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Cl/OH partitioning between hornblende and melt and its implications for the origin of oscillatory zoning of hornblende phenocryst

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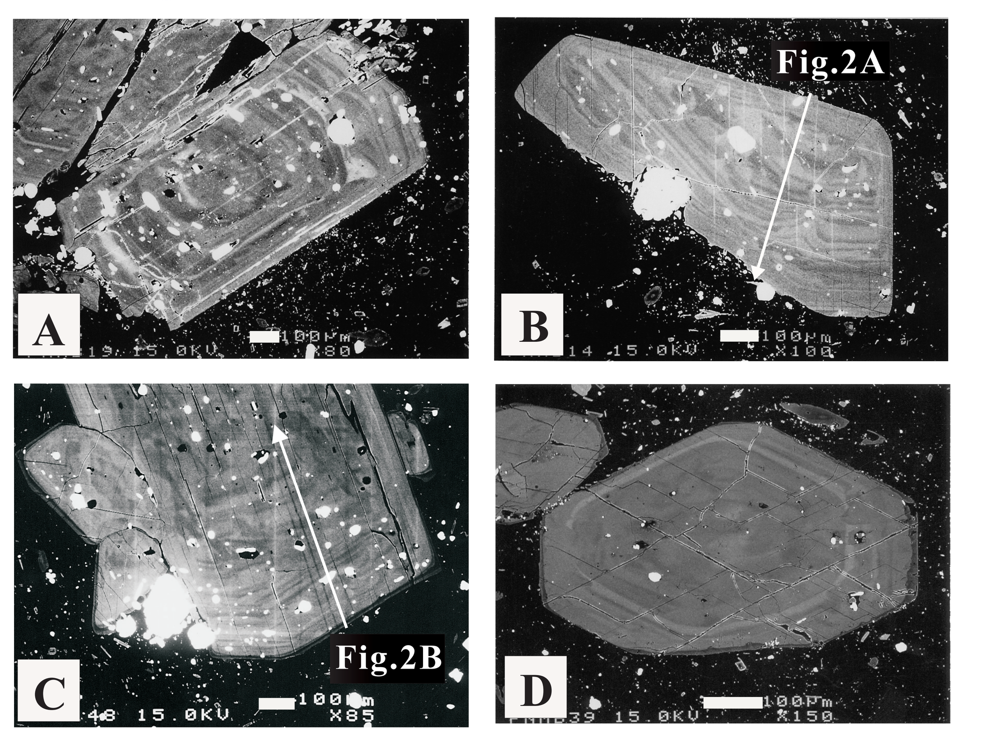
ABSTRACT

