原 著 論 文

Mineralogy of Green Tuff Breccia near Shiroishi-machi, Miyagi Prefecture.

By

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Abstract

Two kinds of green materials are found in deep green coloured tuff breccia near Shiroishi-machi, Miyagi Prefecture: one is apparently isotropic green glass-fragments with vesicular or linear textures of pumice, and the other is aggregates of bluish green fibrous mineral showing clear polarization. The former is predominant and the latter is accessory. Under the high power, a gradation is recognized between these two green materials. Among many green minerals, celadonite most closely resembles these green materials in the mode of occurrence, optical properties, chemical analyses, and X-ray powder patterns. The bluish green fibrous mineral agrees with celadonite in optical characters, which are only available in this fibrous mineral. However, the green glass-fragments show slightly different properties from celadonite, for example, lower refractive index, less potassium (about 4 %), and more water than celadonite; yet the X-ray powder pattern shows a few diffuse powder lines corresponding to the principal lines of celadonite. From the results obtained, it is concluded that the green glass-fragments are volcanic glass stained by submicroscopic celadonite particles, and the bluish green fibrous mineral aggregates are relatively large flakes of celadonite. The celadonite alteration is inferred to have been promoted in the stage of sedimentation of the tuff breccia by a chemical reaction between volcanic glass and hot spring water under sea.

Locality and Geology

Green coloured tuffaceous rocks are commonly found in the Tertiary forma-

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tion in Japan. These rocks are classified into certain types¹⁾ from their geological and mineralogical properties.

The green tuffaceous rocks described in this paper are exposed in the area of about 2 square km, situated about 4 km west of Shiroishi-machi, Miyagi Prefecture (Fukuoka-mura, Katta-gun, Miyagi Prefecture).

The green rocks of this locality are classified into two types: (1) deep green tuff breccia (showing partly bluish, yellowish and dirty green colours), (2) pale green tuff including small green patches (spotted green tuff), showing partial bentonite alteration.

Augite andesite is covered by (1) in which large blocks of the andesite are included. (1) is overlain by strata of (2), alternating with thin beds of sandy shale, and thin sheets of andesite. (2) is overlain by white loose tuff or tuff breccia.

On close examination, the deep green tuff breccia shows a bedded structure marked by alternate zones of deep green and brownish green colours; the thickness of each zone is about 10 cm. The dip and strike of the alternation are almost parallel to those of the upper tuffaceous rocks (N20°W, 30°E). The green patches included in (2) seem to be fragments of (1).

Microscopic Observations

The deep green tuff breccia is a vitric one, being largely composed of green glass-fragments. It also contains altered volcanic rock-fragments, crystal-fragments of plagioclase, augite and biotite, and aggregates of a bluish green fibrous mineral.

The green glass-fragments commonly show a vesicular texture (Fig. 1, (A), (B), (C), (D), (E), (F), and (G), and Fig. 2, (A)). Some possess the linear texture of pumice (Fig. 2, (B)). Most of the glass fragments have an isotropic appearance, but locally show aggregate polarization and sweeping extinction along the margin or central part of each vesicle (Fig. 1, (A), (C), (E), and (F)). Under the high power, the apparently isotropic areas show a mottled appearance which indicates that they are confused aggregates of submicroscopic polarized particles.

Aggregates of the bluish green fibrous mineral are composed of fine flakes or fibers about 0.01mm in mean size, showing birefringence of 0.01~0.02, positive elongation, and pleochroism X: yellowish green, Z: bluish green.

The green glass-fragments and the bluish green fibrous mineral are associated as follows: Commonly the glass fragments are included in areas of the fibrous mineral or partly fill up the interspaces of the latter (Fig. 1, (C), (D), and Fig.

Fig. 1 Microscopic textures of the deep green tuff breccia, near Shiroishi-machi, Miyagi Prefecture (sketches)

g: green glass-fragment. c: bluish green fibrous mineral (celadonite).

o: opal. q: quartz.

The length of the line under each figure shows the length of 0.1mm.

2, (D)). In certain cases, the fibrous mineral is included in the central part of each vesicle (Fig. 1, (B) and (E)). Furthermore, under the high power, a gradation is clearly recognized in the contact between these two kinds of green materials (Fig. 1, (A), (C), and (E)). Rarely, the two green materials are built up a concentric arrangement of alternate thin layers. Obviously there is an intimate relationship between two green constituents.

It is noteworthy that the bluish green mineral aggregates are altered to a brown limonitic material (notation "b" in Fig. 1. (G)) in the brownish green coloured zone of the rock mentioned in the previous paragraph.

