

原 著

Alteration process of basaltic andesite by hydrothermal alteration in Tatun volcanic area, Northern Taiwan

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台湾北部の大屯火山地域における熱水作用による
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要 旨

高温酸性泉の火山岩への影響を解明するために、台湾の大屯地域の梗仔坪 (Jingzaiping) における pH=1.4 および 98℃ の温泉水による玄武岩質安山岩の変質過程に関する鉱物化学的研究を行った。変質した岩石を変質の程度の違いで 8 ゾーンに分け、各ゾーンの鉱物および化学組成の変化を XRD, EPMA, XRF, ICP-MS, 顕微鏡観察によって検討した。この岩石の主成分鉱物である単斜輝石、直方輝石、斜長石は、比較的変質初期に消失し、変質鉱物としてクリストパライトが顕著に認められた。各ゾーンの単位体積当たりの元素存在量 (mol/L) は、変質が進むにつれて Al, Mg, Fe, Mn, Ca, Na, V, Rb, REE は減少したが、Si, Ti, Hf, U, Th は変化しなかった。一方、Pb, Cu は増加し、Co, Ni は変質が進むにつれて基本的に増加し、含有量は少ないが Au も同様な傾向を示した。Cl コンドライトで規格化した LREE は MREE および HREE に比べ反応初期に急激に減少した。同様に規格化した不適合元素 LILE は減少したが、HFSE はほとんど変化しなかった。玄武岩質安山岩の変質生成物中には Cu, Co, Pb が比較的多く含まれ、基本的には変質が進むにつれて増加する傾向を示すが、その変化は変質の程度に必ずしも依存しない。従って、大屯地域の梗仔坪ではこれら含有量が異なる熱水活動が複数回あったことが示唆される。

キーワード：変質作用、玄武岩質安山岩、高温酸性泉、大屯地域、台湾

Abstract

In order to elucidate the effect of hydrothermal alteration on volcanic rock, mineral

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chemistry was conducted on alteration processes of basaltic andesite by hot spring water, which are pH=1.4 and 98°C, in Jingzaiping of Tatun area, Northern Taiwan. The altered part of the collected rock is divided into 8 zones, and the changes of mineral and chemical compositions in each zone during reacted process were studied by XRD, EPMA, microscopic techniques, XRF and ICP-MS. Clinopyroxene, orthopyroxene and plagioclase as the main constituent minerals in the rock show that the minerals disappear in the early alteration zone. Moreover, alteration was advancing rapidly, and cristobalite was predominant from the beginning of alteration. Chemical variations of the altered zones represented by elemental abundance per unit volume (mol/L) show that the contents of Al, Mg, Fe, Mn, Ca, Na, V, Rb and REE decreased as alteration proceeded, and the Si, Ti, Hf, U and Th contents were not changed. On the other hand, the Pb and Cu contents increased, the Co and Ni contents basically increased as the alteration progressed, and the Au contents showed a similar tendency although the content was small. The LREE value normalized by C1 chondrite decreased rapidly by the hot spring water compared to the MREE and the HREE. Incompatible elements such as LILE (Sr, Cs, Rb, K) value normalized by C1 chondrite decreased, but the HFSE (Nb, Ti, Zr, P) hardly changed. It has been shown that the alteration products of basaltic andesite contain relatively large amounts of Cu, Co and Pb. These contents basically tend to increase due to alteration, but they do not necessarily depend on the degree of alteration. Therefore, it was presumed that the hot spring water quality was not constant, and there were multiple hydrothermal activities containing various concentrations such as Cu, Co, and Pb in Jingzaiping of the Tatun area.

Key words : alteration, basaltic andesite, acidic hot spring water, Tatun, Taiwan

