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# Major and Some Trace Elements in the Volcanic Rocks from Ulreung Island, Korea

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## **Abstract**

Geochemical investigation has been carried out for the volcanic rocks from Ulreung island, Korea. The volcanic rock suite is characterized by highly alkalic nature, and some of them contain more than 6 wt.%  $K_2O$  and  $Na_2O$ . The igneous activity may not be related to Pacific plate subduction, or the Japan Sea spreading. It will be hardly possible to explain how to concentrate the abundant incompatible elements in the mantle source in a limited short period beneath Ulreung island.

Most of the chemical features of the volcanic rocks are consistent with simple fractional crystallization. It should be pointed out, however, that significant compositional gap was recognized only in  $K_2O$  content, but not in the other LILEs. The difference between  $K_2O$  and the other LILEs will be hardly explained if fractional crystallization differentiation plays a major role. The volcanic rocks from the island are either highly enriched in  $K_2O$  or not so enriched in  $K_2O$ . No intermediately  $K_2O$ -enriched sample was found. This is contrasted with gradual increase in  $Na_2O$  content. This chemical features will require complicated mechanisms.

## **I. Introduction**

Ulreung island is a volcanic island in the Japan Sea, 130 km off the eastern coast of Korean peninsula. It entirely consists of highly potassic volcanic rocks and volcanoclastic rocks.

In the northeastern Pacific rim, Na-rich alkaline volcanic suite is very common and a number of the volcanoes in Japan and the vicinity are composed of the sodic rock suites. In contrast, K-rich alkaline volcanic suite is rather rare. Especially, highly potassic volcanic suite is scarce. Not only this petrological point of view, the volcanic activity should reflect tectonic evolution of the back arc spreading to form the Japan Sea, and thus investigation of Ulreung island is significant from tectonic point of view as well.

The oldest igneous rocks is 2.7 Ma (Min, 1982) and then the Japan Sea spreading has already completed. However, the dated sample was collected from the subaerial lavas, and the island rises from 2000 m deep sea floor. Therefore, only a few to 5 percent of the entire volcanic edifice is now above sea level. Ulreung island construction could have started right after the Japan Sea spreading or even during the spreading. The erupted igneous materials should carry

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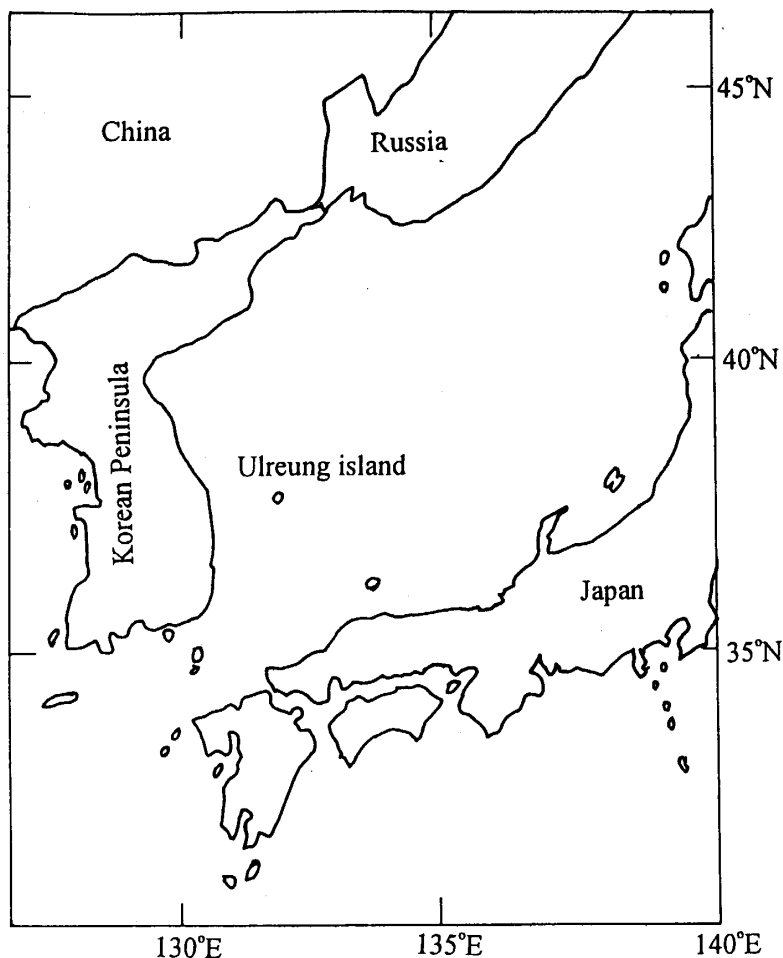


Fig. 1 Location map of Ulreung island.

valuable, physical and chemical information of the mantle beneath the Japan Sea, and possibly the information of what was going on in the mantle during the spreading. It is important to decipher the recorded information in the igneous rocks to understand how the Japan Sea spreading proceeded as well.

We have collected a number of the volcanic rocks and the associated plutonic inclusions from Ulreung island in pursuit for what took place in the mantle during the spreading, and to contribute to the tectonic understanding of the back arc spreading. In this report we present the analytical results of the major and trace element of some of the rocks from Ulreung island, Korea.