Opalization is locally recognized. Opal is commonly found as aggregates of spherulitic grains filling the interspaces of the green glass-fragments (Fig. 1, (H)), or replacing them (Fig. 1, (I)). In such opalized parts, the green glass-

fragments grade into aggregates of deep green spherulitic grains surrounding opal (Fig. 1, (J), and Fig. 2, (F)), or show an aggregate with a concentric texture (Fig. 2, (E), (F)), and the bluish green mineral flakes show a vermicular shape.

The green glass-fragments are also sporadically included in the fragments of altered volcanic rocks (Fig. 2, (E)), or plagioclase fragments (Fig. 2, (E), (F)), and are rarely included as vein filling in plagioclase fragments (Fig. 2, (E)).

The crystal-fragments of plagioclase and augite are commonly free from alterations, such as sericitization and chloritization.

Refractive indices

Precise measurements of the refractive indices of the green materials are difficult, because of their fineness and partial intimate mixture of fine opal grains. However, the following facts are clear, namely, refractive indices of the green glass-fragments are variable in the limit of 1.57~1.60, and are commonly lower than the mean refractive index of the bluish green fibrous mineral (1.59~1.61).

Chemical analyses

First, a specimen of the original rock was analysed chemically; the result is shown in Column (1) in Table 1. Next, the original rock was crushed and

Table 1

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO ₂	50.08%	55.55%	48.62%	54.0%	54.0%	54.22%	51.55%	38.67%
TiO ₂	...	...	...	...	...	...	tr.	0.24
Al ₂ O ₃	11.46	9.45	3.28	3.2	3.6	3.70	4.03	1.54
Fe ₂ O ₃	8.99	10.68	18.29	12.0	11.4	12.50	22.17	26.14
FeO	2.41	2.21	2.63	3.9	2.9	4.75	3.54	2.06
MnO	...	tr.	none	...	...	0.19	tr.	0.31
CaO	3.25	2.69	2.41	1.7	2.7	0.84	0.69	6.77
MgO	5.35	3.28	4.64	4.3	5.2	6.98	3.86	1.72
Na ₂ O	0.85	0.57	0.58	0.1	0.6	0.44	0.55	0.00
K ₂ O	2.29	2.90	3.68	3.8	4.1	6.90	7.03	0.10
H ₂ O (+)	} 15.37	5.55*	6.84*	7.3*	6.0*	} 9.99**	6.62**	9.56
H ₂ O (-)		7.39	8.94	9.8	10.0			12.54
Total	100.05	100.27	99.91	100.1	100.5	100.51	(100.07)	99.65

* Ignition loss above 105°C.

** H₂O

- (1) Chemical analysis of the green tuff breccia (original rock) Analyst: Michio Ôta, Faculty of Agriculture, Tokyo University.
- (2) Specimen consisting of a concentrate of green glass-fragments with a small amount of plagioclase. Analyst: Hideo Minato, Mineralogical Institute, Faculty of Science, Tokyo University.
- (3) Specimen consisting of a concentrate of green glass-fragments with a small amount of brown (limonitic) material. Analyst: same as (2).
- (4) and (5) Specimen composed of the green glass-fragments only. Analyst: the writer
- (6) Celadonite (after L. L. Fermor⁽⁵⁾)
- (7) Glauconite (after Tsuguo Yagi⁽⁶⁾) (P₂O₅: 0.03%)
- (8) Chlorophaeite (after M.A. Peacock and R.E. Fuller⁽¹⁰⁾)

crystal- or rock-fragments with macroscopic sizes were removed by hand picking. Third, the specimens obtained were pulverized to fine powder in an agate mortar and dispersed in water. Finally, by decantation, fine crystal- and rock-fragments were removed and the green glass-fragments were concentrated purely step by step. The chemical analyses of the specimens obtained in these steps are shown in Columns (2), (3), (4), and (5) in Table 1. The last two are those of the specimens, in which the green glass fragments were most highly concentrated. These last two analyses approximate celadonite, except for less potassium and more water. These two analyses differ from analyses of glauconite in that they show more silica and water, and less potassium and ferric iron than glauconite.

X-ray powder patterns

Five X-ray powder patterns were taken with the specimens analysed chemically (Columns (2) and (3)) and with other specimens in which the green glass-fragments were concentrated as much as possible. All of these patterns agreed with each other and with that of glauconite and showed the principal lines of celadonite. Some of these patterns contain a few strongest lines of plagioclase. The mean value of the spacing of each corresponding line appearing on