1. Introduction

The Tatun volcanic group, built up mainly during the last 0.8 to 0.2Ma, is distributed over an area of 300 km² in Northern Taiwan, and consists predominately of a series of andesite to basaltic andesite lava domes in the northern part of Taiwan. There are about 20 volcanoes in only 15km north of the capital city, Taipei, and are constructed along E-W and NE-SW trending ridges (Wang and Chen, 1990 ; Song *et al.*, 2000 ; Lin *et al.*, 2005). One of the major geological structures in the Tatun volcanic group is the Chinshan fault, which is a reverse fault and strikes in the NE-SW direction. The southwestern extension of this fault might be connected to the Hsinchun fault beneath the western Taipei basin. Based on the K-Ar dating (Juang and Chen, 1985 ; Tsai *et al.*, 2010) and fission track analyses (Wang and Chen, 1990), the eruption history of the Tatun area can be divided into two major periods. As for the first eruption, the major one was around 2.5-2.8Ma, whereas the second one started at 1.5Ma and continued until the last eruption around 0.1-0.2Ma (Song *et al.*, 2000). Moreover, more ages dated on volcanic rocks and from sedimentary records indicate the latest eruption may occur younger than 10,000 yrs. (Belousov *et al.*, 2010 ; Zellmer *et al.*, 2015). Chen (1978) conducts petrochemical studies of these volcanic rocks distributed in the Tatun volcanic group and Chilung volcanic group, and analyzed major and trace elements in about 70 types of volcanic rocks, and shows the relationship between the SiO₂ content and some trace elements.

Sato (2006) examined 9 hot springs in Taiwan and nearly 50 hot acid springs (pH<4, Temperature>70°C) in Japan that showed their distributions and chemical characteristics. Hot springs, fumaroles and solfatara are found over wide areas along a zone parallel to the SW-NE-trending the Chinshan fault and extending to the NE coast of Taiwan. These hot springs of Tatun

area related to the volcanic activities are classified into three types based on the Piper diagram, pH value, field occurrence and water-rock interaction by Liu *et al.* (2011). Namely, (1) Type I, SO_4^{2-} acidic water where the reservoir is located in the Wuchishan Formation; (2) Type II, HCO_3^- a near neutral spring water where waters originate from the volcanic terrane (andesite); and (3) Type III, Cl-rich acidic water where waters emanate from shallower Wuchishan Formation. Moreover, they showed that in terms of isotopic ratio, δD and $\delta^{18}\text{O}$ values, two groups of hot spring can be recognized, and based on field occurrences and geochemical characteristics, a model has been proposed to illustrate the origin of these hot springs. After that, Ohsawa *et al.* (2013) studied isotopic and chemical compositions on water samples collected from some hot springs in Tatun volcanic group, Taiwan. The hot spring water showed practically of meteoric origin, and the acidic hot spring water divided into two groups. One is originated from magmatic fluid, and the other is of secondary source from the steam-heated thermal water of acidic- SO_4 type derived from the magmatic fluid.

There have been many studies on the interaction between basaltic rock and hydrothermal solution. For example, Renac *et al.* (2010) studied hydrothermal interactions in basaltic lava from the Kerguelen Archipelago in SW Indian Ocean. It was shown that the source of hot water related to the hydrothermal alteration of basaltic lava was meteoric water from fluid-inclusion micro-thermometry, trace element geochemistry, isotopic composition. Frolova *et al.* (2001) and Ladygin *et al.* (2014) investigated the alteration of basalts on Iturup Island, where a region of modern volcanic and acidic hydrothermal activity, and reported on chemical element mobility, changes in chemical and mineralogical composition, and in physical and mechanical characteristics of the basaltic rock due to alteration. In Fujitaka *et al.* (2020), the artificial chemical weathering of basaltic rock was conducted chemically and mineralogically using H_2SO_4 , HNO_3 and HCl solutions at pH 4, and CO_2 saturated water, and distilled water at 55°C for a different period of time up to 970 days. It shows the secondary products, morphology and chemical changes on the rock surface, and the behavior of leached elements. However, there are few detailed studies on the quantitative transfer of major and trace elements and the change of mineral species with the progress of hydrothermal alteration of naturally occurring rocks although there are researches on leaching of elements from rock surfaces conducted in the laboratory, and mineral chemical researches on alteration products due to weathering alterations in the field.

During the survey of rock alteration in the northern part of Taiwan where hydrothermal activity by various spring waters with high temperature and low pH is recognized, zoning could be observed in basaltic andesite that has been altered by the hydrothermal activities. Therefore, in this study, the altered basaltic andesite is divided into some zones, the results of mineral chemistry studies on the rock by interaction with the hot spring water are reported, and changes in the chemical composition of the hot spring water are also mentioned.

