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# Magma storage prior to the 1912 eruption at Novarupta, Alaska

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Abstract New analytical and experimental data constrain the storage and equilibration conditions of the magmas erupted in 1912 from Novarupta in the 20th century's largest volcanic event. Phase relations at  $H_2O + CO_2$  fluid saturation were determined for an andesite (58.7 wt% SiO<sub>2</sub>) and a dacite (67.7 wt%) from the compositional extremes of intermediate magmas erupted. The phase assemblages, matrix melt composition and modes of natural andesite were reproduced experimentally under H<sub>2</sub>O-saturated conditions (i.e.,  $P_{H2O} = P_{TOT}$ ) in a negatively sloping region in T-P space from 930 °C/100 MPa to 960 °C/75 MPa with  $fO_2 \sim N$ NO+1. The  $H_2O$ -saturated equilibration conditions of the dacite are constrained to a T–P region from 850  $^{\circ}\mathrm{C}/$ 50 MPa to 880 °C/25 MPa. If H<sub>2</sub>O-saturated, these magmas equilibrated at (and above) the level where coerupted rhyolite equilibrated ( $\sim 100$  MPa), suggesting that the andesite-dacite magma reservoir was displaced laterally rather than vertically from the rhyolite magma body. Natural mineral and melt compositions of intermediate magmas were also reproduced experimentally under saturation conditions with a mixed  $(H_2O + CO_2)$ fluid for the same range in  $P_{H2O}$ . Thus, a storage model in which vertically stratified mafic to silicic intermediate magmas underlay H<sub>2</sub>O-saturated rhyolite is consistent with experimental findings only if the intermediates have  $X_{H2O}$ <sup>fl</sup> = 0.7 and 0.9 for the extreme compositions, re-

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spectively. Disequilibrium features in natural pumice and scoria include pristine minerals existing outside their stability fields, and compositional zoning of titanomagnetite in contact with ilmenite. Variable rates of chemical equilibration which would eliminate these features constrain the apparent thermal excursion and re-distribution of minerals to the time scale of days.

## Introduction

The 1912 Novarupta eruption in the Valley of Ten Thousand Smokes (VTTS) is remarkable in many respects, not the least of which has been its impact on diverse areas of volcanological research, such as largevolume ignimbrite emplacement, caldera collapse dynamics, and vapor transport of ore metals from volcanic systems (e.g., Hildreth 1991; Lowenstern 1993; Bursik and Woods 1996). Chief among the outstanding puzzles of this eruption are the striking compositional variety of juvenile erupted material and the subsurface plumbing system which allowed caldera collapse at Mt. Katmai to occur 10 km from the Novarupta vent. During a 60-h period, 13 km<sup>3</sup> magma (dense rock equivalent) was erupted, comprised of 7.5 km<sup>3</sup> high silica rhyolite and an only slightly smaller amount (5.5 km<sup>3</sup>) of intermediate composition material spanning the range from basaltic andesite to dacite. Highly evolved rhyolite is not only extremely rare in the Aleutian arc but completely absent from the Pleistocene record of the local Katmai group of stratovolcanoes (Griggs, Katmai, Trident, Mageik, and Martin). Intermediate compositions are typical of the Katmai group, and the 1912 magmas are compositionally most similar to material erupted from Mt. Katmai itself (Hildreth and Fierstein 2000). Determining the pre-eruptive conditions at which the 1912 magmas last equilibrated is critical to addressing the issues of their relative crustal storage depths, conduit geometry, and ultimately the petrogenesis of the highsilica rhyolite.

The compositions of the intermediate magmas span a continuum between andesite and dacite (58 and 68 wt%  $SiO_2$ ), with rare samples extending to basaltic compositions (50.4 wt% SiO<sub>2</sub>; Hildreth and Fierstein 2000). Thus, the distinction between andesite and dacite magma is simply definitional, and does not imply the presence of two separate magma batches or pumice populations having silica contents clustered below and above 63 wt%. Hereafter, the magma of intermediate composition spanning from andesite to dacite is referred to as the andesite-dacite continuum (ADC). The tephra clasts used in this study represent extremes in this continuum, and the terms "andesite" and "dacite" are used for these particular samples (Fig. 1). The phenocryst crystallinity of the material in the ADC ranges from 30 to 50 wt%. The more evolved pumices typically have slightly greater crystallinities but the range in bulk composition is not simply a result of variable phenocryst content (Hildreth 1983). As expected from their high phenocryst contents, the matrix melts of ADC tephra are highly evolved: rhyodacite to rhyolite in the andesite scoria, and high-silica rhyolite in the dacite pumice (Fig. 1).

The high-silica rhyolite magma erupted in 1912 is separated from the ADC by a compositional gap (8.5 wt% SiO<sub>2</sub>) but appears to be an extension of the ADC Harker trends for all elements except Zr (Hildreth 1987). The discontinuous Zr trend possibly results from saturation and fractionation of zircon. The rhyolite is a liquid multiply-saturated with ~2 vol% unzoned crystals of plagioclase, quartz, orthopyroxene, apatite, pyrrhotite, magnetite and ilmenite. The pumices are white and highly vesicular. The 7–8 km<sup>3</sup> of erupted rhyolite magma is fairly uniform in bulk composition, crystal content, temperature, and  $fO_2$  as determined from Fe-Ti-oxide geothermometry. A small volume of rhyolite

Several models have been proposed for the preeruptive storage geometry for the rhyolite and ADC magmas. A single magma chamber, compositionally layered from mafic at the base to felsic at the top, was proposed on the basis of continuous temperatures and  $fO_2$  values indicated by Fe-Ti-oxide geothermometry in the erupted magmas (Fig. 2; Hildreth 1987; Hildreth and Fierstein 2000). This model links the rhyolite to the ADC by crystal-liquid fractionation, and includes a cumulate mush underlying the pile to account for the large volume of high-silica rhyolite. Another model explains the compositional gap between rhyolite and ADC magmas and provides a triggering event for the eruption, calling for deep origins and pre-eruptive storage of the rhyolite, completely separate from the ADC (Eichelberger and Izbekov 2000). The rhyolite is proposed by those authors to have migrated vertically as a dike which intercepted the surface at Novarupta and the ADC chamber beneath Mt. Katmai simultaneously, drawing the intermediate magmas into the eruption along a shallow dike.

Deposit characteristics and stratigraphic analyses intimate a complex pre-eruption magma storage geometry. The goal of this experimental study is to constrain the pre-eruptive storage conditions for the most- and leastevolved compositions in the ADC, with the implicit assumption that these conditions bracket the storage



Fig. 1. Bulk and matrix glass compositions of 1912 products. Closed circles are from Hildreth (1983). Samples used in this study are shown with error bars indicating  $\pm 1\sigma$  from average microprobe analysis. Lines connect bulk compositions of ADC intermediates with their matrix glass compositions. Percentages are crystal contents of these samples calculated by mass balance assuming that K<sub>2</sub>O is incompatible



Fig. 2. Temperature–oxygen fugacity relationships for 1912 products obtained from Fe-Ti-oxide geothermometry. Bulk compositions of several samples are given in Table 1. Representative uncertainty  $(\pm 1\sigma)$  given for model calculations, this study

conditions for all the intermediate compositions. A combination of analytical and experimental techniques were used to constrain the temperature,  $fO_2$ , total pressure (P<sub>TOT</sub>), and H<sub>2</sub>O contents at which these magmas last equilibrated prior to eruption. Results are compared with a phase-equilibria study of the rhyolite by Coombs and Gardner (2001) to evaluate the magma storage and eruption models described above.

