

HISINGERITE OCCURRING AS A WEATHERING PRODUCT OF IRON-RICH SAPONITE

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Abstract—Hisingerite occurs as a weathering product of iron-rich saponite in rhyolitic tuff of Oya, Tochigi Prefecture. The chemical composition: SiO₂, 40.68%; Al₂O₃, 4.44%; Fe₂O₃, 28.54%; MgO, 1.85%; CaO, 1.42%; Na₂O, 1.50%; K₂O, 0.33%; H₂O⁺, 6.43%; H₂O⁻, 13.70%; total 98.89%. Very broad and weak X-ray powder reflections occur at 16, 4.5, 2.5, 1.7 and 1.5 Å, which correspond to the main peaks of nontronite. It is considered that trioctahedral iron-rich saponite was altered to hisingerite, a very poorly crystalline form of nontronite, by oxidation of iron and advanced leaching of octahedral Mg ions.

INTRODUCTION

Clayey volcanic rock fragments in the tuff of Oya, as already reported in detail (Kohyama *et al.*, 1973), are composed of two kinds of smectite, one is ferrous iron-rich saponite and the other is iron-poor montmorillonite-beidellite. In that report, it was also suggested that a hisingerite was produced by a weathering of the iron-rich saponite. This report describes the mineralogical properties and origin of the hisingerite.

MODE OF OCCURRENCE AND MINERALOGICAL PROPERTIES

Deep green to blue colored fragments are usually found in unexposed parts of the tuff. In open air, however, they easily turn to black within about one hr and finally to brown in a few weeks. The change of color is caused mainly by the oxidation of ferrous iron in the crystal structure of smectite. Exposed surfaces of the clayey rock fragments in the field show various colors such as gray, black, brown, yellow and white. Field observation suggests that they have decolorized with time of exposure in the field. Some fragments show a brindled appearance consisting of a dark brown incrustation coagulating in places over a surface of a completely decolorized part. The dark brown colored incrustation studied here is also found filling small crevices in the tuff.

X-ray powder diffraction patterns show extremely weak diffuse peaks (Table 1) agreeing with those of a dioctahedral smectite. No other diffraction peaks could be observed. On account of much iron, these diffuse peaks may be due to nontronite crystallites. The firing products at 800°C are hematite and cristobalite. An endothermic peak due to dehydroxylation is just visible in its DTA curve (Fig. 1). Infrared absorption spectra show three characteristic peaks: 3540 cm⁻¹ due to OH-vibration and two small peaks at 810 and 665 cm⁻¹ (Fig. 2). These last two peaks

Table 1. X-ray powder diffraction data for hisingerite

1		2		3		4	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
16.1	w					7.53	w
4.51	w	4.44	w	4.51	w	4.33	w
						3.50	w
2.55	wb	2.61	w	2.54	w	2.55	w
2.45	wb						
1.71	vwb			1.70	w		
1.51	vwb	1.50	w	1.53	w	1.55	w
						1.21	w

w—Weak; wb—weak and broad; vwb—very weak and broad.

1—Oya material (present specimen), examined in room air condition.

2—Kawayama material (Sudo and Nakamura, 1952).

3—Beaver Bay complex (Whelan and Goldich, 1961).

4—East Mesabi (Whelan and Goldich, 1961).

are close to the characteristic peaks of nontronite as reported by Farmer and Russell (1964). The chemical composition is shown in Table 2. An electron micrograph (Fig. 3 upper) is composed of thin flakes with a smectite-like shape and shows the layer structure with about 11–13 Å spacing along edges.

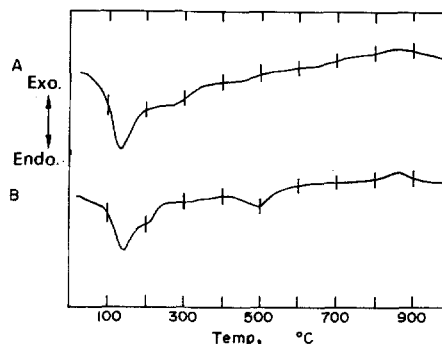


Fig. 1. DTA curve of hisingerite and nontronite. A—Hisingerite from Oya (present specimen); B—Nontronite from Spokane, Washington.