## II. Samples

Topographical descriptions as well as geological frameworks are available elsewhere (e.g., Lee, 1954; Harumoto, 1970; Won and Lee, 1984; Kim, 1985). The samples used in this experiments range from alkali basalts, trachybasalts, trachyandesites, trachytes, and phonolites. Subaerial erupted lavas starts with alkali basalt and trachybasalt, and trachyandesite eruptions followed with a minor amount of trachyte. Both trachyte and phonolitic rocks are dominant in the island, and a small amount of leucite bearing trachyandesite erupted on the top of the volcanic

island. The leucite bearing trachyandesite includes some comagmatic plutonic inclusions. Those were also analyzed. It should be significant to point out that occurrence of leucite as a phenocryst is extremely rare in northwestern Pacific rim. Mineralogical description will be made in detail in a separate paper.

### III. Experimental Procedure

The rock samples were analyzed on the fused glass beads by XRF spectrometric method according to Ohba and Ban (1997). Accelerating voltage was 50 kV and filament current was 50 mA for both major and trace elements. The major elements were determined by conventional calibration line method. Matrix effects were collected using background scattering for the trace elements. Accuracy and precision will be published elsewhere by Ohba (in preparation).

### IV. Results

The analytical results of the rocks are presented in Table 1 and Table 2. Ignition losses are not measured and not included in the tables and total iron is expressed as  $\text{Fe}_2\text{O}_3$ . Since  $\text{SiO}_2$  content does not directly related with the degree of crystallization, the solidification indices were shown with the results. Although the compatible elements like Ni and Cr were determined for the basic rocks, those in the differentiated rocks are below detection limit.

The volcanic rocks of the island range in  $\text{SiO}_2$  content from 42 to 61. Most of them are rather rich in  $\text{Al}_2\text{O}_3$ , and some basic one are highly enriched in  $\text{TiO}_2$ . Although a few basic basalts contain more than several wt. % MgO, the remaining ones are poor in MgO. Total  $\text{Fe}_2\text{O}_3$  exceeds MgO content for all the samples. The rocks are characterized by enriched alkaline elements.  $\text{Na}_2\text{O}$  content ranges from 2.02 wt. % (alkali basalt) to 6.71 wt. % (phonolite), and  $\text{K}_2\text{O}$  from 1.10 wt. % to 6.48 wt. %.  $\text{Na}_2\text{O}$  content seems little more than tripled, and  $\text{K}_2\text{O}$  content increases more than six times. Such highly potassic volcanic rocks are rather rare in circum Japan Sea region, but similar rock suite can be recognized from Iki island (Aoki, 1959), and Jeju island (Lee, 1983). However, most of the rocks from both localities are more enriched in sodium than potassium, and potassium content hardly exceeds sodium content. This is contrasted with highly potassic nature of the Ulreung volcanic suite. Many trachytes from Ulreung island have more potassium than sodium.

Two of the xenoliths are gabbroic, and the other is a monzonitic rock. The gabbroic ones are poor in  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ , but rich in  $\text{TiO}_2$ . The monzonitic rock is rather enriched in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , but not so rich in  $\text{TiO}_2$  as the gabbroic ones. Since they have common chemical characteristics to the volcanic suite, they must be consanguineous with the eruptives. Although they are rather poor in the incompatible elements compared with the volcanics, they have still high abundances of the incompatible elements; the inclusions are not simple cumulated comagmatic rocks.

Table1. Analytical Results of the Rocks from Ulreung Volcanic Island

Sample number	U7 U005	U17 U004	U25	U24	U22	U20 U305	U8 U302	U23 U301	U11 U303	U15 U202	U21	U9	U12 U204
comment	xenolith			xenolith	xenolith							xenolith	
SiO <sub>2</sub>	43.75	43.22	39.68	41.17	42.98	43.56	46.92	48.96	52.24	55.52	55.41	55.55	57.19
TiO <sub>2</sub>	3.31	3.27	5.60	4.63	3.16	3.60	3.25	3.23	2.39	1.21	1.13	1.06	0.96
Al <sub>2</sub> O <sub>3</sub>	12.82	15.00	12.11	13.79	19.10	14.46	17.34	17.45	17.99	18.03	17.39	17.42	19.10
Fe <sub>2</sub> O <sub>3</sub>	13.16	11.85	18.58	17.48	12.64	13.24	10.25	9.12	6.71	6.16	6.03	5.82	4.63
MnO	0.15	0.19	0.14	0.17	0.12	0.19	0.24	0.20	0.24	0.15	0.17	0.16	0.15
MgO	8.86	6.51	7.44	7.10	5.01	4.81	2.92	2.57	1.91	2.20	2.24	2.07	1.11
CaO	11.22	12.72	14.25	10.84	12.26	11.23	9.28	8.32	5.82	3.95	4.00	3.43	2.94
Na <sub>2</sub> O	2.53	1.36	1.44	2.06	2.02	3.20	3.98	4.42	5.23	5.04	5.70	5.72	5.72
K <sub>2</sub> O	1.10	2.15	1.06	1.77	1.35	1.14	1.38	1.20	1.94	5.36	5.68	6.13	6.01
P <sub>2</sub> O <sub>5</sub>	0.60	0.62	0.96	0.48	0.30	0.75	1.08	1.11	0.83	0.40	0.32	0.33	0.27
	97.49	96.87	101.25	99.48	98.92	96.17	96.64	96.55	95.29	98.02	98.06	97.69	98.08
Ni	181	115	5	80	10	88	7	20	2	19	26	21	3
Cr	293	241	15	352	16	160	4	18	n.d.	26	29	29	3
Zr	251	253	182	188	345	243	287	128	418	346	368	364	526
Y	21	23	24	20	31	22	28	22	32	23	27	26	26
Nb	52	55	32	41	88	56	72	24	108	98	110	110	119
Rb	10	35	41	46	134	25	115	48	174	96	179	211	165
Sr	749	820	624	729	1077	913	1102	1114	997	471	373	375	446
Ba	665	724	339	554	1032	884	1020	430	1281	650	485	516	683
FeO/MgO	1.34	1.64	2.25	2.22	3.20	2.48	3.15	2.27	3.17	2.52	2.42	2.53	3.76
Sl	34.5	29.8	26.1	25.0	23.8	21.5	15.8	14.8	12.1	11.7	11.4	10.5	6.3