# **Methods**

Laboratory determination of pre-eruptive magma storage conditions is based on analytical techniques and on experimental reproduction of the phase assemblage, natural compositions of melt and major silicate minerals, and the appropriate mode of mineral phases (e.g., Rutherford et al. 1985; Johnson and Rutherford 1988; Grove et al. 1997; Venezky and Rutherford 1997; Barclay et al. 1998; Moore and Carmichael 1998; Cottrell et al. 1999). The present approach is to constrain  $fO_2$ and temperature using natural samples, then to establish the stability fields of the major phenocryst phases in pressure (P)-temperature (T) space. The compositions of experimental matrix glasses are used to refine the equilibrium conditions, because melts respond to the changing proportions and abundances of crystallizing phases. Finally, the rim compositions of experimentally grown minerals are compared with the rims of phenocrysts in natural samples. Experiments with CO<sub>2</sub> present were run to examine the possibility of H<sub>2</sub>O undersaturation (i.e.,  $P_{H2O} < P_{TOT}$ ) or the presence of a mixed volatile phase. Again, the experimental phase assemblage, glass, and mineral compositions were compared with natural eruptive materials to evaluate the  $P_{H2O}$  and P<sub>TOT</sub> of magma storage.

The materials selected for phase-equilibria experiments are part of a large sample set which defines the compositional range of 1912 ejecta (Hildreth and Fierstein 2000). Pumice samples K1490 (dacite) and K131D (andesite) represent the high- and low-silica extremes of the ADC, respectively (Table 1). The andesite is similar to many analyzed black scoria clasts at the mafic end of the continuum, and it was taken from a late flow unit near the top of the main valley-filling ignimbrite in the central VTTS. The dacite is one of the few pumice blocks to contain trace amounts of hornblende, and is from the distal Ukak lobe of the main VTTS ignimbrite. A large portion of each pumice clast was ground to a powder for bulk compositional analysis by X-ray fluorescence. Splits of the remaining material were used to make mineral separates and thin sections. Bulk compositions determined by XRF fluorescence in USGS laboratories are identical within analytical error to results of electron microprobe analysis of 1-atm fusions (Table 1).

Felsic mineral concentrates were obtained from two dacite clasts (K1490 and K94B) and one andesite clast (K131D) by crushing and sieving to obtain 250–400 mµ fragments, cleaning the grains in an ultrasonic bath, magnetically separating Fe-bearing minerals, and immersing them in fluoroboric acid for 5 h to reduce the amount of glass. A split was used to make polished grain-mount thin sections, and the remaining fraction ground to a powder for analysis by X-ray diffraction. The polished thin sections were etched in HF and stained with barium chloride, saturated Na-cobaltinitrite and amaranth solutions to aid in mineral identification.

#### Experimental techniques

Experiments were run in cold seal TZM and Waspaloy pressure vessels, using an Ar–CH<sub>4</sub> gas mixture and water as the pressurizing medium, respectively (Table 2). The capsule material was either Ag or  $Ag_{70}Pd_{30}$  alloy, depending on run temperature. In most cases, two sample materials were run in separate tubes within the same capsule: finely powdered, crystal-rich andesite/dacite (referenced by "a" in text and tables), and a glass-rich powder of the same bulk composition ("b" part). The glassy material crystallized whereas the natural material either crystallized or melted, depending on the run conditions relative to natural, pre-eruptive magma

Table 1. 1912 magmas and experimental starting materials. N.A. Not applicable, n.a. not analyzed

Sample No.	SiO <sub>2</sub> <sup>c</sup>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>T</sub> <sup>d</sup>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$P_2O_5$	LOI Tot
Andesite											
K131D <sup>a</sup>	59.0	0.72	16.9	7.11	0.14	3.73	7.47	3.51	1.32	0.12	1.5 97.0
K131D <sup>t</sup>	9 59.0 (0.3	3) 0.70 (0.0	3) 17.0 (0.1	) 6.99 (0.1	7) 0.14 (0.05	) 3.73 (0.08	) 7.48 (0.13	) 3.51 (0.15)	1.32 (0.06	0.13 (0.02)	N.A. 99.
K2645A	<sup>b</sup> 60.0 (0.3	3) 0.69 (0.0	5) 17.0 (0.2	) 6.31 (0.1 <sup>°</sup>	7) 0.12 (0.03	3.26 (0.16	0.12	3.95 (0.06	1.43 (0.08	0.16 (0.03)	N.A. 99.5
K2633A	<sup>b</sup> 62.1 (0.4	4) 0.63 (0.0	4) 15.9 (0.1	) 6.41 (0.22	2) 0.15 (0.05	3.23 (0.05	6.43 (0.16	) 3.51 (0.17)	1.52 (0.09	0.13 (0.02)	) N.A. 100.2
Dacite											
K94B <sup>a</sup>	65.4	0.65	15.8	5.16	0.12	2.04	4.78	4.21	1.69	0.15	0.67 99.
K1490 <sup>a</sup>	68.0	0.57	15.2	4.39	0.10	1.60	3.93	4.10	2.04	0.13	1.6 97.7
K1490 <sup>b</sup>	68.3 (0.2	2) 0.58 (0.0	5) 14.8 (0.2	) 4.15 (0.1	7) 0.15 (0.04	) 1.67 (0.06	) 3.96 (0.09	) 4.35 (0.19)	2.00 (0.07)	) n.a.	N.A. 100.3

<sup>a</sup>XRF analyses

<sup>b</sup>Electron microprobe analyses of 1-atm fusions. Numbers in parentheses are standard deviations of  $\geq 5$  analyses

<sup>c</sup>All oxide wt% values normalized to 100

<sup>d</sup>Calculated using  $\text{Fe}^{3+}/\text{Fe}^{2+}$  values obtained using the model of Kilinc et al. (1983) with  $fO_2$  and temperature data from oxide pairs

Table 2. Hydrothermal experiments on 1912 andesite and dacite. N.A. Not applicable