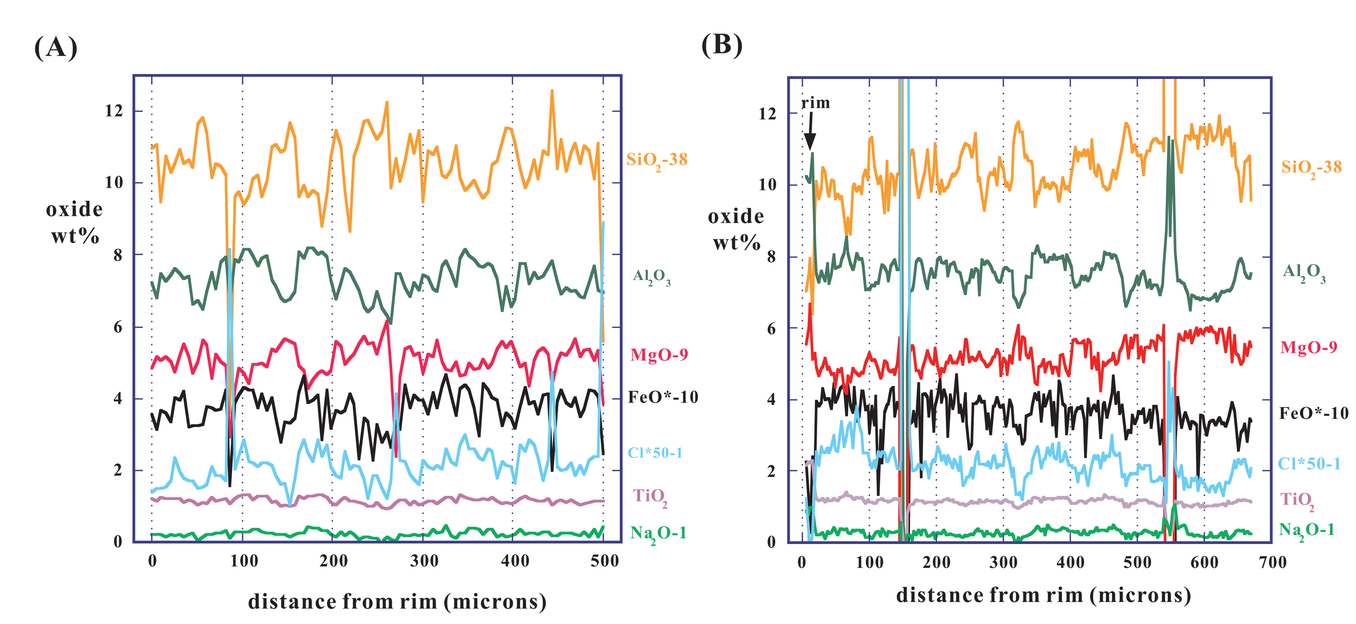
We carried out high temperature-pressure experiments to determine the chlorine-hydroxyl exchange partition coefficient between hornblende and melt on the 1992 dacite of Unzen volcano. Cl in hornblende and melt are analyzed by electron microprobe, whereas OH in hornblende and melt are calculated assuming anion stoichiometry of hornblende and utilizing the dissociation reaction constant for H2O+O=2(OH) in water-saturated melt, respectively. The partition coefficient strongly depends on the Mg/(Mg+Fe) ratio of hornblende, and is expressed as ln K1 = (Cl/OH)hb/(Cl/OH)melt = 2.374.6*[Mg/(Mg+Fe)]hb at 2-3 kb and 800-850−C. It is shown that twofold variation of Cl content in the oscillatory zoned core of hornblende phenocrysts in the 1991-1995 dacite of Unzen volcano is not explained by the dependence of Cl/OH partition coefficient on the Mg/(Mg+Fe)hb, and requires ca. 80% variation of Cl/OH ratio of the coexisting melt. Available experimental data at 200 MPa on Cl/OH fractionation between fluid/melt suggest that ca. 1.2-1.8 wt% degassing of water from the magma explains the required 80% variation of the Cl/OH ratio of the melt. The negative correlation between Al content and Mg/(Mg+Fe) ratio in the oscillatory zoned core of hornblende phenocrysts is consistent with repeated influx and convective degassing of the fluid phase in the magma chamber.

Compositional Zoning of Plagioclase and Hornblende

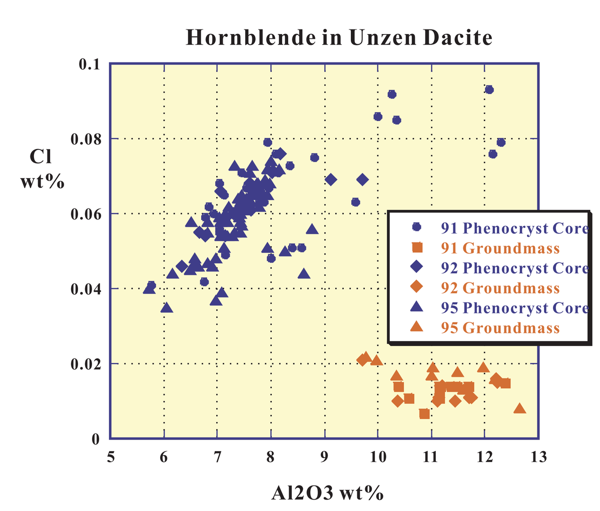
BSE Images of Hornblende Phenocryst in the Unzen Dacite