n.d.: not detected

Table2. Analytical Results of the Rocks from Ulreung Volcanic Island

Sample number	U6 U206	U4 U203	U2 U003	U19	U10 U001	U3 U009	U13 U007	U5 U002	U16 U006	U18 U205	U14 U201	U1 U011
comment	dyke											pumice
SiO <sub>2</sub>	57.85	57.75	57.85	60.88	59.92	61.01	61.24	60.70	60.75	60.67	59.40	58.62
TiO <sub>2</sub>	0.84	0.85	0.84	0.63	0.56	0.62	0.65	0.54	0.47	0.41	0.36	0.41
Al <sub>2</sub> O <sub>3</sub>	19.20	19.18	19.15	16.75	18.28	18.14	18.21	17.93	17.87	18.03	18.72	19.33
Fe <sub>2</sub> O <sub>3</sub>	4.23	4.24	4.19	6.22	4.22	3.54	3.61	3.84	3.68	4.10	4.21	3.23
MnO	0.15	0.15	0.15	0.12	0.18	0.21	0.19	0.24	0.18	0.23	0.18	0.18
MgO	0.90	0.89	0.88	0.80	0.75	0.55	0.53	0.51	0.39	0.38	0.38	0.32
CaO	2.57	2.58	2.57	2.55	1.55	1.25	1.24	1.22	0.72	1.21	1.47	1.47
Na <sub>2</sub> O	5.81	5.79	6.11	5.15	5.43	5.82	6.11	6.38	6.71	6.17	6.37	5.33
K <sub>2</sub> O	6.15	6.15	5.85	4.50	6.48	6.46	6.44	6.11	5.83	5.82	6.35	6.31
P <sub>2</sub> O <sub>5</sub>	0.23	0.22	0.22	0.21	0.19	0.11	0.13	0.10	0.09	0.07	0.09	0.07
	97.92	97.79	97.81	97.82	97.55	97.71	98.35	97.57	96.70	97.09	97.52	95.25
Ni	2	n.d.	1	n.d.	n.d.	n.d.	n.d.	2	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zr	532	546	550	597	437	498	502	804	655	616	696	597
Y	25	25	27	40	32	35	36	49	49	46	35	28
Nb	122	123	125	92	108	121	123	188	157	149	156	148
Rb	161	171	168	119	119	125	126	165	173	139	169	176
Sr	356	344	328	291	112	36	29	2	15	43	45	71
Ba	576	503	477	911	217	61	64	43	37	43	75	120
FeO/MgO	4.21	4.28	4.28	7.00	5.07	5.79	6.15	6.78	8.49	9.84	9.99	9.05
Sl	5.3	5.2	5.2	4.8	4.4	3.4	3.2	3.0	2.3	2.3	2.2	2.1

n.d.: not detected

### V. Discussion

The basic rocks contain only 1 or 2 wt.% Na<sub>2</sub>O and K<sub>2</sub>O. Therefore, they are clearly different from the ultrapotassic rocks reported from African rift (Thompson et al., 1984; Mitchell, 1985). Although the Ulreung volcanics contain kaersutite, biotite, leucite and nepheline, they have no K-richeterite, or phlogopite either. The evolved rocks are considerably enriched in K<sub>2</sub>O, but K<sub>2</sub>O/Na<sub>2</sub>O ratios are not so high as 3. Consequently, it will be inappropriate to name them as lamproite or lamprophyre (e.g., Scott-Smith and Skinner, 1984; Peccerillo and Manetti, 1985; Dawson, 1987; Foley et al., 1987). Interelement relations are examined to understand how the concentrations vary within the rock suite and to find a good parameter to estimate the degree of crystallization differentiation. See Fig. 2; SiO<sub>2</sub> content is usually a good parameter for