Table 2. Chemical analysis and structural formula for hisingerites

	1	2	3	4
SiO ₂	40.68	27.99	42.35	38.19
TiO ₂	—	—	0.13	0.01
Al ₂ O ₃	4.44	—	3.65	0.00
Fe ₂ O ₃	28.32	34.25	23.28	19.91
FeO	0.20	0.54	5.54	24.64
MnO	—	—	0.38	0.66
MgO	1.85	—	8.22	2.36
CaO	1.42	2.33	2.06	0.61
Na ₂ O	1.50	—	—	—
K ₂ O	0.33	—	—	—
H ₂ O ⁺	6.43	7.11	6.85	8.40
H ₂ O ⁻	13.70	27.89	6.95	5.53
Total (%)	98.87	100.11	99.41	100.31
Si	3.52	3.16	3.64	4.00
Al	0.45	—	0.36	—
Fe ³⁺	0.03	0.84	—	—
Al	—	—	0.01	—
Fe ³⁺	1.81	2.07	—	—
Fe ²⁺	0.01	0.05	1.90*	2.57*
Mg	0.24	—	1.05	0.37
Mn	—	—	0.03	0.06
Ca	0.13	0.28	0.38	0.14
Na	0.25	—	—	—
K	0.04	—	—	—

1—Present specimen; 2—Sudo and Nakamura (1952); 3 and 4—Whelan and Goldich (1961).
Structural formulas are calculated on the basis of 10(O) and 2(OH).

* Fe³⁺ recalculated as Fe²⁺ in structure.

DISCUSSION

The question is whether the present sample should be identified as a nontronite from the mineralogical data described. Although the main X-ray diffraction peaks of the present sample agree with those of nontronite or a dioctahedral smectite, they are extremely broad when compared with those of ordinary nontronite, and the DTA curve does not show a characteristic endothermic peak due to dehydroxylation of ordinary nontronite in the region of 400–500°C. Some similarities of hisingerite to nontronite or smectite have been discussed previously by many research workers as mentioned below. Here we discuss the nature of hisingerite, comparing the present data with earlier ones.

(a) Crystallites of hisingerite

Hisingerite has been known as a non-crystalline mineral since olden days of mineralogy and pedology. It has been generally accepted that hisingerite is not completely X-ray amorphous. However, earlier data do not agree with one another concerning the kinds of crystallites described as hisingerite. It has been reported to be nontronite (Gruner, 1935; Sudo and Nakamura, 1952; Bowie, 1955), or iron-rich saponite (Whelan and Goldich, 1961) or mica (Lindqvist and Jansson, 1962).

It is not easy to differentiate nontronite from iron-rich saponite on the basis of the spacing of a broad (060) reflection, because the spacing of nontronite is clearly larger than those of other dioctahedral clay

minerals and rather closer to that of iron-rich saponite. However, when the b_0 -spacing is plotted against the number of Fe + Mg in the chemical formula, as shown in Fig. 4, hisingerite reported by Whelan and Goldich (1961) is clearly plotted in the area of trioctahedral smectite. Hisingerite reported by Sudo and Nakamura (1952) and the present sample both fall in the area of dioctahedral smectite.

In general it is accepted that crystallites of hisingerite are variable and seem to exist, in both cases, as a structure of trioctahedral iron-rich saponite and dioctahedral nontronite. In the present sample the crystallites are considered to be similar to that of a dioctahedral nontronite. This is suggested also from the following consideration of the chemical formulas.

