Solubility of $\text{CaMgSi}_3\text{O}_8$ and $\square\text{Si}_4\text{O}_8$ endmembers in anorthite

Hideki MURAKAMI*, Mitsuyoshi KIMATA*, Susumu SHIMODA*,
Eiji ITO** and Satoshi SASAKI***

*Institute of Geoscience, The University of Tsukuba,
Ibaraki 305, Japan

**Institute for Study of the Earth Interior, Okayama University,
Misasa, Tottori-ken 682-02, Japan

***Research Laboratory of Engineering Materials, Tokyo Institute
of Technology, Midori-ku, Yokohama 227, Japan

Significant amounts of MgO, and excess SiO_2 and Al_2O_3 in anorthites from the island of Miyakejima are estimated by EPMA and X-ray diffraction analysis. The role in the crystal structure establishes Mg, Si and Al cations as $\text{CaMgSi}_3\text{O}_8$, $\square\text{Si}_4\text{O}_8$ and $\text{AlAl}_3\text{SiO}_8$ endmembers for the anorthite solid solution. Syntheses under dry conditions of anorthites along the joins $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\square\text{Si}_4\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{CaMgSi}_3\text{O}_8$ conducted to ascertaining the partial solubility limits of these endmembers in the solid solutions, compared with the anomalous anorthites from Miyakejima. The maximum limit of partial solubility of $\text{CaMgSi}_3\text{O}_8$ is about 25 mol% to $\text{CaAl}_2\text{Si}_2\text{O}_8$, and that of $\square\text{Si}_4\text{O}_8$ is nearly 8 mol%. Nevertheless inhomogeneous distribution of Mg cation within this single crystal has an implication for the unstable behavior of Mg cation in the anorthite structure. Chemical shift of $\text{MgK}\alpha 1$ in the synthetic anorthites affords infallible discrimination of solubility of $\text{CaMgSi}_3\text{O}_8$ endmember rather than $\text{MgAl}_2\text{Si}_2\text{O}_8$.

Condensation of natural occurrences and syntheses of plagioclases with small amounts of $\text{CaMgSi}_3\text{O}_8$ and $\square\text{Si}_4\text{O}_8$ components purifies that anorthites from Miyakejima may have been originally crystallized by super-cooling in SiO_2 -saturated and Mg-rich host magma at the high-temperature more than 1,000°C, and that the phenomenon in anorthite similar to Tschermak substitution, $\text{Mg} + \text{Si} \rightleftharpoons 2\text{Al}$, goes to prove the charge-coupled substitution of $\text{Mg} + \text{Si}$ in only tetrahedral sites. Emphasis is placed upon experimental verification and comparison to observed data is made where possible.

Keywords: Anorthite, $\text{CaMgSi}_3\text{O}_8$, $\square\text{Si}_4\text{O}_8$, Miyakejima, Chemical shift, Four-coordinated Mg

1. Introduction

During the last two decades, there has been extensive controversy about the extent of chemical deviation from the MT_4O_8 ideal formula of feldspar (Smith, 1974; Smith and Brown, 1988), where chemical analyses of most natural plagioclases show that the amount of MgO is less than 0.6 wt.%. Similarly, terrestrial feldspars with a few percent excess SiO_2

or Al_2O_3 have been reviewed. These data, however, are difficult to interpret because of the possibility of mechanical impurities in feldspars, and because of probable uncertainty to ± 0.3 wt.% of MgO by most electron microprobe analyses following the energy dispersive method (Zeng, 1985). The wavelength dispersive method provides more profound sensibility to detection limit of MgO, thus the results are certainly much more reliable (Smith and

Table 1a. Composition of the starting materials

Run	Composition of the starting materials	Method of synthesis
1	$\text{CaAl}_2\text{Si}_2\text{O}_8$ (85mol%) + $\square\text{Si}_4\text{O}_8$ (15mol%)	Dry synthesis method (Super-cooling experiments)
2	$\text{CaAl}_2\text{Si}_2\text{O}_8$ (85mol%) + $\text{CaMgSi}_3\text{O}_8$ (15mol%)	
3	$\text{CaAl}_2\text{Si}_2\text{O}_8$ (80mol%) + $\text{CaMgSi}_3\text{O}_8$ (20mol%)	
4	$\text{CaAl}_2\text{Si}_2\text{O}_8$ (70mol%) + $\text{CaMgSi}_3\text{O}_8$ (30mol%)	
5	$\text{CaMgSi}_3\text{O}_8$ (100mol%)	
6	$\text{CaAl}_2\text{Si}_2\text{O}_8$ (100mol%)	Floating zone method

Brown, 1988). Moreover enhancement of X-ray microdiffractometer (Max. 60 kV, 300 mA) with the PSPC detector enables us to determine mineral species from a single microcrystal of

about 20 μm size (Kimata *et al.*, 1990).

Anorthites from the island of Miyakejima are well-known as euhedral megacrysts very close to the endmember of plagioclase, $\text{CaAl}_2\text{Si}_2\text{O}_8$, and as the sample often used in determining the crystal structure of anorthite (*e.g.*, Foit and Peacor, 1967; Ribbe and Colville, 1968). However chemical compositions of these anorthite megacrysts have never been critically examined in detail.

A major focus of the present works was to develop penetrating insights into the anomalous solubility of MgO and SiO_2 composition in anorthite megacrysts from the Miyakejima, in favor of which syntheses of anorthites along join $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\square\text{Si}_4\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{CaMgSi}_3\text{O}_8$ conduced to ascertaining the partial solubility limits of these endmembers in the solid solutions. Our current work on anorthites concentrates on rigorous EPMA and X-ray diffraction analyses.

II. Field occurrence and petrography

Miyakejima, one of the Izu seven islands, comprises Quaternary volcanoes, and lies at an active island arc extending SSE from Japanese islands. The ejecta and lava flows are predominantly basalts. The eruption carrying the anorthite megacryst presently used is in the

Fig. 1. Photomicrographs of aggregates of acicular Mg-rich, Cu- and Cl-bearing micro-minerals (black) in thin-sectionized anorthite from Miyakejima. Viewed with crossed nicols. Photo B is ten times as large as C in photo A.

