THE PETROGRAPHIC COMPARISON OF SOME VOLCANIC ROCKS FROM JAPAN AND NEW ZEALAND—POTENTIAL REACTIVITY RELATED TO INTERSTITIAL GLASS AND SILICA MINERALS

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1. ABSTRACT

Petrographic comparisons have been made of fresh, volcanic rocks from Japan and New Zealand based on chemical, XRD, and EMP analyses, norm calculations and the ASTM C289 chemical test for the potential reactivity of aggregates with cement alkalies. The results show that where the andesite and basalt compositions are oversaturated with silica much of the silica is present as cristobalite or tridymite in the light-colored, well-crystallized rocks while volcanic glasses predominate in the dark-colored poorly crystallized rocks. It is confirmed that the interstitial glasses in the volcanic rocks are more siliceous than the bulk composition of the host rock. This suggests a higher potential reactivity for these interstitial glasses than would be predicted from the bulk rock composition. An attempt is made to relate the presence of the interstitial glasses, cristobalite and tridymite to the potential alkali-reactivity of these volcanic rocks.

2. INTRODUCTION

Volcanic rocks are used for aggregates in both New Zealand and Japan where they have caused many cases of alkali-aggregate reaction in concrete. In New Zealand the presence of the silica minerals cristobalite and tridymite has not been widely observed in basalts and andesites, although they are common in dacites and rhyolites, and reactivity of the andesites has usually been attributed to the presence of interstitial glass [1]. However, in Japan these silica minerals are widespread in basalts and andesites [2] and it is considered that both cristobalite and tridymite as well as interstitial glass are significant in contributing to the reactivity of Japanese volcanic rocks [3,4].

The presence of significant cristobalite and tridymite in basalts and andesites has not in general been widely observed outside Japan, in spite of the fact that CIPW norms of most andesites and some basalts indicate excess silica to be present in the rocks. For instance in Japan, up to 6% cristobalite in basalt [5] and from 15-25% of cristobalite in andesite [6,7] have been reported. On the other hand in New Zealand significant quantities of cristobalite have been observed in the andesites from the Bay of Prenty region [8] but otherwise it has not been considered of significance in the basalts and andesites.

As both Japan and New Zealand lie along the circum-Pacific belt of volcanism many similarities in their volcanic rocks would be expected. The differences noted above seemed unusual and as a result it was desided to compare volcanic aggregates to determine the extent of any differences and also to relate the presence of the silica minerals and interstitial glass to the reactivity of these volcanic aggregates in concrete.

3. SAMPLING AND TESTING

Thirty four rock samples from New Zealand and fourty two from Japan were collected with emphasis on rocks used for concrete aggregates. The sample collected were primarily andesites but selected examples of basalt, dacite and rhyolite were also included to provide a range of the typical volcanic rocks being used for aggregate. Samples were interchanged and microscopic examination of thin sections made in both countries. Chemical and XRD analyses, calculation of CIPW norms and the ASTM C289 test were carried out by each country on their own rock samples with some intercomparison being made of XRD analyses to see that comparative results were obtained. Determination of silica minerals extracted by phosphoric acid (9) and electron microprobe analyses of interstitial glasses were only performed in Japan. In addition some synthetic glasses made from melting volcanic rocks were prepared in Japan and tested according to ASTM C289.

4. RESULTS AND DISCUSSION

A synopsis of the amounts of normative quartz calculated from the CIPW norms and comparison of the amounts of silica minerals found by microscopic examination and phosphoric acid extraction and the silica content of the interstitial glasses together with reactivities of the samples is given in Table 1, Figs. 1 and 2, with the results of testing the synthetic glasses being shown in Figs. 3 and 4.