(b) Iron in hisingerite

Iron in hisingerite is usually of the ferric form. It is difficult to tell whether a ferrous or ferric form is primary in hisingerite. Assuming a smectite structure, a chemical formula of hisingerite has been calculated on the basis of 10 oxygens and 2 hydroxyl ions. The calculated total number of the octahedral cations for the present sample is close to 2. However, Whelan and Goldich (1961) showed the chemical formulas of their samples by recalculating all ferric ions as ferrous ions and found the total number of the octahedral cations to be close to 3. We consider that the primary form of iron in the present sample is ferric in the light of the mode of occurrence and origin.

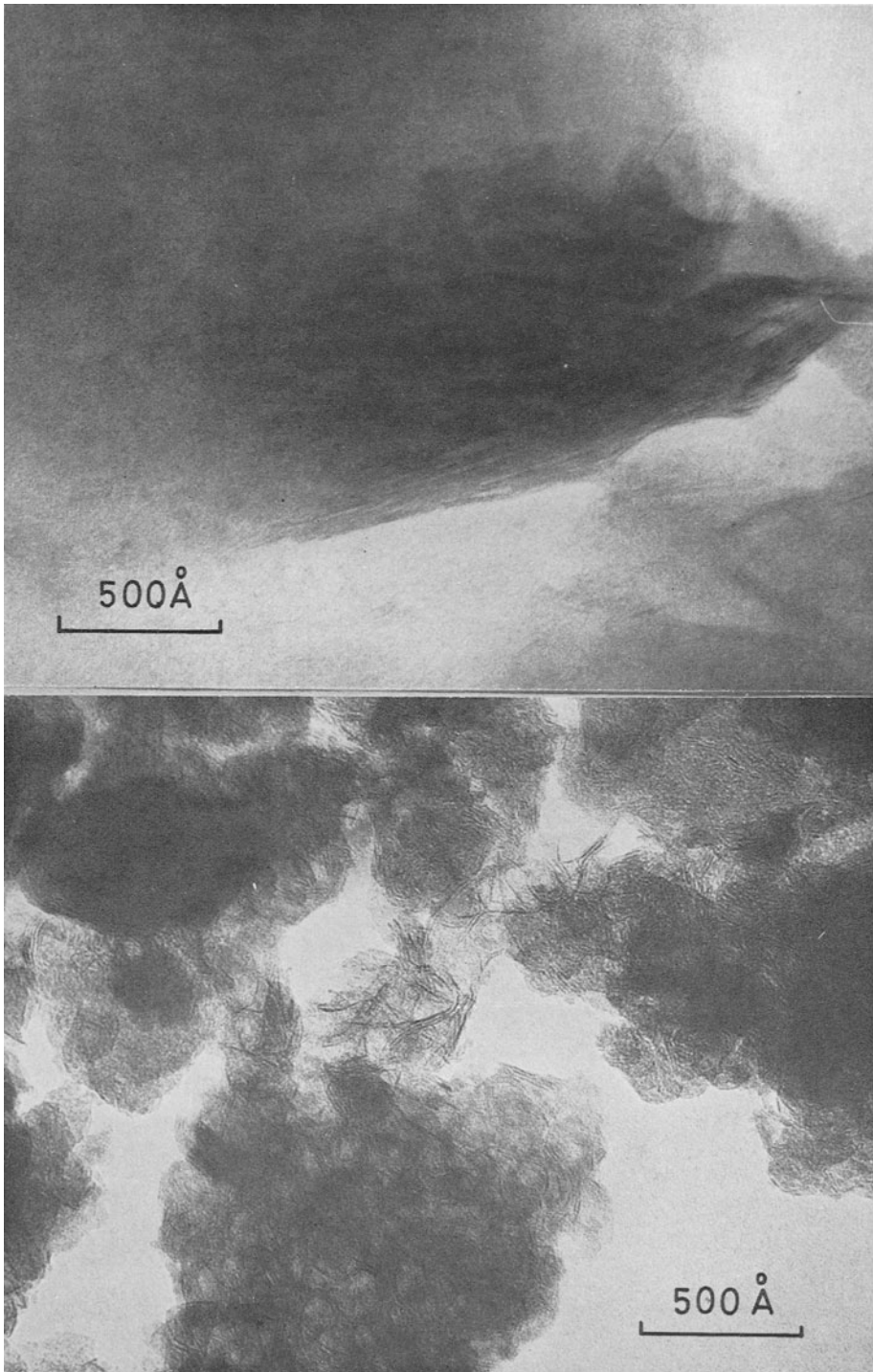


Fig. 3. Electron micrographs of hisingerite. Upper—Hisingerite from Oya (present specimen). Lower—Hisingerite from Kawayama.

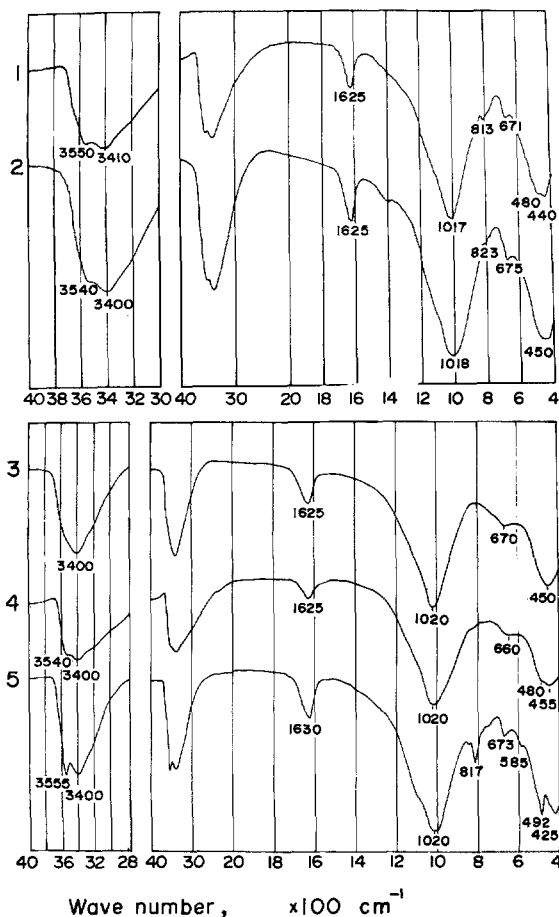


Fig. 2. Infrared absorption spectra of hisingerites and nontronite. 1—Hisingerite from Oya (present specimen); 2—Hisingerite from Kawayama; 3—Hisingerite from Beaver Bay complex; 4—Hisingerite from E. Mesabi; and 5—Nontronite from Spokane, Washington.

(c) Mode of occurrence

Hisingerite has been found in various differing modes of occurrence. It occurs as alteration products of ferro-magnesian silicates such as olivine, pyroxene,

amphiboles, garnets and iron-rich sulphides such as pyrite and pyrrhotite. Whelan and Goldich (1961) indicated that ferromagnesian silicates or sulphides had altered to hisingerite. The mode of occurrence and origin of the present sample seems to be close to that reported by Whelan and Goldich (1961).

(d) Comparison of the present sample to hisingerite from Kawayama

The occurrence of hisingerite from Kawayama Mine was reported by Sudo and Nakamura (1952). This material gave the first data of hisingerite in Japan and we compared the present sample with hisingerite from Kawayama as shown in Table 3. The mode of occurrence and some properties do not fully agree with each other. Hisingerite from Kawayama occurs in close association with pyrrhotite. There is no indication that the parent material is smectite. An electron micrograph of hisingerite from Kawayama (Fig. 3 lower) shows that it is composed of aggregates of fine curled fibers, which show a lattice

