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NATURAL ANALOGUE STUDY OF VOLCANIC GLASS

—A Case Study of Basaltic Glasses in Pyroclastic Fall Deposits of Fuji Volcano, Japan—

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要　旨

高レベルガラス固化体の地層処分における長期の変質挙動を解明するため，富士火山噴山物中の玄武岩質火山ガラスの変質について調査を行った。従来の研究では，火力ガラスの変質速度は環境条件によってかなりの幅を持つことが報告されているが，環境条件について詳細な検討は行われていない。本研究では宝永スコリア（280 年前）と砂沢スコリア（2800 年前）という比較的新しい火山噴出物を研究対象とし，気象データや地下水の分析に基づき環境条件を明確にした上で変質速度や変質層の性状について検討した。

ガラスの変質温度は約 13℃，地下水の流量は 0.2ℓ/cm²/y と見積もられ，この条件下で淡水と反応したガラスの変質速度は数μm/1000y であることがわかった。これらの玄武岩質ガラスに形成された変質層の形態は，浸出試験でホウケイ酸ガラスに形成された変質層と類似していた。また地下水中の元素濃度は，ガラスの浸出の結果としてほぼ説明されることがわかった。

なお本論文は 1988 年 10 月にベルリンで開催された Materials Research Society のScientific Basis for Nuclear Waste Management 第 12 回国際シンポジウムでの発表をまとめたものである。

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ABSTRACT

A considerable range in alteration rates of basaltic glasses in various environments has been reported in previous studies. However, these studies paid only cursory attention to the environmental conditions under which the glass had been altered. In this study, the alteration of basaltic glasses was investigated and the environmental conditions and the alteration rate were discussed. Two sample ages were represented: 280 years and 2800 years. Basaltic glasses and their alteration layers were analyzed by electron probe microanalyzer (EMPA) and the thickness of the alteration layers were measured by scanning electron microscope (SEM). The ground water collected near the sampling point of Zunazawa Scoria (2800 years) and the pore water of both samples were analyzed. The alteration temperature and flow rate of water are estimated to be about 13°C and 0.2 $l/m^2/y$ respectively on the basis of meteorological data. The alteration layers of young aged basaltic glasses in freshwater conditions are similar to those of leached borosilicate glasses. The alteration rates of these basaltic glasses are estimated to be several μm/1000y. The elemental concentrations in the ground water can be roughly explained as the result of leaching of the glasses.

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INTRODUCTION

Many natural analogue studies of the alteration of natural glasses have been carried out to assess the long-term durability of waste form glasses [1,2]. Basaltic glasses have been considered as appropriate natural analogues for low-silica borosilicate glass because of their similar silica contents. Alteration layers formed on experimentally leached borosilicate glass are similar to those on basaltic glass formed in nature [3]. Basaltic glass is similar to waste glass with respect to alteration products, alteration layer morphologies and alteration rates in laboratory experiments [4]. The alteration rates of basaltic glasses under the following environments have been studied: (a) ocean floor environment [5,6,7], (b) subglacial environment [7,8], (c) hydrothermal environment [9]. The alteration rates at low temperature in these studies vary from 0.001 μm/1000y to 30 μm/1000y. The variation is interpreted as the result of the differences of the environmental conditions. However, few detailed studies have been reported on the environmental conditions (for example, water flow rate and water chemistry).

This paper describes the alteration of basaltic glasses in clear environmental conditions and of well-known ages. The alteration is a long-term leach test carried out by nature with rain water as leachant and ground water as leachate. Few papers have been published on the alteration of basaltic glass of young age. The young aged samples were selected in this study to discuss the environmental conditions during alteration on the basis of present meteorological data.