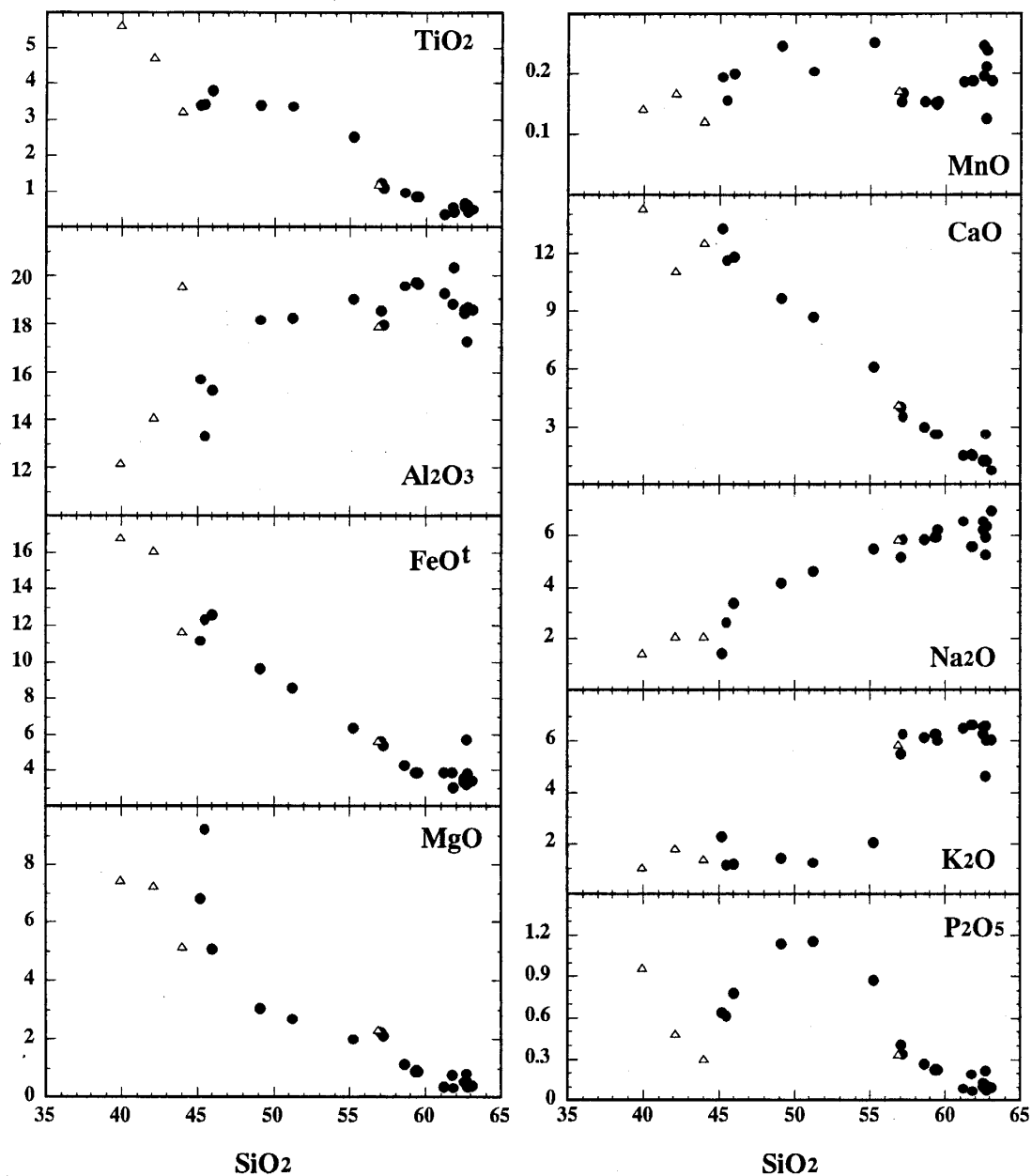


Fig. 2. Major elements versus SiO<sub>2</sub> variation diagram. Solid circle, volcanic rock; open triangle, plutonic inclusion. Both scales are wt. %.

crystallization. It seems the parameter works in the CaO–SiO<sub>2</sub> and FeO<sup>t</sup>–SiO<sub>2</sub>, and MgO–SiO<sub>2</sub> diagrams, but the K<sub>2</sub>O–SiO<sub>2</sub>, and Na<sub>2</sub>O–SiO<sub>2</sub> relations demonstrate that the parameter works only in the narrow range (45 wt.% to 55 wt.%). Note the substantial compositional gap between 56 and 57 of the parameter in the K<sub>2</sub>O–SiO<sub>2</sub> diagram. Also the data points scatter considerably between 57 and 63 in K<sub>2</sub>O–SiO<sub>2</sub>, Na<sub>2</sub>O–SiO<sub>2</sub>, and some other diagrams. Similar scattering is promptly recognizable in the trace elements–SiO<sub>2</sub> diagrams in Fig. 3. The chemical variations of such highly incompatible elements as Nb, Zr, and Y seem smooth between 45 and 55, but their trends are complicated. In Y–SiO<sub>2</sub> diagram, Y abundance increases till SiO<sub>2</sub> reaches 55, then drops drastically and again starts to increase almost twice instantly while the SiO<sub>2</sub> changes from 62 to 63. Since none of the major mineral phases includes so much Y, there will be no proper reason to account for such decrease and prompt increase. Data scattering similar to those in the Na<sub>2</sub>O–SiO<sub>2</sub> and K<sub>2</sub>O–SiO<sub>2</sub> can be noticed in Nb–SiO<sub>2</sub>, Zr–SiO<sub>2</sub>, Zr–SiO<sub>2</sub> diagrams as well. Although the data scatter in Ba–SiO<sub>2</sub> and Rb–SiO<sub>2</sub> diagrams, this could be caused by different modal abundances of mica and k-feldspar: Ba and Rb are compatible with them.

The xenoliths are plotted in the low SiO<sub>2</sub> ranges in Figs. 2 and 3. They seem to be on the common variation trends in the most of major elements – SiO<sub>2</sub> and incompatible–SiO<sub>2</sub> diagram. In contrast, the xenoliths plot off the simple and coherent variations in Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, Cr–SiO<sub>2</sub>, and Ni–SiO<sub>2</sub> diagrams. They may not represent liquid magmas, but may be cumulated rocks from variably differentiated magmas.