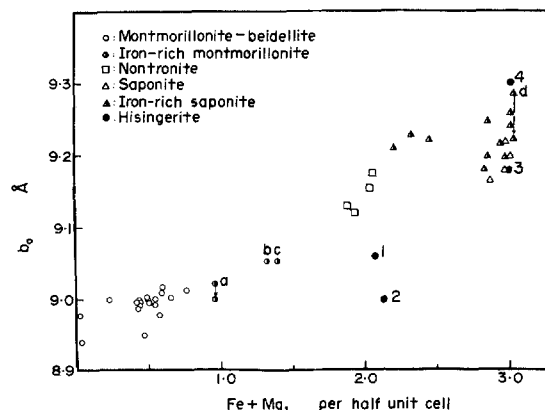


Fig. 4. *b*-Parameter plotted against Fe + Mg in octahedral sheet of hisingerite with various kinds of smectite. 1,2,3 and 4—Correspond to the number of Table 1. a—Iron-rich montmorillonite—beidellite from Oya (Kohyama *et al.*, 1973); b and c—iron-rich montmorillonite from deep sea sediments (Aoki, Kohyama and Sudo, 1974); d—iron-rich saponite from Oya (ferrous form) (Kohyama *et al.*, 1973). Arrow indicates the shrinkage by oxidation in air.

Table 3. Comparison of Oya- and Kawayama-hisingerite

	Oya-hisingerite	Kawayama-hisingerite
X-ray reflections	Broad reflections of nontronite are observed. The weak basal peaks are also observed	Broad reflections of nontronite are observed but the basal peaks are not observed
DTA curve	Endothermic peak due to dehydroxylation is scarcely observed	Endothermic peak due to dehydroxylation is absent
IR spectra	Diffuse bands of nontronite and a weak OH-vibration at 3550 cm ⁻¹ are observed	Diffuse bands of nontronite and a weak OH-vibration at 3540 cm ⁻¹ are observed
Chemical composition	Most of the iron is ferric and when calculated on the basis of 10(O) and 2(OH), it shows a dioctahedral structure	Most of the iron is ferric and when calculated on the basis of 10(O) and 2(OH), it shows a dioctahedral structure
Electron micrograph	Thin small flakes with curled edges, preserving a smectite-like shape	Fine curled fibers
Electron diffraction	Clear <i>hk</i> reflections are observed	Clear <i>hk</i> reflections are observed

image of about 12 Å, which is close to the basal reflection of smectite. The lattice image can be seen more frequently in hisingerite from Kawayama than the present sample. The characteristic difference also appears in the X-ray diffraction patterns. Although crystallites in both samples are considered to be nontronite in structure, the basal reflections of hisingerite from Kawayama are scarcely visible but can be seen weakly in the Oya sample.

(e) *Definition of non-crystalline minerals*

Non-crystalline minerals have been found as precipitates from contemporaneous hot springs and in rocks after the lapse of geological time. The former is usually in a completely non-crystalline state while the latter is usually in a poorly crystalline state. Hisingerite from Kawayama originated from gels of Fe and Si, and was formed by a chemical reaction between surface and circulating water in the pyrrhotite deposit. Therefore the nontronite-like crystallites would be formed by crystal nucleation in the gel. The present sample occurs as a weathering product of iron-rich saponite, and therefore crystallites in the present sample are apt to show the nature of smectite more clearly than in the case of hisingerite from Kawayama. In any case, the degree of crystallinity of hisingerite is variable, and it is not easy to distinguish hisingerite from nontronite or usual iron-rich saponite. The present sample should be named hisingerite, a very poorly crystalline form of nontronite, rather than nontronite on the basis of the mode of occurrence and some mineralogical properties.

(f) *Origin of the present sample*

The origin of the present sample is as follows: at first, ferrous iron-rich saponite is oxidized into

ferric iron-rich saponite in open air accompanied by loss of hydroxyl ions in order to balance the electric charges (Kohyama *et al.*, 1973). Subsequently advanced leaching of Mg ions from the octahedral sheets by surface water, including rain fall, and regeneration of the lost hydroxyl ions would play a role in reconstructing the trioctahedral sheets into dioctahedral ones.

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