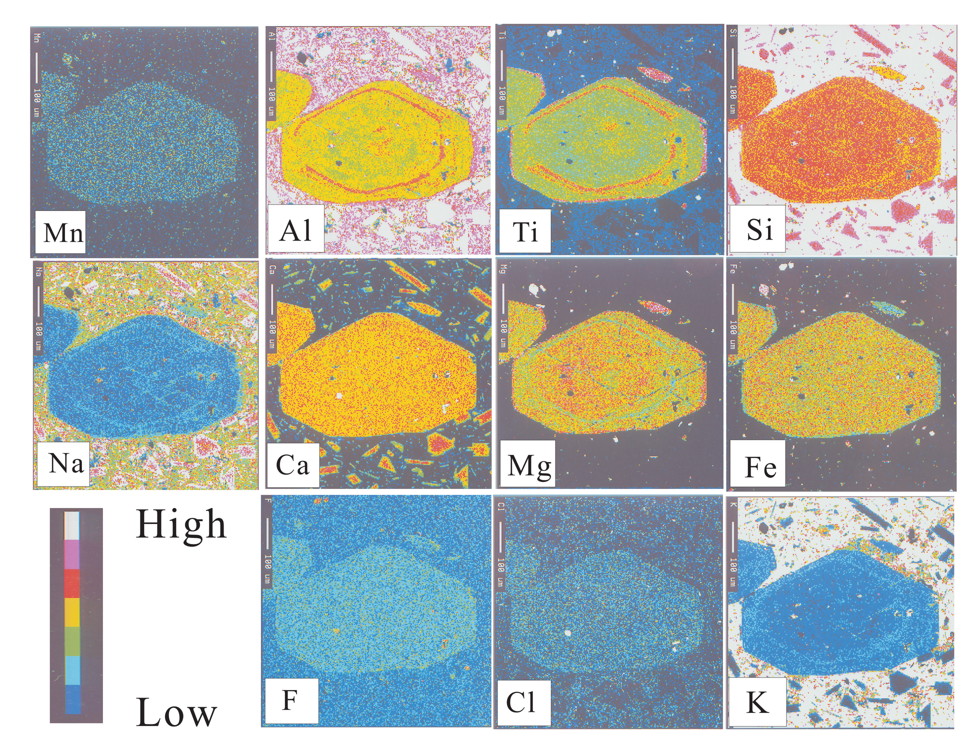
Line Profiles of Hornblende Phenocrysts



Elemental Correlations: Al, Fe, Cl, Ti, Na versus Si, Mg

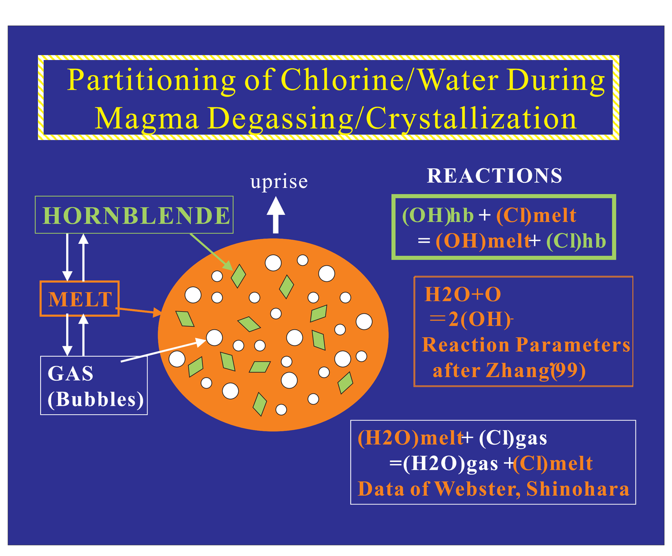


X-Ray Mapping of Hornblende



Note the different compositional correlation between the core and rim zonings

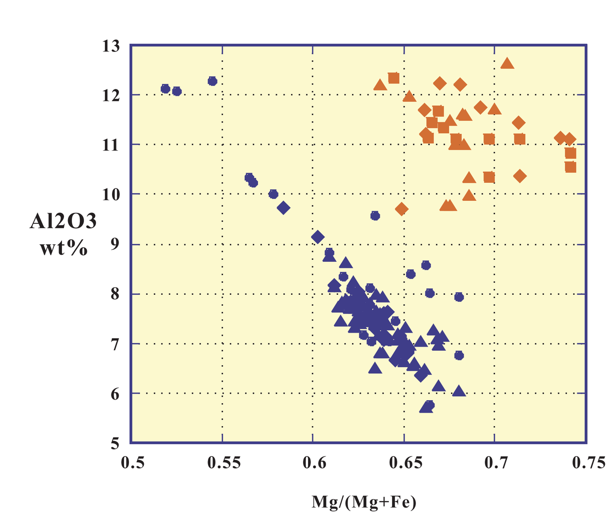
Experimental Determination of Cl/OH Partition Coefficient between Hornblende and Melt



