ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES IN JAPAN. II. COMPOSITION AND GENESIS OF SOLUBLE SULPHATES PRODUCED IN THE ENVIRONMENTS OF A SULPHUROUS SPRING.

By Ichizo SUGANUMA.

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The so-called sulphurous gas gushing out from the cavities which are located in a region of sulphurous spring, chiefly consists of H_2S, CO_2, and steam or vapour. If the gas contains steam or vapour in a large amount, the temperature of the gas mostly attains about 100 degrees.

The sulphurous gas above explained, gushing from the fissure of the andesite rock or the cavity of clay which is formed by the decomposition of the andesite, gradually acts physically and chemically on the surface of the rock or clay above mentioned.

As the result of these action, a long needle-like crystalline efflorescence of white or light yellow with a silky appearance, is deposited on the surface.

An alum spring in the vicinity of Beppu in Oita-ken, a province of Kyushu, Japan, gives us a large amount of these crystalline masses by the natural production above mentioned, and in Nasu-Motoyu in the vicinity of Nikko, and also in Owaku-dani in Hakone. These natural crystalline products are collected and utilized for both bathing and medical purposes.

These crystals under microscope have a fibrous structure mostly with a few opaque nodes as on grasses, generally white in colour, but sometimes of light yellowish white, or yellow, or even mixed with yellowish powder of native sulphur.

The needle-like, silky white crystals, which are of the commonest kind, have a melting point 105°C., are soluble in water, and the aqueous solution of them is strongly acid.

The composition of the crystals is $Al_2(SO_4)_3$ and $FeSO_4$, and contains the same molecules of water of crystallization as in the common alum. In mineralogy, these crystals are called *halotrichite.*

The author obtained these crystals experimentally by passing steam mixed with H_2S and CO_2 on the Hakone andesite finely powdered and well washed, and on another experiment obtained the same result by passing steam through the andesite powder which was percolated with a dilute H_2SO_4, and allowing it to stand on a glass plate for a few days.

Therefore we know that the genesis of the crystals above mentioned is due to the weathering action of aluminium silicate and iron silicate contained in the andesite by carbonic acid or the other acids, and at the same time, to the formation of aluminium sulphate and iron sulphate by the action of H_2SO_4 produced by the oxidation of H_2S.

In the same region of sulphurous spring that produces halotrichite, there are found other snow-white crystalline masses similar in appearance to the above mineral.

These crystals under a microscope are found to be transparent, colourless and scaly, and they have a melting point 115°C.

The composition obtained by chemical analysis corresponds to $Al_2(SO_4)_3 \cdot 16H_2O$ i.e. a mineral called *alunogen* mineralogically. The author observed certain samples which consist of halotrichite on the top and of alunogen on the base, and sometimes observed the facts that alunogen is chiefly formed on clay longly exposed to air and sulphurous gas and fully decomposed by acids.

On these facts it is supposed that alunogen is formed from the clay poor in iron, subjected under the action of sulphurous gas, while the clay at first rich in iron, produces halotrichite.

Furthermore, the author observed the existence of light green crystalline masses as efflorescence on a black volcanic rock in Taiwan or some dark green clay in Fukeno-yu, Akita prefecture. The formation of these crystals is probably due to the action of sulphurous gas on rocks or clay very rich in iron, and the composition and properties of the crystals correspond to $FeSO_4 \cdot 7H_2O$ i.e. native green vitriol or *melanterite* in mineralogy. The fact that the samples of these crystals are frequently contaminated with halo-

trichite when tested under a microscope, is easily accounted for by the above reasoning of their formation.

Now, rocks with melanterite and halotrichite formed on their surfaces, are found to contain some fine crystalline particles of FeS_2 i. e. iron pyrites in their small cavities. Probably this is the case of the formation of FeS_2 by the interaction of hydrogen sulphide and iron silicate in the absence of air.

The author has frequently observed the fact that gypsum exists on a rock surface where the steam in sulphurous gas is gradually condensed. This mineral is, no doubt, formed from calcium silicate contained in rocks by the action of H_2SO_4, which is an oxidized product of H_2S.

It is a noticeable fact that a sulphurous gas containing only a small proportion of water vapour and naturally dry gas mixture composed of H_2S and CO_2 of ordinary temperature, frequently acts as a very poisonous gas as war gas. Some examples of this are found in the sulphurous gas in Sessho-seki in Nasu, and Sessho-dani in Akita Shika-yu, Akita Prefecture, Japan.

TABLE 1.

Analytical results of alunogen.

Component	Observed value	Calc. value as $Al_2(SO_4)_3 \cdot 16H_2O$
Al_2O_3	16.17	16.22
FeO	tr.	—
MgO	tr.	—
CaO	0.30	—
SO_3	38.01	38.09
H_2O	45.13 (at 325°C.)	45.69
SiO_2 (in sol. in acids)	0.23	—
total	99.84	100.00

TABLE 2.

Analytical results of halotrichite.

Component	Observed value	Calc. value as $Al_2(SO_4)_3 \cdot FeSO_4 \cdot 24H_2O$
Al_2O_3	10.28	11.03
FeO	8.56	7.75
MgO	0.12	—
CaO	0.46	—
SO_3	34.85	34.56
H_2O	44.82 (at 325°C.)	46.66
SiO_2 (insol. in acids)	1.24	—
total	100.33	100.00

TABLE 3.

Analytical results of melanterite.

Component	Observed value	Calc. value as $FeSO_4 \cdot 7H_2O$
FeO	25.25	25.90
Al_2O_3	2.12	—
CaO	0.46	—
MgO	0.36	—
SO_3	27.65	28.77
H_2O	—	45.33
total	—	100.00

The First Higher School, Tokyo.