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Groundmass pargasite in the 1991–1995 dacite of Unzen volcano: phase stability experiments and volcanological implications

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Abstract

Pargasite commonly occurs in the dacitic groundmass of the 1991–1995 eruption products of Unzen volcano. We described the occurrence and chemical compositions of amphibole in the dacite, and also carried out melting experiments to determine the low-pressure stability limit of amphibole in the dacite. The 1991–1995 ejecta of the Unzen volcano show petrographic evidence of magma mixing, such as reverse compositional zoning of plagioclase and amphibole phenocrysts, and we used a groundmass separate as a starting material for the experiments. Reversed experiments show that the maximum temperature for the crystallization of amphibole is 930°C at 196 MPa, 900°C at 98 MPa, and 820°C at 49 MPa. Compared with the experimental results on the Mount St. Helens dacite, present experiments on the Unzen dacitic groundmass show that amphibole is stable to pressures ca. 50 MPa lower at 850°C. Available Fe–Ti oxide thermometry indicates the crystallization temperature of the groundmass of the Unzen dacite to be 880 ± 30°C, suggesting that the groundmass pargasite crystallized at > 70 MPa, corresponding to a depth of more than 3 km in the conduit. The chlorine content of the groundmass pargasite is much lower than that of phenocrystic magnesiohornblende in the 1991–1995 dacite of Unzen volcano, indicating that vesiculation/degassing of magma took place before the crystallization of the groundmass pargasite. The present study shows that the magma was water oversaturated and that the degassing of magma along with magma mixing caused crystallization of the groundmass amphibole at depths of more than 3 km in the conduit. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: pargasite; Cl content of amphibole; degassing; magma mixing; groundmass crystallization; Unzen volcano

1. Introduction

Amphibole is a common phenocryst component of calc-alkalic andesites and dacites (Jakes and White, 1972; Sakuyama, 1983). The 1991 dacite of Unzen volcano, however, contains pargasite in the ground-mass along with phenocrystic magnesiohornblende. The presence of amphibole in the groundmass is unusual, because the crystallization of amphibole generally requires high water pressures (e.g., Helz, 1982), whereas groundmass minerals are commonly

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Fig. 1. X-ray mapping of the groundmass of the 5/24, 1991 dacite lava of Unzen volcano. X-ray intensity of Al K α , Ca K α , Si K α , and Fe K α are shown. Fe–Ti oxides (high Fe), amphibole (moderate Fe, Ca, Al, low Si), orthopyroxene (moderate Fe, low Ca, Al), Ca-rich pyroxene (high Ca low Al), plagioclase (high Ca, Al, low Si, Fe), and matrix glass are discerned. Note that most of the amphibole crystals are corroded, whereas orthopyroxene crystals have idiomorphic outline.

920113	920113	951017	951017	951017	951017
gmhb-	gmhb-	hb-1-1c	hb-1-4c	gmhb-	gmhb-
4c gm	4r gm	phen-c	phen-c	2c gm	2r gm
42.13	43.21	48.59	47.00	42.74	43.76
2.45	2.37	1.16	1.29	2.12	2.32
12.52	11.19	6.98	7.92	12.44	11.21
13.89	13.85	13.60	14.86	12.67	13.31
0.24	0.23	0.49	0.57	0.16	0.22
12.57	13.04	14.54	13.47	13.83	14.06
11.01	10.97	10.81	10.88	11.29	11.01
2.10	2.00	1.33	1.49	2.27	2.06
0.61	0.55	0.45	0.59	0.40	0.45
0.06	0.07	0.06	0.08	0.05	0.10
0.02	0.03	0.07	0.08	0.02	0.02
97.59	97.50	98.08	98.23	97.99	98.51
6.257	6.411	7.078	6.911	6.279	6.403
1.743	1.589	0.922	1.089	1.721	1.597
0.449	0.367	0.277	0.283	0.433	0.337
0.274	0.264	0.127	0.143	0.234	0.256
1.725	1.719	1.657	1.827	1.557	1.629
0.03	0.029	0.06	0.071	0.02	0.027
2.783	2.883	3.156	2.953	3.028	3.066
1.752	1.745	1.688	1.715	1.778	1.726
0.605	0.574	0.376	0.425	0.646	0.585
0.116	0.104	0.083	0.11	0.075	0.084
15.734	15.685	15.424	15.527	15.771	15.710
0.617	0.626	0.656	0.618	0.660	0.653

Table 1 Chemical composition of amphibole in the 1991–1995 eruption products of Unzen volcano

91524

gmhb-

4r gm

44.86

1.96

11.35

12.08

0.15

14.68

11.03

2.02

0.47

0.02

0.01

98.64

6.492

1.508

0.428

0.214

1.462

0.019

3.167

1.71

0.567

0.086

15.653

0.684

920113

hb-2-1c

phen-c

47.47

1.37

7.55

14.34

0.52

13.88

11.06

1.46

0.37

0.05

0.07

98.15

6.955

1.045

0.259

0.151

1.757

0.065

3.032

1.737

0.414

0.07

15.485

0.633

920113

hb-2-4c

phen-c

47.82

1.18

7.03

14.17

0.53

13.75

11.20

2.07

0.36

0.08

0.06

98.23

7.011

0.989

0.225

0.13

1.737

0.065

3.006

1.76

0.589

0.066

15.578

0.634

920113

hb-2-6r

phen-r

43.18

2.55

11.64

11.33

0.14

14.62

11.52

2.28

0.40

0.04

0.01

97.70

6.327

1.673

0.337

0.281

1.388

0.017

3.193

1.808

0.649

0.075

15.748

0.697

91524

gmhb-

4c gm

43.32

2.74

11.16

12.77

0.17

13.78

11.34

1.92

0.60

0.02

0.02

97.83

6.377

1.623

0.313

0.304

1.572

0.021

3.024

1.788

0.547

0.112

15.681

0.658

^aphen-c: phenocryst core, phen-r: phenocryst rim, gm: groundmass.

^bTotal Fe as ferrous.