SAMPLES

Volcanic glasses constituting scoriae generated by pyroclastic falls were studied. The scoriae are black grains composed of vesicular low silica glasses, which include some crystals. Two kinds of scoria samples were collected from the two selected sites at the foot of Fuji Volcano, where the stratigraphy and chronology of pyroclastic fall deposits have been studied in detail. One is named Houei Scoria and the other Zunazawa Scoria. Houei Scoria is black and Zunazawa Scoria is yellowish-brown when dry. Samples are mainly composed of grains several mm in diameter. Both samples were collected from exposures resulting from recent road cutting. Fig.1 shows the location of sampling sites. Site stratigraphy

is summarized in Fig.2. The samples of Houei Scoria were collected from four horizons (HS1, HS2, HS3 and HS4). The deposits of these sites are composed mostly of scoria beds except one thin pumice bed. The ages of the deposits shown in Fig.2 (compiled after Miyaji [10] and Machida [11]) are known by historical records of eruptions and by radiocarbon dating. Historical documents record that Houei Scoria was deposited in 1707 A.D. (280 years ago). The age of Zunazawa Scoria is considered to be about 2800 years based on the radiocarbon age of the immediately underlying deposit.

These scoria samples contain pore water, and spring water was found about 2.5 m below Zunazawa Scoria bed (Fig.2). These waters were sampled for chemical analysis.

METHODS

Density, water content and grain size distribution of samples were measured. Density was calculated from the unit weight of samples in the field. Grain size distribution was obtained by sieve analysis (diameter: 75 μm ~ 19 mm).

Glass compositions were determined by EPMA (SHIMAZU EMX-SM) using a broad electron beam (30 μm). Alteration layers were studied by optical microscope, EPMA (using a smaller electron beam (3 μm)) and SEM with energy dispersive X-ray spectrometer (EDS). A synthetic basaltic glass whose composition was determined by wet chemical analysis was used for the standard of the analyses by EPMA. The thickness of alteration layers was measured from SEM photos of the sections oriented nearly normal to the layers. Alteration layers were mechanically scraped off and their clay-size fractions prepared for X-ray diffraction analysis.

In the field, pH and Eh of the spring water were measured by portable meters. The spring water was filtrated through 0.45 μm filter and the filtrate was analyzed by absorption spectrophotometry, flame spectrometry and atomic absorption spectrometry. For the analysis of pore water, scoria samples of 1 kg were shaken in 1 liter of distilled water for 1 hour, then the dilute solutions were analyzed. The elemental concentrations of pore waters were calculated from the data of these analyses and the water contents of samples.

RESULTS

Physical Properties and Glass Composition

The physical properties of samples are summarized in Table I. The chemical compositions of glasses are given in Table II. The SiO_2-contents of Houei glass (HS2) and Zunazawa glass (ZS) are approximately 59 wt% and 53 wt% respectively. These values are a little higher than the general value of basaltic glass (SiO_2 content of 45 ~ 52 wt%).

Alteration Layer

SEM images of Houei Scoria show the presence of thin alteration layers on grain surfaces and vesicle walls (Fig.3). The layers are not distinguishable with the optical microscope. Reddish or yellowish-brown alteration layers on grain surfaces and vesicle walls of glass in Zunazawa Scoria can be seen with the optical microscope. This alteration layer is optically isotropic and X-ray amorphous. The surface form of the alteration layer of Houei Scoria (HS1, HS2, HS3, HS4) is grainy and that of Zunazawa Scoria (ZS) is flaky (Fig.3). Despite the difference in morphology, EDS data indicate that the chemical composition of the alteration layer of Houei Scoria is similar to that of Zunazawa Scoria. The morphology of alteration layers of both scoriae is strikingly similar to that observed on the surface of experimentally altered borosilicate glasses [12] (Fig.3). Alteration layer thicknesses are summarized in Fig.4. Average thicknesses are: HS1, 0.33 μm; HS2, 0.44 μm; HS3, 0.49 μm; HS4, 0.70 μm; ZS, 8.8 μm. EPMA line profiles across the alteration layer of ZS are illustrated in Fig.5. All the X-ray intensites decrease from the glass/alteration layer boundary to the surface of scoria. This implies the increase of H_2O-content and the decrease of density. The elemental concentrations in the alteration layer are characterized by more depletion of Mg, Ca, Na, and K, as compared to that of Si, Al, Fe, and Ti (Fig.6).