4.1 Comparison of Japanese and New Zealand Rocks

The results clearly indicate that similar types of volcanic rocks in Japan and New Zealand contain the same ranges of interstitial glass, cristobalite and tridymite. New Zealand basalts used for concrete aggregates all tend to be undersaturated with silica and the one sample from Ongaroto which is the exception is only just over saturated. Observation in both countries reported a small amount of interstitial glass in this sample, but neither cristobalite nor tridymite were noted. All the Japanese basalts, with the exception of a sample from Genbudo, are oversaturated with silica and similar amounts of interstitial glass and silica minerals were reported from both countries. Similarly, all the andesite, dacite and rhyolite samples examined from both countries are oversaturated with silica as would be expected. The amounts of glass, cristobalite and tridymite present in any one sample were primarily dependent on whether the sample was a light-colored well-crystallized rock or a dark-colored glassy variety. Since both dark and light-colored rocks may be present in an aggregate source this variation presented sampling problems. However, the intercomparison of samples show that up to 20% of cristobalite and 17% of tridymite may be present in the andesites and the silica minerals are more widespread in New Zealand rocks than previously thought.

4.2. Silica Minerals Observed by Microscopy

Silica minerals occur interstitially, filling interstices in the groundmass of light-colored, well-crystallized volcanic rocks. Cristobalite appears in the basalts and andesites as fine mosaic aggregates, intergrown with microlites of feldspars and pyroxene in the groundmass, or rounded patches with a roof-tile texture. Tridymite usually occurs as coarse mosaics filling interstices of the groundmass in andesites, but sometimes forms wedge-shaped plates projecting into the cavities of the rock. It may also occur as slender platelets parallel to the flow texture, or surrounded by glass altered to smectite clay. These observations suggest that these silica minerals crystallized before the solidification of the magma and hence are of primary rather than secondary origin.

Quartz, which may also occur as a silica mineral, appear as rounded patches of sponge-like aggregates with uniform extinction in a poorly crystallized groundmass of the slightly altered rocks. The quartz sometimes contains pseudomorphs of other silica minerals suggesting it has been formed through recrystallization and in these cases indicates an initial stage of alteration (2). Where there is a significant percentage of the silica minerals in a sample there are few problems in observing them in thin section, but where the minerals are finely disseminated they are easily underestimated or

sometimes overlooked unless a careful search is made.

4.3 Silica Minerals Determined by Phosphoric Acid Extraction

Another method of determining silica minerals in rocks is to extract them with phosphoric acid (9) and carry out an XRD analysis of the residue to determine cristobalite, tridymite and quartz. This determination can be used to confirm the results of microscopic examination and clearly shows that in the light-colored well-crystallized rocks most of the normative quartz is present as cristobalite or tridymite. For instance a Japanese andesite with 18.7% normative quartz yielded 17.1% residue on acid extraction which consisted of tridymite with lesser amounts of cristobalite and quartz. Likewise, a New Zealand andesite with 21.5% norative quartz yielded 19.1% residue on acid extraction largely composed of cristobalite. The above results confirm that the method is of considerable use in detecting the silica minerals in volcanic rocks. The amounts detected substantially exceed those observed by microscopy, suggesting that the silica minerals are present as a finely divided form in the groundmass and thus could be highly reactive.

4.4 Volcanic Glass Observed by Microscopy

Volcanic glass is either contained interstitially in the groundmass or sometimes enclosed in phenocryst minerals. It is usually dark brown in glassy basalts and pale brown in andesites containing more then 30% of glass. In well-crystallized rocks containing less than 7% of glass, the interstitial glass tends to be dusty in texture because of dark inclusions which are up to 10 microns in size. These inclusions may be formed of globules of dark brown glass with a higher refractive index than the host glass or small spheres of opaque magnetite. The occurrence of these dark inclusions of glass was discovered in lunar rocks (10) and their terrestrial counterparts were found later in many volcanic rocks around the world (11,12). Interstitial glass is very likely overlooked where the groundmass is either cryptocrystalline or partly devitrified.

4.5 Compositions of Volcanic Glass

Because the process of crystallization of a magma increases the silica content of the residual melt, the interstitial glass in volcanic rocks has a higher silica content than the bulk composition of the rock. For instance Mielenz et al.(13) found that a reactive olivine basalt contained 20% of andesitic glass. This aspect was investigated by electron microprobe analysis to try and relate the composition of the interstitial glasses to the reactivity of the rocks.