Sample

grain^a

SiO₂

TiO₂

 Al_2O_3

FeO^b

MnO

MgO

CaO

Na₂O

K₂O

F

Cl

Total

A1(4)

Al(6)

Ti

Fe^b

Mn

Mg

Ca

Na

Κ

Total

Mg/

(Mg + Fe)

O = 23 Si 910524

hb-5-2c

phen-c

47.22

1.30

7.80

14.27

0.57

13.28

11.22

1.36

0.61

0.08

0.08

97.80

6.954

1.046

0.312

0.144

1.758

0.071

2.915

1.771

0.389

0.114

15.474

0.624

910524

hb-5-5c

phen-c

48.35

1.11

6.72

13.84

0.57

13.97

11.12

1.21

0.46

0.04

0.06

97.46

7.105

0.895

0.269

0.122

1.701

0.071

3.061

1.751

0.344

0.087

15.406

0.643



UNZEN AMPHIBOLE

Fig. 2. Al_2O_3 vs. Mg/(Mg+Fe) ratio of amphibole in the 1991 and 1995 dome dacites of Unzen volcano, Japan.

considered to crystallize at shallow depths either after effusion or in the conduit. One of the purposes of the present study is to determine whether groundmass amphibole crystallized deep in the conduit or at shallow depth. The secondary purpose of this study arose from a volcanological view point. The 1991-1995 eruption of Unzen volcano was mostly effusive, although the dome lava showed a variable degree of self explosivity, generating pyroclastic flows and two Vulcanian explosions (Sato et al., 1992: Nakada and Fujii, 1993). The self explosive nature of the dacite lava was caused by high excess pore gas pressure (Sato et al., 1992; Sparks, 1997), and the presence of the groundmass amphibole in the ejecta may be related to the high excess pore gas pressure in the extruded viscous lavas or in the shallow conduit. These ideas led us to conduct experimental work on the low-pressure stability limit of amphibole in the Unzen 1991-1995 dacite.

The stability of amphibole has been investigated for more than 3 decades, though few detailed works have been done in the low-pressure range (e.g., review by Helz, 1982). Pure pargasite stability was investigated by Boyd (1959). It was demonstrated that at 900°C, pargasite is stable to pressures of ca. 30 MPa. In volcanic rock systems, many experimental works have been concerned with the role of

amphibole in the generation of calc-alkalic magmas and experiments have been conducted mainly in the pressure range of 200 MPa to 3 GPa (Green and Ringwood, 1968: Kushiro et al., 1968: Holloway and Burnham, 1972; Helz, 1973; Cawthorn, 1976; Allen and Boettcher, 1983; Sisson and Grove, 1993). The low-pressure stability limit of amphibole in calc-alkalic volcanic rocks has been experimentally examined only in the Mount St. Helens dacites. Rutherford et al. (1985) and Rutherford and Hill (1993) demonstrated that amphibole is unstable at less than 100 MPa in a Mount St. Helens dacite by reversed experiments, although the experiments of Mertzbacher and Eggler (1984) showed the presence of amphibole at 800°C and 100 MPa in another Mount St. Helens dacite. Therefore, the low-pressure stability of amphibole in calc-alkalic systems has not been well constrained experimentally.

In this paper, we first describe the composition and texture of the groundmass amphiboles in the 1991–1995 dome dacite of Unzen volcano, and then present the results of experiments on the groundmass composition of the Unzen dacite designed to constrain amphibole stability. Finally, we discuss the crystallization conditions of amphibole in the 1991–



UNZEN AMPHIBOLE

Fig. 3. Cl vs. Mg/(Mg+Fe) ratio of amphibole in the 1991 and 1995 dome dacites of Unzen volcano, Japan.

Table 2	
Chemical composition of starting material	of the present study and relevant rock compositions

	(1 ^a) Unzen 1991–1995 groundmass	(2) Unzen 1991–1995 groundmass	(3) Unzen 1991–1995 bulk rock	(4) Mount St. Helens 1980 bulk rock
SiO ₂	68.24	68.14	65.31	63.80
TiO ₂	0.53	0.57	0.66	0.61
Al_2O_3	14.95	15.08	16.01	18.17
FeO	4.05	3.78	4.40	3.97
MnO	0.09	0.09	0.10	0.07
MgO	1.91	1.80	2.37	1.73
CaO	3.86	4.10	5.00	5.38
Na_2O	3.48	3.51	3.58	4.96
K ₂ O	2.85	2.78	2.40	1.31
P_2O_5	0.14	0.14	0.16	
Total	100.00	99.99	99.99	100.00

(1^a) Starting material used for the experiment XRF analyses by Sato.

(2) XRF analyses of groundmass separate by Nakada.

(3) XRF analyses by Nakada.

(4) Rutherford et al., 1985.

1995 Unzen dacite and its volcanological implications.

2. Groundmass amphibole in the 1991–1995 dacite of Unzen volcano

The 1991–1995 eruption products of the Unzen volcano show limited variations in petrography and

[Phase relation at ca. 196 MPa]

1100 0 glass no amph. (heating) \wedge 1050 ∇ no amph. (cooling) \cap amph. (heating) ۸ amph. (cooling) 1000 temperature (C) ∇ ∇ 95 ∇ \wedge 900 850 amp+px+pl+ox+liq+vap amp+px+ ox+liq pl 800 750 10 12 H,O wt.%



bulk rock chemistry (Nakada and Motomura, 1999). The SiO_2 contents range from 64–66 wt.%, and total phenocryst contents vary from 20 to 30 vol.%. Phenocryst phases are plagioclase, magnesiohornblende, biotite, quartz, magnetite, ilmenite, apatite, and rare orthopyroxene and clinopyroxene. Magnesiohorn-



Fig. 5. Temperature $-H_2O$ relations at about 98 MPa for Unzen groundmass compositions.