Water Chemistry

The chemistry of pore water, spring water and average rain water in Japan [13] is listed in Table III. The followings are noteworthy: (1) the elemental concentrations in ZS pore water are higher than those in HS2 pore water (implying that elemental concentration in ground water increases with depth), (2) the elemental concentrations in the spring

water are lower than those in ZS pore water except for Ca, Mg, and HCO_3, (3) SiO_2-concentrations in HS2 pore water and ZS pore water are much higher than in the spring water. The calculated SiO_2-concentration increases directly with the amount of distilled water for dilution, indicating that SiO_2 gel is present in pore water, and it dissolves at the time of dilution.

DISCUSSION

Environmental Conditions

Records of meteorological conditions for the last 2800 years do not exist; however, analyses of paleosea-level variations [14] and paleoclimatological data [15,16], indicate that the climatic conditions in Japan have not changed significantly for the last 2800 years. Therefore, the temperature and the water supply rate are estimated as follows on the basis of the data at the meteorological station which is 7 km from the sampling sites: average effective temperature, 13°C (mean annual temperature); water supply rate, 0.2 $l/cm^2/y$ (calculated value from the annual amounts of rain fall and of evapotranspiration). On the assumption of the water content in Table I, the following water flow rate can be estimated: HS2, 11 m/y; ZS, 9 m/y. These values are high in comparison with the estimated water flow rate in the deep underground (for example [17]).

The samples were situated in the unsaturated zone, therefore, percolating meteoric water is the only source of pore water. The pore water flows downward in the deposits and dissolves the components of scoria. This natural phenomenon can be regarded as a renewed freshwater leach test. The composition of the ground water which had been supplied to Houei Scoria and Zunazawa Scoria is considered to be intermediate between the compositions of rain water and of spring water. Some elemental concentrations of analyzed pore water are higher than those of spring water. This indicates that the elemental concentrations of the pore water in vesicles are high because of the low flow rate in vesicles. Although attention should be paid to the seasonal fluctuations of temperature, water content and water chemistry, it is inferred that these factors at the sampling points (except HS3 and HS4) do not vary significantly [18].

Alteration Rate

In natural alteration systems, it is generally difficult to know the exposure age of a sample, that is, the time that the glass has actually been in contact with water [8]. The exposure ages of the samples in this study are equivalent to the sample ages because the surface of the samples were always in wet conditions and in contact with renewed pore water. The alteration layer thickness varies widely within a scoria grain. In general, the thickness of the alteration layer on the wall of a vesicle is less than that on the outside surface of the scoria grain. This may be due to the low flow rate in a vesicle. The alteration rates calculated from the average thicknesses of alteration layers on the surface of scoria grains are as follows: HS1, 1.2 μm/1000y; HS2, 1.6 μm/1000y; HS3, 1.8 μm/1000y; HS4, 2.5 μm/1000y; ZS, 3.1 μm/1000y.

The alteration rate of Houei Scoria decreases with the increase of burial depth (Fig.7). The decrease of alteration rate can be explained by the following: (1) the increase of elemental concentrations of environmental water due to the reaction with scoriae, (2) the decrease of maximum temperature (the decrease of daily variations of temperature). The burial history (the relationship between time and burial depth) must be taken into consideration in interpreting the alteration rate. Fig.8 shows the schematic relationship between time and burial depth of the samples. This burial history is obtained on the basis of Fig.2. The scoria that experiences a long history of shallow burial is more likely to be altered during shallow burial than the scoria that experiences relatively rapid burial soon after deposition.

The relation between alteration layer thickness and age are shown in Fig.9. The two kinds of alteration rates, the forward rate of alterration (3-20 μm/1000y, under silica-unsaturated conditions) and the final rate (0.1 μm/1000y, under silica-saturated conditions) indicated by Grambow et al.[7], are also shown in Fig.9. The alteration rates estimated in this study are near or below the forward rate. Although very little data on the alteration rate under freshwater conditions have been reported, it may be stated that the alteration rate near the surface of the earth in freshwater conditions is similar to the forward rate.