2. Samples and experimental methods

There are many hot spring spots in the Tatun volcanic area, many of which have high temperatures above 90°C , are acidic with sulfuric acid and/or hydrochloric acid with pH of 1 to 2. In this study, 7 hot springs were mainly investigated in Tatun volcanic group (Fig. 1). Most of

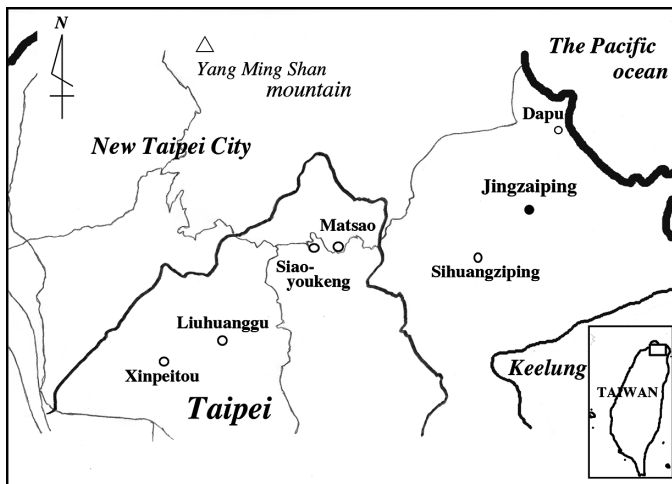


Fig. 1 Map showing hot springs at the Tatun volcanic group in the Northern Taiwan. The point examined in this study is indicated by solid circle.

the rocks in this area are altered by the hot spring waters, and are significantly altered from the core to the rim, so-called onion-like weathering (Fig. 2A). Altered rock samples of basaltic andesite were collected from the point near Jingzaiping, Keelung where is hot spring water with the highest temperature (98°C) and lowest pH (1.4), and the alteration process was studied in detail. The hot spring water corresponds to Type 1 by Liu *et al.* (2011). As shown in Fig. 2B, the collected rock was divided into eight zones from the almost unaltered core (7B-a) to the strongly altered rim one (7B-h) according to the degree of apparent alteration. The chemical composition of each zone was analyzed by XRF (X-ray fluorescence, Hitachi High-Tech Science Corporation RIX · SEA5120A) and ICP-MS (Analyzed by Actlabs Co., Ltd., Canada), and shown in Table 1. Micrograph of the 7B-a, which is almost unaltered rock, shows porphyritic texture mainly composed of orthopyroxene (OPX), clinopyroxene (CPX) and plagioclase (PL), and contain magnetite as an opaque mineral. The rock is classified as basaltic andesite based on the texture and the SiO_2 vs. $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ diagram (Le Bas *et al.*, 1986). The main constituent minerals of the basaltic andesite studied by an electron probe microanalysis (EPMA) showed $\text{En}_{97-98}\text{Fs}_1\text{Wo}_{0-1}$ for OPX, $\text{En}_{65-66}\text{Fs}_1\text{Wo}_{31-32}$ for CPX, and $\text{An}_{85-88}\text{Ab}_{9-11}\text{Or}_{1-2}$ for PL. For the EPMA analysis, a JEOL JXA-8230 at the Okayama University of Science was used with an acceleration voltage of 15 kV,

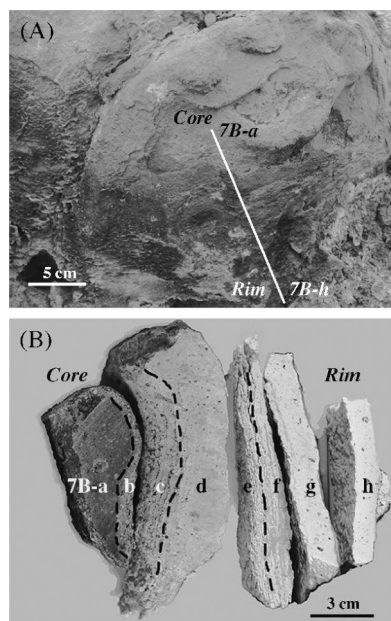


Fig. 2 Occurrence of representative sample collected from Jingzaiping, Northern Taiwan. (A) Hydrothermally altered basaltic andesite. (B) Cross section of the altered basaltic andesite divided into zones from 7B-a to -h.