[Phase relation at 98 MPa]

Table 3	
Experimental resul	t

$\overline{(1)}$ Heating exp	(1) Heating experiments						
Sample #	P (MPa)	<i>T</i> (°C)	Time (h)	H ₂ O wt.%	Phases		
104	196	900	28.0	1.8	opx, cpx, mt, pl, gl		
105	196	900	28.0	5.7	hb, opx, cpx, mt, pl, gl		
106	196	950	443.5	443.5 1.0 opx, cpx, mt, pl,			
107	196	950	443.5 2.3 opx, cpx, mt, pl		opx, cpx, mt, pl, gl		
108	196	950	443.5	3.5	opx, cpx, mt, pl, gl		
109	196	932	68.1	2.0	opx, cpx, mt, pl, gl		
110	196	882	65.2	0.0	opx, cpx, mt, pl, gl		
111	196	882	65.2	2.0	hb, opx, cpx, mt, pl, gl		
112	196	882	65.2	4.3	hb, opx, cpx, mt, pl, gl		
113	196	882	65.2	6.6	hb, opx, cpx, mt, pl, gl		
114	196	1032	25.0	2.1	opx, pl, gl		
115	196	1032	25.0	3.8	opx, gl		
116	196	1032	25.0	0.0	opx, cpx, mt, pl, gl		
117	196	1032	25.0	6.0	gl		
122	196	932	68.1	1.2	opx, cpx, mt, pl, gl		
123	196	932	68.1	2.8	opx, cpx, mt, pl, gl		
124	196	932	68.1	4.6	hb, opx, cpx, mt, pl, gl		
125	196	850	111.1	11.4	hb, opx, mt, pl, gl		
126	196	850	111.1	1.6	hb, opx, cpx, mt, pl, gl		
127	196	850	111.1	4.1	hb, opx, mt, pl, gl		
128	196	850	111.1	2.6	hb, opx, cpx, mt, pl, gl		
129	196	800	140.3	1.8	hb, opx, cpx, mt, pl, gl		
130	196	800	140.3	3.4	hb, opx, cpx, mt, pl, gl		
131	196	800	140.3	5.2	hb, opx, mt, pl, gl		
133	98	964	46.2	1.3	opx, cpx, mt, pl, gl		
134	98	964	46.2	2.9	opx, cpx, mt, pl, gl		
135	98	964	46.2	4.3	opx, cpx, mt, pl, gl		
139	98	922	144.5	1.8	opx, cpx, mt, pl, gl		
141	98	922	144.5	4.1	opx, cpx, mt, pl, gl		
145	98	861	166.5	1.4	hb, opx, cpx, mt, pl, gl		
146	98	861	166.5	3.4	hb, opx, cpx, mt, pl, gl		
147	98	861	166.5	5.5	hb, opx, cpx, mt, pl, gl		
148	98	821	168.2	1.9	hb, opx, cpx, mt, pl, gl		
149	98	821	168.2	3.0	hb, opx, cpx, mt, pl, gl		
150	98	821	168.2	4.4	hb, opx, cpx, mt, pl, gl		
154	78	800	117.4	1.6	hb, opx, cpx, mt, pl, gl		
155	78	800	117.4	3.5	hb, opx, cpx, mt, pl, gl		
156	78	800	117.4	4.2	hb, opx, cpx, mt, pl, gl		
158	78	862	27.8	3.4	hb, opx, cpx, mt, pl, gl		
159	78	862	27.8	4.3	hb, opx, cpx, mt, pl, gl		

(2) Cooling experiments

Sample #	P (MPa)	T_0/T_t (°C)	Time (h)	H ₂ O wt.%	Phases
136	196	1014/964	1/19.9	1.4	opx, cpx, mt, pl, gl
138	196	1014/964	1/19.11	2.7	opx, mt, pl, gl
151	98	1021/871	1/133.5	1.5	opx, cpx, mt, pl, gl
152	98	1021/871	1/133.6	3.3	hb, opx, cpx, mt, pl, gl
162	98	969/819	2/157.4	5.9	hb, opx, cpx, mt, pl, gl
163	49	1050/813	1/113.8	2.0	hb, opx, cpx, mt, pl, gl
164	49	1050/813	1/113.8	3.5	hb, opx, cpx, mt, pl, gl

(=) = =

(2) Cooling exp	bernnents				
Sample #	P (MPa)	$T_0 / T_t (^{\circ}C)$	Time (h)	H ₂ O wt.%	Phases
165	49	1050/813	1/113.8	5.5	hb, opx, cpx, mt, pl, gl
166	49	1047/847	1/47.4	2.1	opx, cpx, mt, pl, gl
167	49	1047/847	1/47.4	4.7	opx, cpx, mt, pl, gl
168	49	1047/847	1/47.4	0	opx, cpx, mt, pl, gl
172	29.4	1044/794	1/105.5	2.4	opx, cpx, mt, pl, gl
174	29.4	1044/794	1/105.5	0	opx, cpx, mt, pl, gl
175	193	1051/901	1/25.6	4.3	hb, opx, cpx, mt, pl, gl
176	193	1051/901	1/25.6	2.1	opx, cpx, mt, pl, gl
177	193	1051/901	1/25.6	0	opx, cpx, mt, pl, gl
178	98	1050/900	4.2/140.4	2.0	opx, cpx, mt, pl, gl
179	193	1050/950	1/94.8	3.8	opx, mt, gl
180	193	1050/950	1/94.8	0	opx, cpx, mt, pl, gl
181	98	1050/900	4.2/140.4	5.9	hb, opx, cpx, mt, pl, gl
182	193	1050/950	1/94.8	6.6	cpx, mt, gl
183	193	950/930	8.5/185.6	5.1	opx, cpx, mt, gl
186	193	950/930	8.5/185.6	7.3	opx, cpx, mt, gl
189	98	1050/1030	2.6/41.0	4.4	gl
192	98	1050/1030	2.6/41.0	5.7	gl
195	98	1050/1030	2.6/41.0	2.8	gl
196	193	1050/980	15.1/50.5	5.7	gl
198	193	1050/980	15.1/50.5	3.9	opx, gl

Abbreviations of the phases; hb: amphibole, opx: orthopyroxene, cpx: clinopyroxene, mt: iron-titanium oxides, pl: plagioclase, gl: glass.

blende phenocrysts are 0.3-5 mm in length, sometimes with a thin rim of pargasite. The boundary between the core and rim is generally sharp, and the core often shows a corroded outline. A thin breakdown zone, consisting of fine iron-titanium oxides, pyroxenes, plagioclase and glass, is rarely observed along the margins of the phenocrystic magnesiohornblende. The groundmass is composed of plagioclase, pargasite, orthopyroxene, clinopyroxene, magnetite, ilmenite, apatite and glass. The modal proportion of glass in the matrix groundmass is ca. 50-80 vol.%. Pargasite constitutes 1-2 vol.% of the groundmass. Groundmass pargasite is elongate (100–300 microns long and 5-50 microns wide) and prismatic. It is often rounded and shows a hollow skeletal shape (Fig. 1). Pyroxenes usually occur as detached minute needle-like crystallites in the matrix glass of the 1991–1995 Unzen dacite (Fig. 1).