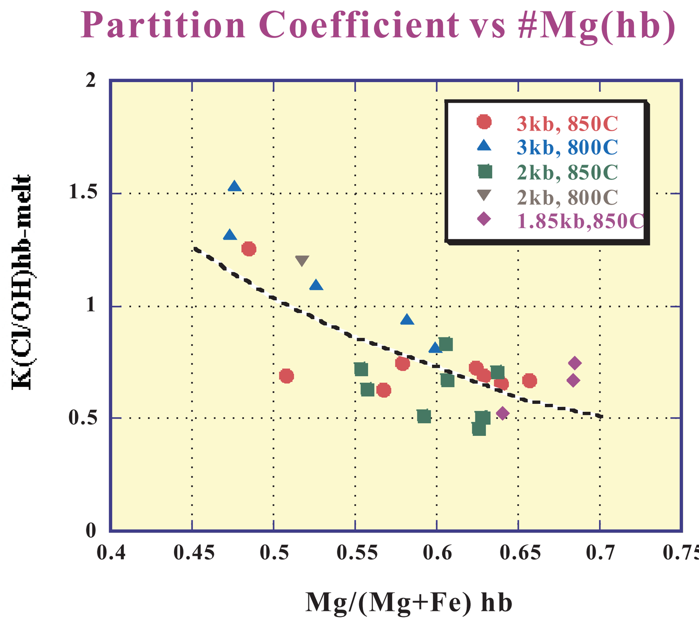
Starting Material

	UZBulk*	Fe-doped UZBulk**	Uzgm*	Fe-doped Uzgm**
SiO2	65.31	63.32	68.24	66.44
TiO2	0.66	0.58	0.53	0.47
Al2O3	16.01	15.05	14.95	13.94
FeO	4.40	6.74	4.05	6.28
MnO	0.10	0.10	0.09	0.08
MgO	2.37	2.21	1.91	1.74
CaO	5.00	4.93	3.86	3.82
Na2O	3.58	3.33	3.48	3.01
K2O	2.40	2.41	2.85	3.00
P2O5	0.16	0.27	0.14	0.17
total	99.99	98.93	100.00	98.94

*XRF analyses, **epma analyses

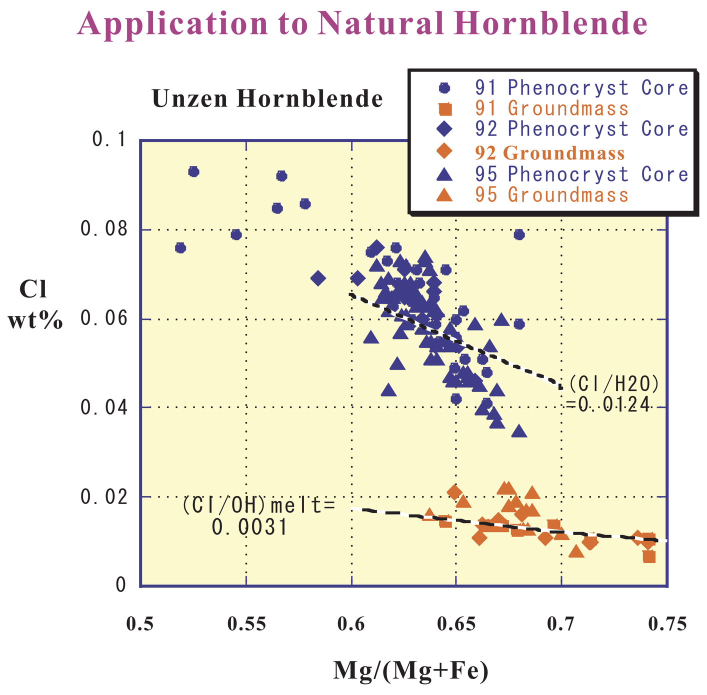


Partition Coefficient vs #Mg(hb)