Table 1b. Run conditions and the results of experiments (Dry synthesis method)

Run	Starting temperature (°C)	Keeping time (hours)	Cooling rate (°C/hour)	Final temperature (°C)*	Products and size**
1	1550	120	1	1500	anorthite (fine) + glass
2	1550	5	5	1350	anorthite (micro)
3	1550	5	5	1350	anorthite (large)
4	1550	5	5	1350	anorthite (large)
5	1550	120	1	1500	cristobalite (fine) + glass

* After the experiments the products in a Pt crucible are quenched in the air.

** micro<10 μm, 10 μm<fine<40 μm, 40 μm<large

activity of 1940, and it created the Hyoutanyama volcano.

The basaltic lava is a dark-gray, melanocratic, olivine+anorthite-bearing rock, and accessory phases include hypersthene, augite and magnetite (Isshiki, 1960). To date, several minerals included by anorthite megacrysts from Miyakejima have been reported macro- and micro-scopically: olivine (Fo₈₂Fe₁₈), iron minerals (ilmenite or hematite?), clinopyroxene (Isshiki, 1960), native copper and unidentified micro-minerals (Murakami *et al.*, 1991). By appearance, these anorthite megacrysts are classified into two types: transparent and wine-red ones. The latter color is chiefly attributed to oriented flattening of native copper straggling in the wine red part (Murakami *et al.*, 1991). Aggregates of micro-minerals less than 1 μm which are of acicular shape and rich in Mg, Cu and Cl, are lining up in the red part of anorthite megacrysts (Fig. 1).

III. Syntheses of anorthites in the An-□Si₄O₈ and An-Mac (CaMgSi₃O₈) series

In order to examine the chemical anomaly

in Si and Mg of anorthites from Miyakejima, super-cooling experiments in the An-□Si₄O₈ and An-Mac systems were carried out following the dry-synthesis method at 1 atm in the electric furnace. Moreover the standard anorthite of CaAl₂Si₂O₈ composition as pure as possible was synthesized by the floating zone method. Starting materials were powdered mixtures of chemical reagents; calcium carbonate (CaCO₃, calcite), silicon dioxide (SiO₂, amorphous), aluminum hydroxide (Al(OH)₃, gibbsite and bayerite) and magnesium hydroxide (Mg(OH)₂, brucite). For synthesis of anorthite endmember, a small amount of Fe₂O₃ as the optical absorbent was added to the starting material following the floating-zone method.

Table 1c. Run conditions and the result of experiment (Floating zone method)

Run	Rotation rate (rpm)	Growth rate (mm/hour)	Temperature (°C)	Products and Size
6	400	0.28	1660	anorthite large***

The atmosphere was nitrogen and the temperature of anorthite melt was measured by using a pyro-meter.

*** 1cm<large

Table 2. Representative microprobe analyses of anorthites from Miyakejima

Sp.No.	121	124	127	128	130	132	135
SiO ₂	44.56	44.77	44.30	44.47	44.49	45.00	44.56
Al ₂ O ₃	34.82	34.90	35.36	34.96	35.24	35.03	34.96
FeO*	0.44	0.34	0.39	0.37	0.42	0.35	0.35
MgO	0.05	0.07	0.07	0.07	0.06	0.08	0.09
CaO	19.48	19.12	19.25	19.32	19.19	18.81	19.36
Na ₂ O	0.45	0.46	0.45	0.47	0.47	0.38	0.43
Total	99.80	99.66	99.82	99.66	99.87	99.65	99.75
Numbers of ions on the basis of eight O							
Si	2.067	2.075	2.053	2.063	2.060	2.082	2.065
Al	1.904	1.907	1.932	1.912	1.923	1.911	1.910
Fe	0.017	0.013	0.015	0.015	0.016	0.014	0.014
Mg	0.004	0.005	0.005	0.005	0.004	0.005	0.006
Ca	0.968	0.949	0.956	0.960	0.952	0.932	0.961
Na	0.041	0.042	0.040	0.042	0.043	0.035	0.039
Total	5.001	4.991	5.001	4.997	4.998	4.979	4.995

* Total iron as FeO

The conditions and products of each synthesis are summarized in Table 1. All phase identifications were made by the petrographic microscope, X-ray powder diffractometer, enhanced X-ray microdiffractometer (Kimata *et al.*, 1990) and EPMA.

IV. Chemical composition

Natural and synthetic anorthites were analyzed using JEOL JXA-8621 electron microprobe. The analytical conditions are the same as used by Murakami *et al.* (1991). Owing to an unavoidable problem of secondary fluorescence, there is considerable uncertainty on the iron contents in EPMA analyses (Smith and Brown, 1988). Moreover quantity of Fe in Miyakejima anorthites is so small that the FeO and Fe₂O₃ content cannot be determined by EPMA. Therefore, the Fe content was calculated as FeO in these anorthites. Probably some of the scatter in the data is attributable to individual differences in Fe²⁺/Fe³⁺ ratio. Assumption of Fe²⁺ in the presents anorthite leads to the minimum deviation from the MT₄O₈ ideal formula. Numbers of cations on the basis of eight oxygens have been estimated for the present anorthites. The fractions of

NaAlSi₃O₈, CaAl₂Si₂O₈, CaMgSi₃O₈, CaFeSi₃O₈, □Si₄O₈ and AlAl₃SiO₈ could be calculated by the following method: the amount of Al equal to all Na are combined to give the NaAlSi₃O₈. All Mg and treble amount of Si are subtracted as CaMgSi₃O₈, and so do total iron as Fe²⁺ and treble amount of Si as CaFeSi₃O₈. The remaining Al is used to form CaAl₂Si₂O₈. In case Al still remains, all the rest are used for making of AlAl₃SiO₈. Finally the residuary Si is consumed to form □Si₄O₈.

