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QUALITY AND QUANTITY DETERMINATIONS OF REACTIVE SUBSTANCES IN VOLCANIC ROCKS

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1. INTRODUCTION

Andesite is a volcanic rock generally used in Japan as aggregate for concrete. It often contains reactive substances such as volcanic glass, cristobalite and tridymite.

The chemical and mortar bar tests specified in ASTM are employed to estimate the alkali reactivity of aggregates. It is, however, necessary to know the species and contents of the reactive substances in aggregates for a proper understanding of reactivity of aggregates. Therefore, development of simple and convenient methods to determine the contents of reactive substances will bring a great advance in studies on alkali aggregate reaction.

An attempt has been made in this study to utilize image analysis and electron probe microanalyzer (EPMA) for the purpose of determination of contents of reactive substances in andesites. The present study also examines the relation between expansive characteristics of andesites and their physical properties such as porosity.

2. SAMPLES

Six andesites containing reactive substances were collected from various parts in Japan. Five of them contain volcanic glass and one has cristobalite as reactive substance. Petrological characteristics of the samples are summarized in Table 1.

3. PETROLOGICAL DESCRIPTION OF REACTIVE SUBSTANCES IN ANDESITES

Volcanic rocks are formed by quenching of silicate melts

Table 1: Petrological properties of samples

Sample	Rock type	Locality	Texture	Reactive species	Substance content(%)
A	Two pyroxene andesite	Hokkaido	prophyritic	glass	11
B	Two pyroxene andesite	Yamagata	porphyritic	glass	40
C	Clinopyroxene andesite	Ishikawa	porphyritic	glass	45
D	Two pyroxene andesite	Ishikawa	porphyritic	glass	40
E	Orthopyroxene andesite	Kagawa	aphyric	glass	50
F	Two pyroxene andesite	Kanagawa	aphyric	cristobalite	1.8

during volcanic eruptions. Phenocrysts are relatively larger crystals that grow by crystallization in subsurface area due to slow cooling of magma before an eruption. On the other hand, rapid cooling of residual magma at the surface results in the formation of tiny microcrystals. Glass is formed as uncrystallized phase in a case of imperfect growth of microcrystals with especially rapid cooling rate, so that it is contained in interstices of microcrystals in groundmass. Photo 1 shows groundmass of a glassy andesite. Some phenocrystic minerals also, however, contain glass phase as shown in Photos 2 and 3. Photo 2 shows the glassy phase in a phenocryst as formed by the magma trapped in the growing phenocrystic crystals. Also, glass in phenocryst can be formed by the partial melting of previously formed phenocryst upon in contact with higher temperature magma (1). Photo 3 shows this type of glass. It is an important characteristic of volcanic glass to appear brown when observed in single Nicol under a microscope.

Cristobalite and tridymite are stable in 1470 - 1723°C and 870 - 1470°C, respectively (2). They are considered to be formed under metastable range of temperature at the late stage of the crystallization of magma and to remain in the rocks even at low temperatures because of the hardness of transition from

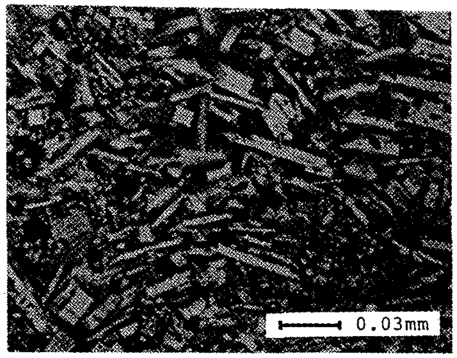

Photo 1: Groundmass of glassy andesite (Sample C) (Single Nicol, x400)

Photo 2: Phenocryst bearing glass inclusions in sample D (Crossed Nicols, x200)

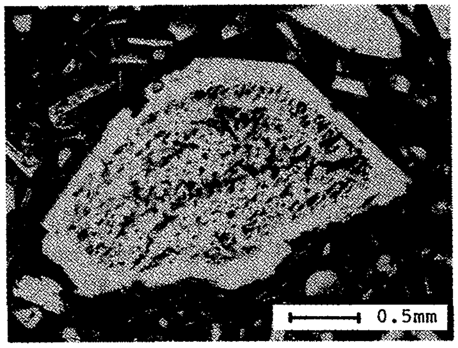

Photo 3: Phenocryst bearing glass inclusions in sample B (Single Nicol, x40)