Charge	Crystal-rich starting material "a"	Glass-rich starting material "b"	Temperature (°C)	Pressure (MPa)	X <sub>H2O</sub> fl	Duration (h)	Products <sup>b</sup>
Andesite	experiments $-fO_2 \approx NN$	JO + 1					
K01	K131d <sup>a</sup>	None	990	200	1	47.5	Gl, (opx), (cpx)
K03	K131d <sup>a</sup>	K01	990	150	1	48.5	Gl, plag, opx, cpx, mt
K04	K131d <sup>a</sup>	K01	990	100	1	49.5	Gl, plag, opx, cpx, mt
K05	K131d <sup>a</sup>	K01	990	50	1	47.8	Gl, plag, opx, cpx, mt, (ilm)
K08	K131d <sup>a</sup>	K01	930	100	1	49.0	Gl, plag, opx, cpx, mt
K09	K131d <sup>a</sup>	K01	960	150	1	48.8	Gl, plag, opx, cpx, mt
K10	K131d <sup>a</sup>	K01	930	150	1	48.3	Gl, plag, opx, cpx, mt
K11	K131d <sup>a</sup>	None	870	100	1	48.2	Plag, gl, opx, cpx, mt
K12	K11	K01	960	200	1	48.5	Gl, plag, opx, cpx, mt
K14	K11	K01	930	200	1	57.5	Gl, plag, opx, cpx, hbd, mt
K15	K11	K01	900	200	1	48.9	Gl, plag, hbd, opx, mt, (cpx)
K16	K11	K01	870	200	1	48.7	Gl, plag, hbd, opx, mt, (cpx)
K17	K11	K01	900	150	1	103.6	Gl, plag, opx, cpx, hbd, mt
K18	K11	K01	870	150	1	71.8	Gl, plag, hbd, opx, mt, (cpx)
K21	KII KINI IN	K08b	870	100	1	139.2	Plag, gl, opx, cpx, mt
K22	K131d <sup>a</sup>	K10b	900	100	1	139.6	Plag, gl, opx, cpx, mt
K23	K131d <sup>a</sup>	None	850	/5	1	136.2	Plag, gl, opx, cpx, mt
K24	K131d <sup>a</sup>	None	900	75	1	140.0	Plag, gl, opx, cpx, mt
K25	K131d <sup>a</sup>	None	900	100	1	139.2	Plag, gl, opx, cpx, mt
K26	K131d <sup>a</sup>	None	990	200	1	48.6	Gl, opx, cpx
K2/	K131d <sup>4</sup>	K26	960	125		95.6	Gl, plag, opx, cpx, mt
K28	K2/a	None	960	214	N.A.°	119.7	Gl, plag, opx, cpx, mt
K29	K131d <sup>a</sup>	K01	960	50	1	141.0	Plag, gl, opx, cpx, mt
K 32	K26	None	1,050	100	1	21.8	Gl
K33 1/24	K131d	None	960	220	1	48.8	GI, opx, cpx, mt
K 34 V 26	$K_{20}$ $V_{121} J^a$	None V 26	1,050	50	1	23.0	GI Clarlag any any mt
K 30 K 27	K13IU V26	K20 None	900	110	1	92.9	$G_{1}$ , plag, opx, cpx, int $G_{1}$ ( $n_{1}$ ) ( $n_{2}$ )
K3/ V29	$K_{20}$ V 121 d <sup>a</sup>	None	1,020	100	1	37.0 45.0	GI, (pI), (opx)
K 30 K 20	$\mathbf{K}_{121}$	None V 26	900	75	1	43.9	Gl, plag, opx, cpx, int
K 40	K131da	K 20 K 26	900	100	1	90.5	Gl, plag, opx, cpx, mt
K40 K41	$K_{121}d^a$	K20 K26	900	200	0.52	93.9 42.4	Cl. plag, opx, cpx, int
K / 3	K131d <sup>a</sup>	None	960	200	1	88.8	Gl plag opy cpy mt
K44 K44	K131d <sup>a</sup>	K 37a	990	75	1	107.1	Gl plag opy cpy mt
K46	K131d <sup>a</sup>	None	960	200	0 454	48.1	Gl plag opy cpy mt
K47	K131d <sup>a</sup>	None	960	150	0.751	48.2	Gl plag opx cpx, mt
K49	K131d <sup>a</sup>	None	960	125	0.852	53.6	Gl plag opx cpx mt
K 50	K131d <sup>a</sup>	None	960	225	0.341	59.7	Gl plag opx cpx mt
Decite of	$r_{\rm maximanta}$ NNO $< t_{\rm O}$	$<$ NNO $\pm 2$	900	220	0.5 11	59.1	Gi, ping, opa, opa, int
	$V_{1400}$	$2 \le \text{ININO} \pm 2$	020	200	1	40.6	Cl any any mt
KD01	K 1490	None V D01	920	200	1	49.0	$G_{1}$ , $Op_{X}$ , $Cp_{X}$ , $Int$
KD02	K 1490	KD01	850	100	1	242.1	Gl plag cpy opy mt
KD03	K 1490 K 1490	KD01	880	100	1	241.7	Gl plag cpx, opx, mt ilm
KD04	K 1490	KD01	850	50	1	241.0	Gl plag cpx opx atz mt
K D05	K 1490	KD01	880	50	1	241.1	Gl plag cpx opx mt
KD12	K 1490	KD01	850	25	1	278.6	Gl plag cpx opx atz mt
KD12 KD13	K1490	KD01	880	25	1	228.0	Gl plag cpx opx, qtz mt
KD13 KD14	K 1490	KD01	820	50	1	228.7	Plag gl gtz opy cpy mt
KD14	K 1490	KD01	820	150	1	124.2	Gl plag cpy opy mt
KD15 KD16	K1490	None	950	200	1	47 7	Gl
KD17	K1490	None	850	15	1	542.6	Plag gl atz ony cny mt
KD18	K1490	None	880	15	1	542.0	Plag gl gtz opx cpx mt
KD10	<sup>1</sup> None	KD15h	880	150	1	954	Gl plag cpx opx mt
KD20	K 1490	None	850	75	0.816	182.0	Gl plag cpx opx mt (atz)
KD20	K1490	None	850	75	0.733	182.5	Gl plag cpx opx mt ( $dtz$ )
KD21	K1490	None	850	100	0.57	167.7	$Gl_{1}$ plag_ cpx, opx, mt, (qtz)
KD23	K1490	None	850	100	0.495	168.0	$Gl_{1}$ plag cpx, opx, mt, (qtz)
KD24	K1490	None	850	125	0.439	164.9	Gl. plag, cpx, opx, mt. (qtz)
KD25	K1490	None	850	150	0.275	164.3	Gl, plag, cpx, opx, qtz, mt

 $^cFluid-undersaturated experiment, 1.0 wt% H_2O dissolved in melt <math display="inline">^dProgrammed$  cooling from 950 °C at 5 °C/h

<sup>a</sup>Powdered end-member mafic andesite <sup>b</sup>Phases listed in decreasing abundance. Phases in parentheses are trace. Gl, Glass; plag, plagioclase; opx, low-Ca pyroxene; cpx, high-Ca pyroxene; mt, magnetite; ilm, ilmenite; hbd, hornblende; qtz, quartz

storage conditions. Thus, many of the experiments represent "reversals", in which equilibrium is approached from both melting and crystallization directions. We found that a close approach to equilibrium was attained within 96 h for all of the andesite experiments. Equilibrium in the dacite experiments required 48 to 250 h, depending on temperature and H<sub>2</sub>O content. Several samples were fused to create homogeneous glasses for electron microprobe bulk compositional analysis (Table 1). Powders were wrapped in Mo foil, sealed in evacuated Si glass tubes, held at 1,300 °C for 3 h, reground and then re-melted at 1,300 °C for 5 h.