Representative compositions of the anorthites in question are summarized in Table 2. All analytical totals are ranging from 98.9 to 100.8 wt.% (Tables 2 to 7). Several analyses in Table 4 are of slightly less satisfactory stoichiometry, perhaps because of alkali instability against the electron beam. Microprobe analyses for all elements heavier than sodium are usually accurate to within 2 to 3 wt.% (Buseck *et al.*, 1980). Their statistical treatment contributes to penetrating the essential components. Actually, neither mean value less than one for Na+Ca in M-site nor less than four for Si+Al+Mg+Fe in T-sites, except for the case of AlAl₃SiO₈ endmember is produced in

Fig. 2a. X-ray element "map" for MgK α aggregates of acicular Mg-rich, Cu- and Cl-bearing micro-minerals in anorthite.

The examined area is in accord with the one in Fig. 1(A). White dotted line is electron microprobe traverse of Fig. 2b.

Fig. 2b. Electron microprobe traverse for MgK α across aggregates of acicular Mg-rich, Cu- and Cl-bearing micro-minerals in anorthite from Miyakejima.

The anorthite (D) around microminerals is depleted in Mg, while (N) distant from them is less.

Table 14. Their values strictly conform structural formula of feldspar (Tables 8 to 13).

The X-ray element map by MgK α radiation for the polished thin section of anorthite from Miyakejima is illustrated in Fig. 2a. As

perceived in comparison with Fig. 1, this mapping area represents two kinds of minerals; aggregates of acicular Mg-rich, Cu- and Cl-bearing micro-minerals in the preferred orientation (Murakami *et al.*, 1991), and relatively Mg-poor anorthite adjoining to them. Generally speaking, compositional zoning is not developed in anorthite megacrysts from Miyakejima. The anorthite hereabout can be classified broadly into two divisions (Fig. 2b); one is adjacent to Mg-rich micro-minerals (D1 and D2) and fatally depleted in Mg, while the other is distant from them (N) and is of Mg-bearing normal type. Except for this Mg-variety, lack of chemical zoning common to natural plagioclase limited is within a single crystal.

The analyses of synthetic anorthite prepared by the floating-zone method are given in

Table 3. Representative microprobe analyses of synthetic anorthites with ideal formula

Sp.No.	1	4	19	31	35	56	I.F.*
SiO ₂	42.66	42.72	43.54	42.27	43.02	43.30	43.2
Al ₂ O ₃	36.27	36.30	36.51	36.69	36.18	36.75	36.6
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.0
CaO	19.87	19.98	20.08	20.34	19.87	20.06	20.2
Na ₂ O	0.10	0.08	0.07	0.08	0.13	0.09	0.0
Total	98.90	99.08	100.20	99.38	99.20	100.20	100.0
Numbers of ions on the basis of eight O							
Si	1.996	1.995	2.010	1.972	2.005	2.000	2.000
Al	2.000	1.998	1.986	2.018	1.988	2.001	2.000
Fe	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.996	1.000	0.993	1.017	0.993	0.993	1.000
Na	0.009	0.007	0.006	0.007	0.012	0.008	0.000
Total	5.001	5.000	4.995	5.014	4.998	5.002	5.000

* Ideal formula

Table 4. Representative microprobe analyses of synthetic Mg-bearing anorthites

Sp.No.	1	4	8	9	15	19	57
SiO ₂	44.81	44.92	44.27	44.50	43.95	43.69	48.38
Al ₂ O ₃	35.01	32.76	35.70	35.30	35.67	35.43	27.49
MgO	0.37	1.48	0.26	0.37	0.29	0.34	3.74
CaO	19.45	20.39	19.78	19.92	19.85	20.06	20.04
Na ₂ O	0.26	0.23	0.18	0.17	0.17	0.17	0.14
Total	99.90	99.78	100.19	100.26	99.93	99.69	99.78
Numbers of ions on the basis of eight O							
Si	2.068	2.087	2.041	2.051	2.033	2.028	2.241
Al	1.905	1.794	1.939	1.917	1.945	1.939	1.501
Mg	0.025	0.103	0.018	0.026	0.020	0.023	0.258
Ca	0.962	1.015	0.977	0.983	0.984	0.998	0.994
Na	0.023	0.021	0.016	0.015	0.015	0.015	0.013
Total	4.983	5.020	4.991	4.992	4.997	5.003	5.007

Table 3, together with the ideal formula. Despite of Na included in a small amount, the crystal hereat was standardized in the present study.

Chemical compositions of synthetic Mg-bearing anorthites are given in Table 4. Every confidence is reposed in that these synthetic anorthites must be in solid solution, because no exsolved Mg-oxide phase has been observed under the microscope with high magnification (e.g. VANOX made in Olympus, Fig. 3a). They are notable for their relatively high Mg contents as compared with Miyakejima anorth-

ites. The maldistribution of Mg within a single crystal of synthetic anorthite informs us of the unstable behavior of Mg cation in the framework silicate (Fig. 3b). To a rough approximation, the maximum limit of partial solubility of CaMgSi₃O₈ is about 25 mol% to CaAl₂Si₂O₈.

Chemical compositions of synthetic anorthites in the An-□Si₄O₈ series are shown in Tables 5 to 7. The product of this experiment is constituted of anorthite and glass (Fig. 4). The synthesized anorthites are divided into two types; one is tabular crystals with excess SiO₂

Fig. 3a. Photomicrographs of synthetic Mg-bearing anorthite thin-sectionized. Viewed with plane-polarized light.

Fig. 4. Photomicrographs of thin section of synthetic anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\square\text{Si}_4\text{O}_8$ series). Viewed with plane-polarized light (A) and crossed nicols (B).

Fig. 3b. X-ray element "maps" for $\text{MgK}\alpha$ of synthetic Mg-bearing anorthite. A2 and B2 are as A1 and B1 in Fig. 3a.