The results of analyzing interstitial glass in selected samples are noteworthy (Table 2). Apart from the reactive Egmont andesites from New Zealand which appear to contain interstitial glass with 65% silica, all the reactive rocks analyzed contained glasses that fall in the narrow range of 72-78% silica. That is rhyolitic glass is present in these reactive rocks irrespective of whether they are a basalt, andesite, dacite or rhyolite. These results agree with Philpotts (12), who found that most basalt and andesite contain interstitial glass with silica contents ranging from 65-77%. Similarly, Graham (14) reports analyses which show rhyolitic glass to be present in a potentially reactive basalt in New Zealand. In contrast the analysis of the unreactive New Zealand basalts showed that the interstitial glass in these rocks is an andesitic glass with a silica content of 52%. A glass of this composition would be expected to be less reactive than rhyolitic glass. However, the small amount of glass present in these rocks could also explain their lack of reactivity.

4.6 The Reactivity of Synthesized Materials

The reactivity of synthetic cristobalite, glasses prepared by fusing volcanic rocks and some common glassy materials such as blast-furnace slag, fused fly ash and silica glass was determined using the ASTM C289 test (Figs.3 and 4). The plot of the log of the amount of silica in solution (Sc) against the total silica present in the test sample indicates a linear relationship between these variables. When these results are compared

with the results shown in Fig.4, it is apparent that glasses of less than 65% silica are not particularly reactive. These observations are in general agreement with results reported by Stanton (15) and Tang et al.(16). On the other hand, synthetic cristobalite proved to be potentially deleterious and the result serves to explain the reason why the well-crystallized volcanic rocks containing appreciable amounts of cristobalite without glass, tend to be potentially deleterious in this test. Both cristobalite (17) and tridymite (18) have been noted as reactive in the mortar bar test.

5. CORRELATION OF RESULTS WITH REACTIVITY

An attempt was made to correlate reactivity based on the ASTM C289 quick chemical test with the amount and type of interstitial glass, cristobalite and tridymite present in a volcanic rock (Figs.1 and 2). As a result some clear trends were noted between the bulk chemistry of fresh volcanic rocks and reactivity. For fresh volcanic rocks to show potential reactivity they must contain approximately >50% silica. That is they must be saturated or oversaturated with silica so that either highly siliceous glasses or the silica minerals cristobalite and tridymite may be present. Whether the rock will have pessimum proportion will depend on the relative proportions of glass to silica minerals. For example, andesites containing cristobalite and/or tridymite will tend to be potentially deleterious (2) whereas glassy andesites and obsidians will be deleterious with low dissolved silica (Sc) and low reduction in alkalinities (Rc). This type of relationship probably applies right across the spectrum of fresh volcanic rocks from basalt to rhyolite. However, many rock deposits may contain a range of both light-colored crystalline and dark-colored glassy rocks. Thus the contributions of the glass and the silica minerals may be difficult to determine in aggregate deposits.

Where the matrix of the rocks is completely glassy, as tends to be the case with Japanese Sanukites and New Zealand Egmont andesites, the interstitial glasses will all exceed 65% silica and in general fall in the range of 72-78% silica. In these cases the reactivity probably solely depends on the amounts of glass present. That is rocks that contain more than 20% of fresh and/or partly devitrified glass, have a Sc less than 250 mmol/l. The greater the content of interstitial glass in andesites, the lower the Sc value becomes approaching those of obsidian and rhyolitic glass. In contrast, where glass is completely absent reactivity depends on the amount of silica minerals present. Rocks in which over 10% of cristobalite and/or tridymite was detected by the phosphoric acid extraction, have a Sc over 500 mmo/l. However, in the case of altered rocks the presence of devitrified glass presents problems as the mineralogy and contribution to reactivity of these devitrified matrices is not known. But calulation of the CIPW norms of the rhyolitic interstitial glasses suggests excess silica to be present as either cristobalite, tridymite or quartz if these glasses were devitrified.

Thus, in making a petrological assessment to predict the reactivity of a basalt, a knowledge of the bulk chemistry and amount of glass and silica minerals is essential. For volcanic rocks ranging from andesite to rhyolite a knowledge of the excess silica in the composition should alert the petrographer to the probable extent of silica minerals that should be present, especially if interstitial glass is not dominant in the matrix. If silica minerals cannot be observed their presence can be unequivocally determined by performing a phosphoric acid extraction test. Thus the above techniques enable the petrographer to better assess the potential reactivity of a volcanic rock and allow a better interpretation to be made of any results of the ASTM C289 quick chemical test.