In the experiments with  $P_{H2O} = P_{TOT}$ , distilled deionized H<sub>2</sub>O sufficient to saturate the melt at run conditions was placed in the capsule along with starting materials and solid buffer tubes. The mass fraction of fluid in the charges never exceeded 0.28. Capsules were crimped, welded shut and weighed before and after heating for 1 h in a drying oven to verify the integrity of the welds. After running at high temperature and pressure, capsules were re-weighed and then checked for the presence of liquid water when opened. Charges which did not fizz when pierced or otherwise indicated H<sub>2</sub>O loss during the experiment were discarded.

Fluid-saturated experiments with  $a_{H2O} < 1$  in the fluid phase (i.e.,  $P_{H2O} = P_{TOT} - P_{CO2}$ ) were run using Ag<sub>2</sub>CO<sub>3</sub> as a source of  $CO_2$  (Holloway et al. 1968). The fluid composition of these so-termed "H2O-undersaturated" experiments is given by the total pressure  $(P_{TOT})$  and mole fraction of H<sub>2</sub>O in the fluid  $(X_{H2O}^{fl})$ , which in combination specify P<sub>H2O</sub>:  $(P_{TOT})(X_{H2O}^{fl}) = P_{H2O}$ . The weight fraction of H<sub>2</sub>O in the melt was calculated using the initial masses of  $H_2O$ ,  $Ag_2CO_3$ , starting material, a mass-balance calculation of melt fraction at the end of the experiment, and an empirical, composition-based  $H_2O$  solubility model (Moore et al. 1998).  $X_{H2O}^{ff}$  was calculated by subtracting moles of H<sub>2</sub>O dissolved in the melt from the total water added to the charge and dividing by the total moles of volatiles (H<sub>2</sub>O +  $\dot{CO}_2$ ), with estimated uncertainty in X<sub>H2O</sub><sup>fl</sup> of ±0.026. Previous experimental studies show that decreasing P<sub>H2O</sub> below  $P_{TOT}$  by means of either running at fluid-absent conditions or adding CO<sub>2</sub> gas produces identical results with respect to phase equilibria of high-Si melts at P<sub>TOT</sub> < 1,500 MPa (Ebadi and Johannes 1991; Johannes and Holtz 1996). Thus, results from CO<sub>2</sub>-bearing, H<sub>2</sub>Oundersaturated experiments apply equally well to magmas with  $H_2O$  present in quantities insufficient to form a separate fluid phase (Rutherford et al. 1985; Gardner et al. 1995).

The oxygen fugacity of the experiments was controlled in the TZM runs by varying the composition of the Ar–CH<sub>4</sub> pressurizing gas mixture according to an independent calibration of sample  $fO_2$  as a function of P<sub>CH4</sub>, P<sub>TOT</sub>, and temperature. Small amounts of two solid buffer assemblages (Ni–NiO and Re–ReO<sub>2</sub>) were included as  $fO_2$  monitors in separate tubes (Pt and Ag<sub>70</sub>Pd<sub>30</sub>, respectively) within each capsule. We interpreted the absence of Ni metal and ReO<sub>2</sub> at the end of the experiment as indicating the experimental  $fO_2$  was above the NNO buffer and below NNO+2 (Pownceby and O'Neill 1994). Experiments run in the Waspaloy bombs with aged Ni filler rods were maintained at  $fO_2$  of NNO+1±0.5, according to previous calibrations in this laboratory (Geschwind and Rutherford 1992; Gardner et al. 1995).

#### Microprobe analysis

Minerals and matrix glasses in the natural and experimental samples were analyzed using the Cameca Camebax electron microprobe at Brown University. Glass analyses were obtained using 15-keV accelerating voltage, 10-nA beam current, and a defocused beam having the largest spot size allowed by crystal texture. Accuracy and precision were monitored by repeated analysis of a well-characterized comenditic obsidian. Sodium loss from hydrated experimental glasses under the electron beam was accounted for using the time-zero extrapolation technique of Nielsen and Sigurdsson (1988), and by obtaining test analyses of variably hydrated, standard reference glasses prior to and following analyses of unknowns (Devine et al. 1995). Minerals were analyzed with a focused 15-nA beam and accelerating voltage of 15 keV. Data were reduced using the ZAF correction procedure of Bence and Albee (1968).

#### Results

#### Natural phase assemblages

The phase assemblage of silicic ADC tephra, as reported in previous studies (e.g. Hildreth 1983; Lowenstern 1993) includes plagioclase, augite, orthopyroxene, magnetite, ilmenite, and accessory phases apatite and pyrrhotite. Although quartz (or any SiO<sub>2</sub> polymorph) was not previously identified in any of the ADC tephra, the high SiO<sub>2</sub> content of the matrix glass of K1490 (79.1 wt%) indicated that this melt must have been saturated (or very nearly so) with an  $SiO_2$  phase. The distinctive alpha quartz peaks at 20.86 and  $26.64^{\circ}2\theta$ (Cu) were not identified in any of the replicate XRD analyses, indicating that if present, quartz accounts for less than 5 vol% of the felsic mineral split. No quartz was found in K94B dacite, but seven of the estimated 1,000 grains in K1490 dacite concentrate were identified as quartz in stained, felsic concentrate grain mounts. These determinations were verified with the electron microprobe, and the glass selvages clinging to several grains were identical to other matrix glass analyses. The presence of even a small amount of quartz in equilibrium with the melt is an important phase-equilibrium constraint  $(a_{quartz} = 1)$  for determining pre-eruption storage conditions.

Several quartz grains were also found in the andesite sample, although none of the fragments had glassy selvages. Unlike the dacite, the matrix glass of K131D andesite is not highly evolved ( $68 \text{ wt}\% \text{ SiO}_2$ ). Thus, it is extremely unlikely that these quartz crystals were in equilibrium with the andesite matrix melt. To verify this, a large euhedral quartz crystal was placed in contact with K131D powder and brought to 930 °C and 100-MPa conditions at which the experimental melt ( $67.7 \text{ wt}\% \text{ SiO}_2$ ) is otherwise very similar to the natural matrix melt (67.6 wt%). After 48 h, this grain had begun to dissolve and the surrounding matrix glass was significantly SiO<sub>2</sub>-enriched (77 wt%). Thus, quartz is not considered part of the andesite phase assemblage; the significance of observing it in K131D is discussed below.

# Temperature, $fO_2$ and $P_{H2O}$ constraints from natural samples: andesite

Pre-eruptive magmatic temperature estimates were obtained from analyses of Fe-Ti oxides in the andesite. Examination of thousands of grains in a magnetic concentrate yielded just two magnetite-ilmenite pairs in contact. These pairs satisfy the Bacon and Hirschmann (1988) Mg-Mn distribution criteria, and give equilibration temperatures of 953 and 962 °C (both  $\pm 21$  °C) and log  $fO_2$  of -9.85 and -9.91 (±0.11), respectively, according to the mineral formula calculation method of Stormer (1983) with the algorithm of Anderson and Lindsley (1988). Three pairs in a slightly more evolved andesite (K2645A, Table 1 and Fig. 2) also give similar values (954–959 °C and -10.1) using this method. These values are within the range of previously reported data for the 1912 andesite (Hildreth 1983; Coombs and Gardner 2001). Phase-equilibria experiments were conducted across a range of temperatures (850–1,050 °C) and pressures (50-220 MPa) in order to locate mineralin curves. In view of the thermometry data, coverage was especially focused at 960 °C for the purpose of ascertaining magma storage pressure.