Representative analyses of amphibole in the Unzen 1991–1995 lavas are shown in Table 1. Analyses were made by using the electron-probe microanalyzer JXA-8900R at Kobe University. Analytical conditions are 15 kV acceleration voltage, 12 nA of electron beam current with a focused beam used for mineral analyses. Glass analyses were made with a defocused beam, ca. 20 microns across. The following standards were used to obtain quantitative analyses; Si: SiO₂, Ti: TiO₂, Al: Al₂O₃, Fe: Fe₂O₃, Mn: MnO, Mg: MgO, Ca: CaSiO₃, Na: natural albite, K: natural adularia, F: CaF₂, Cl: NaCl. Counting periods for X-ray peaks are 20 s for major elements and 100 s for fluorine and chlorine. The background intensities were measured on both sides of the X-ray peak. The background-corrected intensities are processed according to the ZAF method to obtain quantitative analyses.

Al₂O₃ contents and Mg/(Mg + Fe) ratios are generally 6–9 wt.% and 0.60–0.67 for phenocrystic magnesiohornblende, and 10–13 wt.% and 0.62–0.72 for groundmass pargasite (Fig. 2). Silicon contents per formula unit (pfu) of the groundmass amphibole and rim of phenocrystic amphibole are 6.2–6.5, and correspond to pargasite after the nomenclature of Leak et al. (1997). TiO₂ contents are generally 0.8– 1.6 wt.% for phenocrystic magnesiohornblende and 2.0–2.8 wt.% for groundmass pargasite. The fluorine content of both phenocrystic magnesiohornblende and groundmass pargasite is 0.02-0.10 wt.%. The chlorine content of amphibole in the Unzen dacite shows marked variation from the phenocryst core to the groundmass. The core of phenocrystic magnesiohornblende contains ca. 0.05-0.08 wt.% of chlorine, whereas, groundmass pargasite generally contains 0.01-0.03 wt.% of chlorine (Fig. 3). The change of the chlorine contents of the magnesiohornblende and pargasite may be related either to degassing of magmas or to magma mixing processes as will be discussed later. Nakada and Fujii (1993) suggested that magma mixing of phyric silicic magma and aphyric andesitic magma caused the change of amphibole composition from magnesiohornblende to pargasite associated with the increase of crystallization temperature and change of melt composition. Other petrographic features, such as the coarse reaction corona around biotite phenocryst, the high FeO* (total Fe as FeO) and MgO contents of the reversely zoned rim of plagioclase phenocryst (Sato, 1996) indicate that magma mixing took place just before the crystallization of the rim of phenocrysts and groundmass minerals in the Unzen dacite.

The temperature and oxygen fugacity of crystallization of groundmass minerals in the 1991–1995 dacites of Unzen volcano have been estimated to be $880 \pm 30^{\circ}$ C and 1–2 log units higher oxygen fugacity than quartz–fayalite–magnetite (QFM) buffer by analyses of iron–titanium oxides in the groundmass (Nakamura, 1995; Nakada and Motomura, 1999-this volume; Venezky and Rutherford, 1999-this volume).

3. Experimental studies

3.1. Starting material

The 1991–1995 dacite of Unzen volcano showed petrographic evidence of magma mixing, and the bulk rock sample is not appropriate as a starting material for the study of amphibole stability in the groundmass. Therefore, we used a groundmass separate of the 1992 dacite of Unzen volcano. Part of a hot block, ca. 2 m across, in the mud flow deposit of May 28, 1992 was sampled, crushed and sieved to 0.15-0.25 mm in diameter. The hot block is > 500°C 20 cm interior from the surface at the time of

sampling, and might have been just produced from the dome lava as a block in a pyroclastic flow and subsequently incorporated in the mud flow. Phenocryst minerals (quartz, plagioclase, and Fe-Ti oxides) are first separated by isodynamic magnetic separator. The residual fraction was processed by heavy liquid (methylene iodide) to separate mafic phenocrysts. The residual groundmass fraction was repeatedly rinsed by deionized water, dried, and further pulverized by agate mortar for ca. 1 h. Table 2 shows the bulk chemical composition of the starting material, representing the 'groundmass composition' of the 1992 Unzen dacite. The groundmass composition has an SiO₂ content of 68 wt.%, and is consistent with the composition of the groundmass separate of (Nakada and Motomura, 1999-this volume) (Table 2). These separates are, in fact, a mixture of the interstitial melt of the pre-existing rhvodacite, and the newly injected magma (which appears to be free of phenocrysts).

3.2. Experimental procedure

The experiments were carried out using the internally heated pressure vessel of KOBELCO installed at Kobe University. The apparatus uses Ar as a pressurising medium, attaining a maximum pressure of 196 MPa. Pressure is maintained to ca. 3% of the nominal values. The heating assemblage was placed only in the upper part of the vessel, where a homogeneous temperature (within 3°C, over 2 cm height) was maintained. The lower part of the vessel was at ca. 300°C, where the charges were dropped and quenched after each run by electrically cutting the molybdenum wire hanging the charges. Temperature was monitored by W-Re5/26 thermocouples and controlled by an automatic regulator. Temperature at the sample site was repeatedly calibrated against melting points of gold (1064°C) and/or copper (1085°C). The temperature is accurate to within ca. 5°C at the sample site.