Mass Balance Between Alteration Layer and Spring Water

As mentioned before, spring water can be regarded as leachate. In order to discuss the leaching behavior of glass, it is necessary to clari-

fy the relation between the elemental concentration in leachate and the elemental loss from the alteration layer. The calculations of elemental concentrations in ground water were based on the following: (1) the physical and the chemical properties of the scoriae deposited over Zunazawa Scoria are similar to those of Zunazawa Scoria; (2) the rate of deposition was nearly constant (Fig.8); (3) the alteration was isovolumetric [8,19]; (4) density of basaltic glass was 2.8 g/cm^3; (5) the specific surface area was 80 cm^2/cm^3 (estimated from the grain size distribution of Zunazawa Scoria); (6) the composition of ground water at the depth of 6.8 m was similar to that of the spring water; (7) the water supply was 560 l/cm^2 ($0.2(l/cm^2/y) \times 2800(y)$); (8) the composition of rain water was similar to the average composition of the rain water in Japan [13]. The calculation for Na-concentration, for instance, is as follows.

$$\underset{(a)}{2.80(g/cm^3)} \times \underset{(b)}{0.021} \times \underset{(c)}{(1-0.29)} \times \underset{(d)}{80(cm^2/cm^3)} \times \underset{(e)}{8.8(\mu m)} = \underset{(f)}{0.0029\ (g/cm^3)}$$

$$\underset{(f)}{0.0029(g/cm^3)} \div (\underset{(g)}{560(l/cm^2)} \div \underset{(h)}{680(cm)}) + \underset{(i)}{1.1(mg/l)} = \underset{(j)}{4.6\ (mg/l)}$$

where (a) density of basaltic glass, (b) Na-content in Zunazawa glass, (c) ratio of Na-concentration in alteration layer and pristine glass, (d) specific surface area, (e) thickness of alteration layer, (f) Na-mass loss per unit volume of Zunazawa Scoria, (g) water supply, (h) thickness of deposits, (i) Na-concentration in rain water, (j) Na-concentration in calculated ground water.

Fig.10 shows the results of mass balance calculations. The result indicates that the calculated composition of ground water is in fair agreement with the composition of spring water. The discrepancies in the concentrations of Fe and SiO_2 can be explained by the precipitation of iron hydroxides and silica gel respectively among scoria grains.

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REFERENCES

1. R.C. Ewing and M.J. Jercinovic, in Scientific Basis for Nuclear Waste Management Vol.X, edited by J.K. Bates and W.B. Seefeldt (Material Research Society, Pittsburgh, 1987), pp. 67-83.
2. W. Lutze, B. Grambow, R.C. Ewing and M.J. Jercinovic, in Natural Analogues in Radioactive Waste Disposal, edited by B. Come and N.A. Chapman (Graham Trotoman, 1987), pp. 142-152.
3. C.C. Allen, in Scientific Basis for Nuclear Waste Management Vol.V, edited by W. Lutze (North-Holland, New York, 1982), pp. 37-44.
4. W. Lutze, G. Malow, R.C. Ewing, M.J. Jercinovic and K. Keil, Nature, 314, 252 (1985).
5. H. Hekinian and M. Hoffert, Marine Geology, 19, 91 (1975).
6. W.B. Bryan and J.G. Moore, Geol. Soc. Amer. Bull., 88, 556 (1977).
7. B. Grambow, M.J. Jercinovic, R.C. Ewing and C.D. Byers, in Scientific Basis for Nuclear Waste Management Vol.IX, edited by L. Werme (Material Research Society, Pittsburgh, 1986), pp. 263-272.
8. M.J. Jercinovic and R.C. Ewing, JSS Project Technical Report, 88-01, 21 (1988).
9. S.P. Jacobsson and J.G. Moore, Geol. Soc. Amer. Bull., 97, 648 (1986).
10. N. Miyaji, Jour. Geol. Soc. Japan, 94, 433 (1988).
11. H. Machida, Jour. Geol., 73, 23 (1964).
12. I. Hirose, (unpublished data).
13. K. Sugawara, Chemistry of the Earth' Crust, 2, 501 (1967).
14. T. Yamamoto, Tenki, 27, 76 (1980).
15. I. Maejima, Jour. Geol., 93, 413 (1984).
16. S. Sugimura, Kagaku, 47, 749 (1977).
17. KBS, in Final Storage of Spent Nuclear Fuel: KBS-3, (SKBF/KBS, Stockholm, 1983), pp. 20:11-20:17.
18. J. Ossaka, N. Otsuka, J. Hirabayashi, K. Okada and K. Matsui, Nendo Kagaku, 24, 116 (1984).
19. R. Cowan and R.C. Ewing, in Microbeam Analysis - 1986, edited by A.D. Roming, Jr. and W.F. Chambers (San Francisco Press, San Francisco, 1986), pp. 131-133.