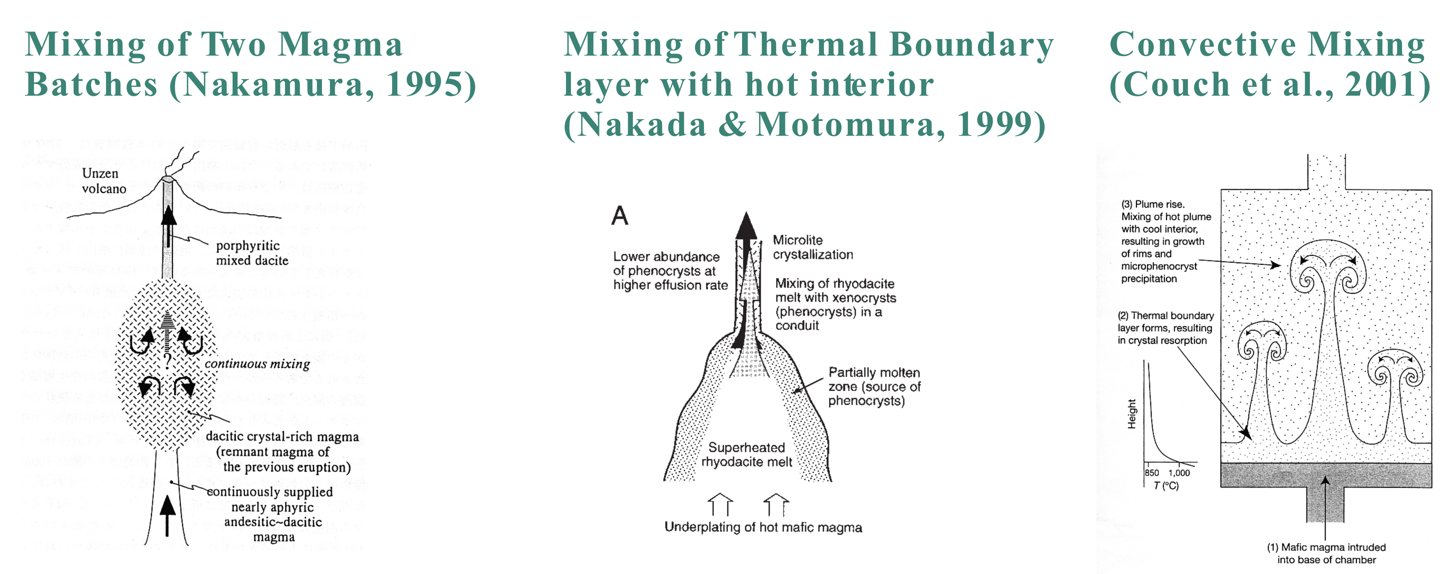
K = 2.37-4.6(Mg/(Mg+Fe))
Temperature, pressure show small effects

Application to Natural Hornblende



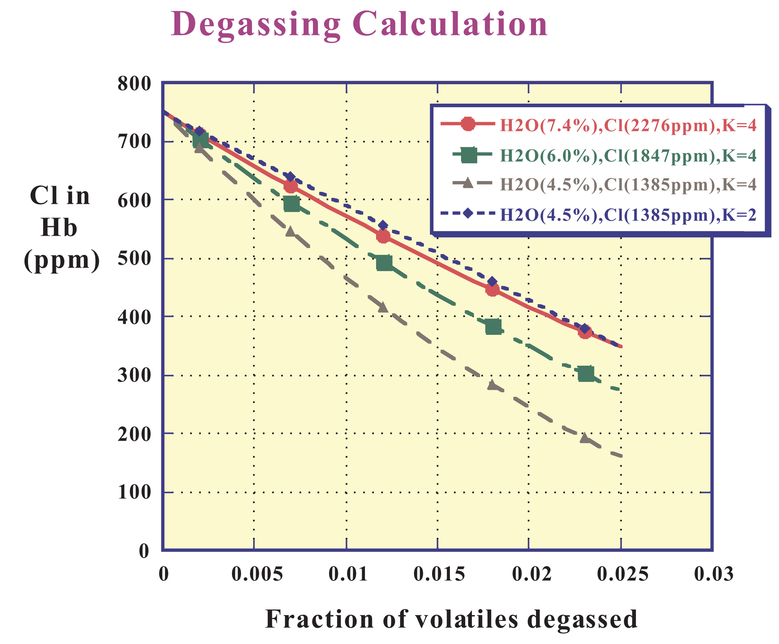
Large variation of Cl in the core of hb does not be accounted for by compositional dependence of K.