The starting material powder was sealed in a Ag50Pd50 capsule with a known amount of distilled water. The procedure of charge preparation is as follows. A Ag50Pd50 tube (2.3 mm o.d., 2.0 i.d. and 20 mm long) was welded on one end and weighed, then 20–30 mg of starting material powder was inserted, and weighed. Distilled water was then in-

jected, the total capsule weighed, and then welded on the other end and weighed. The weight loss during welding was very small compared with the amount of water added. The sealed capsule was kept at 110°C in an oven for several tens of minutes, then weighed to ensure the good sealing of the capsule. The charge is run in the high pressure and temperature vessel, quenched, and weighed to ensure that water did not escape during the run. Oxygen fugacity was not controlled in the present experiments. The chemical composition of titanomagnetite (ulvospinel content = 10%) and titanohematite (ilmenite content = 37%) in some runs suggest that the oxygen fugacity was about equal to that defined by the MNO buffer reaction: $3MnO + \frac{1}{2}O_2 = Mn_3O_4$ (Lindsley,

Table 4	
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Phase	chemistry	of	some	experimental	products
1 mase	chemisuy	or	some	experimental	produces

1991). This redox state is 3 log units higher than the NNO buffer reaction: $2Ni + O_2 = 2NiO$, and about one f_{O_2} log unit lower than that of HM buffer reaction: $2Fe_3O_4 + \frac{1}{2}O_2 = 3Fe_2O_3$. The run duration was 1–3 days for higher temperature (>900°C) runs, and more than 4 days for lower temperature runs. Reversed experiments, both in the heating and the cooling run procedures, were carried out to ensure the equilibrium phase boundary. In heating experiments, 2–4 capsules with different water contents were heated, and held at a constant temperature. After a certain run duration, the capsules were quenched by dropping them in the cool lower part of the vessel. In cooling experiments, the charges were first heated to a higher temperature (usually at

Run #	Phase	п	SiO_2	TiO_2	Al_2O_3	FeO*	MnO	MgO	CaO	Na_2O	K_2O	F	Cl	Total
152	amp		45.65	2.40	10.29	10.30	0.29	15.47	11.01	1.84	0.55	0.22	0.02	98.02
		3	0.48	0.15	0.52	0.77	0.04	0.31	0.26	0.07	0.03	0.12	0.00	
	pl		53.80	0.03	29.14	0.40	0.00	0.08	12.70	4.04	0.23	0.06	0.00	100.48
	op		54.14	0.25	2.26	15.29	0.58	26.77	0.86	0.04	0.03	0.00	0.01	100.23
		2	0.54	0.02	0.31	0.20	0.21	0.36	0.09	0.02	0.01	0.00	0.01	
	Ti-hem		0.17	16.44	0.64	72.02	0.19	1.70	0.03	0.05	0.08	0.00	0.00	91.31
		2	0.06	0.87	0.02	0.87	0.02	0.05	0.01	0.02	0.01	0.00	0.00	
	gl		74.17	0.37	11.81	0.96	0.03	0.39	1.49	2.79	4.18	0.01	0.04	96.23
		4	0.26	0.05	0.04	0.07	0.01	1.01	0.03	0.05	0.05	0.01	0.01	
162	amp		48.43	1.60	9.15	10.08	0.38	14.66	10.69	1.39	0.66	0.16	0.02	97.20
	-	2	0.14	0.12	0.29	0.47	0.00	0.41	0.13	0.03	0.06	0.10	0.00	
	pl		54.27	0.01	28.56	0.55	0.00	0.05	12.31	4.09	0.30	0.00	0.01	100.16
	op		54.04	0.18	1.22	17.31	0.72	24.19	1.85	0.06	0.07	0.00	0.01	99.64
	•	2	0.17	0.04	0.13	0.95	0.08	0.74	0.35	0.01	0.01	0.00	0.00	
	ср		52.77	0.61	4.78	7.48	0.19	14.28	18.34	0.45	0.27	0.00	0.01	99.17
	gl		75.20	0.17	10.98	0.74	0.03	0.24	1.05	2.57	4.37	0.09	0.03	95.46
		3	0.37	0.05	0.12	0.12	0.01	0.01	0.03	0.08	0.03	0.02	0.00	
164	amp		45.79	1.81	12.10	10.99	0.40	13.10	12.14	1.52	0.47	0.08	0.02	98.42
	1	2	0.81	0.09	0.01	0.73	0.04	1.00	0.37	0.04	0.10	0.06	0.00	
	pl-1		54.12	0.02	28.28	0.77	0.00	0.10	12.29	4.24	0.26	0.09	0.01	100.17
	•	3	0.81	0.01	0.62	0.08	0.01	0.01	0.45	0.27	0.02	0.11	0.00	
	ср		47.44	0.63	8.97	12.14	0.37	9.64	20.08	0.39	0.22	0.00	0.01	99.87
	1	4	0.70	0.06	0.33	0.24	0.04	0.56	0.97	0.07	0.10	0.00	0.00	
	Ti-hem		0.09	27.27	0.46	61.19	0.32	2.40	0.06	0.05	0.03	0.00	0.00	91.88
165	amp		44.73	1.98	13.36	9.69	0.29	14.06	11.27	1.83	0.53	0.10	0.02	97.86
	1	2	0.85	0.01	0.63	0.18	0.02	0.09	0.02	0.05	0.06	0.10	0.00	
	pl		65.16	0.06	22.39	0.56	0.02	0.05	6.28	5.70	0.97	0.00	0.01	101.19
	•	2	0.40	0.01	0.26	0.02	0.02	0.02	0.19	0.15	0.03	0.00	0.00	
	gl		71.65	0.24	14.35	0.73	0.05	0.29	2.35	2.89	4.30	0.07	0.03	96.94
	J	3	0.27	0.02	0.09	0.07	0.01	0.04	0.05	0.09	0.05	0.05	0.00	

1050°C) for 1 h, then cooled down to the run temperature in 10-20 min, and kept at that temperature for 1 to 7 days before quenching.

The run products were checked for water loss, and mounted in epoxy resins. Polished thin sections were made, and examined by optical microscope, and analytical electron microscope. For phase analyses, the JXA-8800R (JEOL) electron probe microanalyzers of the Earthquake Research Institute, the University of Tokyo, and the JXA-8900R, of Kobe University, were used.