Table I Physical properties of scoria beds

Sample	Wet density (g/cm^3)	Water content (%)	Grain size distribution (wt%)						
			- 0.074	- 0.25	- 0.84	- 2.00	- 4.76	- 9.52	- 19.1 (mm)
HS2	1.14	19.1	1.0	0.8	6.3	31.0	44.2	15.3	1.4
ZS	0.94	29.7	3.7	6.0	11.9	17.7	26.1	26.0	8.6

Table II Chemical compositions of glasses

Sample	Oxide (wt%)								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Total
HS2 glass	58.9	1.0	15.9	6.9	3.8	6.8	2.6	0.6	96.5
ZS glass	52.8	1.5	14.7	10.2	4.5	8.0	2.9	0.9	95.5

Table III Chemistry of pore water, spring water and rain water

Sample	Chemical composition (mg/l)									pH	Eh (mV)
	Na	K	Ca	Mg	Fe	HCO_3	SO_4	Cl	SiO_2		
HS2 pore water	6.2	2.6	4.0	1.0	0.7	33	2.9	1.5	62	-	-
ZS pore water	8.4	3.3	4.6	1.3	5.0	35	6.4	4.3	218	-	-
Spring water	4.8	1.3	8.7	6.6	2.9	67	4.7	2.8	36	7.0	178
Rain water [13]	1.1	0.3	0.4	1.0	0.2	-	1.5	1.1	0.8	-	-