Although ilmenite crystals in the natural andesite are unzoned, with  $\sim 40\%$  TiO<sub>2</sub>, titanomagnetites are compositionally variable both grain to grain and within individual crystals. TiO<sub>2</sub> contents of the titanomagnetites span two ranges with a gap between 9.18 and 9.97 wt%. The lower-Ti grains are isolated, euhedral-faceted crystals surrounded by matrix melt or are completely enclosed within pyroxene grains, and thus are *not* in contact with ilmenite. These crystals are homogeneous in composition. Titanomagnetites in contact with ilmenite grade from high TiO<sub>2</sub> near the ilmenite contact downward away from it (Fig. 3). Assuming that the change in TiO<sub>2</sub> concentration in the ilmenite upon heating is small in comparison with that of the magnetite, the temperatures indicated by the interior magnetite compositions are lower than the contact compositions by  $\sim$ 35 °C (temperatures in Fig. 2 are obtained from the near-contact magnetite compositions and the adjacent ilmenite).



**Fig. 3.** End-member percentages of ulvospinel (*usp* spinel phase) and ilmenite (*ilm* rhombohedral phase) in K131D Fe-Ti oxides. Analytical error is equal to or less than *symbol* size. *Horizontal lines* of outside rim (in contact with glass) are composition shown for reference

Melt inclusions in phenocrysts of K131D are commonly partly crystallized or fractured, and thus unsuitable for microprobe analysis. Unfortunately, this precludes gathering information directly about mixing and thermal history from their volatile contents and host compositions (Lowenstern and Mahood 1991; Cottrell et al. 1999; Anderson et al. 2000). Several melt inclusions in plagioclase hosts from other 1912 andesites were previously analyzed by ion probe (Westrich et al. 1991). These inclusions contain gas bubbles and glass with very low dissolved H<sub>2</sub>O contents ( $\sim 1 \text{ wt\%}$ ). Westrich et al. (1991) conclude that they represent trapping of degassing melt, but it is also possible they experienced decompression during magma ascent. These melt inclusions give a minimum  $H_2O$  content for the melt present during crystal growth in the andesite. Beyond this, there are no constraints on pressure or the partial pressure of  $H_2O(P_{H2O})$  from the melt inclusions in natural andesite samples.

Constraints from natural samples: dacite

More information on pre-eruptive temperature and H<sub>2</sub>O content is available for the dacite (K1490) which contains relatively abundant (0.5 wt%) ilmenite. Individual titanomagnetite and ilmenite crystals in the dacite are unzoned but are not uniform in composition as a population. For example, TiO<sub>2</sub> contents in magnetites range from 8.4 to 10.0. Pairs of magnetite and ilmenite grains in contact give equilibration temperatures which cluster in the range 848 to 878 °C ( $\pm$  20 °C average error), with corresponding log *f*O<sub>2</sub> values of -11.7 to -11.4 ( $\pm$ 0.14). Two "outlier" pairs, corresponding to high-TiO<sub>2</sub> magnetites, give values of 936 °C/–9.8 and 964 °C/–9.4 for temperature/log *f*O<sub>2</sub>. The *f*O<sub>2</sub> values indicated by the

Melt inclusions in the dacite phenocrysts are generally less crystalline than those in andesite, with many crystal-free vitreous inclusions. A previous FTIR study of the melt inclusions in plagioclase phenocrysts in 1912 dacite estimated that the magma contained  $2.8 \pm 0.5$  wt% dissolved H<sub>2</sub>O (with CO<sub>2</sub> below minimum detection limit of 50 ppm; Lowenstern 1993), and thus could have coexisted with a separate, H<sub>2</sub>O-rich fluid phase if stored at ~47 MPa (Moore et al. 1998).

#### Experimental results

#### $H_2O$ -saturated experiments: and esite

The K131D andesite is saturated with augite, orthopyroxene, and magnetite at 990 °C over the 0–200 MPa pressure range examined. At this temperature, plagioclase appears at 150 MPa and is stable at all lower pressures. Hornblende, not present in the natural phenocryst assemblage, is stable below 930 °C when the pressure is greater than ~130 MPa. Thus, the phenocryst assemblage of K131D is produced experimentally in the lightly shaded region of P–T space shown in Fig. 4. This region includes the temperature range obtained from the Fe-Ti-oxide pairs, shown as a darker shaded strip at 960 °C±5.

Changing phase proportions and abundances during crystallization with varying pressure (isothermal series) and at varying temperature (isobaric series) are reflected in the evolution of matrix melts along characteristic liquid lines of descent (LLD). Thus, the compositions of glasses from H<sub>2</sub>O-saturated experiments (Table 3) can be compared with natural matrix glass to indicate the pressure of magma storage under H<sub>2</sub>O-saturated conditions. At 960 °C, the SiO<sub>2</sub> contents of experimental melts increase from  $\sim 60$  to 73 wt%, and crystallinity increases from 10 to 60% as P<sub>H2O</sub> decreases from 220 to 50 MPa (Fig. 5a). The glass compositions from a series of experiments at 100 MPa show the effect of temperature on melt composition during isobaric crystallization (Fig. 5b). The melts produced at 75 and 100 MPa bracket the natural matrix glass in the 960 °C series, and a close match to the natural matrix glass composition is attained in the 100-MPa series at 930 °C. Thus, the isobaric and isothermal experimental results describe a narrow  $P_{H2O}$ -T space in which the natural melt compositions are produced (Fig. 4). This range encompasses the temperature range indicated by the two Fe-Ti-oxide pairs.

The modes of glass and mineral phases in selected experimental samples were calculated by mass balance using a linear least-squares regression of nine major and minor oxide components distributed among seven phases (melt, augite, orthopyroxene, two plagioclase

**Fig. 4.** Phase diagram for K131D andesite under  $H_2O$ -saturated conditions. Experiments are given by *triangles* which point in the direction of approach to equilibrium. Mineral-in curves are shown for orthopyroxene (*opx*), clinopyroxene (*cpx*), titanomagnetite (*mt*), plagioclase feldspar (*plag*), and hornblende (*hbd*). The natural phase assemblage is stable in the *lightly shaded* region, Fe-Ti-oxide temperatures are bracketed by the narrow, vertical *darker shaded bar*, and the experimental matrix glass compositions closely match the natural compositions within the diagonally *hatched region*. *Dashed lines* are calculated  $H_2O$  solubilities using the algorithm of Moore et al. (1998) with composition and experimental conditions as model inputs

compositions, magnetite, and ilmenite), using the K131D whole-rock analysis as the bulk composition. The crystallinity calculated for the natural andesite K131D is 43%, consisting of 23% plagioclase, 10% Carich pyroxene, 7.4% orthopyroxene, 3% magnetite, and <1% ilmenite. The modes of H<sub>2</sub>O-saturated experiments K08 and K43 at 930 °C/100 MPa and 960 °C/ 75 MPa, respectively, most closely match the mode and mineral compositions of the natural sample (Table 4), indicating that these T-P<sub>H2O</sub> conditions bracket the natural pre-eruptive storage conditions of the K131D andesite magma if H<sub>2</sub>O-saturated. Discrepancies between experimental and natural samples are higher proportion of plagioclase to pyroxene, higher proportion of orthopyroxene to clinopyroxene, and greater CaO content of matrix melt in the experimental samples. The crystal-rich starting materials (a experiments) produced higher matrix CaO than the glassy starting materials (b experiments) in 10 out of 15 paired experiments. One possibility is that the cores of zoned phenocrysts (Shearer et al. 1991) which were exposed to matrix melt in the finely powdered, crystal-rich starting material caused the disproportionate crystallization of orthopyroxene with respect to clinopyroxene, raising residual melt CaO content.