Table 2

(1)		(2)		(3)		(1)		(2)		(3)	
I	d	I	d	I	d	I	d	I	d	I	d
(st)	(10A)	5	9.97A	4	10.00A	•	...	•	...	2	2.20
•	...	•	...	1	4.99	1	2.18	1	2.14	2	2.14
9	4.43	5	4.50	4	5.52	1	1.95	1/2	1.99	2	1.99
•	...	•	...	3	4.32	1	1.83	•	...	2	1.95
•	...	•	...	3	4.11	•	...	•	...	1	1.82
2	3.67	2	3.64	4	3.62	•	...	•	...	1	1.71
1	3.31	3	3.31	4	3.31	3	1.66	1	1.65	3	1.65
•	...	2	3.07	4	3.08	•	...	•	...	2	1.59
1	2.86	•	...	2	2.89	6	1.51	5	1.51	4	1.51
•	...	•	...	3	2.67	1	1.36	•	...	2	1.34
8	2.60	5	2.58	5	2.57	2	1.32	3	1.30	3	1.30
•	...	•	...	1	2.48	•	...	•	...	1	1.28
4	2.39	4	2.39	4	2.39	1	1.26	•	...	2	1.25
•	...	1	2.25	2	2.25						

(1) The X-ray powder pattern of green glass-fragments

I: intensity, d: spacing. The powdered lines are measured on the film taken by the camera with the radius of 30.7mm, and by Cu radiation, except the line of 10 A, which was measured on the film by the camera with the radius of 57.3 mm. No corrections are applied on the readings of the spacings.

(2) Glauconite (after W. E. Maegdefrau and U. Hofmann⁽⁹⁾)

(3) Celadonite (after W. E. Maegdefrau and U. Hofmann⁽⁹⁾)

each of these patterns is shown in Column (1) in Table 2.

Interpretation and Discussion

The mineralogical properties of the green materials from Shiroishi show that, among many green minerals, the two minerals glauconite and celadonite are most similar to these green materials.

Before further discussion, we must call attention to the interesting report of K. Hummel⁽²⁾, who described a green material called "Schlerngrünerde" which is approximate to, but slightly different from glauconite and celadonite; it has the lower refractive index (1.571~1.593), more water and alumina, less potassium and ferric iron than these two minerals. Hummel's material is found as a filling of amygdales or as pseudomorphs after pyroxene in the porphyrite. The occurrence is quite different from the Shiroishi materials now under consideration; however, Hummel's paper is very pertinent to this study.

The mineral name of glauconite was originally given to bluish green grains found in certain sediments formed under muddy sedimentation accompanied by organic substances, which seem to have an important role in forming glauconite grains. Mutual colloid chemical and biochemical reactions are considered to occur between organic substances and inorganic ions in sea water. On the other hand, celadonite is a secondary alteration product found in vesicular tuff or volcanic rocks. The grains of glauconite are commonly composed of extremely fine submicroscopic flakes. On the other hand, celadonite shows commonly an aggregate of fine flakes, each of which is clearly recognized under the microscope. In these respects, the occurrence of the Shiroishi materials resembles that of celadonite rather than glauconite, because the rock containing these green materials is tuff breccia free from organic substances.

The mean refractive indices of glauconite and celadonite generally reported in the literature⁽³⁾⁽⁴⁾ are embraced in the range 1.61~1.63, but K. Hummel noticed that some glauconite and celadonite show lower refractive indices than those reported, showing that the mean refractive indices of these two green minerals may be as low as 1.60. He found that the mean refractive index of celadonite increases after dryness in the air for several months and also decreases in weathered specimens. Considering these data, the mean refractive index of the bluish green fibrous mineral from Shiroishi is not in conflict with that of celadonite, but, those of the green glass fragments are slightly lower than the range above mentioned.

The chemical analyses of glauconite and celadonite closely resemble each

other; however, pure specimens of celadonite and glauconite reported in the literature show the following chemical differences from each other⁽⁶⁾⁽⁷⁾: silica is higher in celadonite than in glauconite, and the ferric iron and the ratio of R_2O_3 to RO are greater in glauconite than in celadonite. (The amounts of potassium and water are almost alike in these two minerals). On this basis, the chemical analyses of the green glass fragments agree with celadonite, except for less potassium and more water.

J. W. Gruner,⁽⁸⁾ M. E. Maegdefrau, and U. Hofmann⁽⁹⁾ found that glauconite and celadonite belong to the mica group showing X-ray powder patterns which agree well with the mica type, although the powder lines of glauconite are more diffuse than those of celadonite. Referring to these X-ray data, the X-ray powder pattern of the green glass fragments agrees with that of glauconite and also the principal part of the celadonite pattern.

In conclusion, bluish green fibrous mineral agrees with celadonite in its optical character and mode of occurrence. The green glass fragments seem to be composed of a mineral which is slightly different from celadonite, that is, a mineral having a lower degree of crystallinity, lower refractive index, less potassium and more water than celadonite. This suggests that the unknown green mineral and typical celadonite are related in the manner of hydrous micas and muscovite.