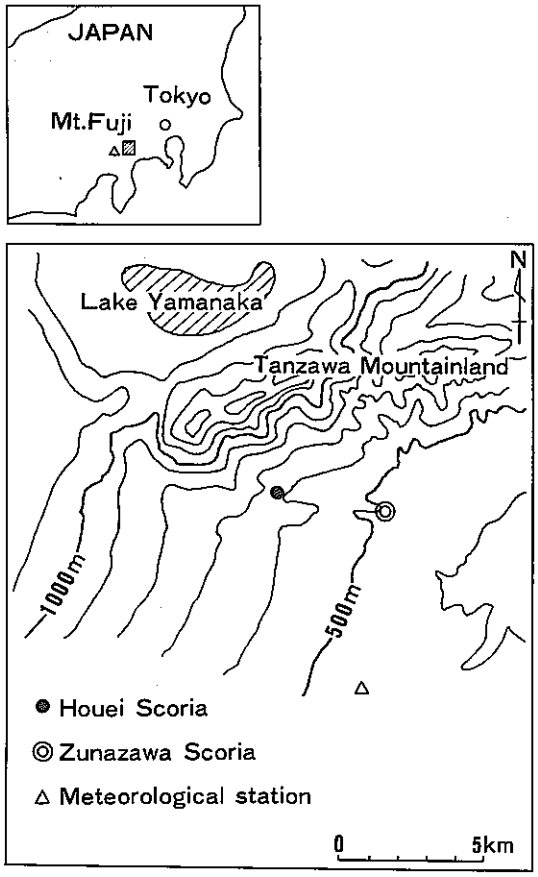

Fig.1 Sample location map

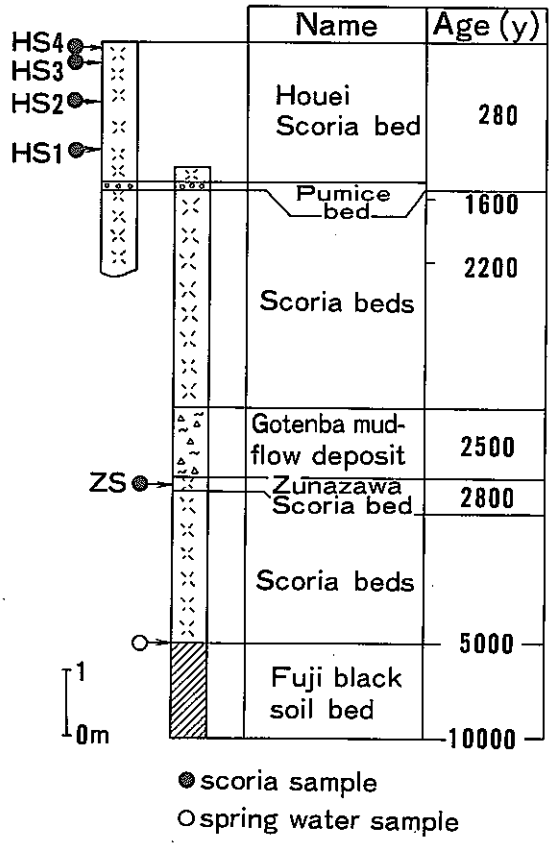

Fig.2 Stratigraphic section of Mt. Fuji Pyroclastics
Sampling horizons are indicated by marks on the left.