Table 1 Chemical composition of each zone in basaltic andesite

wt(%)	7B-a	7B-b	7B-c	7B-d	7B-e	7B-f	7B-g	7B-h
SiO ₂	54.56	68.06	69.94	73.06	79.55	81.22	81.50	78.49
TiO ₂	0.56	0.65	0.80	0.84	0.40	0.37	0.70	0.75
Al ₂ O ₃	16.58	9.07	7.11	5.79	4.20	4.04	4.32	4.45
Fe ₂ O ₃ [*]	7.88	6.52	4.40	1.88	2.00	1.26	1.21	1.65
MnO	0.16	0.13	0.11	0.04	0.06	0.01	0.02	0.04
MgO	5.21	3.91	2.37	0.34	0.37	0.26	0.11	0.19
CaO	8.78	4.76	2.45	0.57	0.61	0.35	0.20	0.22
Na ₂ O	2.78	0.70	0.00	0.01	0.00	0.03	0.01	0.00
K ₂ O	1.56	1.78	2.15	0.80	0.26	0.25	0.30	0.26
P ₂ O ₅	0.05	0.04	0.07	0.10	0.06	0.08	0.08	0.08
H ₂ O(+) ^{**}	1.80	3.97	6.47	12.12	8.27	8.53	6.38	8.58
H ₂ O(-) ^{***}	0.07	0.41	4.16	4.44	4.21	3.61	5.16	5.29
Total	100	100	100	100	100	100	100	100
(ppm)								
Sr	449	284	68	61	48	47	38	38
Rb	66	68	58	25	2	2	2	2
Cs	3.8	4	4	1.9	1.1	1.2	1	1
Ba	356	475	510	598	621	616	597	589
Nb	3	4	4	3	4	4	4	5
Zr	55	65	64	64	49	58	45	49
Y	15	10	3	1	2	2	1	1
La	12.3	8.3	2.8	2.6	3.9	3.5	2.5	2.6
Ce	23.3	15.1	4.3	2.9	4.3	4.0	2.6	2.7
Pr	2.78	1.75	0.41	0.24	0.36	0.32	0.19	0.22
Nd	11.5	7.1	1.5	0.8	1.1	1.0	0.7	0.7
Sm	2.5	1.5	0.3	0.1	0.2	0.2	0.1	0.2
Eu	0.76	0.50	0.10	0.05	< 0.05	< 0.05	< 0.05	< 0.05
Gd	2.2	1.4	0.4	0.1	0.2	0.2	0.2	0.2
Tb	0.4	0.2	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dy	2.5	1.7	0.6	0.2	0.3	0.2	0.2	0.2
Ho	0.5	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Er	1.5	1.0	0.4	0.1	0.2	0.2	0.1	0.2
Tm	0.24	0.18	0.06	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Yb	1.7	1.2	0.4	0.1	0.2	0.3	0.2	0.2
Lu	0.25	0.2	0.06	< 0.01	< 0.01	0.04	< 0.01	< 0.01
V	253	183	81	25	11	13	6	6
Cr	110	115	100	30	30	30	50	60
Zn	190.3	145.3	96.3	103.3	93.7	97.7	70.3	75.3
Ga	13	7	4	3	1	1	2	2
Co	399	767	1002	7	3	3	1366	1405
Cu	4.0	29.7	23.7	31.0	73.3	41.0	19.0	87.7
Ni	32.3	45.7	1.3	2.3	0.7	1.0	0.7	29.3
Ag	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Au	< 0.001	< 0.001	0.046	0.037	0.018	0.018	0.030	0.129
Hf	1.6	1.8	1.9	2.1	1.7	2.1	1.5	1.4
Ta	0.4	0.5	0.5	0.3	0.3	0.3	0.5	0.6
Pb	6	8	9	13	28	20	17	18
Sn	2	2	2	< 1	1	2	2	2
Th	4.8	4.4	3.3	2.2	3.3	3	2.1	2.6
U	1.7	1.8	1.5	1.1	1.3	1.2	0.8	0.9
Density(g/cm ³)	2.80	2.40	2.23	2.07	2.15	2.12	1.99	1.97

* Total iron as Fe₂O₃, ** Loss on ignition, *** Loss on drying.

a beam current of 12 nA and beam diameter of 5 μm . The peak and backgrounds were measured for 10 and 5 seconds, respectively. The ZAF method was used for corrections. The standard minerals were ; quartz (Si), corundum (Al), rutile (Ti), eskolaite (Cr), hematite (Fe), periclase (Mg), manganosite (Mn), wollastonite (Ca), jadeite (Na) and adularia (K). The altered products of the basaltic andesite were identified using XRD (X-ray powder diffractometer, Rigaku RINT-2500V) with graphite-monochromatized $\text{CuK}\alpha$ radiation generated at 40 kV and 160 mA.