Table 5. Representative microprobe analyses of synthetic anorthites containing excess SiO₂

Sp.No.	2	5	20	42	49	52	55
SiO ₂	47.29	47.23	45.35	46.50	47.23	48.03	46.33
Al ₂ O ₃	33.93	33.88	34.82	34.30	33.50	33.29	35.50
FeO*	0.15	0.15	0.06	0.13	0.05	0.08	0.10
CaO	18.59	18.60	19.09	18.43	18.39	18.18	18.73
Na ₂ O	0.32	0.28	0.27	0.35	0.38	0.28	0.17
Total	100.28	100.12	99.59	99.71	99.55	99.84	100.83
Numbers of ions on the basis of eight O							
Si	2.161	2.162	2.096	2.140	2.172	2.198	2.107
Al	1.828	1.828	1.897	1.860	1.816	1.796	1.903
Fe	0.006	0.006	0.002	0.005	0.002	0.002	0.004
Ca	0.910	0.912	0.946	0.909	0.906	0.891	0.913
Na	0.026	0.021	0.022	0.029	0.032	0.021	0.013
Total	4.931	4.929	4.963	4.943	4.928	4.908	4.940

* Total iron as FeO

Table 6. Representative microprobe analyses of synthetic anorthites containing excess SiO₂ and Al₂O₃

Sp.No.	4	5	6	9	11	24	33
SiO ₂	43.74	43.51	43.90	43.89	43.48	43.54	44.08
Al ₂ O ₃	36.84	37.13	36.84	36.97	37.14	36.64	37.04
FeO*	0.02	0.03	0.00	0.03	0.00	0.02	0.00
CaO	19.95	19.64	19.75	19.66	19.72	19.43	19.39
Na ₂ O	0.15	0.10	0.09	0.09	0.12	0.11	0.13
Total	100.70	100.41	100.58	100.64	100.46	99.74	100.64
Numbers of ions on the basis of eight O							
Si	2.009	2.002	2.016	2.014	2.000	2.015	2.019
Al	1.994	2.014	1.994	1.999	2.013	1.998	2.000
Fe	0.001	0.001	0.000	0.001	0.000	0.001	0.000
Ca	0.982	0.968	0.972	0.966	0.972	0.963	0.952
Na	0.014	0.009	0.008	0.008	0.011	0.010	0.012
Total	5.000	4.994	4.990	5.018	4.996	4.987	4.983

* Total iron as FeO

Table 7. Representative microprobe analyses of synthetic glasses

Sp.No.	2	13	29	30	40	50	56
SiO ₂	56.23	49.65	53.97	52.61	49.72	54.96	56.01
Al ₂ O ₃	26.34	31.59	28.16	29.05	31.52	27.56	26.27
FeO*	0.22	0.19	0.19	0.27	0.13	0.25	0.24
CaO	16.06	17.95	16.67	17.17	18.13	16.44	16.28
Na ₂ O	0.85	0.47	0.64	0.51	0.35	0.56	0.66
Total	99.50	99.85	99.63	99.61	99.85	99.77	99.46
Numbers of ions on the basis of eight O							
Si	2.538	2.287	2.444	2.392	2.271	2.481	2.531
Al	1.401	1.700	1.504	1.557	1.897	1.466	1.399
Fe	0.009	0.007	0.007	0.010	0.005	0.009	0.009
Ca	0.777	0.878	0.809	0.836	0.887	0.795	0.788
Na	0.049	0.036	0.050	0.039	0.028	0.042	0.049
Total	4.774	4.888	4.814	4.834	4.888	4.793	4.776

* Total iron as FeO

Fig. 5. Si/(Al+Ca)-plot for synthetic anorthites containing excess SiO₂.

(Table 5), and the other contains excess Al₂O₃, and elongated to c-axis (Table 6). Thus residual glasses are rich in CaO and SiO₂, and depleted in Al₂O₃ (Table 7). Synthetic anorthites containing an excess of Al₂O₃ ranging from 0.8 to 4.2 mol% gave a distinctively different feature. These have well-developed twinings on a very fine scale (less than 1.5 μm), along the c-axis, and the chemistry of excess Al₂O₃ did not appear as a separate alumina-bearing phase or corundum (α -Al₂O₃). The stoichiometry harmonizes well with chemical analyses, because

consumption of excess Al in minor amounts is assumed to be an AlAl₃SiO₈ endmember within the anorthite. Aluminum avoidance rule has no measurable effect on anorthite structure, on account of minor amount of excess Al₂O₃ and the quenching experiment from 1,500°C to room temperature.

The synthesized crystals are too fine to examine the distribution of Si within a single crystal. Implication from Fig. 5 infers that up to 8 mol% 4SiO₂ can be solved into anorthite.

V. X-ray crystallography

X-ray data for Mg-bearing anorthites were collected using an automated Enraf-Nonius CAD-4 diffractometer and graphite monochromatized MoK α radiation ($\lambda = 0.71069\text{\AA}$) and the four-circle diffractometer combined with synchrotron radiation at the BL-10A station, Photon Factory, KEK in Tsukuba City. The unit-cell parameters were determined by the least-squares refinement of 25 reflections in the 2θ range of 20 to 25°. Measurement of Bragg reflections on the automated four-circle X-ray diffractometer confirmed that the present synthetic anorthites containing Mg belong to a group of triclinic C $\bar{1}$ feldspars with $c = 7\text{ \AA}$. Detection of diffraction

Table 8. Crystal chemical data for anorthites from Miyakejima

Cell dimensions		Chemical composition (wt.%)		Endmember	Numbers of ions on the basis of eight O			
						(1)	(2)	
a(Å)	8.179(1)	SiO ₂	44.47	CaAl ₂ Si ₂ O ₈	93.8	Si	2.062	2.061
b(Å)	12.885(1)	Al ₂ O ₃	35.08	NaAlSi ₃ O ₈	4.0	Al	1.918	1.920
c(Å)	14.177(1)	FeO*	0.39	CaFeSi ₃ O ₈	1.5	Fe	0.015	0.015
α (°)	93.208(8)	MgO	0.07	CaMgSi ₃ O ₈	0.5	Mg	0.005	0.005
β (°)	115.886(9)	CaO	19.28	□Si ₄ O ₈	0.1	Ca	0.958	0.958
γ (°)	91.191(8)	Na ₂ O	0.44	AlAl ₃ SiO ₈	0.1	Na	0.040	0.040
V(Å ³)	1340.3	Total		99.73	100.0	Total		4.998 4.999