plag

hbd

(cpx

mt

срх

K131D Andesite

250

Temperature (°C)

151

**Table 3.** Natural and experimental matrix and inclusion glass compositions (all analyses are for matrix glass unless noted; natural samplesare identified as "scoria" or "pumice"; all others are experimental charges)

Sample No.	SiO <sub>2</sub>		TiO <sub>2</sub>		Al <sub>2</sub> O	3	FeO	Г	MnC	)	MgC	)	CaO		Na <sub>2</sub> C	)	K <sub>2</sub> O		Tot <sup>a</sup>	n <sup>b</sup>
Andesite	67.6	(0,4)	0.65	(0.08)	15.5	(0, 2)	1 65	(0.32)	0.00	(0.05)	1 20	(0.16)	2.61	(0.11)	4 21	(0, 16)	2.24	(0.07)	08.7	10
(scoria) K 2645A	71.4	(0.4)	0.05	(0.08)	13.5	(0.2)	3.28	(0.32)	0.09	(0.03)	0.68	(0.10)	2.62	(0.11)	4.51	(0.10)	2.24	(0.07)	98.7	5
(scoria) K2633A	74.2	(1.4)	0.67	(0.13)	12.8	(0.1)	3.02	(0.48)	0.09	(0.06)	0.35	(0.11)	1.64	(0.27)	4.09	(0.12)	3.15	(0.04)	98.4	3
(scoria) K03a	60.7	(0.2)	0.68	(0.04)	17.7	(0.1)	5.24	(0.12)	0.13	(0.05)	3.32	(0.09)	6.99	(0.04)	3.76	(0.10)	1.44	(0.02)	94.5	5
K04a	64.0	(0.3)	0.73	(0.09)	15.9	(0.2)	4.94	(0.25)	0.12	(0.05)	2.42	(0.05)	6.27	(0.13)	3.98	(0.16)	1.67	(0.09)	95.9	9
K04b	63.2	(0.1)	0.77	(0.07)	16.8	(0.2)	4.92	(0.13)	0.13	(0.07)	2.61	(0.11)	5.79	(0.25)	3.99	(0.16)	1.79	(0.07)	93.8	6
K030 K08a	67.7	(0.3)	0.77	(0.04)	13.4	(0.2)	5.18 4.09	(0.18) (0.14)	0.09	(0.05) (0.06)	1 20	(0.09) (0.08)	2.95 4 44	(0.18) (0.20)	4.10	(0.23) (0.15)	2.00	(0.03) (0.12)	95.5	9
K08b	67.1	(0.2)	0.75	(0.03)	15.9	(0.1)	4.18	(0.23)	0.10	(0.03)	1.24	(0.13)	3.94	(0.09)	4.44	(0.16)	2.38	(0.03)	94.6	5
K09a	64.0	(0.5)	0.94	(0.09)	15.9	(0.3)	5.56	(0.22)	0.09	(0.05)	1.81	(0.06)	5.60	(0.24)	4.33	(0.15)	1.81	(0.11)	93.7	5
K09b	63.2	(0.3)	0.90	(0.07)	16.4	(0.1)	6.22	(0.27)	0.12	(0.05)	1.88	(0.14)	5.46	(0.21)	3.94	(0.21)	1.83	(0.13)	94.3	5
K100 K12a	62 7	(0.4)	0.81	(0.10) (0.07)	17.1	(0.3)	3.00	(0.34) (0.16)	0.11	(0.03) (0.03)	2 53	(0.18) (0.19)	4.38	(0.23) (0.20)	4.12	(0.10) (0.20)	1 49	(0.17) (0.08)	90.2	7
K12b	63.2	(0.3)	0.66	(0.08)	18.1	(0.1)	4.03	(0.10) (0.20)	0.12	(0.05)	2.18	(0.19)	6.80	(0.16)	3.63	(0.10)	1.29	(0.05)	92.0	8
K21a	72.8	(0.3)	0.49	(0.04)	13.9	(0.1)	3.02	(0.14)	0.08	(0.07)	0.64	(0.03)	2.59	(0.07)	3.95	(0.19)	2.61	(0.07)	94.5	9
K21b	73.2	(0.6)	0.53	(0.05)	14.1	(0.2)	2.91	(0.15)	0.07	(0.04)	0.63	(0.03)	2.70	(0.10)	3.37	(0.29)	2.49	(0.19)	92.4	7
K25 K27a	72.1 66.1	(0.7)	0.50	(0.05)	15.9	(0.1)	3.10	(0.17) (0.24)	0.06	(0.06) (0.07)	0.64	(0.05) (0.09)	5.24 5.46	(0.13) (0.19)	3.95 4 40	(0.36) (0.16)	2.46	(0.17) (0.08)	93.7	8
K27b	66.5	(0.1)	0.78	(0.06)	16.1	(0.1)	3.39	(0.21)	0.09	(0.07)	1.82	(0.0) (0.12)	5.29	(0.19) (0.18)	4.17	(0.10) (0.21)	1.84	(0.00) (0.11)	93.9	7
K28	67.4	(0.3)	0.71	(0.07)	15.9	(0.1)	2.68	(0.11)	0.10	(0.06)	1.91	(0.06)	5.02	(0.16)	4.44	(0.18)	1.82	(0.07)	94.6	9
K29a	71.2	(1.1)	0.75	(0.04)	13.2	(0.4)	4.16	(0.43)	0.13	(0.03)	0.70	(0.11)	2.64	(0.32)	4.46	(0.34)	2.75	(0.10)	97.3	7
K 290 K 32	/3.5	(0.3)	0.74	(0.05) (0.04)	12.2	(0.2)	5.52 6.31	(0.18) (0.27)	0.06	(0.04)	0.41	(0.02)	1.88	(0.06) (0.14)	4.4/	(0.13)	3.37	(0.05) (0.04)	97.8	9
K32 K33	59.2	(0.3)	0.74	(0.04)	16.6	(0.1)	6.68	(0.27) (0.12)	0.14	(0.05) (0.06)	3.70	(0.00)	8.19	(0.14) (0.18)	3.60	(0.0)	1.17	(0.04)	94.8	10
K36a	67.9	(0.4)	0.74	(0.07)	15.0	(0.2)	3.79	(0.19)	0.11	(0.06)	1.51	(0.04)	4.77	(0.11)	4.32	(0.17)	1.89	(0.05)	95.4	11
K36b	68.5	(0.4)	0.79	(0.05)	14.8	(0.2)	3.67	(0.22)	0.13	(0.05)	1.46	(0.05)	4.90	(0.09)	4.00	(0.18)	1.73	(0.12)	94.6	8