Models of Magma Chamber Processes



Above previous models do not account for the inverse correlation between Al and #Mg, and large variation of chlorine in hornblende.

Degassing Calculation



Behavior of Elements During Various Magmatic Processes Normalized against Mg/(Mg+Fe) of Hornblende

	Observation		Model		
Hornblende	core	rim	cryst.frac	mixing	degassing
Al	-	+	+	+	-
Ti	-	+	+	+	-
Na	-	+	+	+	-
K	-		-	-	
Ca					
Mg	+	+	+	+	+
Mn		+	-	-	
Fe	-	-	-	-	-
Si	+	-	-	-	+
Cl	-	-			-
Plagioclase	core	rim			
Ca	-	+	+	+	-
Na	+	-	-	-	+
Mg		+	+	+	
Fe		+			

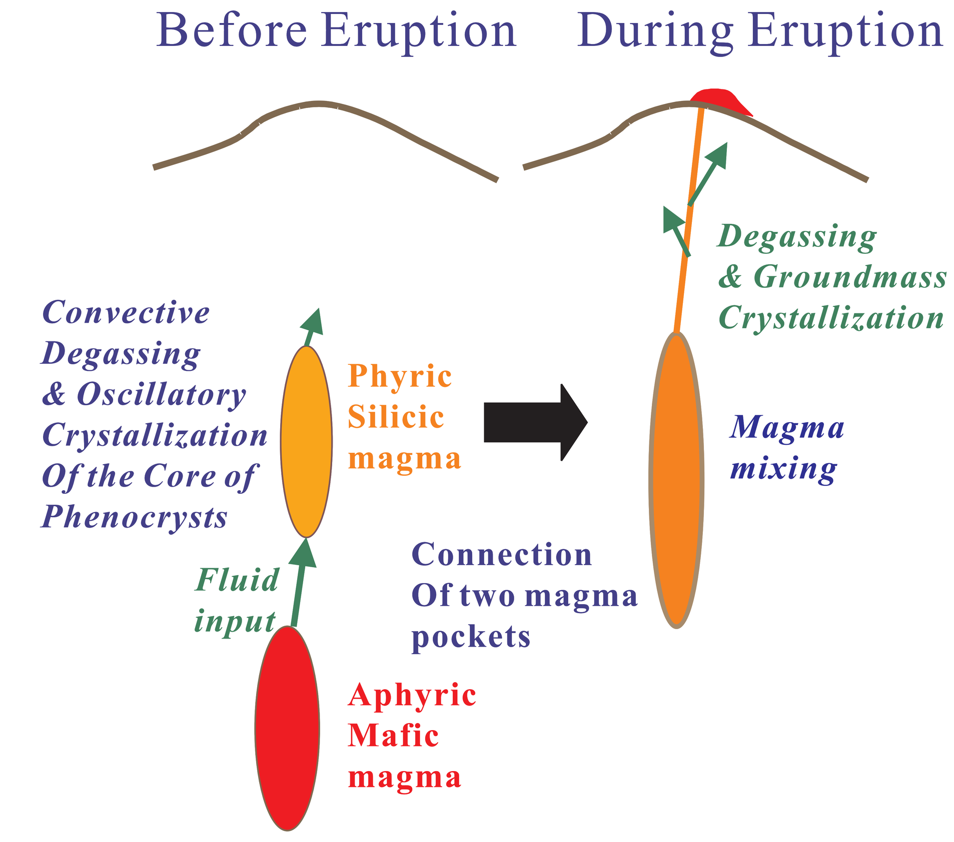
Experimental Run Conditions

#	capsule	sample	Cl in fluid	NaCl or HCl conc. wt%	aqueous solution wt%	T C	P MPa	duration day	fO2	phases in run products
278	Ag70Pd30	UZ Bulk Glass	NaCl	4	7.40	850	300	7	NNO	hb,mt,pl,gl
283	Ag70Pd30	UZ Bulk Glass	NaCl	4	7.10	850	300	7	NNO	hb,mt,pl,gl
286	Ag70Pd30	UZ Bulk Glass	NaCl	4	7.30	850	300	7	NNO	hb,mt,cpx,pl,gl
290	Au	UZ Bulk Glass	NaCl	4	5.20	850	300	7	NNO	hb,mt,pl,gl
291	Au	UZ Bulk Glass	NaCl	4	4.60	850	200	7	NNO	hb,mt,pl,gl
298	Au	Fedoped UZ Bulk Glass	NaCl	4	3.60	800	300	7	NNO	hb,mt,opx,pl,gl
299	Au	Fedoped UZ Bulk Glass	NaCl	4	4.10	850	200	7	NNO	hb,mt,opx,pl,gl
300	Au	Fedoped UZ Bulk Glass	NaCl	4	4.85	850	300	7	NNO	hb,mt,pl,gl
307	Ag70Pd30	UZ Bulk Glass	NaCl	4	5.99	850	200	7	NNO	hb,mt,opx,pl,gl
309	Ag70Pd30	UZ Bulk Glass	NaCl	4	6.79	850	200	7	NNO	hb,mt,pl,gl
313	Ag70Pd30	Fedoped UZ Bulk Glass	NaCl	4	6.88	850	300	7	NNO	hb,mt,pl,gl
314	Ag70Pd30	UZ Bulk Glass	NaCl	4	5.81	850	185	1	NNO+4	hb,mt,gl
315	Ag70Pd30	UZ Bulk Glass	NaCl	4	4.55	850	185	1	NNO+4	hb,mt,pl,gl
316	Ag70Pd30	Fedoped UZ Bulk Glass	NaCl	4	6.49	850	185	1	NNO+4	hb,mt,gl