Instead of the silica content parameter, how the solidification index (SI =  $100 \times \text{MgO} / (\text{MgO} + \text{FeO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ) works will be examined in Fig. 4. The solidification index is fairly a good parameter to evaluate the degree of crystallization for many and various kinds of rock suites. However, the data point similarly scatter or cluster in such diagrams as Al<sub>2</sub>O<sub>3</sub>–SI, K<sub>2</sub>O–SI, and Na<sub>2</sub>O–SI. Almost no improvement was recognized, and this should have been possibly caused by fractional crystallization of biotite and K-feldspar. No change in K<sub>2</sub>O abundances in the SI range of 36–15 is inconsistent with crystallization, and the abrupt increase of K<sub>2</sub>O between SI 13 and SI 12 cannot be accounted for by mineral fractionation observed as phenocrysts. Therefore, the practical fractionation process should be clarified in future. The gabbroic and monzonitic xenoliths are plotted between SI 30 and SI 25. The SI numbers are smaller than two basaltic rocks, and may imply that those xenoliths could have been precipitated from rather evolved magmas.

Let us emphasize the curiosity of the abrupt change of the K<sub>2</sub>O abundance of the Ulreung rock suite in Fig. 5 in which six LIL elements are plotted against K<sub>2</sub>O content. Excluding Sr, the other elements are highly incompatible. Since biotite and K-feldspar appear as phenocrysts in rather early differentiation stage, Ba starts to decrease in the middle of the crystallization course, and Rb does not increase much. Rb and K<sub>2</sub>O should change coherently. The data distribution in the Rb–K<sub>2</sub>O diagram, however, is substantially scattered and is conflict with the simple expectation. If both alkaline elements are evenly incorporated in the minerals, the data points should make a kind of linear distribution in the Rb–K<sub>2</sub>O diagram.

It should be significant to point out the compositional gap between 2.5 and 4.5 wt.% K<sub>2</sub>O.

Similar compositional gap can be recognized for Sr abundance between approximately 800 ppm to 500 ppm. This is nearly the equivalent gap to that of  $K_2O$ . In contrast, such a clear gap does not appear in the other incompatible elements- $K_2O$  diagrams. Although it seems as if there exists a gap in the diagram, it should be caused solely by the abrupt change of  $K_2O$ . Therefore, a complicated process will be required to increase  $K_2O$  content discontinuously, but Zr, Y, and Nb abundances continuously. Also the process should account for sudden drop of Sr abundance as well. During this sequence, Ba abundance should jump once and decrease very rapidly. Any possible and expected process will be highly elaborate.