Numbers of measurement points 77

* Total iron as FeO

(1) observed

(2) calculated

Table 9. Crystal chemical data for synthetic anorthites*

Cell dimensions		Chemical composition (wt.%)		Endmember		Numbers of ions on the basis of eight O		
						(1)	(2)	
a(Å)	8.178(1)	SiO ₂	43.42	CaAl ₂ Si ₂ O ₈	99.3	Si	2.005	2.007
b(Å)	12.883(2)	Al ₂ O ₃	36.63	NaAlSi ₃ O ₈	0.7	Al	1.993	1.993
c(Å)	14.169(1)	FeO**	0.00	CaFeSi ₃ O ₈	-	Fe	0.000	0.000
α(°)	93.120(9)	CaO	20.07	□Si ₄ O ₈	-	Ca	0.993	0.993
β(°)	115.889(7)	Na ₂ O	0.08	AlAl ₃ SiO ₈	-	Na	0.007	0.007
γ(°)	91.259(8)							
V(Å ³)	1339.2	Total	100.20		100.0	Total	4.998	5.000

Numbers of measurement points 40

* Floating zone method

** Total iron as FeO

(1) observed

(2) calculated

Table 10. Crystal chemical data for synthetic Mg-bearing anorthites

Cell dimensions		Chemical composition (wt.%)		Endmember		Numbers of ions on the basis of eight O		
						(1)	(2)	
a(Å)	8.177(1)	SiO ₂	44.80	CaAl ₂ Si ₂ O ₈	92.9	Si	2.087	2.087
b(Å)	12.867(1)	Al ₂ O ₃	34.75	NaAlSi ₃ O ₈	2.8	Al	1.885	1.886
c(Å)	7.083(1)	MgO	0.34	CaMgSi ₃ O ₈	2.3	Mg	0.023	0.023
α(°)	93.214(8)	CaO	19.54	□Si ₄ O ₈	1.9	Ca	0.954	0.952
β(°)	115.835(1)	Na ₂ O	0.30	AlAl ₃ SiO ₈	-	Na	0.028	0.028
γ(°)	91.192(2)							
V(Å ³)	668.8(2)	Total	99.73		99.9	Total	4.977	4.976

Numbers of measurement points 62

(1) observed

(2) calculated

spots from synthetic anorthites with excess SiO₂ was escaped owing to micron-size of their single crystals. These atoms may disintegrate completely Si/Al ordering over the tetrahedral sites of anorthite. The relationship between their cell parameters and chemical compositions of synthetic and natural anorthites is represented in Tables 8 to 12. Lattice constants of their Mg-bearing anorthites seem to be synchronous with concentration of

CaMgSi₃O₈ in the solid solution.

VI. Chemical shift for Mg atom

In order to comprehend the coordination state of Mg in synthetic anorthites, chemical shift of MgK α lines was accurately estimated by EPMA. Measurement of their lines of Mg²⁺ octahedrally or tetrahedrally coordinated in oxide crystals was first tried using a high resolution spectrometer of the 2-crystal type

Table 11. Crystal chemical data for synthetic Mg-bearing anorthites

Cell dimensions		Chemical composition (wt.%)		Endmember		Numbers of ions on the basis of eight O		
						(1)	(2)	
a(Å)	8.176(1)	SiO ₂	44.69	CaAl ₂ Si ₂ O ₈	95.1	Si	2.065	2.065
b(Å)	12.860(1)	Al ₂ O ₃	35.23	NaAlSi ₃ O ₈	1.7	Al	1.919	1.919
c(Å)	7.073(1)	MgO	0.16	CaMgSi ₃ O ₈	1.2	Mg	0.012	0.012
α(°)	93.221(9)	CaO	19.55	□Si ₄ O ₈	1.9	Ca	0.966	0.963
β(°)	115.848(1)	Na ₂ O	0.19	AlAl ₃ SiO ₈	-	Na	0.017	0.017
γ(°)	91.184(2)							
V(Å ³)	668.3(2)	Total	99.82		99.9	Total	4.979	4.976

Numbers of measurement points 83

(1) observed

(2) calculated

Table 12. Crystal chemical data for synthetic Mg-bearing anorthites

Cell dimensions		Chemical composition (wt.%)		Endmember		Numbers of ions on the basis of eight O		
						(1)	(2)	
a(Å)	8.171(5)	SiO ₂	44.47	CaAl ₂ Si ₂ O ₈	96.3	Si	2.048	2.050
b(Å)	12.855(9)	Al ₂ O ₃	35.77	NaAlSi ₃ O ₈	1.6	Al	1.941	1.942
c(Å)	7.072(4)	MgO	0.12	CaMgSi ₃ O ₈	0.8	Mg	0.008	0.008
α(°)	93.10(6)	CaO	19.73	□Si ₄ O ₈	1.3	Ca	0.972	0.971
β(°)	115.72(5)	Na ₂ O	0.18	AlAl ₃ SiO ₈	-	Na	0.016	0.016
γ(°)	91.33(8)							
V(Å ³)	667.4(8)	Total	100.27		100.0	Total	4.985	4.987

Numbers of measurement points 105

(1) observed

(2) calculated

(Kawazoe *et al.*, 1981). Our samples were analyzed by wavelength dispersive techniques using the accelerating potential of 15 and 20 kV, probe currents of 5.0×10^{-8} and 1×10^{-7} A, respectively, and the defocused electron spot of about 8 μ m on the target surface. TAP crystal ($2d=25.757$ Å) was utilized to obtain the $K\alpha$ emission band of Mg atom, for which the detector was a gas-flow proportional counter made in JEOL. Measurements were made under the conditions of high vacuum, 3×10^{-5} Torr, and a

flow gas composited of 90% argon and 10% methane. Each peak-profile trace was derived from the average of five measurements. $MgK\alpha I$ line detected from akermanite, $Ca_2MgSi_2O_7$, (Kimata and Ii, 1981) was used as normalization of wavelength value obtained by Kawazoe *et al.* (1981).