320	Ag70Pd30	Fedoped UZBulk Glass	NaCl	4	4.40	800	300	7	NNO	hb,mt,opx,pl,gl
322	Ag70Pd30	UZ GM Glass	NaCl	4	4.57	850	200	7	NNO	hb,opx,mt,pl,gl
323	Ag70Pd30	UZ GM Glass	NaCl	4	4.87	800	300	7	NNO	hb,opx,mt,pl,gl
324	Ag70Pd30	UZ GM Glass	NaCl	4	6.26	850	300	7	NNO	hb,mt,pl,gl
325	Ag70Pd30	UZ GM Glass	NaCl	4	3.75	800	200	7	NNO	hb,opx,pl,gl
326	Ag70Pd30	Fedoped UZGM glass	NaCl	4	4.52	800	300	7	NNO	hb,mt,gl
329	Ag70Pd30	Fedoped UZGM glass	NaCl	4	6.02	850	300	7	NNO	hb,mt,opx,gl
330	Ag70Pd30	UZ Bulk Glass	NaCl	4	4.61	850	200	7	NNO	hb,mt,opx,pl,gl
331	Ag50Pd50	UZ Bulk Glass	NaCl	4	4.43	800	300	7	NNO	hb,mt,opx,pl,gl
333	Ag70Pd30	Fedoped UZBulk Glass	NaCl	4	5.15	850	200	7	NNO	hb,mt,opx,pl,gl
B51	Au	UZ GM Glass	HCl	2.8	9.83	850	200	5	NNO	hb,mt,opx,pl,gl
B52	Au	UZ GM Glass	HCl	5.6	10.02	850	200	5	NNO	hb,mt,opx,pl,gl
B53	Au	UZ GM Glass	HCl	11.2	10.30	850	200	5	NNO	hb,mt,opx,pl,gl
B57	Au	UZ GM Glass	HCl	2.8	10.05	850	300	5	NNO	hb,mt,gl
B58	Au	UZ GM Glass	HCl	5.6	10.15	850	300	5	NNO	hb,mt,gl
B59	Au	UZ GM Glass	HCl	11.2	10.46	850	300	5	NNO	hb,mt,gl

* Run 314, 315, 316 are processed by IHPV at Kobe Univ., other runs were carried out by CSPV at Univ. of Hannover

Conclusive Image of Magma Chamber Processes

Fluid Input/Outgassing before connection of Two Magma Batches (This study, modified from Hattori, 1993)



Abstract

Compositional zoning of phenocryst minerals in volcanic rocks are often interpreted as record of repeated magma replenishments. Here, we present evidences of fluid input/outgassing processes as a model of formation of compositional zonings of hornblende and plagioclase phenocrysts in the 1991-1995 dacite of Unzen volcano.