K3/ K38	61.2 67.4	(0.1)	0.78	(0.07)	16.9	(0.1)	6.24 4 31	(0.13) (0.11)	0.14	(0.06)	3.83	(0.08)	7.61	(0.11) (0.12)	2.57	(0.09)	0.//	(0.03)	95.0 04.8	10
K39a	69.1	(0.2)	0.87	(0.07)	13.7	(0.2)	4.71	(0.11) (0.42)	0.14	(0.07) (0.04)	1.86	(0.00)	5.61	(0.12) (0.24)	2.69	(0.10) (0.17)	1.26	(0.07)	94.9	10
K39b	69.9	(0.2)	0.89	(0.07)	15.0	(0.1)	3.83	(0.16)	0.09	(0.04)	2.00	(0.04)	3.82	(0.14)	3.37	(0.14)	1.14	(0.05)	95.6	9
K40a	67.6	(0.6)	0.75	(0.12)	14.7	(0.1)	4.12	(0.46)	0.10	(0.04)	1.57	(0.02)	5.62	(0.35)	3.78	(0.17)	1.75	(0.11)	94.4	6
K40b	68.6	(0.3)	0.86	(0.07)	14.7	(0.2)	3.58	(0.30)	0.16	(0.05)	1.57	(0.01)	5.22	(0.33)	3.70	(0.18)	1.61	(0.10)	94.7	6
K41a K41b	66 2	(0.4) (0.3)	0.82	(0.00)	14.9	(0.3)	4.25	(0.24) (0.24)	0.14	(0.00) (0.03)	1.72	(0.11) (0.10)	6.12	(0.13) (0.13)	3.69	(0.20) (0.09)	1.37	(0.21) (0.05)	94.9	6
K43	68.8	(0.5)	0.84	(0.10)	14.7	(0.2)	2.86	(0.21)	0.11	(0.05)	1.45	(0.06)	4.49	(0.24)	4.62	(0.19)	2.16	(0.11)	99.1	8
K44a	65.8	(0.5)	0.90	(0.07)	14.7	(0.7)	4.64	(0.28)	0.11	(0.04)	2.26	(0.13)	6.51	(0.39)	3.57	(0.15)	1.50	(0.09)	97.4	8
K44b	67.2	(0.6)	0.92	(0.06)	15.1	(0.2)	4.26	(0.28)	0.13	(0.07)	2.23	(0.18)	5.28	(0.13)	3.57	(0.14)	1.34	(0.07)	95.0	8
K40 K47	67.0	(0.2) (0.4)	0.76	(0.08)	13.3	(0.1) (0.2)	4.12	(0.19) (0.18)	0.12	(0.03)	1.85	(0.09) (0.05)	5.74	(0.11) (0.12)	4.10	(0.10) (0.10)	1.92	(0.07)	96.0	12
K49	69.3	(0.4)	0.89	(0.06)	14.4	(0.2)	3.08	(0.08)	0.11	(0.04)	1.69	(0.04)	5.29	(0.21)	3.38	(0.14)	1.88	(0.10)	95.1	10
K50	72.1	(0.5)	0.80	(0.08)	13.6	(0.3)	2.61	(0.18)	0.08	(0.04)	1.17	(0.03)	3.93	(0.24)	3.81	(0.14)	1.90	(0.08)	96.8	9
K38 glass	75.1		0.41		11.7		3.18		0.12		0.55		1.67		4.01		3.26		97.4	1
K38 glass incl.	70.8		0.57		14.0		3.60		0.17		0.82		3.35		4.39		2.21		96.2	1
Dacite K1490	79.1	(0.2)	0.24	(0.05)	11.7	(0.1)	0.71	(0.23)	0.01	(0.02)	0.10	(0.04)	0.81	(0.05)	4.12	(0.11)	3.22	(0.09)	98.6	7
(pumice)				· /		( )				( )		· /		· /		( )		· /		
KD01	68.3	(0.3)	0.54	(0.05)	15.3	(0.1)	3.87	(0.14)	0.09	(0.04)	1.19	(0.03)	4.34	(0.13)	4.41	(0.22)	1.99	(0.05)	93.7	11
KD02a	73.8	(0.2)	0.32	(0.05)	13.9	(0.1)	1.74	(0.15)	0.03	(0.03)	0.49	(0.03)	2.57	(0.08)	4.56	(0.20)	2.58	(0.10)	95.1	8
KD020 KD03a	75.7	(0.3)	0.33	(0.08) (0.04)	12.9	(0.1)	2.05	(0.33) (0.08)	0.03	(0.03) (0.04)	0.33	(0.11) (0.03)	2.65	(0.09) (0.09)	4.30	(0.13) (0.35)	2.39	(0.07) (0.12)	94.5	7
KD03b	75.7	(0.3)	0.22	(0.04)	12.8	(0.1)	2.01	(0.08)	0.07	(0.06)	0.28	(0.02)	2.03	(0.14)	4.12	(0.16)	2.78	(0.07)	94.7	, 7
KD04a	72.9	(0.2)	0.35	(0.04)	14.0	(0.2)	2.56	(0.18)	0.05	(0.04)	0.45	(0.03)	2.54	(0.14)	4.49	(0.10)	2.68	(0.09)	95.7	8
KD04b	72.9	(0.4)	0.39	(0.04)	13.8	(0.2)	2.66	(0.15)	0.09	(0.05)	0.47	(0.04)	2.60	(0.10)	4.54	(0.21)	2.53	(0.07)	95.1	8
KD05b	79.0 79.8	(0.5) (0.2)	0.26	(0.04) (0.05)	11.4 11.1	(0.1) (0.2)	1.45	(0.13) (0.13)	0.05	(0.03)	0.15	(0.01) (0.14)	0.99	(0.10) (0.07)	5.55 3.16	(0.22) (0.13)	5.15 3.12	(0.14) (0.25)	90.5 93.6	0 8
KD050	78.2	(0.2) (0.3)	0.20	(0.03)	11.6	(0.2) (0.2)	1.20	(0.13) (0.08)	0.04	(0.03)	0.17	(0.17) (0.01)	1.04	(0.07)	3.75	(0.13) (0.21)	3.12	(0.23) (0.09)	95.8	8
KD06b	79.0	(0.3)	0.30	(0.05)	11.4	(0.1)	1.51	(0.11)	0.05	(0.04)	0.20	(0.05)	1.10	(0.08)	3.32	(0.23)	3.18	(0.21)	94.2	8
KD12a	80.3	(0.2)	0.22	(0.06)	10.8	(0.2)	1.15	(0.12)	0.04	(0.03)	0.09	(0.02)	0.59	(0.04)	3.39	(0.10)	3.40	(0.24)	96.0	8
KD12b	79.4	(0.5)	0.35	(0.04)	11.2	(0.3)	1.33	(0.14)	0.04	(0.05)	0.15	(0.06)	0.97	(0.10)	2.98	(0.32)	3.56	(0.10)	93.4	8
KD13a	10.9	(0.3)	0.50	(0.03)	11.1	(0.1)	1.34	(0.11)	0.00	(0.02)	0.12	(0.05)	0.79	(0.05)	5.88	(0.17)	5.30	(0.13)	91.3	0

