An Iron-Rich Variety of Montmorillonite
found in "Ōya-ishi"

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(Read, 1st May, 1949; Received, 10, June, 1952)

Introduction: "Ōya-ishi" is one of Japanese important building stones found in Ōya, Shiroyama-mura, Kawachi-gun, Tochigi Prefecture. The rock is a thick vitric tuffaceous rock, composed largely of volcanic glass fragments commonly fresh, free from alterations except a slight alteration to montmorillonite on an exposed surface, and in places, a slight alteration to celadonite. "Ōya-ishi" usually contains many rock fragments of various sizes. The fragments are commonly perfectly altered to clay substances of various colours, such as gray, black, yellow, brown, and green. In the clay substances, the writers identified an interesting iron-rich variety of montmorillonite.

Megasopic observations: Rock fragments with sizes of about 1 cm to 50 cm are included in "Ōya-ishi" showing the following zonal distribution: a zone, concentrated with especially large fragments, alternates regularly in parallel with a zone of no large fragments; the alternation forms a bedding structure, which reveals a clear parallel banding on a cutting surface; the dip of the bedding plane is nearly 10° and is parallel to that of the shale overlain with "Ōya-ishi". Generally, the concentration of the fragments is relatively higher in an upper zone than in a lower one. Selecting several zones with many fragments, the writers estimated the relative concentration of fragments with the result that it is higher in the southwest area than in the other ones.

The shape of the rock fragments is commonly flat and angular; each fragment is usually arranged in the flat plane and is nearly parallel to the bedding plane. The rock fragments are massive or show a clear linear texture like a wooden block, and rarely contain phenocrysts of quartz and plagioclase, the latter having the same mineralogical composition (oligoclase to andesine) as that in "Ōya-ishi".

Green coloured fragments are usually found from unexposed parts of "Ōya-ishi". However, on its exposed surfaces, fragments show various colours, such

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as gray, black, yellow, and brown. A green fragment collected from a deep place easily turns, in daylight, to gray or black within about one hour and finally to brown in a few weeks.

The rock fragments are perfectly altered to clay materials which commonly swell in water like bentonite. On an exposed surface, some fragments are found to be white porous skeletons in which a linear texture remains alone. The skeletons are inferred to be fragments from which clay substances have been perfectly leached out by surface water.

**Microscopic observations:** Both massive and linear fragments reveal aggregates of a very fine clay mineral with moderate birefringence and positive elongation. The aggregates show a vesicular texture in massive fragments (Fig. 1, A), and a fluidal texture in a linear fragment (Fig. 1, B). A brown opaque

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**Fig. 1** Microscopic textures of altered rock fragments in “Ōya-ishi”. (×80)
(A) Altered green massive rock fragment collected from a deep place of “Ōya-ishi”.
(B) Altered yellow coloured rock fragment with a linear texture collected on an exposed surface of “Ōya-ishi”.

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**Fig. 2** Differential thermal analysis curves of altered rock fragments in “Ōya-ishi” compared with one of the typical examples of Japanese montmorillonite.
(EX: Endothermic reaction. EX: Exothermic reaction.)

2. Altered pale yellow rock fragment with a linear texture collected on an exposed surface of “Ōya-ishi”.
3. Altered brown coloured rock fragment with a massive texture collected from an exposed surface of “Ōya-ishi”.
4. Altered green massive rock fragment collected from a deep place of “Ōya-ishi”.
material is found mixed with the clay materials which fill up some of the vesicles (Fig. 1).

Chemical analysis: The chemical analyses of yellow; brown, and green fragments show largely silica, alumina, ferric iron and considerable water, and the content of ferric iron is more in green or brown fragments than in yellow fragments (Table 1). A green coloured fragment collected from a deep place has been analyzed chemically. The specimen, of course, turned easily to brown colour. The chemical analysis was carried out with the brown specimen. The result (Table 2) seems to show an intermediate chemical composition between montmorillonite and nontronite.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>Benzidine colour reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellowish white to pale yellow</td>
<td>12.61%</td>
<td>4.97%</td>
<td>0.48%</td>
<td>very strong</td>
</tr>
<tr>
<td>Brown</td>
<td>9.87</td>
<td>9.74</td>
<td>2.27</td>
<td>very strong</td>
</tr>
<tr>
<td>White porous skeleton of a rock fragment</td>
<td>9.26</td>
<td>11.03</td>
<td>2.55</td>
<td>strong</td>
</tr>
<tr>
<td></td>
<td>12.05</td>
<td>1.80</td>
<td>n. d.</td>
<td>none</td>
</tr>
</tbody>
</table>

Differential thermal analysis curve: The differential thermal analysis curves of yellow and brown specimens are shown with the curve of a green fragment collected from a deep place (Fig. 2). The rate of heating is 10°C per minute. All of these curves agree well with that for montmorillonite with the following peaks clearly recognizable: a sharp endothermic peak \( n \) between 100°C and 200°C, a clear endothermic peak \( n' \) between 600°C and 700°C, a weak endothermic peak \( n'' \) between 800°C and 900°C followed by a clear exothermic peak \( x \).

On close examination, the following three points are noteworthy: (1) the temperature of the last exothermic peak is slightly shifted from that of a typical montmorillonite because of the iron content; this fact is a general thermal characteristic of montmorillonites; (2) a clear characteristic endothermic peak of nontronite at about 500°C is not recognizable in the thermal curves obtained;
(3) the characteristic peak of limonite is not recognized. This confirms the fact that an opaque brown material mixed with clay mineral as observed under the microscope is not limonite, but is a part of the clay mineral which has turned brown.

Thus, the thermal studies confirm the fact that the clay mineral is a variety of montmorillonite without the impurities of limonite and typical nontronite. From this confirmation, the writers attempted to apply the result of chemical analysis given in Table 2 to the general formula for the montmorillonite group according to the method proposed by C. S. Ross and S. B. Hendricks. The result is as follows:

\[(\text{Al}_{1.33}\cdot\text{Fe}^{3+}_{0.67}\cdot\text{Fe}^{2+}_{0.33}\cdot\text{M}_{0.67})\cdot(\text{Al}_{3.33}\text{Si}_{2.67})\cdot\text{O}_{10}\cdot(\text{OH})_2\cdot\text{nH}_2\text{O}\cdot(\text{K}, \text{Na}, (\text{Ca}/2))_{0.5}\]

The number of atoms having octahedral coordination is 2.18 which is slightly higher than the ordinal number of 2, and the iron content of octahedral coordination does not reach the amount for typical nontronite.

**Considerations:** From every respect, the clay mineral under consideration is an iron-rich variety of montmorillonite.

The writers believe that a considerable amount of ferrous iron substituting montmorillonite lattice is usually unstable and easily turns to the ferric state even in an exposed condition in daylight. The oxidation may have an important role in the discoloration of the clay mineral. Furthermore, in some cases, the iron is gradually leached out from the clay mineral on the exposed surface by being washed with surface water.

The above observations lead to the conclusion that the rock fragments are bombs of acidic, volcanic rocks altered to clay materials. The explanation of the alteration is very difficult, but it is inferred that alteration was mainly promoted by a volcanic vapour saturated in them, and the iron was mostly concentrated in the rock fragments in the process of alteration.

**References**