6. CONCLUSIONS

1. Intercomparison of fresh, volcanic rocks from Japan and New Zealand show that the volcanic rocks in both countries contain similar amounts of cristobalite and/or tridymite. Thus the contribution of these materials to reactivity should be similar in both countries.

2. Analyses of interstitial glass in the reactive rock sample showed that this glass tends to be rhyolitic in composition and thus highly reactive. In contrast the glass in some basalts only contained 52% silica which explains their lack of reactivity.

3. Testing of synthetic glass materials showed that where the glass contained less than 65% silica the glass was not reactive.

4. Correlation of the presence of interstitial glass, cristobalite and tridymite with reactivity indicates that where glass dominates the matrix of the rock the rock will test as deleterious in the ASTM C289 test, and where silica minerals dominate the rock will test as potentially deleterious.

5. The results show that a knowledge of the bulk chemical composition of a rock, combined with a microscopic determination of glass content and silica minerals confirmed by a phosphoric acid extraction test, will assist a petrographer in assessing the potential reactivity of a volcanic rock.

7. ACKNOWLEDGEMENTS

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(*) in Japanese

TABLE 1 SUMMARY OF PETROGRAPHY OF VOLCANIC ROCKS

		NEW ZEALAND					
		ANALYSIS			MICROSCOPY		
ROCK TYPE	SIO_2	Q^1	RES^2	$SIO_2{}^3$	GL	CR	TR
BASALT A	43-44	0	--	52	0-25	0	0
BASALT B	51	1	--	76	5	0	0
ANDESITE							
EGMONT C	55-56	7-8	2-8	65	5-40	0-10	0-1
TONGARIRO D	58-62	6-19	3-9	72-73	20-50	0-7	0
PRE-QUATERNARY	55-64	9-26	7-19		10-80	0-20	0-2
DACITE	68-72	27-32	24		5-60	0-15	0-10
RHYOLITE	78	42	22		15-55	0-15	0-1

		JAPAN					
		ANALYSIS			MICROSCOPY		
ROCK TYPE	SIO_2	Q^1	RES^2	$SIO_2{}^3$	GL	CR	TR
BASALT E	51-56	0-12	2-8	72-74	0-20	0-7	0
ANDESITE							
EAST JAPAN F	55-62	8-21	1-16	72-77	5-20	0-15	0-10
WEST JAPAN G	57-64	13-24	8-17	75-78	5-20	0-15	0-17
PRE-QUATERNARY H	58-62	16-23	7-19	75	0-65	0-20	0-10
SANUKITE I	65-67	19-23	9-12	78	5-50	0-15	0-10
DACITE	66	31	15		5	5	
RHYOLITE	75	38	33		40	10	5

(1) EXCESS SILICA AS NORMATIVE QUARTZ
(2) RESIDUE FROM PHOSPHORIC ACID EXTRACTION
(3) SIO_2 OF INTERSTITIAL GLASS
A-I SAMPLE IDENTIFICATION IN TABLE 2

TABLE 2 EPMA COMPOSITIONS OF INTERSTITIAL GLASS

	NEW ZEALAND						JAPAN	
	A	B	C	D	D	D	E	E
$SIO_2{}^1$	43.3	50.8	54.9	58.9	59.9	62.1	50.8	52.0
SIO_2	52.1	76.1	65.4	72.7	72.2	73.4	74.0	72.0
TIO_2	2.0	0.6	0.9	0.7	1.1	0.7	0.9	0.1
AL_2O_3	18.9	11.4	15.2	11.1	12.0	11.9	10.4	14.6
FEO	10.5	1.4	4.5	2.5	4.4	2.4	2.9	1.3
MGO	0.1	0.0	0.8	0.2	0.5	0.3	0.0	0.2
CAO	3.6	0.6	2.4	1.4	2.3	1.2	0.5	1.0
NA_2O	4.3	2.8	4.3	2.8	3.3	3.1	2.3	5.4
K_2O	4.5	6.2	5.0	4.1	4.2	4.7	6.2	6.0
TOTAL	96.0	99.1	98.5	95.5	99.9	97.7	97.2	100.6
Q^2	0.0	34.7	13.3	35.8	29.9	32.9	34.5	15.6
GLASS	25	2*	40	20	30	35	1*	2*