Inasmuch as the feldspar structure consists of two kinds of tetrahedral and extraframework sites (Smith and Brown, 1988), two standards of Mg-silicates, where the Mg occupies

Table 13. Endmember presentation for synthetic anorthites containing excess SiO_2

Chemical composition (wt.%)	Endmember			Numbers of ions on the basis of eight O	
				(1)	(2)
SiO_2	46.85	$\text{CaAl}_2\text{Si}_2\text{O}_8$	90.8	Si 2.148	2.147
Al_2O_3	34.17	$\text{NaAlSi}_3\text{O}_8$	2.3	Al 1.847	1.847
FeO^*	0.10	$\text{CaFeSi}_3\text{O}_8$	0.4	Fe 0.004	0.004
CaO	18.57	$\square\text{Si}_4\text{O}_8$	6.2	Ca 0.912	0.912
Na_2O	0.29	$\text{AlAl}_3\text{SiO}_8$	0.2	Na 0.023	0.023
Total	99.98		99.9	Total 4.934	4.933

Numbers of measurement points 26

* Total iron as FeO

(1) observed

(2) calculated

Table 14. Endmember presentation for synthetic anorthites containing excess SiO_2 and Al_2O_3

Chemical composition (wt.%)	Endmember			Numbers of ions on the basis of eight O	
				(1)	(2)
SiO_2	43.73	$\text{CaAl}_2\text{Si}_2\text{O}_8$	97.2	Si 2.011	2.010
Al_2O_3	36.94	$\text{NaAlSi}_3\text{O}_8$	1.0	Al 2.002	2.002
FeO^*	0.01	$\text{CaFeSi}_3\text{O}_8$	0.0	Fe 0.001	0.000
CaO	19.65	$\square\text{Si}_4\text{O}_8$	0.6	Ca 0.972	0.972
Na_2O	0.11	$\text{AlAl}_3\text{SiO}_8$	1.2	Na 0.010	0.010
Total	100.44		100.0	Total 4.996	4.994

Numbers of measurement points 54

* Total iron as FeO

(1) observed

(2) calculated

these two sites respectively, are necessary for comparison of $\text{MgK}\alpha$ spectra. Majorite, $^{[VIII]}\text{Mg}_3^{[VI]}\text{Mg}^{[VI]}\text{Si}^{[IV]}\text{Si}_3\text{O}_{12}$, with the garnet structure (Ito *et al.*, 1987) has three magnesiums eight-coordinated and one six-coordinated, and akermanite, $\text{Ca}_2^{[IV]}\text{MgSi}_2\text{O}_7$, with the melilite structure, has one magnesium tetrahedrally coordinated. These two minerals were selected as the reference crystals.

$\text{K}\alpha\text{I}$ and $\text{K}\alpha\text{II}$ for Mg in akermanite and majorite, are shown in Figs. 6a and 6b, respec-

Fig. 6a. WD spectra for the $\text{K}\alpha\text{I}$ emission peaks of Mg in akermanite and majorite. Fig. 6b. WD spectra for the $\text{K}\alpha\text{II}$ emission peaks of Mg in akermanite and majorite.

tively. Chemical shift of $\text{MgK}\alpha$ caused by the difference in bond energy between four- and eight-coordinated states proved to be larger for $\text{MgK}\alpha\text{II}$ than for $\text{MgK}\alpha\text{I}$. In the present anorthites synthesized, however, $\text{MgK}\alpha\text{II}$ peaks were too weak to detect. Fig. 7 indicates that the wavelength range of $^{[IV]}\text{Mg}$ does not coincide with that of $^{[VIII]}\text{Mg}$ and that the present anorthites are plotted within the range of $^{[IV]}\text{Mg}$. Accordingly crystal-chemical behavior of Mg in anorthites leads to solubility of $\text{CaMgSi}_3\text{O}_8$ endmember rather than $\text{MgAl}_2\text{Si}_2\text{O}_8$.

Fig. 7. WD spectra and intensity for the $K\alpha$ emission peaks of Mg in akermanite, majorite and synthetic Mg-bearing anorthite.

VII. Discussion

For the feldspar endmember, varieties of crystal chemical substitutions are represented by all of the charge-balanced types; $M^0Si_4O_8$, $M^+T^{3+}Si_3O_8$, $M^{2+}T^{2+}Si_3O_8$, $M^{2+}T^{3+}_2Si_2O_8$ and $M^{3+}T^{3+}_3SiO_8$. The cation imperatively necessary for characterization of Miyakejima anorthites are as follows: M^0 =vacancy; M^+ =Na; M^{2+} =Ca; M^{3+} =Al; T^{2+} =Mg, Fe²⁺; T^{3+} =Al, Fe³⁺. Inasmuch as the current EPMA cannot distinguish between Fe²⁺ and Fe³⁺, quantity of Fe in Miyakejima anorthites was estimated as FeO. Therefore, in order to account for anomaly of SiO₂ and MgO in the present anorthites, the complexed substitutions are introduced:

- (1) $Na + Si \rightleftharpoons Ca + Al$,
- (2) $\square + 2Si \rightleftharpoons Ca + 2Al$,
- (3) $Mg + Si \rightleftharpoons 2Al$,
- (4) $Fe + Si \rightleftharpoons 2Al$,
- (5) $Al + Al \rightleftharpoons Ca + Si$

It was examined whether or not substitution (1) and (2) occur in Miyakejima anorthites (Figs. 8 and 9). There is no definite correlation between Na and Si (Fig. 8). Si cations are

approximately constant against increase of Na. However, a plot of (Ca + Na) as a function of Si (Fig. 9) reveals some significant correlation prevailing the coupled substitution. Accordingly subtraction of the correlation in Fig. 8 from that in Fig. 9 indicates that increase of Ca has linked in synchronous connection with decrease of Si, which amply justifies the complexed substitution (2) for Miyakejima anorthites. As a result, conjugated replacement in the extraframework and tetrahedral positions occurs with complete compensation of a surplus charge on a scheme;

This formula means the solid solution between silica (Si₄O₈) and anorthite, namely the existence of vacancy in M-site of anorthite. This interpretation is consistent with structural explanation by Megaw (1970) that coesite, a high-pressure polymorph of SiO₂, has the crystal structure similar to the feldspar with the same sub-unit. This phenomenon concerning the solid solution can be regarded as formation of a precursory Ca-feldspar to myrmekite (Smith and Brown, 1988), following the equa-

Fig. 8. Si/Na-plot for anorthites from Miyakejima.