3.3. Phase stability

Figs. 4 and 5 illustrate the temperature $-H_2O$ phase relationships for the groundmass of the Unzen dacite at about 196 MPa and 98 MPa, respectively. These phase equilibria are based on the experiments summarized in Table 3. At 196 MPa, amphibole stability increases as the water content of the system increases, from 880°C at 2 wt.% to ca. 930°C at 6 wt.%. It is also noted that amphibole is a near-liquidus phase at 196 MPa. The crystallization sequence at water-saturated conditions is orthopyroxene (ca. 970°C), magnetite (ca. 970°C), clinopyroxene (ca. 940°C), amphibole (930°C), and plagioclase (ca. 910°C). At 98 MPa, amphibole crystallized at 900°C in cooling experiments. The charge contains relict pyroxenes and plagioclase, and new crystals of plagioclase, pyroxenes, magnetite, and amphibole. The proportion of the relict crystals depends on the melting conditions of a run (temperature, pressure, and water content). Amphibole shows overgrowth textures both in heating and cooling experiments. In some run products of heating experiments, the zoning of amphibole shows an iron-rich hornblende relict core with overgrown pargasite rim. In a few run products of cooling experiments, relict orthopyroxene is surrounded by pargasite. Amphibole in cooling experiments is usually elongate and prismatic with strong pleochroism. Some of the cooling experiments contain long prismatic pale green clinopyroxene which lacks strong pleochroism and distinguish it from amphibole. Plagioclase often shows a skeletal fork-shaped outline. Plagioclase rarely occurs as dendritic crystals. The run product of #165 (1050/813°C, 49 MPa, 5.9 wt.% H₂O) showed heterogeneous distribution of dendritic plagioclase. Crystallinity of the charge varied from ca. 20% to 60%. The glass in the glassy part shows less evolved composition compared with those in the higher pressure run product (#162) of otherwise similar run conditions (Table 4), and may retain disequilibrium composition when the melt was supercooled from above the liquidus temperature. Most of the run products of both heating and cooling experiments are homogeneous in terms of crystallinity and vesicularity.

Fig. 6 illustrates the temperature–pressure phase relations of the groundmass of the 1992 dacite of Unzen volcano for water-saturated conditions. The stability field of amphibole is delineated by a smooth curve, ca. 930°C at 196 MPa, ca. 900°C at 98 MPa, and ca. 820°C at 49 MPa. Above the amphibole stability limit, plagioclase, magnetite, and pyroxenes are present. The stability of amphibole extends toward lower pressures compared with those in the Mount St. Helens dacite by Rutherford and Hill (1993) as illustrated in Fig. 6.

3.4. Phase chemistry

The chemical compositions of phases in some of the experimental run products are shown in Table 4.



Fig. 6. Pressure-temperature relations for Unzen groundmass compositions near water-saturated conditions. Stability limit of amphibole in the Mount St. Helens dacite is after (Rutherford and Hill, 1993).

Mg/(Mg + Fe) ratio of amphiboles in the experimental run products are 0.60 to 0.78. Among these compositions, amphiboles grown during experiments are mostly in the range of 71 to 78, and the iron rich amphiboles represent relict crystals from the starting material. The high Mg/(Mg + Fe) ratio of the experimentally grown amphibole may reflect the high oxidation state of the coexisting melt: the oxygen fugacity of the unbuffered charges is at or near the MNO buffer as previously noted. The Al₂O₃ contents of amphiboles produced in the experiments are 9.2-10.3 at 819-871°C and 98 MPa, and 12.2-13.3 wt.% at 813°C and 49 MPa. These values are consistent with the natural amphibole composition, i.e., most of the groundmass pargasite contained 10-13 wt.% of Al₂O₃ (Fig. 2). TiO₂ content of the experimentally grown amphibole is 1.5-2.5 wt.%, and is similar to those in the natural groundmass pargasite.

4. Discussions

4.1. Amphibole stability and chemistry

Here we compare our experimental data on the stability and composition of amphiboles in the groundmass of the Unzen 1991 lava with those of previously studied systems. Pargasite stability has been studied by Boyd (1959) and Westrich and Holloway (1981). The former study determined the low pressure stability of pargasite to be ca. 1000°C at 100 MPa and 910°C at 50 MPa. Although incorporation of iron in the system may decrease the high-temperature stability limit of amphibole (Gilbert et al., 1982), these synthetic end-member stability data include the stability range of amphibole obtained in the present study.

Amphibole stability in volcanic rock systems have been experimentally studied by many workers as previously mentioned. Among these the works of Rutherford et al. (1985) and Rutherford and Hill (1993) on the stability relations of amphibole in the Mount St. Helens dacite is directly relevant to the present experimental data. The present study showed a much lower pressure stability of pargasite in the Unzen groundmass composition compared with those of the Mount St. Helens dacite by Rutherford and

Hill (1993). Both experimental studies performed reversed runs of 4–7 days duration, eliminating possible disequilibrium conditions. The main composition differences in these two systems are the higher SiO₂ contents and higher K₂O/Na₂O ratio of the Unzen groundmass starting composition (Table 2). Cawthorn (1976) showed that Na₂O content of the system is crucial for the stability of amphibole, and suggested that Na₂O content more than 3 wt.% is requisite for the crystallization of amphibole in calcalkalic rock systems. Na₂O contents of Unzen groundmass and Mount St. Helens dacite are 3.3 wt.%, and 4.5 wt.%, respectively, and fulfill the Cawthorn's criterion. There are no data on the effect of the K_2O/Na_2O ratio of the system on the stability of amphibole. The K₂O/Na₂O ratio of coexisting liquid is 1.1 and 0.5 for Unzen and Mount St. Helens, respectively. It is possible that elements entering the A site (vacant site) of amphibole are important for stability relations (Gilbert et al., 1982). Potassium is readily accommodated by the vacant site according to the presence of the peak of distribution coefficient near the size of potassium in ionic radius vs. distribution coefficient diagram (Matsui et al., 1977). Therefore, it is most likely that the high K/Na ratio of the system increases the relative stability of amphibole, causing the lower pressure extension of amphibole in the Unzen dacite compared with those in the Mount St. Helens dacite.