3. Results and discussions

3.1 Altered product

In the zone from 7B-d to 7B-h near the rock surface of the altered zones, the CPX, OPX and PL as the main primary minerals from Jingzaiping were changed to altered minerals by the high temperature with low pH acidic hot spring waters, and the original minerals could not be detected by XRD. The PL is rapidly replaced by altered products than OPX and CPX. In any case, these primary minerals of the rock disappeared in the 7B-d zone, and in the more altered zones 7B-d to 7B-g, only cristobalite was detected as an altered mineral. In the most altered zone (7B-h), in addition to sulfur, diffraction lines indicating the possibility of linarite ($\text{PbCu}(\text{SO}_4)(\text{OH})_2$) and bieberite ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) of hydrous sulfate minerals were also detected with cristobalite. No clay minerals, which are often associated with alteration products, were observed.

On the other hand, Chen and Yang (1984) reported cristobalite, tridymite, quartz, smectite, illite, hydromica, anhydrite, pyrite, calcite, sphene, chlorite, epidote, and actinolite as the hydrothermal altered minerals from Tatun area. Since the weathered sample used in this study were close to the active fumaroles, it was considered that even if clay minerals were formed, they were washed away by the flows, and did not remain.

3.2 Chemistry of altered product

Fig. 3, 4 and 5 show the chemical variation of the altered zones represented by the elemental abundance per unit volume (mol/L). Figs. 4 and 5 were shown in logarithmic notation. Each value was calculated from the chemical composition, and density, which determined by the pycnometer, shown in Table 1. In Fig. 3, which shows the major elements, Al, Ca, Mg, Fe and Na are rapidly leached by hot spring water. The value of H tends to increase toward the highly altered zones. The Si value has some variation but is almost constant as well as the Ti and P. Therefore, it is consistent with the results of XRD, which indicates that CPX, OPX and PL in the rock have been altered rapidly. Since the amount of oxygen is basically constant, it is presumed that the alteration process is progressing under the constant volume.

Similarly, the REE is shown in Fig. 4, but the Eu, Tb, Ho, Tm and Lu are excluded from the figure because they were below the detection limit in the ICP-MS analyses in some altered zones. The REE value decreases rapidly from 7B-a to 7B-d, then the Y, Pr, Sm, Er, Dy and Yb values increase somewhat in the 7B-e and 7B-f zones, but hardly moves until 7B-h on the rim.

In some of other minor metallic elements shown in Fig. 5, the Pb and Cu values increase by the alteration process, and the Co and Ni decreases in the middle alteration zones, but increase again in the outer zone, and Cu basically increase overall. The V and Cr values decrease, but

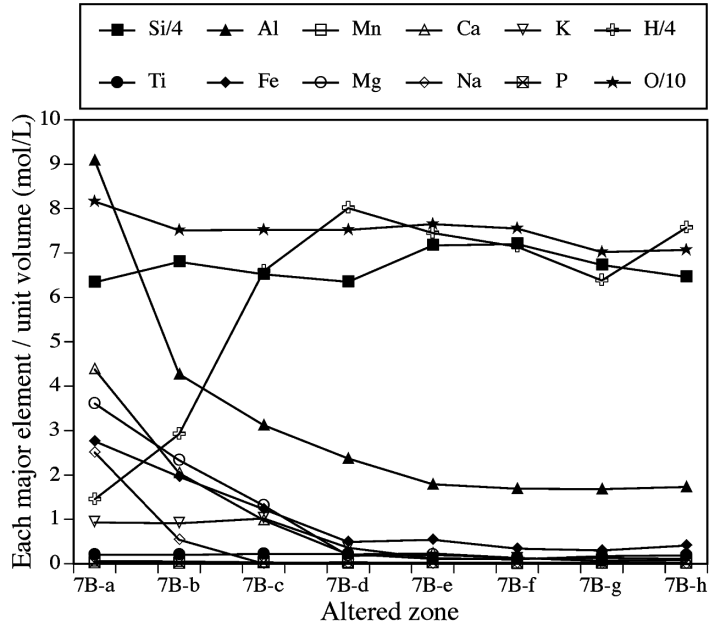


Fig. 3 Change in amount of each major element per unit volume by the acidic hot spring alteration. The values of silicon, hydrogen and oxygen are divided by 4, 4 and 10, respectively. The zone's name is the same as in Fig. 2B.