Strong evidence for the relevance of fluid to the compositional zoning is the variation of Cl in hornblende phenocryst. The hornblende phenocrysts often show reverse zoning at the rim and oscillatory or spike zoning within the core. The Cl content of hornblende ranges from 0.04-0.08 wt.% within the core and 0.01-0.02 wt% in the rim. The marked decrease of Cl from the core to the rim indicate that degassing of magma caused the decrease of Cl/OH in the magma. To quatify the amount of degassing, we carried out volatile-saturated high-pressure experiments to determine the partition coefficent for the exchange reaction: (OH)magma + (Cl)hornblende = (Cl)magma + (OH)hornblende at 800-850 C and 2-3 kb under NNO conditions. The amount of (OH) is calculated by assuming water saturation in the melt (Zhang, 1999, Rev. Geophys), and using the reaction constant of Novak and Behrens(2001, EPSL). Although the obtained partition coefficient: K = (Cl/OH)hb/(Cl/OH)melt, is somehow scatted, they show dependence on Mg/(Mg+Fe) ratio of hornblende, and gives an equation: K = -12.2*exp(-4.60*XMg) (r=0.77). The strong dependence of K on XMg has been interpreted as the effect of large ionic size (r=181pm) of Cl to be accommodated in larger cell size of Fe-rich hornblende (Volfinger et al., 1985, GCA). From the obtained partition coefficient, we calculated the (Cl/OH) ratio of magma for crystallization of the core of hornblende to be in a range of 0.015-0.025 and for crystallization of the rim to be ca. 0.008. Although the composition of hornblende and plagioclase suggest mixing of magmas just before the crystallization of the rim of phenocrysts, the two-fold lowering of Cl/OH ratio of magma may be caused by magma degassing before the crystallization of the rim of hornblende phenocryst.

The variation of Cl content within the core of hornblende phenocryst may reflect fluid input/outgassing in the chamber. If replenishment of phyric magma pocket by high- temperature aphyric magmas takes place, we expect increase of both XMg and

Fluid Input/Outgassing Processes Recorded in the Compositional Zonings of Hornblende and Plagioclase Phenocrysts in Unzen Dacite

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(preferred session: I)
(preferred mode: oral)

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The variation of Cl content within the core of hornblende phenocryst may reflect fluid input/outgassing in the chamber. If replenishment of phyric magma pocket by high- temperature aphyric magmas takes place, we expect increase of both XMg and Al in the crystallizing hornblende, because the replenishment increases XMg and decreases silica activity in the melt. This is contrary to the observed compositional correlation; i.e., Al is negatively correlated with XMg in the core of hornblende phenocryst. Al content in the core of hornblende phenocryst is positively correlated with Cl, suggesting that fluid input into the magma decreased silica activity, and increased Cl content of the melt. Before the replenishment of the chamber, fluid from the deeper high-temperature magma pocket may be migrated into the upper low-temperature phyric magma chamber, just like the case of 1991 eruption of Mt. Pinatubo (Hattori, 1993, Geology). The low-temperature phyric magma, supplied by fluid may show dissolution of phenocrysts and then crystallize high-Cl and Al hornblende, and buoyantly uprose towards the upper part of the chamber, where oversaturation of the melt caused degassing. The repeated fluid input/outgassing process is consistent with wide variation of Ca/(Ca+Na) ratio (0.38-0.76) of the core of plagioclase phenocryst with consistently lower MgO (<0.02) and FeO* (0.16-0.20wt) contents compared with the rim of plagioclase phenocrysts (Ca/(Ca+Na)=0.55-0.70, MgO=0.05-0.08, FeO*=0.45-0.60wt%).