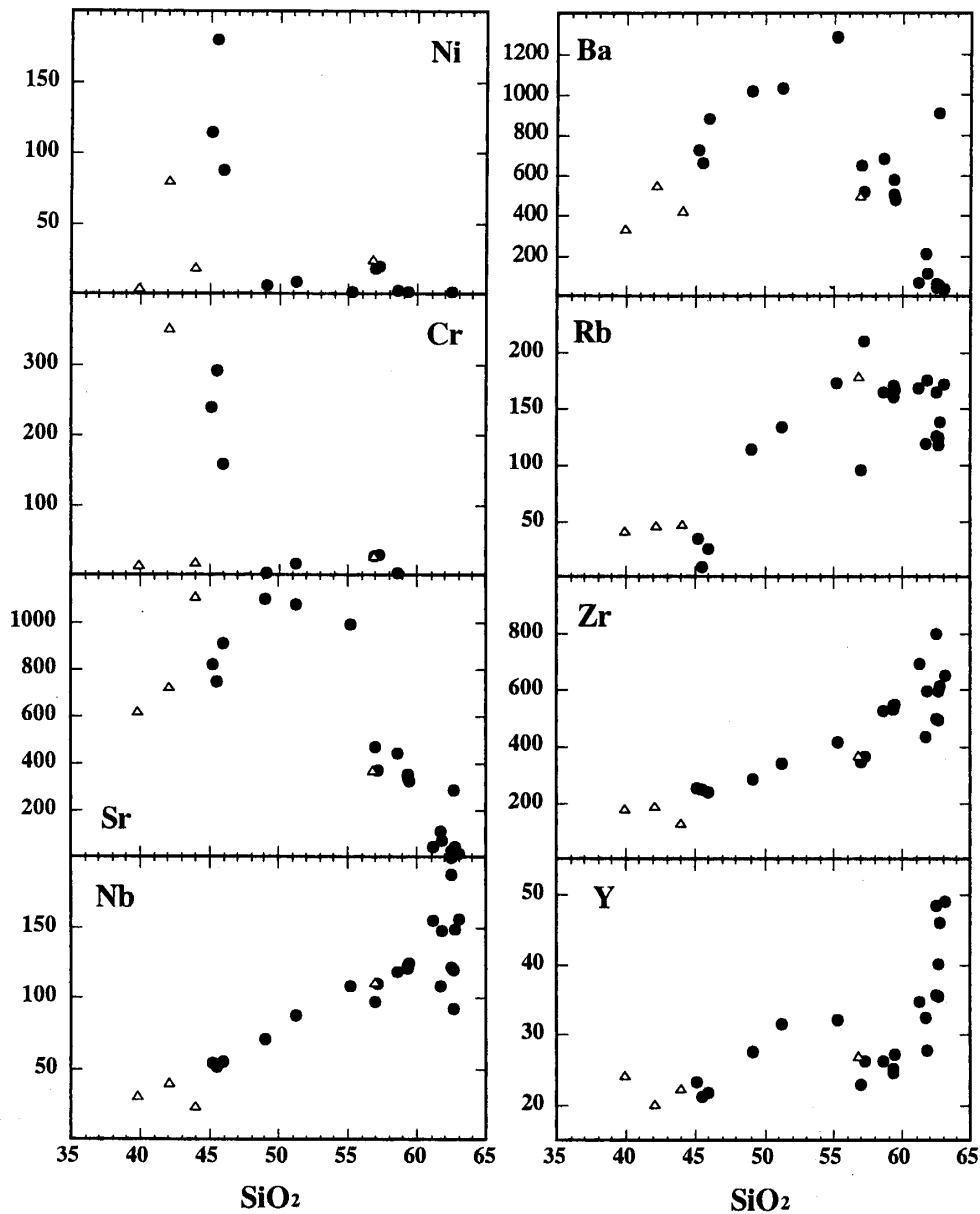


Fig.3. Trace elements versus  $SiO_2$  variation diagram. Symbols are the same as those in Fig.2. Vertical scale is ppm.



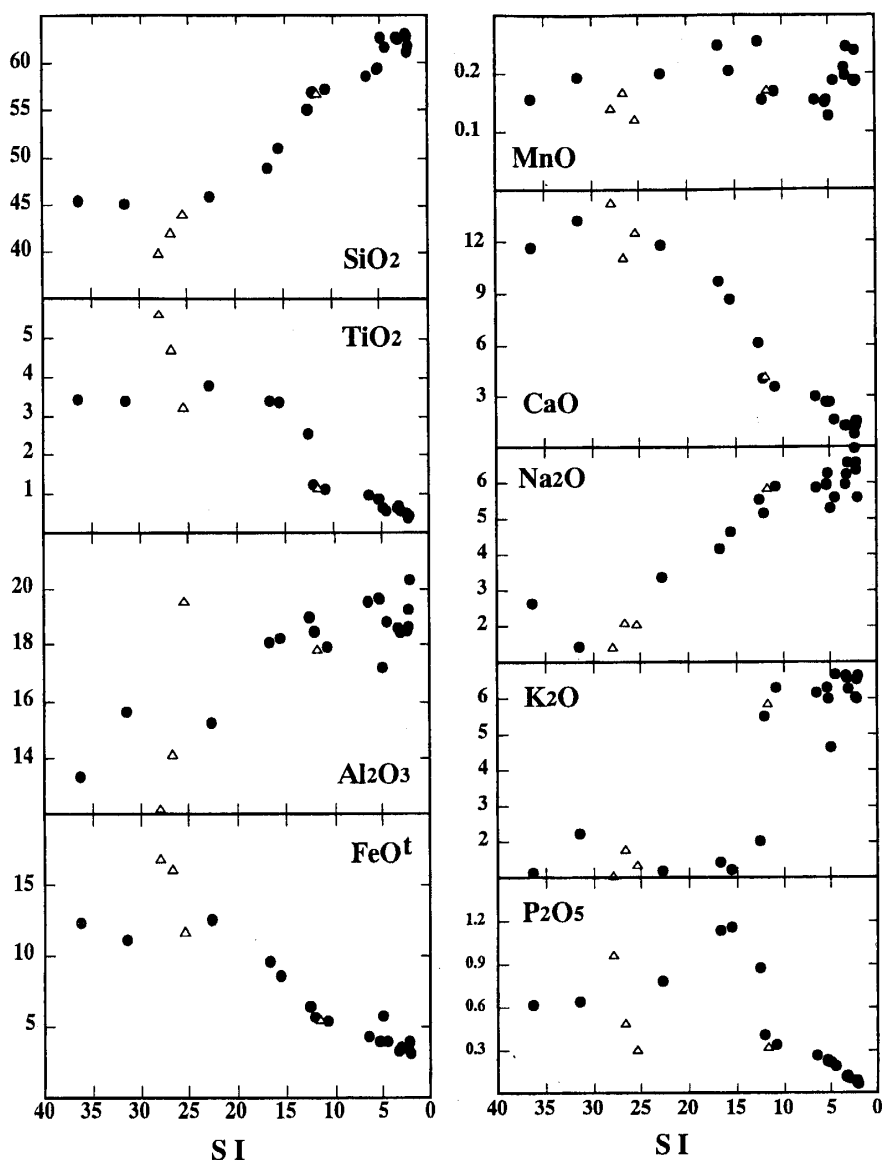


Fig.4. Major element versus solidification index variation diagram. Symbols are the same as those in Fig. 2. Horizontal scale is elemental ratios,  $SI = 100 \times MgO / (MgO + FeO + Na_2O + K_2O)$ .