Considering the following facts: (1) the green glass-fragments show the general outline of vesicular glass-fragments or of pumice, (2) a gradation is clearly recognized, under the high power, between the fragments and the bluish green mineral aggregates, (3) there is a variation in the refractive indices of the green glass fragments, - it is concluded that the green glass fragments are volcanic glass stained by submicroscopic celadonite particles. The postulated submicroscopic mixture of glass particles and celadonite grains is believed to produce the slightly different mineralogical properties from typical celadonite.

The minerals palagonite and chlorophaeite⁽¹⁰⁾ have been described in alteration products from vesicular glass-fragments. However, their mineralogical properties have not been described in detail, except the chemical analysis and refractive index, both of which are quite different from those of the green materials now under consideration.

Genesis

The above descriptions indicate that the main part of the deep green tuff breccia is composed of volcanic glass fragments altered to celadonite. It is very difficult to decide in what stage of the rock formation, the celadonite alteration

took place. Three hypotheses may be considered: (1) the glass-fragments were altered before their accumulation, (2) the alteration was mostly promoted in the stage of the sedimentation of the green fragments, (2) alteration was caused by a later hydrothermal action.

The second hypothesis is favoured, for the following reasons. The deep green tuff breccia is locally found in the area of acidic tuffaceous rocks covering the augite andesite mass, and on close examination, the tuff breccia shows a bedded structure indicated by alternating zones of especially deep green (or bluish green) and brownish tint. The brownish zones are considered to be oxidized parts of the formation. The colonred zones are almost parallel to the beds of sandy shale in the overlying tuffaceous sediments. These facts show that the green clouring is intimately related to and controlled by a bedded structure. However, the tuff breccia shows microscopic features which suggest an alteration by hot spring water; for example, opalization and dissemination of aggregates of bluish green flakes of celadonite. The alteration is inferred to be somewhat different from ordinary hydrothermal alterations such as sericitization and chloritization, because these two alterations are lacking in crystal-fragments of plagioclase and augite.

These two characters point to the conclusion that the celadanite alteration mostly took place in the stage of sedimentation of the rock by a special inorganic chemical reaction between glass fragments and a hot spring water, which may be related to the augite andesite and which saturated the original sediment of the tuff breccia.

Acknowledgment

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Fig. 2 Microscopic textures of the deep green tuff breccia, near Shiroishi-machi, Miyagi Prefecture (X 80)

- A: Green glass-fragments (g) showing a vesicular texture.
- B: A green glass-fragment (g) showing a linear texture of pumice.
- C: Bluish green fibrous mineral aggregates (c) in green glass-fragments (g).
- D: Microscopic texture of an opalized part. Green glass-fragments (g) enclosed in opal (o).
- E: A green glass-fragment (g) in a rock-fragment of an altered volcanic rock, and vein filling of the green glassy material in a crystal-fragment of plagioclase (f).
- F: Patches of green glass-fragments (g) in a rock-fragment of plagioclase (f).

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宮城縣白石町附近の緑色角礫凝灰岩の鑛物學的研究

(摘要)

須藤 俊 男

宮城縣白石町附近に分布する濃緑色角礫凝灰岩は緑色の玻璃片が主體をなし、所々に青緑色の纖維狀鑛物の集合體を伴う。前者は見掛上等方性を示し、純粹に濃集した試料に就いて調べた結果、X線粉末寫眞はセラドナイトの主線と一致するが、屈折率はそれより低く、カリウムの含有量少なく、含水量大である。後者は、その光學性のみしか調べ得なかつたが、その性質はセラドナイトの範圍に落ちる。高倍率の下で觀察すれば、上の兩者は接觸する部分で互に漸移化している。要するに、この緑色玻璃片は超顯微鏡的の微細なセラドナイト片で交代されたものであつて、この角礫凝灰岩の緑色化は、セラドナイト化であると結論し、斯くの如き變質は、主として、原岩の生成當時に、火山玻璃と海底湧泉との間の化學反應により生成したものであらうと推定した。

抄 録

American Permian Nautiloids by A. K. Miller and W. Youngquist.

Geol. Soc. Am. Mem. 41, pp. 218, 59 pls. 1949

戦後間もなく Gooper 氏からテキサスで珪化して素晴らしい二疊紀化石の資料を發見したと云う吉報を得たが、その内の鸚鵡貝が此研究の主體をなしている。此類は北米二疊系に廣く分布し、約 100 種を容している本書では Pseudorthoceratidae, Bactritidae, koninkoceratidae Domastoceratidae, Tainoceratidae,

Liroceratidae Sphippioceratidae の 7 科 21 屬が識別されているが、初めの 3 科は直錐(及至曲錐)型で他、は螺型で、筋や結びや棘のあるものが多い。此の保存のよい豊富な資料の研究によつて古生代末期の此類が急に分明した事は誠に喜ばしい。(小林貞一)