Fig. 10. Al/(Si+Mg+Fe)-plot for anorthites from Miyakejima.

Fig. 9. (Ca+Na)/Si-plot for anorthites from Miyakejima.

Fig. 11. Al/(Si+Mg)-plot for a single synthetic crystal with the averaged composition of $An_{96.1}Mac_{3.9}$.

tion: $CaAl_2Si_6O_{16} \rightleftharpoons CaAl_2Si_2O_8 + 4SiO_2$.

The coupled substitutions (3) and (4) were examined by a plot of (Si+Mg+Fe) as a function of Al (Fig. 10), where the substitutions seem to occur at a first approximation. Not only $CaFeSi_3O_8$ but also $CaMgSi_3O_8$ is a candidate for endmembers of anorthite solid solutions.

For anorthite solid solutions in the

$CaAl_2Si_2O_8$ - $CaMgSi_3O_8$ series, plots of Al against Mg+Si elucidate the coupled substitution, $2Al \rightleftharpoons Mg+Si$, as shown in Figs. 11 and 12. This elucidation suggests that Mg coupled with Si can occupy tetrahedral Al sites in the crystal structure of anorthite, which is stringently enforced by two observations: (1) that chemical shift of $MgK\alpha I$ in the synthetic

Fig. 12. Al/(Si+Mg)-plot for several synthesized Mg-bearing anorthites.

anorthites is within the range of variability revealing the tetrahedral coordination of Mg cation and (2) that the amount of Mg in anorthite does not have any systematic relation to that of Na.

The anorthites of up to 10 mol% excess Al₂O₃ and of a well-developed twinning were synthesized by Bhatti *et al.* (1970). The electron diffraction by TEM indicates that this twinning is made up of albite twinning and Carlsbad twinning with a mirror imaging across the planes (010) and (100), respectively. The (100) mirroring, however, would seem to be in better accord with complex albite-Carlsbad twins than with Carlsbad twins (Torske, 1974). From its unique occurrence, the twinning is believed to be associated with the inclusion of an excess of Al³⁺ in the anorthite (Bhatti *et al.*, 1970 and Torske, 1974). The coupled substitution (5) is indeed rare in anorthites from Miyakejima, because very little excess Al₂O₃ gives rise to no systematic twinning in question.

VIII. Genesis of Mg-bearing and Si-excess anorthite

The minor element content of feldspars has

petrogenetic significance, especially with regard to the overall trend of crystal-liquid differentiation. Some attention has been directed to the role of Mg in the plagioclase structure. Sector-zoned plagioclase from submarine basalts involved the formula Ca(Fe, Mg)Si₃O₈ (Bryan, 1974), besides Mg-rich plagioclases were described from Allende meteorite (Yang, 1973) and lunar basalt (Bruno and Facchinelli, 1975). Success in synthesis of CaMgSi₃O₈ crystal was achieved by Sclar and Benimoff (1980), who have not published the crystallographic data in full. It should be surprised, however, that the upper solubility limit of MgO is 5.01 wt.% for plagioclase in meteorite (Miura, 1984). Plagioclases of such various occurrences, albeit difficult for substitution of ¹¹Mg in a feldspar (Burt, 1991), can accommodate magnesium following a substitution of the form, Mg + Si $\rightleftharpoons$ 2Al. As a mineralogical citizenship to one of minor feldspar components, MacKenzie's molecule (Mac), the name of CaMgSi₃O₈ component, was proposed by Zeng (1985), who synthesized plagioclase with up to 5.17 mol% CaMgSi₃O₈. This molecule seems to be more common to natural and synthetic plagioclases than Schwantke's component, Ca_{0.5}AlSi₃O₈ (Sch), (Schwantke, 1909). Survey of the existing data probes that the Mg-content in feldspars depends mainly on that in the host magma, the temperature of crystallization and the degree of recrystallization (Smith, 1974), especially reflecting very rapid cooling histories.

The component Ca_{0.5}AlSi₃O₈ introduced by Schwantke (1909) has been too uncertain in the analyses to permit demonstration of the existence (Smith and Brown, 1988). Stimulating is the report by Longhi and Hays (1979), however, that excess silica in synthetic anorthite can be incorporated up to Ca_{0.88}Na_{0.01}Al_{1.80}Si_{2.20}O₈, because the estimation of endmembers for this compound, in utter disregard of Na, casts light

on forming the solid solution of $0.76\text{CaAl}_2\text{Si}_2\text{O}_8 + 0.24\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$. Nevertheless anorthites with 15 mol% excess silica were synthesized (Bruno and Facchinelli, 1974), and some plagioclases from lunar basalts were found to contain up to 7 mol% $\square\text{Si}_4\text{O}_8$ (Beaty and Albee, 1980). These examples evince the intricacy of anorthite solid solution. The present inspection of Miyakejima anorthite (Fig. 9) signifies the existence of $\square\text{Si}_4\text{O}_8$ endmember in anorthite solid solution. Furthermore Kim and Burley (1971) reported about 5% excess SiO_2 in albite synthesized at 5 kb. and 670°C , and subsequently Chatterjee (1972) and Chatterjee and Johannes (1974) found that hydrothermal synthesis near 700°C can yield solid solutions between sanidine and quartz. This $\square\text{Si}_4\text{O}_8$ component seems to be common and realistic not only to plagioclases but also to alkali feldspars. Therefore in honor of Megaw (1970) for her penetration concerning the crystal structure of coesite and for her contribution to feldspar mineralogy and crystallography, it is natural that Megaw's molecule (Meg) should be given to the name of $\square\text{Si}_4\text{O}_8$ endmember in feldspars. The crystal structure of non-stoichiometric Eu-anorthite (Kimata, 1988) has lent further support for being identified as the solid solution between $\text{EuAl}_2\text{Si}_2\text{O}_8$ and $\square\text{Si}_4\text{O}_8$. Condensed summaries of the formation environment emerge that the solid solution of Ca-plagioclase with $\square\text{Si}_4\text{O}_8$ requires genetic conditions of more than $1,000^\circ\text{C}$ and super-cooling, and those of alkali feldspar does for hydrothermal condition of less than 700°C .