The analytical results are plotted in Fig. 6 in which  $K_2O$ - $Na_2O$  relation is visualized. The division of the alkaline rocks into high-K series, K-series, and Na-series is the same as Middlemost (1975) proposed. According to Kim (1985), the volcanic suite of Ulreung island belongs to potassic series. The rocks make K enrichment curved alley (upward convex) in  $Na_2O$ - $K_2O$  diagram (Kim, 1985). However, our analytical results are inconsistent with his report. Although  $Na_2O$  increases gradually, significant increase of  $K_2O$  cannot be noticed before  $Na_2O$  exceeds 5 wt.%. Once  $Na_2O$  exceeds 5 wt.%,  $K_2O$  content jumps to more than 4 wt.%. Similar variations were found in some other places in the world like Iki island, Japan (Aoki, 1959), Jeju island Korea (Lee, 1983), Tristan da Cunha (Baker et al., 1964) and Gough island (Le Maitre, 1962). Those are well known for their highly alkalic rocks. Among them, the

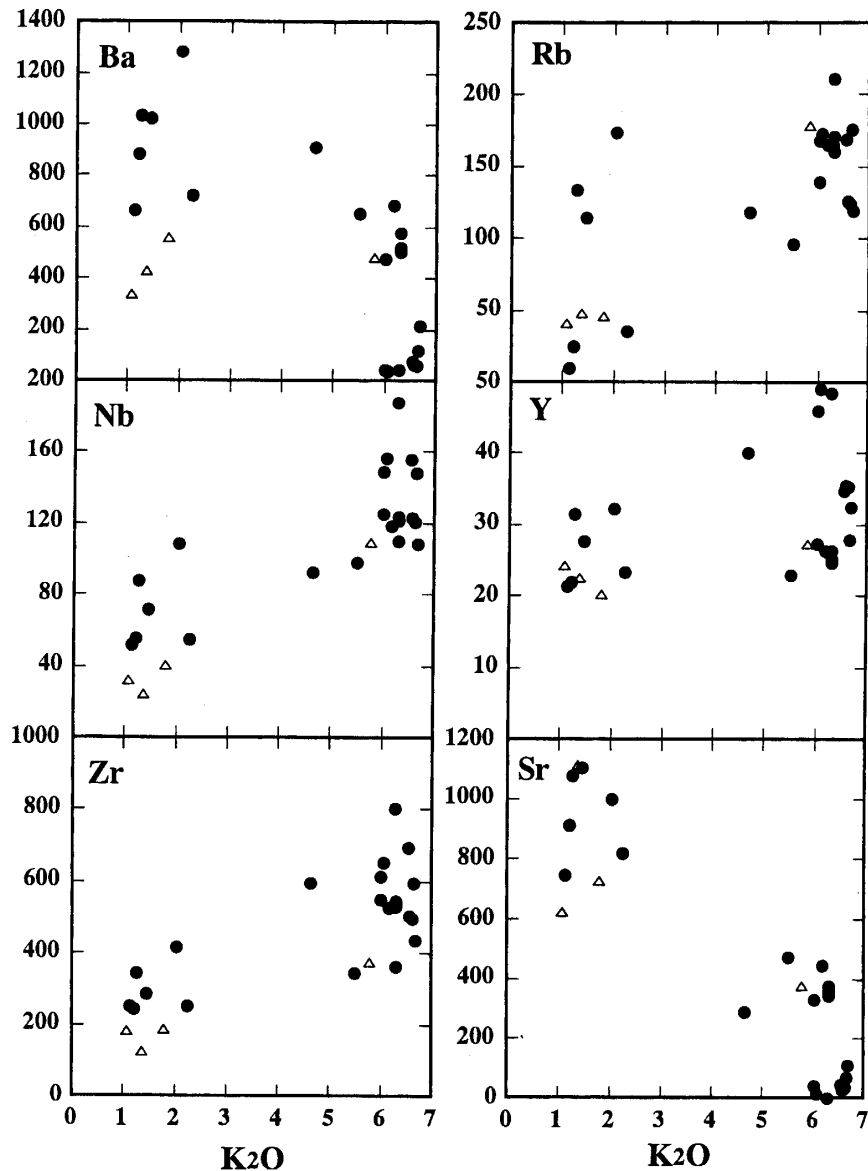


Fig. 5.  $K_2O$  versus  $Na_2O$  relation. Plutonic inclusions are not shown. Scales are wt.%.

Ultreung rock suite takes an extreme course of in  $Na_2O$ - $K_2O$  diagram, and the increasing trend from 2 to 5 wt.%  $Na_2O$  will not be reasonable. It is hardly possible to increase only  $Na_2O$  without  $K_2O$  enrichment by simple and acceptable processes.

The total variation of the Ulreung rock suite is presented in the AFM diagram (Fig. 7) together with plutonic inclusions. It is similar to the reported tendency (Kim, 1985), and common to the other alkaline rock suite elsewhere. In combination of three major parameters (alkalies,  $FeO^t$  and  $MgO$ ), no compositional gap is recognized. The variation trend seems consistent with the simple fractional crystallization. The most primitive rocks starts from 1.34 of  $FeO^t/MgO$  ratio. The rock suite takes an Fe-enrichment course, and after it reaches to the peak of 2.48 of  $FeO^t/MgO$ , it is heading toward the alkaline apex. While the trend approaches to the  $Na_2O+K_2O$  corner, the  $FeO^t/MgO$  ratio changes from 2-3 to 9-10. The change of the ratio