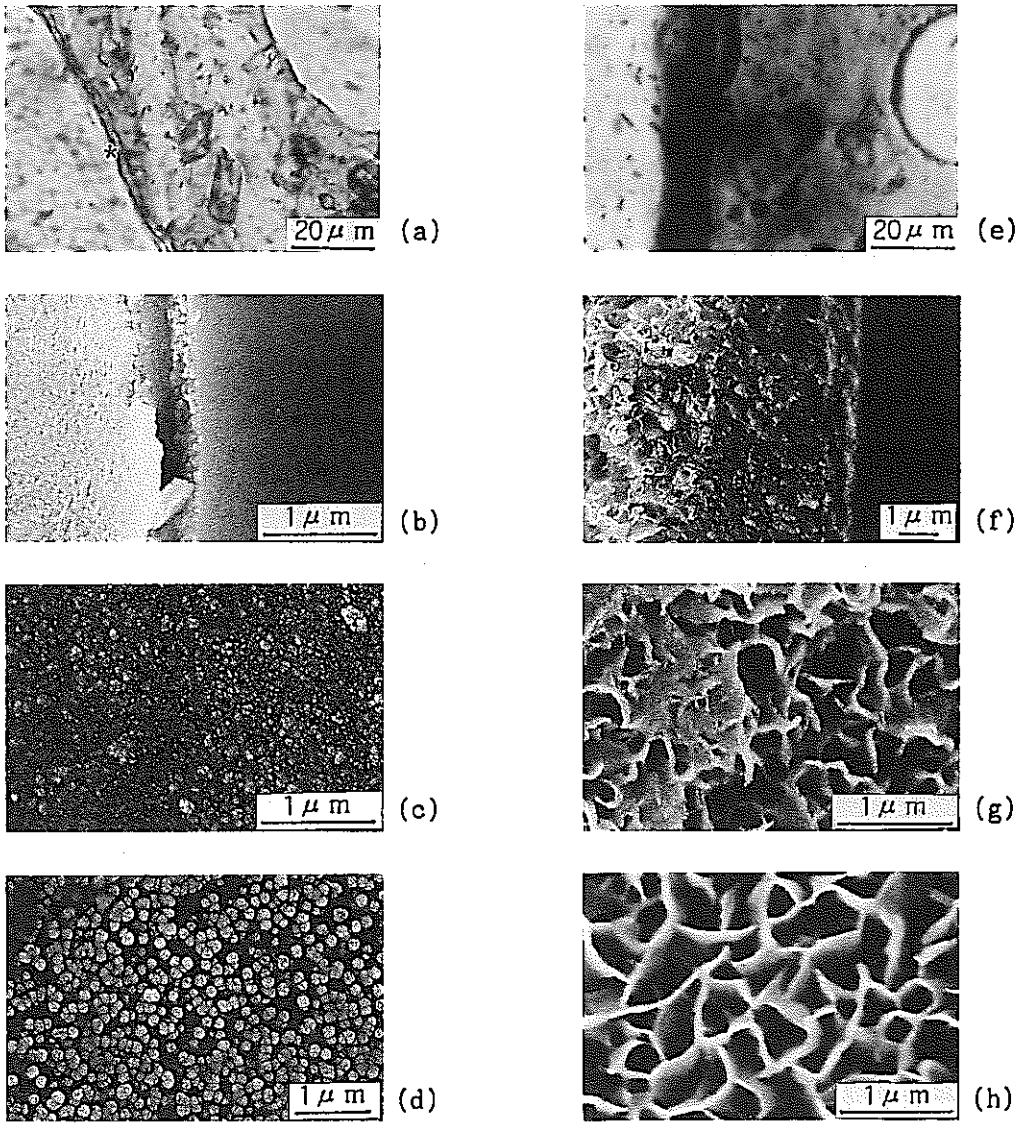

Fig.3 Alteration layers of Houei Scoria (HS2) and Zunazawa Scoria (ZS) (a) Photomicrograph of HS2. Distinct alteration layer is not observed on the grain surface (*). (b) SEM photo of the cross section of HS2. (c) SEM photo of the surface of HS2. (d) SEM photo of the surface of simulated waste glass leached in ground water at 19°C for 1 year [12]. (e) Photomicrograph of ZS. (f) SEM photo of the cross section of ZS. (g) SEM photo of the surface of ZS. (h) SEM photo of the surface of simulated waste glass leached in distilled water at 98°C for 90 days [12].

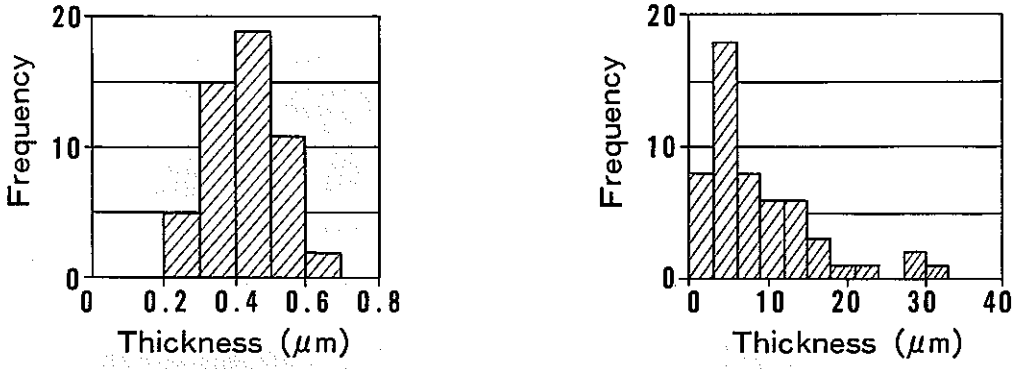

Fig.4 Frequency histograms of the thickness of alteration layers of Houei Scoria (HS2) and Zunazawa Scoria (ZS)
Thicknesses were measured by SEM.

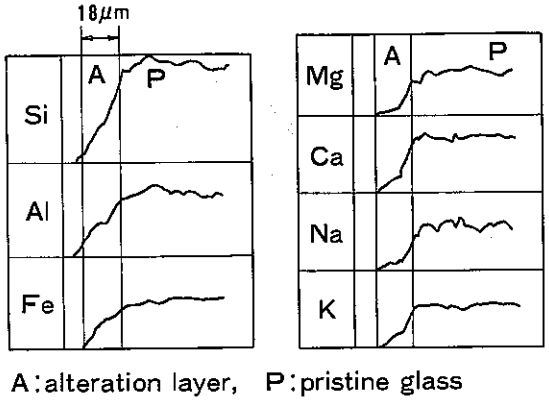

Fig.5 X-ray line profiles across the alteration layer of Zunazawa Scoria (ordinate: X-ray intensity)

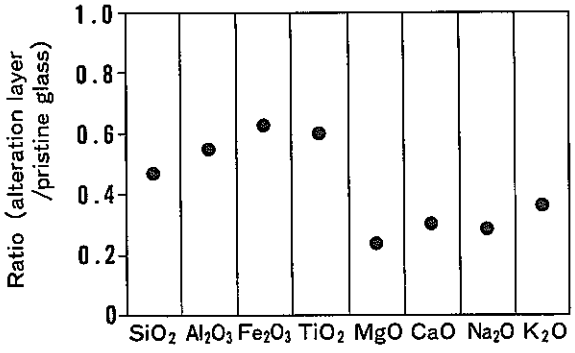

Fig.6 Ratio of elemental concentration in alteration layer (average) and pristine glass of Zunazawa Scoria