Simultaneous solubility of Meg and Mac molecules into anorthite was examined by Grove and Bence (1979), who showed that Meg and Mac components increase in anorthites of simulated lunar basalts with increased cooling rate and with lower temperature at constant cooling rate.

The solid solution between anorthite and

Mac molecule reminds us of Tschermak substitution, $\text{Mg} + \text{Si} \rightleftharpoons \text{Al} + \text{Al}$. This coupled substitution is common to mica, amphibole and pyroxene groups, and it defines that these Mg and Si cations can be simultaneously substituted for tetrahedral and octahedral Al. Such phenomenon in anorthite similar to Tschermak substitution, however, proves the coupled substitution in only tetrahedral sites. And so in the difference between the unit-cell volumes of the endmembers, the type with the tetrahedrally coupled cations $\text{Mg} + \text{Si}$ must be larger than with the $\text{Al} + \text{Al}$, which has been already demonstrated by the crystallographic relation of melilite groups in the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ series (Kimata and Ii, 1981 and 1982). Therefore the former substitution has an implication for preference of the crystal structure of larger thermal expansion. Representative occurrences of melilites are 1) such alkaline volcanic rocks as the nepheline-aggregate-lavas from the active Nyiragongo volcano (Sahama, 1978) and such carbonatites as okaite from the Oka complex, Quebec (Gold, 1966), 2) carbonaceous chondrites containing the CAI (calcium- and aluminum-rich inclusion) first crystallized from the solar nebula in the high-temperature state (Clark *et al.*, 1970; Grossman, 1975), and 3) a blast-furnace slag crystallized at atmospheric pressure and in the range $1,250$ - $1,450^\circ\text{C}$ (Butler, 1977). These occurrences indicate that high temperature above $1,000^\circ\text{C}$ and rapid cooling are requisite to this kind of Tschermak substitution in only tetrahedral sites of melilites. The general concept that high temperatures and low pressures favor low coordination (Mason, 1966) is applicable to the behavior of Mg cation. The crystallization over $1,000^\circ\text{C}$ is common to the rare silicates with tetrahedrally coordinated Mg cation (Kimata, 1983).

The euhedral anorthite megacrysts from Miyakejima substantially contain both Meg and Mac molecules, furthermore the lack of

chemical zoning appears to be entirely attributable to formation of these megacrysts under conditions of relatively rapid cooling, specially caused by super-cooling. A reasoning faith in the model that invokes some high-temperature and relatively shallow region beneath the volcanic front (Murakami *et al.*, 1991) is fortified not only by the present paragenesis with fused olivines, native coppers and unidentified Cu-rich, Mg- and Cl-bearing microminerals implicitly included by the host anorthite, but also by solubility of Meg and Mac molecules and the lack of chemical zoning.

IX. Conclusions

Such phenomenon in anorthite as similar to Tschermak substitution proves the coupled substitution in only tetrahedral sites; $\text{Mg} + \text{Si} \rightleftharpoons \text{Al} + \text{Al}$. Moreover a substitution of the type, $\text{Ca} + 2\text{Al} \rightleftharpoons \square + 2\text{Si}$, can accommodate excess Si in anorthite. Reviews of these natural occurrences and syntheses unfold that high temperatures above 1,000°C and rapid cooling are indispensable for realization of these substitutions.

Progress in studies of the petrogenetic importance of Mg-bearing and Si-excess feldspars has served to quicken the collective appetite for crystal-liquid differentiation. Stoichiometric arguments alone cannot determine whether these Mg and Si cations occupy specific tetrahedral sites. Quantitative determination of their contents and states in feldspars at lower-crust conditions must await improvements in both experimental and simulation techniques proffering their direct evidences.

Chemical shift of $\text{MgK}\alpha$ I affords infallible discrimination of the coordinated sites common to silicates, namely eight-coordinated and tetrahedral sites. This method serves as a useful tool for attempts at understanding and optimizing the crystallographic sites occupied

by Mg^{2+} cation.

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灰長石における CaMgSi₃O₈, □Si₄O₈ 端成分の固溶

村上英樹・木股三善・下田 右・伊藤 英司・佐々木 聡

合成された純粋な灰長石, それぞれ MgO, SiO₂ に富んだ灰長石を, EPMA と四軸自動 X 線回折装置を用いて化学組成と格子定数の測定を行い, 三宅島産灰長石との比較を行った。複合イオン置換に基づく検討から, 天然及び合成の灰長石は, Mg を CaMgSi₃O₈, 過剰の Si は □Si₄O₈ 端成分として, 固溶する可能性が指摘された。さらに Mg に対するこの端成分を確認するため, EPMA による Mg の化学シフトを解析した。その結果, 合成灰長石に固溶される Mg は, オケルマナイト (Ca₂MgSi₂O₇) 中の Mg と同じ四配位席を占有することが示唆された。また, X 線単結晶回折法からは, Mg の固溶量が増加するに従って, 単位格子の体積が増加する傾向が明らかになった。以上のことから灰長石における Mg の固溶は, 雲母, 角閃石, 輝石に認められる通常の Tschermak 置換, $\text{Mg} + \text{Si} \rightleftharpoons 2\text{Al}$, とは異なり, 四配位席だけの Tschermak 置換が, メリライトと同様に灰長石においても成立することを明示している。