	JAPAN							
	F	F	F	F	G	G	H	I
$SIO_2{}^1$	55.4	57.7	59.0	59.2	59.8	60.9	62.0	67.1
SIO_2	73.6	73.0	77.2	74.5	74.5	77.6	75.7	78.0
TIO_2	0.5	0.8	0.5	0.3	0.1	0.8	0.7	0.5
AL_2O_3	10.5	11.4	11.3	12.1	13.8	10.4	11.1	9.6
FEO	0.5	3.8	1.0	1.8	0.4	2.2	2.2	1.1
MGO	0.1	0.1	0.0	0.1	0.0	0.0	0.1	0.1
CAO	0.5	1.2	0.4	1.4	1.0	0.2	0.7	0.6
NA_2O	2.5	2.3	2.4	2.8	4.9	2.7	2.3	2.3
K_2O	5.7	5.4	6.5	5.2	5.3	6.1	4.4	4.5
TOTAL	93.9	98.0	99.3	98.2	99.9	99.9	97.2	96.7
Q^2	36.4	34.1	37.6	34.3	24.4	37.4	42.6	45.5
GLASS	5*	70	5*	20	5*	7*	65	40

(1) BULK ROCK COMPOSITION
(2) EXCESS SILICA AS NORMATIVE QUARTZ
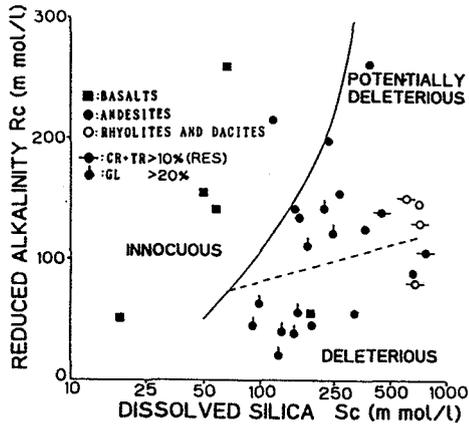(*) CONTAINS DARK INCLUSIONS

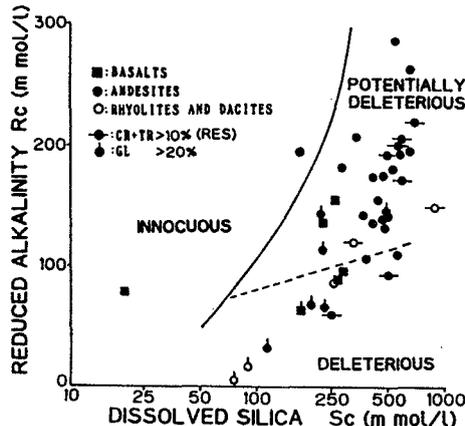FIG. 1 ASTM C 289 CHEMICAL TEST OF NEW ZEALAND VOLCANIC ROCKS

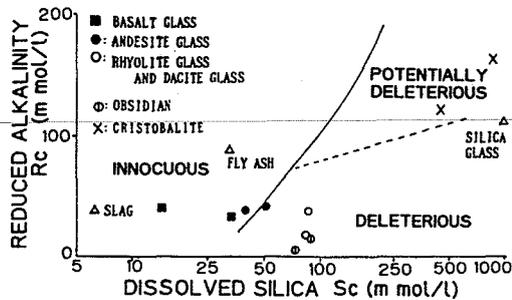FIG. 2 ASTM C 289 CHEMICAL TEST OF JAPANESE VOLCANIC ROCKS

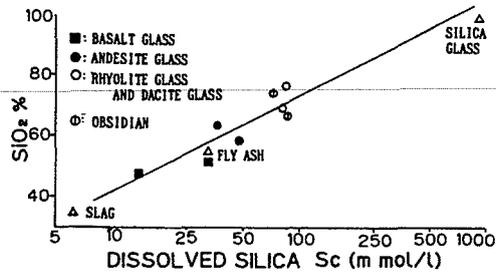FIG. 3 ASTM C 289 CHEMICAL TEST OF SYNTHETIC MATERIALS

FIG. 4 PLOTS OF SC AGAINST SIO_2 CONTENT OF SYNTHETIC MATERIALS