gases from the high-temperature fumaroles appeared to have once passed through, were found masses of very fine, deep-red powdered material consisting for the most part of SiO_2, together with 8% Fe_2O_3. Microscopic examination has shown that the silica occurs in grains coated with finer particles of rouge (ferric oxide).

Low-temperature fumaroles. At the writer's visit, the low-temperature fumaroles were exhaling dense white vapor-clouds from small clefts and openings in the ground on and about the second dome. Inside the fumaroles, temperatures varying from 120° to 230°C were measured at a depth of about 1 cm, although at the orifice of the fumaroles, the escaping vapors showed 100°C, the boiling temperature of water at that place. The vapors consist mainly of steam, besides a little acidic gases (HCl, H_2S) and some contaminating air, as shown in Table III.

Table III. Composition of gases from the low-temperature fumaroles.

	(Vol. %)
Water vapor	98.5
Acidic gases	0.1
Air.	1.4

(T. Shirai, analyst)

The low-temperature fumaroles are rich in variegated masses of sublimates and other deposits accumulated by the action of their exhalations. Sulphur, boric acid, free silica, and salts such as hydrated aluminium-sulphates and calcium-sulphate are the predominant ones among them.

Sulphur occupies the main part of the sublimates, occurring as acicular crystals on the walls of the fumaroles and also in a massive layer, a few millimeters in thickness, on the ground thereabout. The sulphur layer is often dotted with many scaly lumps, a few centimeters in diameter, of white salts having a chemical composition as shown in Table IV. From the composition, it is inferred that the salts are a mixture of gypsum ($CaSO_4 2H_2O$) and alunogen ($Al_2(SO_4)_3 18H_2O$).

At the bottom of the sulphur layer lies in places a layer of white powdery material cemented with sulphur particles. The material is pure but more or less hydrated silica, as shown by the chemical analysis: 91% SiO_2, 9% H_2O. This silica, together with the rouge-coated silica around the high-temprature fumaroles, must have been produced by some action of the exhaling gases. So far as the writers know, such a mode of occurrence of free silica like this is very remarkable, and has not been reported by anyone up to this time. Although the process of formation of the silica is not demonstrative, it seems to have been connected with the presence of hydrogen fluoride in the fumarole gases.

The sulphur deposit near the orifice of some of the low-temprature fumaroles is covered densely with fine silky crystal flakes. Both microscopic examination aud chemical test have shown them to be sassolite, native boric acid H_3BO_3 (Fig. 3).

Moreover, the wall of some of the low-temperature fumaroles is covered with lumps, white, pale yellow or brilliant green, of a fibrous mineral, as if it were a moss-grown rock. Chemical analysis has shown the mineral to be one of the halotrichite group (iron alum), having a composition as shown in Table V. The chemical composition corresponds approximately to the formula $Al_2(SO_4)_3 20H_2 0$, if the small quantity of iron component is neglected. This is close in composition to alunogen, $Al_2(SO_4)_3 18H_2O$.

Table IV. Chemical composition of a scaly mass of white salts around the low-temperature fumaroles.

	(Wt. %)
CaO	15.8
Al_2O_3	7.2
SO_3	40.2
H_2O	37.0

(T. Shirai, analyst)

Table V. Chemical composition of a fibrous mineral collected from the wall of a low-temperature fumarole.

	(Wt. %)
Al_2O_3	13.3
FeO	0.9
Fe_2O_3	0.7
SO_3	34.5
H_2O	50.6

(T. Shirai, analyst)

Résumé. The fumaroles on the new dome "Showa-Shinzan", Volcano Usu, are divided into two types—the high-temperature fumaroles exhaling gases directly from the red-hot lava, and the low-temperature fumaroles exhaling white vapors through a deposit of volcanic ash and other detritus.

The principal emanation from the fumaroles of both types is steam,

Fig. 1. High-temperature fumaroles exhaling superheated and invisible gases from fissures in the new lave exposed on the southwest side of the dome "Showa-Shinzan." Most of the fissures were glowing inside. (May, 1943)

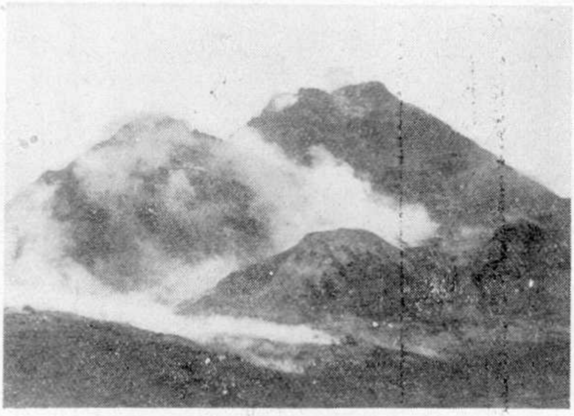

Fig. 2. Low-temperature fumaroles exhaling white vapor-clouds, on the southwest side of the dome "Showa-Shinzan." whose top is seen in the centre of the figure.

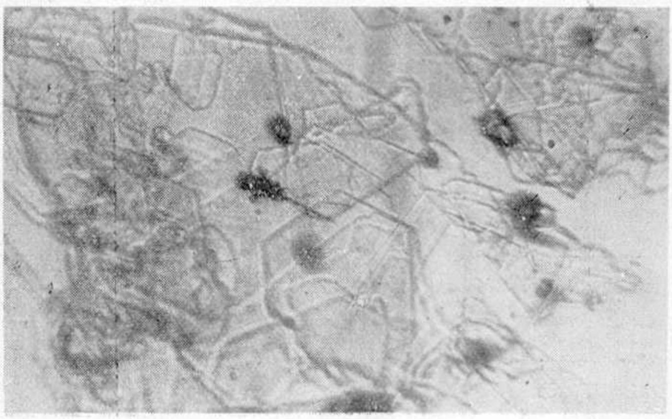

Fig. 3. Sassolite crystals from the sublimates around the low-temperature fumaroles on the dome "Showa-Shinzan." ×200. Black spots in the figure are particles of sulphur.

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but some acids are present, among which hydrogen chloride, hydrogen fluoride and boric acid may be mentioned in particular. Although these acids are poor in amount in the emanation from the low-temperature fumaroles, they must have once been fairly abundant, as inferred from incrustations around the fumaroles.

Sulphur, sassoltie, gypsum, alunogen, halotrichite, free and rouge-coated silica are the main products fron the fumaroles.

Further investigations are desirable for the elucidation of the mode of formation of these products, especially of the free silica.