Although the phase stability relation of the present experiments represent conditions near MNO buffer, the stability of amphibole may not differ from those near NNO buffer condition. Rutherford et al. (1985) showed little difference for amphibole stability between the NNO and MNO buffers in a Mount St. Helens dacite. Helz (1973), in her experimental study of partial melting of Hawaiian tholeiite at 5 kbar, observed decrease of the thermal stability of amphibole in HM buffer condition compared with those in QFM buffer condition. Spear (1981), on the other hand, demonstrated little effect of oxygen fugacity on the stability limit of amphibole in a MORB system between QFM and HM buffer conditions at 1-2 kbar. Venezky and Rutherford (1999-this volume) show low-pressure stability field for amphibole at NNO + 0.5 in a mixed magma bulk composition of Unzen dacite very similar to the present result under oxidized condition. Therefore, the difference

of the low-pressure stabilities of amphibole in the Unzen groundmass and Mount St. Helens dacite may not be ascribed to the difference of the oxidation conditions of the experiments.

Other factors that may be relevant to amphibole stability include TiO_2 , SiO_2 , and fluorine contents of the system. The TiO₂ content of the Unzen and Mount St. Helens systems are both ca. 0.5 wt.%, and the amphiboles in both of the experimental charges have ca. 2 wt.% of TiO_2 , suggesting that TiO_2 is not a factor in producing the different low pressure stability limit of amphibole in the Unzen and Mount St. Helens experiments. Concerning the effect of SiO_2 content of the system on the stability of amphibole, compilation of 46 pairs of amphibole-melt compositional data (Allen and Boettcher, 1983; Rutherford et al., 1985: Conrad et al., 1988: Johnson and Rutherford, 1989a: Foden and Green, 1992: Sisson and Grove, 1993; Kawamoto, 1996; Grove et al., 1997; this study) indicates that the maximum temperature for amphibole stability generally decreases as the coexisting melt becomes more silicic. The SiO₂ contents of the starting material of Unzen and Mount St. Helens experiments are 68 and 64 wt.%, and apparently contradictory to the observed extension of the amphibole stability in the Unzen experiment. The experimental work of Venezky and Rutherford (1999-this volume) on the bulk rock Unzen sample (SiO₂ = 64.5 wt.%) showed similar amphibole stability to those on the groundmass separate in our experiment. Therefore, it seems that extension of amphibole stability toward lower pressure in the Unzen sample may not be ascribed to higher SiO_2 content of the system. Fluorine may be another important factor. Troll and Gilbert (1972) reported the 1 atm stability of fluor-tremolite, and it is likely that fluorine expands the thermal stability of amphibole at low pressure. The fluorine contents of the 1991–1995 Unzen lavas are 250–280 ppm (J. Hirabayashi, pers. commun.), whereas, that of the Mount St. Helens dacite is 0.01–0.06 wt.% (average, 0.024 wt.% for 12 samples; Lipman et al., 1981). The very similar fluorine contents of both dacites, as well as the low fluorine content of the groundmass pargasite in Unzen dacite (0.02–0.10 wt.%) suggest that the fluorine content is not a factor that influenced the different amphibole stability. At present, it seems most likely that the higher K/Na ratio of the

Unzen groundmass separate compared with those of the Mount St. Helens dacite caused the extension of the stability limit of pargasitic amphibole in the Unzen groundmass.

 Al_2O_2 content and/or Al(IV) in amphibole have been used as an igneous geobarometer or geothermometer. Hammerstrom and Zen (1986) proposed that Al_2O_2 and Al(T) contents of amphibole in granitic rocks coexisting with biotite, plagioclase, quartz, sanidine, sphene, ilmenite, melt and fluid are positively correlated with the pressure of consolidation, based on empirical experimental evidence. Johnson and Rutherford (1989b) experimentally calibrated the geobarometer at ca. 780°C. The Al_2O_3 contents of amphiboles in the present experimental study, however, show an apparently reversed relation with pressure. As shown in Table 4, Al₂O₃ contents of amphibole in lower-pressure run products have higher Al₂O₃ content than those in higher pressure run products. This apparent discrepancy is not serious, because the present experiments were conducted at higher temperatures and did not include many of the phases required to buffer the Al₂O₃ content of amphibole. In particular, the absence of quartz in most of the experiments would have a major effect on the Al content of the magnesiohornblende according to Johnson and Rutherford (1989b). Recent experimental and theoretical modeling of Sharma (1996) in the subsolidus system Na₂O-CaO-MgO- Al_2O_3 -SiO₂-H₂O shows that Al_2O_3 and Al(IV) are dependent on both pressure and temperature of crystallization. The fairly high Al₂O₂ contents of amphiboles in the present low pressure experiments may be affected not only by pressure but also by temperatures and coexisting melt compositions.

On the other hand, Holland and Blundy (1994) calibrated a thermometer based on the reactions between amphibole and plagioclase in both silicasaturated and -undersaturated conditions. We applied the thermometer in the silica-undersaturated condition (reaction: Edenite + Albite = Richterite + Anorthite) to the natural pairs of amphibole and plagioclase for both phenocryst core and rim in Unzen samples, and obtained $783 \pm 22^{\circ}$ C for the phenocryst core pairs and 878° C for the phenocryst rim pairs. These temperatures are consistent with those obtained by Fe–Ti oxide thermometer for both pairs (Nakamura, 1995; Nakada and Motomura, 1999-this volume; Venezky and Rutherford, 1999-this volume).

4.2. Processes of the crystallization of the groundmass amphibole

Although amphibole is a common phenocryst phase in calc-alkalic volcanic rocks, its presence in the groundmass has been paid little attention in previous studies. Most of the groundmass of large plinian eruption products are microlite-free glass. whereas effusive eruption products contain microlites, crystallites and nanolites in the groundmass. This may partly be due to slower cooling rate and to longer periods of degassing-induced crystallization in the effusive eruption products (Eichelberger et al., 1986; Cashman, 1990). Present experimental data suggest that in the Unzen 1991 lavas, at magmatic temperatures of $880 \pm 30^{\circ}$ C, crystallization of pargasite in the groundmass should have occurred at pressures more than 70 MPa, corresponding to a depth of more than 3 km. The crystallization of groundmass minerals at depth in the conduit may be caused either by (1) crystallization during magma mixing, (2) cooling induced crystallization near the margin of the conduit, and (3) degassing-induced crystallization of magmas. These three processes are examined below in terms of the crystallization of the groundmass pargasite in the Unzen dacite.