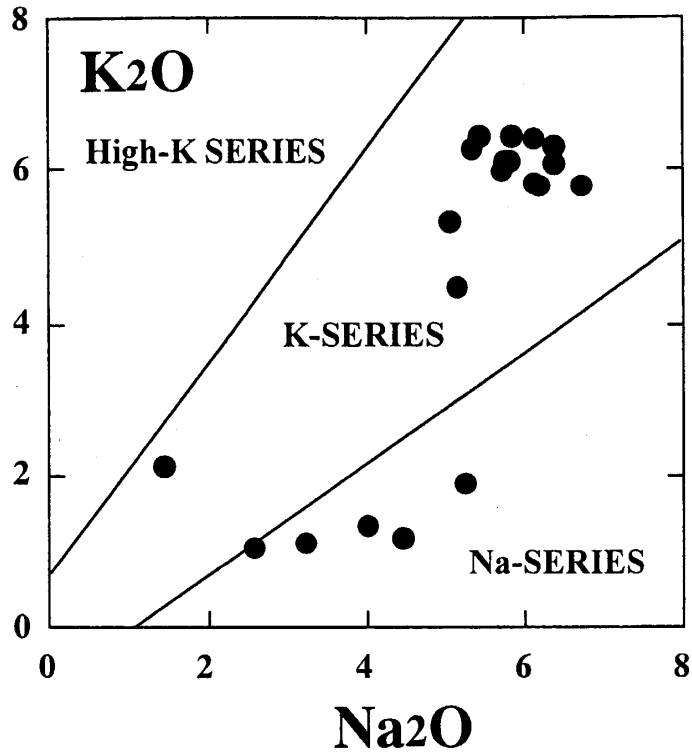


Fig. 6.  $K_2O$  versus  $Na_2O$  relation. Plutonic inclusions are not shown. Scales are wt.%.

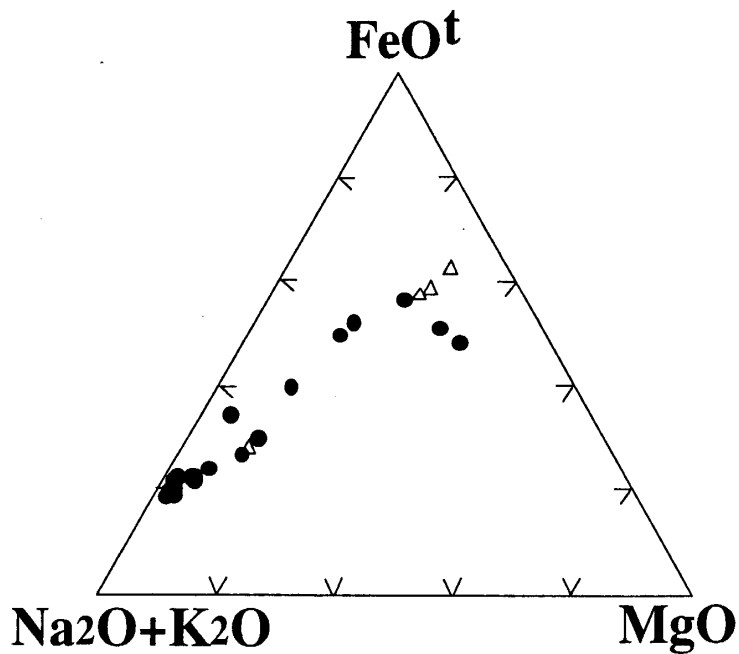


Fig. 7. A (alkaline elements) - F (total iron as  $FeO$ ) - M (magnesium) diagram. Symbols are the same as those in Fig. 2.

should be controlled by mafic mineral fractionation including abundant opaque mineral precipitation. The Fe-enrichment should imply the opaque mineral crystallization has been should be controlled by mafic mineral fractionation including abundant opaque mineral precipitation. The Fe-enrichment should imply the opaque mineral crystallization has been should be controlled by mafic mineral fractionation including abundant opaque mineral precipitation. The Fe-enrichment should imply the opaque mineral crystallization has been delayed like tholeiitic rock suite.

The xenolithic rocks are not on the general trend of the Ulreung volcanic suite, but on the extension from the end of the course to the most Fe-enriched point. This may imply that the inclusions are related with the rather differentiated rocks, but not related with basaltic rocks.

## VI. Summary

The Ulreung volcanic rock suite is characterized by highly alkalic nature. Especially, the evolved trachyte as well as phonolite contain more than 6 wt.%  $K_2O$  and  $Na_2O$ . If the igneous activity is related to Pacific plate subduction, the chemical feature and magma generation might be recognized as one variety of the island arc volcanism. However, it is not clear whether the subducted plate exists beneath Ulreung island, and thus very special reason will be needed to provoke igneous activity beneath Ulreung island. The Japan Sea spreading has ended probably long before the igneous activity of Ulreung island started (oldest available data, 2.4 Ma, Min, 1982). If the Ulreung island igneous activity started right after the Japan Sea has been completed, how the abundant incompatible elements were accumulated in the mantle source in a limited short period beneath Ulreung island must be accounted for. It will not be simple to concentrate  $K_2O$ , and the other LILE in the source mantle.

All the volcanic rocks are enriched in alkaline elements and the other LILE as well. The elemental variations generally seem to be consistent with simple fractional crystallization. It should be pointed out that significant compositional gap exists in  $K_2O$  content, but the gap was not recognized in the other LILEs. The observed discrepancy will be hardly explained if fractional crystallization differentiation plays a major role. Our chemical data are somewhat different from the reported data set (Kim, 1985) in  $K_2O$  content. No intermediately  $K_2O$ -enriched sample was found. Then, the volcanic rocks from the island are either highly enriched in  $K_2O$  or not so enriched in  $K_2O$ . In contrast,  $Na_2O$  content increases gradually in the rock suite. This chemical features will require complicated mechanisms.

## VII. Acknowledgements

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