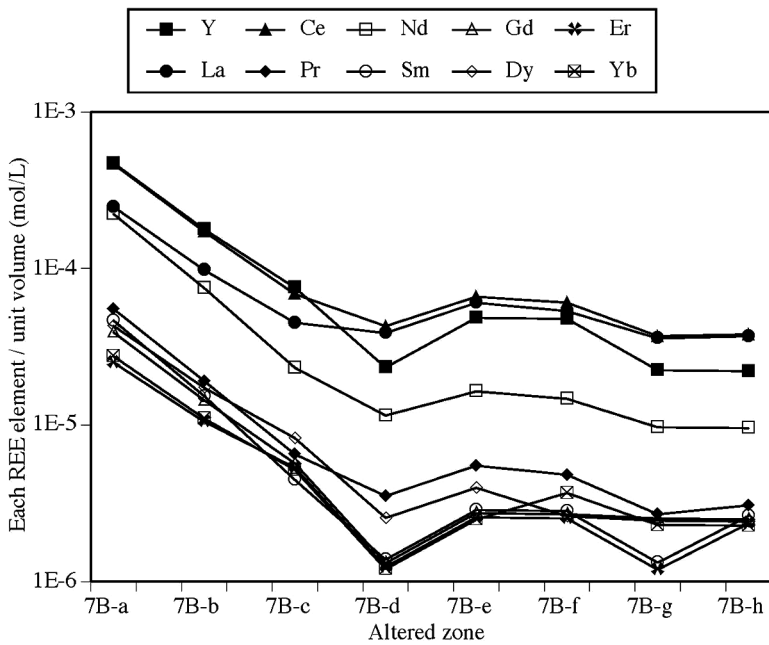


Fig. 4 Change in amount of REE element per unit volume by the acidic hot spring alteration. The zone's name is the same as in Fig. 2B.

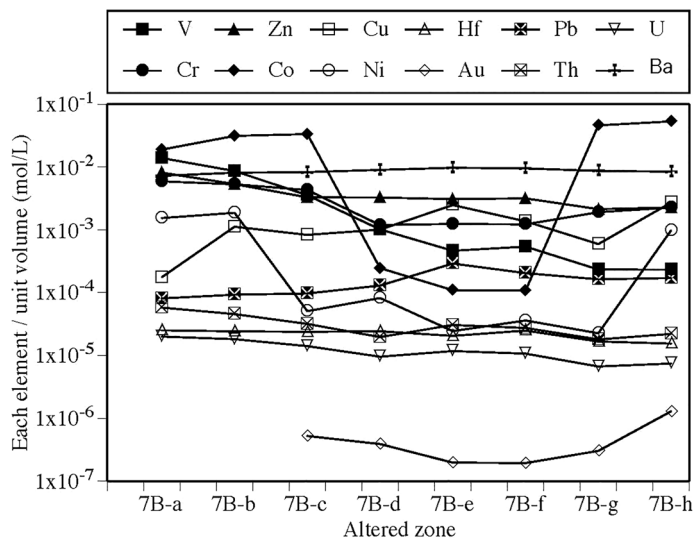


Fig. 5 Change in the selected minor element content per unit volume by the acidic hot spring alteration. The zone's name is the same as in Fig. 2B.

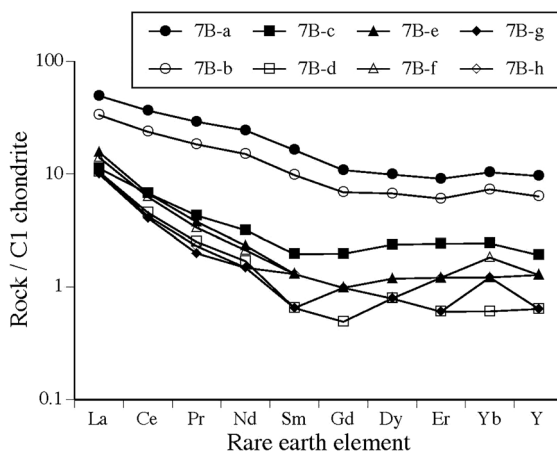


Fig. 6 C1 chondrite normalized REE variation diagram for each zone. The zone's name is the same as in Fig. 2B.

the Zn, Hf, U and Th hardly change. The presence of Au is not detected in the inner zone of the rock, but it is somewhat contained in the intermediate zone and tends to increase slightly in the near the surface zone where alteration has progressed.