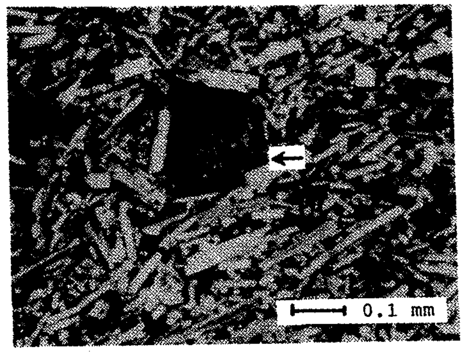

Photo 4: Cristobalite in a vesicle in sample F (Crossed Nicols, x100)

these minerals to quartz which is stable at low temperatures. These minerals are contained in groundmass and/or in vesicles and not as phenocrysts. Photo 4 shows cristobalite existing in a vesicle of an andesite. There are some cases when volcanic glass crystallizes into cristobalite and tridymite through alteration. It is difficult to identify these minerals by a microscope because of their small size. X-ray diffractometry is a suitable method to identify this kind of cristobalite and tridymite (3).

4. DETERMINATION OF CONTENTS OF REACTIVE SUBSTANCES

4.1 Method using an image analyzer

This method takes advantages of the fact that volcanic glass appears brown under single Nicol. A microscopic image in high magnification is input to an image analyzer through a color television camera connected with the microscope. Certain thresholds are determined in the intensities of the three primary colors of red, green and blue, and then the glassy area is binarized. The ratio of the binarized area to the total area is adopted as the volumetric ratio of glass. For samples having porphyritic texture, the ratio of phenocrysts is determined by the similar binarization using low magnification images. If this

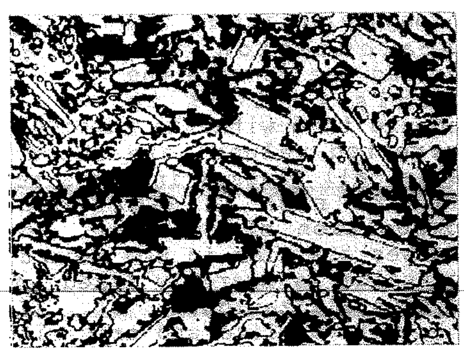

Fig. 1: Binarized pattern of glass portion of sample C by an image analyzer (dark area)

ratio is taken as A% and the ratio of glass in groundmass as B%, the volumetric ratio of glass to the whole rock is taken to be (100 - A)x(B/100). Fig. 1 is an example of the binarization of glassy area in the area of Photo 1. Results obtained by this methods are given in Table 1. The conventional linear traverse method was carried out using sample B for comparison with this method and found to be in good agreement with the results obtained from binarization.

It is, however, difficult to apply this method to the determination of contents of cristobalite and tridymite, because these minerals do not show distinct differences from plagioclase in both single and crossed Nicols.

4.2 Method using an EPMA

This method takes advantage of the difference in chemical compositions between reactive substances and other minerals.

4.2.1 Chemical compositions of reactive substances

There are few studies on the chemical composition of glass in volcanic rocks (4). Chemical composition of glass was, therefore, determined by EPMA in the present study. The sum of major conponents did not total to 100% (Observed values were between 88% and 95%.), and the difference between the observed total and 100% was assumed to arise due to the hydration of glass through alteration. The recalculation was carried out to make the totals to 100% to compare them with the chemical composition of fresh andesite. The corrected values are shown in Table 2. As is clear from the table, all glasses in andesites have SiO_2 in excess of 70 percent and are rich in SiO_2 compared with the average chemical composition of andesite. Another characteristic is that the glasses are rich in K_2O except for sample B. This could be because potassium is scarcely fixed in minerals formed in the early stage of crystallization.

Table 2: Chemical composition of glass in andesite

Sample	A	B	C	D	E	X**
SiO_2	78.55	76.35	73.09	77.30	78.96	59.59
TiO_2	0.61	0.57	0.99	0.92	0.59	0.77
Al_2O_3	11.10	14.02	14.40	13.30	10.20	17.31
Fe_2O_3*	1.85	4.71	3.40	2.78	1.65	3.33
FeO						3.13
MgO	0.08	0.12	0.23	0.12	0.07	2.75
MnO	0.11	0.07	0.14	0.29	0.02	0.18
CaO	0.51	2.60	0.90	0.58	0.21	5.80
Na_2O	1.17	1.04	1.67	1.21	2.60	3.58
K_2O	6.23	0.50	5.33	4.06	5.96	2.04
Total	100.24	99.98	100.15	100.56	100.26	

* Total iron was calculated as Fe_2O_3.
** Average of chemical composition of andesites (6)

Cristobalite and tridymite have nearly pure SiO_2 composition with very little impurites (5).