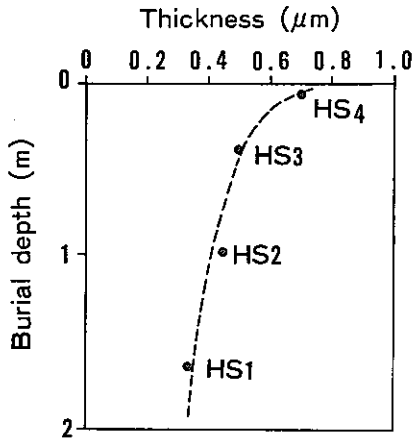

Fig.7 The relation between burial depth and alteration layer thickness of Houei Scoria (HS1-HS4)

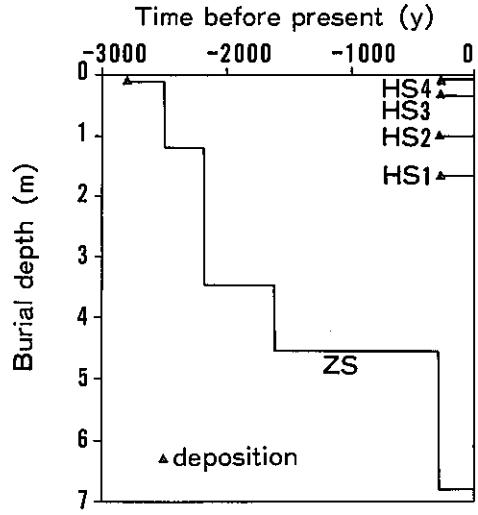

Fig.8 Schematic burial history curves for Houei Scoria (HS1-HS4) and Zunazawa Scoria (ZS)

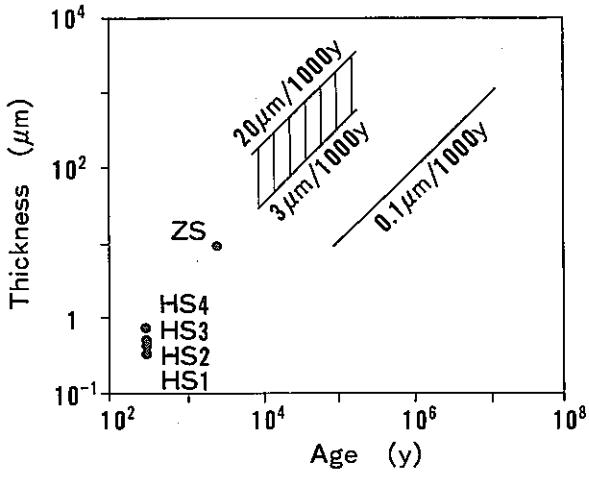

Fig.9 The relation between alteration layer thickness and age of samples
The diagonal lines (alteration rates) are after Grambow et al.[7].

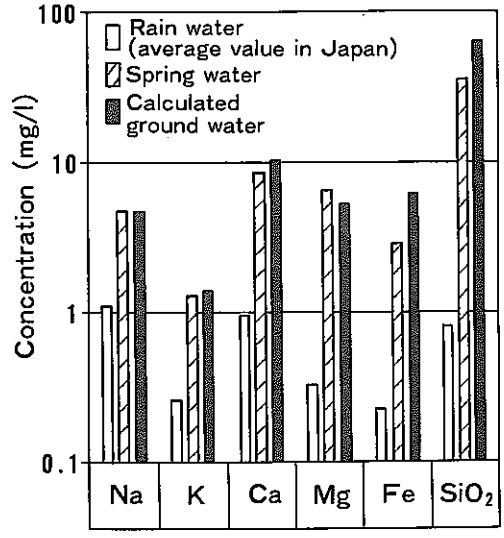

Fig.10 The comparison between elemental concentrations of spring water and calculated ground water
Calculation is based on the elemental weight loss from alteration layer and flow rate.