The C1-chondrite normalized REE patterns for each altered zone are shown in Fig. 6. The decrease in LREE (La, Ce, Pr and Nd) value in each zone due to alteration is remarkably between 7B-b to 7B-c of the early stage of alteration compared to the MREE (Sm, Gd and Dy) and HREE (Er and Yb). There is a clear gap between the 7B-b and 7B-c zones.

The changes of C1 chondrite normalized incompatible trace element patterns for each altered zone are shown in Fig. 7. The contents of Sr, K, Rb, Ce and Y which are large-ion lithophile elements (LILE) decrease, and in particular, the Rb value is decreased remarkably. The contents

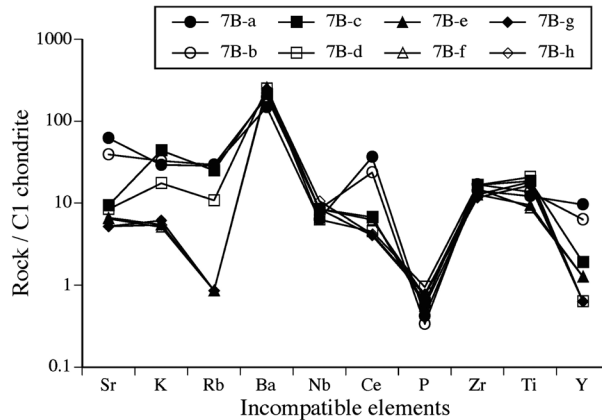


Fig. 7 C1 chondrite normalized incompatible trace element patterns for each zone. The zone's name is the same as in Fig. 2B.

of Nb, P, Zr and Ti of high field strength elements (HFSE) tend not to change.

Fig. 8 shows the relation between the change in molar ratio with respect to the mol/L by the hydrothermal alteration and the ionic radius as a 6-coordination. The molar ratio is calculated from the mole of each ion in each alteration zone divided by the mole of individual ion in almost unaltered basaltic andesite (7B-a). That is, a horizontal thick line with a molar ratio of 1×10^0 indicates 7B-a. Therefore, the molar ratio decreases when ions are leached due to alteration by hot spring water, and non-leached ions remain unchanged and increase when supplied from outside the system. Among the major elements (Fig. 8A), those with an ionic radius of around 75 pm such as Fe and Mg and around 100 pm such as Ca and Na are relatively low. These ionic radius elements are the main components excluding Si in OPX, CPX and PL, which are the main minerals in basaltic andesite. The Ti is almost unchanged. In more detail, the change of the molar ratio from 7B-a to 7B-b or 7B-c zone at the early stage of alteration is large for Na in PL, relatively small for Mg, Fe and Mn in OPX and CPX, and intermediate for Ca in both minerals. Therefore, leaching from PL occurs more rapidly from an earlier stage than OPX and CPX.

Most of the minor elements are reduced by alteration, but the molar ratio of Cu, Co, Pb and Ba is higher than that of the unaltered basaltic andesite (Fig. 8B). That is, from 7B-a zone to the most altered one (7B-h), the Cu, Co and Pb increase from 4 to 88 ppm, from 399 to 1405 ppm, and from 6 to 18 ppm, respectively (Table 1). These elements dissolved from basalt and/or supplied from outside may remain in alteration products such as hydrous sulfate minerals. Chen (1978) reported that the contents of Cu and Co in andesite to basalt in the Tatun volcanic area were 80 to 116 and 73 to 87 ppm, respectively. Compared with the results of this study, the Cu content is almost the same as the maximum value of basaltic andesite in this study, and that of Co is low. Sato (2006) reported barite containing Pb from Hokuto (Peito), Taiwan, and Tamagawa and Kawarage, Japan, which are hot springs containing sulfate ion. Barite has not been detected here by XRD, but Ba with a relatively high molar ratio may have precipitated as insoluble barite during the alteration process with sulfuric acid solution. It is possible that Pb was precipitated in also barite and remained.