4.2.2 Method using an EPMA

EPMA used in the present study has a high speed mapping system which indicates X-ray intensities of 512x512 dots using 16 colors. Fig. 2 shows a mapping image of potassium of sample C. As is shown in section 2.1 above, the glass is rich in patassium,

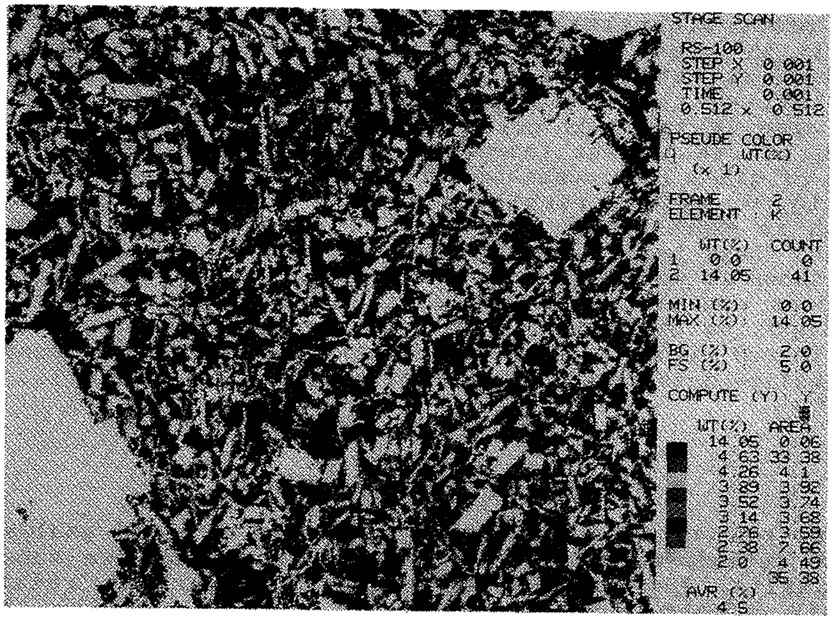

Fig. 2: EPMA mapping image of potassium in sample C (0.512 x 0.512 mm)

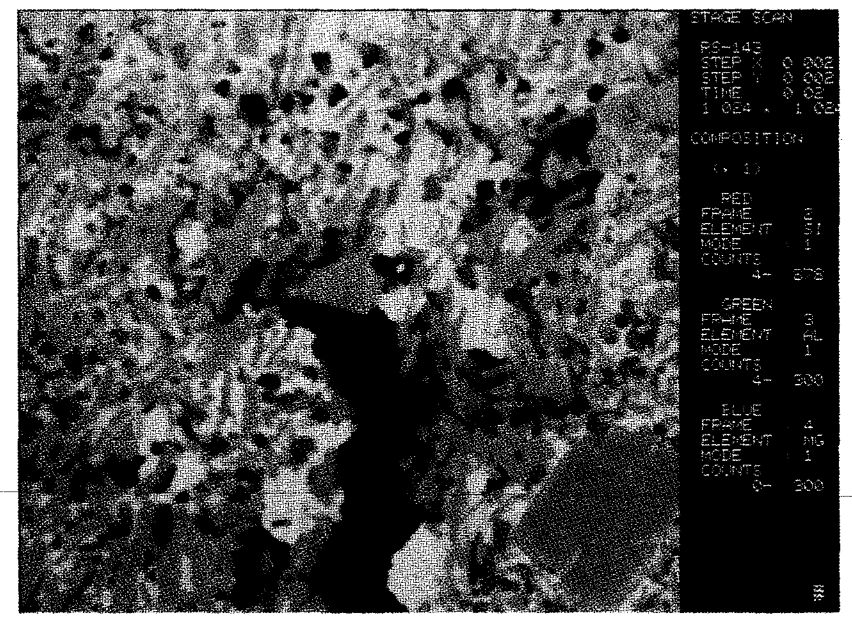

Fig. 3: Superimposed EPMA mapping image of Si, Al and Mg in sample F (1.024 x 1.024 mm)

while other minerals are not. It is, therefore, possible to identify the glass portion through a mapping image of potassium. A certain threshold value is set regarding X-ray intensity of potassium, and then the ratio of the area above this value to the total area is taken as glass content. The result gives a glass content of 48 percent indicating good agreement with the result (those of glass in groundmass) obtained by image analysis.

Fig. 3 shows a mapping image of sample F. In this case, silicon is expressed in red, aluminum by green and magnesium by blue and these images are superimposed. Feldspar containing Si and Al is shown in yellow through the combination of red and green and pyroxenes containing Si and Mg is done in purple through the superimposing of red and blue. The portion of cristobalite is shown in red without superimposing of other colors. The content of cristobalite determined by this method was 1.8 % (Table 1).

5. CONCLUDING REMARKS

The present study shows the usefulness of image analysis and EPMA as methods to determine the contents of reactive substances in andesite. The authors are presently trying to relate the physical property of glassy andesite such as porosity, thermal history etc. to the deleteriuos expansion of mortar bars on account of alkali reaction with reactive glass, and hope to present the results at the Conference.

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