The much lower chlorine contents of the groundmass pargasite compared with those of the phenocrystic magnesiohornblende (Fig. 3) suggest either the chlorine content of the mafic aphyric magma was very low to produce the low chlorine concentration in the mixed magma, or degassing (vesiculation) took place before the crystallization of the groundmass pargasite. Yamaguchi (1997) reported that chlorine contents of glass inclusion in the plagioclase and quartz phenocrysts in the 1991-1995 dacite of Unzen volcano are 800-850 ppm. These compositions may represent the chlorine content of the melt of the silicic end-member, which was in equilibrium with the core of the magnesiohornlbnede phenocryst. The chlorine content of the core of magnesiohornblende phenocryst ranges from 500-800 ppm, suggesting that distribution coefficient of chlorine be-

tween magnesiohornblende and magma is 0.6-1.0. Studies of melt inclusions in phenocrysts in subduction zone magmas shows that basic to intermediate magmas generally have 300 to 3000 ppm of chlorine (Harris and Anderson, 1984; Devine et al., 1984). The mixing ratio of mafic and silicic magmas have been estimated between ca. 0.5 to 2 (Nakamura, 1995; Venezky and Rutherford, 1999-this volume). Therefore, one-third lowering of the concentration of chlorine in the groundmass pargasite compared to the phenocrystic magnesiohornblende is difficult to explain by mixing of mafic and silicic magmas. Chlorine is strongly partitioned into water vapor phase compared to the silicate melt by a factor of more than 100 at high pressures (Webster, 1992); therefore, the degassing (or vesiculation) of 1 wt.% of water from magma may decrease the chlorine content of the magma by half. It is most likely that groundmass pargasite crystallized from mixed magma by magma vesiculation/degassing of fairly large amount of volatiles.

M. Rutherford (pers. commun.) suggested that microlite amphibole may crystallize during magma mixing, because the high-temperature mafic magma will be quenched against the cooler felsic magma. It is possible that during mixing of hot mafic and cooler silicic magma, any temperature-composition state between two end-members would be achieved, because thermal diffusivity is much faster than chemical diffusivity. Mingling of magmas may occur in laminar flow in the conduit (simple Hagen Poiseuille flow model suggest Raynolds number below 0.1) by laminar overturning (Koyaguchi and Blake, 1989), or by the disturbed flow along the irregular conduit wall, or by convective movement of heterogeneously vesiculated magma due to gravitational instability. Here, we consider a localized patch of mingling magma, ca. 10 cm in size, within which thermal homogenization may occur within several hours. Local migling ratio of mafic and silicic magmas may vary from 0 to 1, which mostly determine the temperature of the patch, but the magma composition is not homogenized in it. There, mafic magma part (or band) would be cooled to crystallize, whereas silicic magma (porphyritic) part would be heated and phenocrysts would be resorpt. Similar phenomena in magma may take place in the successive magma mingling processes. In this way magma mixing would

proceed during the magma ascent in the conduit. Geodetic observations (Ishihara, 1993) showed that there are at least 3 minor magma pockets at depth of 1.5, 5, and 8 km under Unzen volcano, suggesting wide variation of the conduit diameter from the magma chamber (at depth of 10.5 km, Nishi et al., 1995) to the surface. Therefore, we expect complex history of magma mixing in the erupted ejecta. Actually, we observed that thickness of the rim of phenocrysts (plagioclase and amphibole) varies from grain to grain. Some plagioclase show thick dusty zone at the rim, whereas others are clear and equant at the rim. Thickness of the reaction corona around biotite phenocryst varies from 0 to more than 100 microns. These observations of phenocryst phases in a thin section suggest that each phenocryst experienced much complex thermal and chemical histories.

The slight negative correlation between chlorine content and the Mg/(Mg + Fe) of groundmass amphibole (Fig. 3) indicates that degassing proceeded along with the magma mixing. The negative correlation is difficult to explain with a model involving crystallization along the cooler margin of a volcanic conduit. The cooling near the conduit margin may be associated with crystallization differentiation, together with degassing of volatiles (Stasiuk et al., 1996), inducing the composition of amphibole toward lower Mg/(Mg + Fe) and lower chlorine content, which contradicts the actual negative correlation (Fig. 3). Therefore, we infer that the groundmass amphibole crystallized during magma mixing and volatile degassing at depth more than ca. 3 km in the conduit.

Concerning the relationship between the self-explosive nature of the dacite (Sato et al., 1992) and the presence of pargasite in the groundmass, present experiments and the H_2O content of the groundmass of the Unzen dacite demonstrated that there is no direct link. Kusakabe et al. (1999-this volume) reported that ejecta of the 1991 Unzen eruption contained 0.2–0.6 wt.% of water in the groundmass. The corresponding equilibrium pressure for water saturation is 0.3–2 MPa, much lower pressure compared to the minimum stability pressure of pargasite in the groundmass (ca. 70 MPa). This indicates that there is no direct link between the self-explosivity of lavas and the presence of amphibole in the groundmass.

5. Conclusions

(A) Pargasite constitutes 1-2 vol.% of the groundmass of the 1991–1995 dacite of Unzen volcano. It is long prismatic and often shows rounded outline. Al₂O₃ content of the pargasite is ca. 10–13 wt.% with Mg/(Mg + Fe) of ca. 0.66–0.72, whereas those of phenocrystic magnesiohornblende is ca. 7–9 wt.% and 0.60–0.67. Chlorine content of amphibole is 0.05–0.08 wt.% in the core of phenocryst and is 0.01–0.03 wt.% in the rim of phenocryst and the groundmass.

(B) Experimental study showed that pargasite is stable only at more than ca. 70 MPa at magmatic temperatures of $880 \pm 30^{\circ}$ C.

(C) The groundmass pargasite crystallized during magma mixing at depths more than ca. 3 km in the conduit, and vesiculation/degassing of magma preceded the crystallization of the pargasite to reduce their chlorine contents.

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