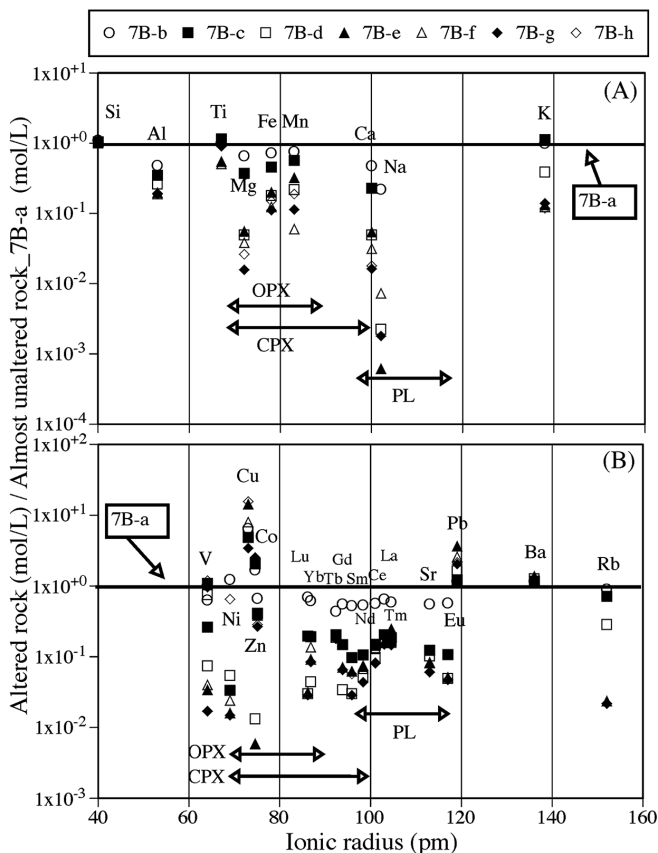


Fig. 8 Logarithmic molar ratios of the major and minor elements in each zone against ionic radius. The left and right arrows indicate the range of ionic radii of the main constituent elements in plagioclase (PL), orthopyroxene (OPX) and clinopyroxene (CPX). (A) major element, (B) minor element. The zone's name is the same as in Fig. 2B.

On the other hand, in artificial weathering experiments using sulfuric acid at pH 4 and 50°C for basalt and gabbro, it is shown that elements such as Cu, Co and Pb are relatively easily dissolved by this acidic extraction solution (Fujitaka *et al.*, 2020, Kobayashi *et al.*, 2005). It has also been shown that the Tatun area has many hydrothermal activities involving various elements (e.g., Liu *et al.*, 2011). Therefore, it is considered that the concentrated elements in the altered basaltic andesite were supplied from the hot spring water rather than due to the weathering alteration. In addition, since the molar ratios of Cu, Co, Pb and so on do not simply change depending on the degree of alteration from the inside to the surface of the altered rock, it is suggested that the chemical composition of the hot spring water in this area may have changed depending on the activity stage.

4. Conclusions

In order to elucidate the effect of the acidic hot spring water on volcanic rock, mineral

chemistry studies were conducted on the alteration processes by the sulfuric acid hot spring water at pH=1.4 and 98°C or higher using the altered basaltic andesite showing zoning from Jingzaiping, Tatun volcanic area, Northern Taiwan. PL was altered earlier than OPX and CPX by the hot spring water from XRD data and behavior of leaching elements. Cristobalite was the only major alteration product, and in addition to this, sulfur, linarite and bieberite-like minerals were slightly detected in the most altered surface zone.

The Al, Mg, Fe, Mn, Ca, Na, V, Rb, and REE, expressed in terms of mass per unit volume (mol/L), were leached out of the rock and decreased during the alteration process. The Si, Ti, Hf, U, Th and O contents were not changed. On the other hand, the Pb, Cu, Ba and H increased, and the Co, Ni and Au basically increased in the outer zone. The LREE normalized by C1 chondrite decreased remarkably at the early stage compared to the MREE and the HREE. The LILE (Sr, K, Rb, Ce, Y) value of incompatible element decreased, but the HFSE (Nb, P, Zr, Ti) hardly changed.

The contents of Cu, Co, Pb and so on in alteration products of the rock basically tended to increase as alteration progressed, but an increase or decrease was observed in each zone. In the Tatun area, it was suggested that the chemical composition of the hot spring water may change depending on each activity stage.

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