Table	3.	(Contd.)	)

Sample No.	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>T</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Tot <sup>a</sup> n <sup>b</sup>
KD13b	78.8 (0.2)	0.40 (0.08)	11.3 (0.1)	1.68 (0.05)	0.04 (0.05)	0.23 (0.01)	1.41 (0.09)	3.37 (0.24)	2.72 (0.08)	93.4 5
KD14a	79.1 (0.3)	0.16 (0.04)	11.2 (0.1)	1.24 (0.14)	0.05 (0.03)	0.11 (0.06)	0.72 (0.11)	3.70 (0.21)	3.76 (0.24)	95.4 8
KD14b	79.3 (0.5)	0.31 (0.14)	11.1 (0.2)	1.17 (0.19)	0.03 (0.04)	0.10 (0.01)	0.83 (0.10)	2.96 (0.13)	4.17 (0.05)	94.0 7
KD15a	72.5 (0.3)	0.42 (0.07)	14.1 (0.2)	2.63 (0.26)	0.07 (0.05)	0.58 (0.04)	2.68 (0.10)	4.56 (0.14)	2.51 (0.09)	94.5 10
KD17	78.5 (0.5)	0.28 (0.03)	11.5 (0.4)	1.05 (0.11)	0.04 (0.03)	0.06 (0.01)	0.61 (0.28)	3.72 (0.13)	4.22 (0.27)	94.3 4
KD19	72.4 (0.4)	0.51 (0.06)	13.9 (0.1)	2.41 (0.13)	0.08 (0.05)	0.73 (0.04)	3.19 (0.09)	4.39 (0.18)	2.35 (0.05)	97.7 7
KD20	78.2 (0.3)	0.25 (0.04)	11.8 (0.1)	1.73 (0.10)	0.09 (0.06)	0.16 (0.01)	1.18 (0.07)	3.72 (0.18)	2.92 (0.09)	96.1 12
KD21	78.2 (0.2)	0.25 (0.05)	11.7 (0.1)	1.77 (0.07)	0.04 (0.05)	0.16(0.02)	1.15 (0.04)	3.66 (0.20)	3.05 (0.08)	96.1 11
KD22	78.5 (0.2)	0.23 (0.02)	11.6 (0.1)	1.86 (0.08)	0.04 (0.04)	0.14(0.02)	1.19 (0.14)	3.53 (0.14)	2.96 (0.06)	95.9 10
KD23	78.5 (0.2)	0.23 (0.05)	11.5 (0.1)	1.78 (0.10)	0.04 (0.03)	0.13 (0.03)	1.12 (0.06)	3.65 (0.13)	3.10 (0.06)	96.2 10
KD24	78.4 (0.2)	0.22 (0.04)	11.5 (0.1)	1.73 (0.16)	0.02(0.02)	0.12(0.02)	1.04 (0.08)	3.74 (0.13)	3.17 (0.12)	96.2 6
KD25	77.7 (0.3)	0.22 (0.03)	11.7 (0.1)	1.63 (0.12)	0.04 (0.03)	0.11 (0.01)	0.85 (0.17)	3.82 (0.22)	3.87 (0.11)	97.0 8

<sup>a</sup>Total prior to normalization

<sup>b</sup>Number of analyses

### $H_2O$ -saturated experiments: dacite

The mineral-in curves in P–T space for K1490 dacite are shown in Fig. 6. The stability region for the natural phase assemblage is lightly shaded, and the temperature constraints from the Fe-Ti-oxide pairs are shown as a darker shaded region. Orthopyroxene is the first mineral to appear, followed by clinopyroxene and titanomagnetite with decreasing temperature. Plagioclase joins the assemblage below 860 °C at 150 MPa, and is stable below 910 °C at 50 MPa. Amphibole occurred in only one experiment, at 150 MPa and 850 °C. Quartz saturation occurs at low P and T, and provides the tightest constraint on the pre-eruptive  $P_{H2O}$  of the natural magma ( $P_{H2O} = 50$  MPa).

Comparison of the experimental liquid line of descent as a function of  $P_{H2O}$  with the natural melt composition is shown for several oxide components in Fig. 7 for 850 and 880 °C. At the lower temperature, the natural melt composition is achieved at 50 MPa. At 880 °C, the natural melt is exactly reproduced at 25 MPa, with the 50-MPa experiment also a close match. The insensitivity of the melt composition to pressure in this range is presumably a consequence of its highly evolved nature (~79.0 wt% SiO<sub>2</sub> anhydrous). In fact, the H<sub>2</sub>O-saturated solidus pressure for the high-silica rhyolite matrix of K1490 at 850 °C is approximately 20 MPa (Tuttle and Bowen 1958).

Experiments in which the matrix glass composition matches natural matrix glass also reproduce natural mineral compositions and modes: 29% plagioclase, 4.6% augite, 4.3% orthopyroxene, and 2.7% Fe-Ti oxides (Table 4). Several dacite experiments closely match the natural material in all respects. If the natural magma was H<sub>2</sub>O-saturated at depth, experiments indicate that the dacite equilibrated between P<sub>H2O</sub> of 50 and 25 MPa at temperatures of 850–880 °C. The agreement between natural and experimental phase compositions and modes at P<sub>TOT</sub> = P<sub>H2O</sub> = 50 MPa is consistent with the idea that the 1912 dacite equilibrated with an H<sub>2</sub>O-rich volatile phase prior to eruption. H<sub>2</sub>O saturation at ~50 MPa (Moore et al. 1998) is also consistent with the

measured  $H_2O$  contents of melt inclusions in plagioclase phenocrysts trapped under  $H_2O$ -saturated conditions (Lowenstern 1993).

#### Amphibole in natural samples

Dacite starting material (K1490) contains a trace quantity of euhedral hornblende crystals. The only other



Fig. 5. Matrix glass compositions in H<sub>2</sub>O-saturated andesite experiments **a** at 960 °C, and **b** at 100 MPa. Shaded horizontal *bars* represent natural matrix glass composition and  $\pm 1\sigma$  uncertainty. Analytical variation in experimental glass compositions is smaller than the *symbols* in all cases except for K<sub>2</sub>O (as shown). Temperatures and pressures are accurate to within  $\pm 5$  °C and  $\pm 1$  MPa, respectively. *Triangles* point in the direction of approach to equilibrium; *closed symbols* for crystal-rich starting material (crushed K131D), *open symbols* for glassy starting material

			nadva i				nd nn	ion nem	enomeodu									
Sample	Total	Mode	e by n	ass b	alance	•			Plag/Cpx	Orthopyro	xene rims		Augite rim			Plagioclase	rims	
	(%)	Glass	: Plag	Opx	Cpx	Mt	Ilm	rms		MO	EN	FS	МО	EN	FS	AN	AB	OR
Andesite	r T	22	90	0 v		( (		(10.0)	r -	0.02			030 045	0.30.0.40	0 10 0 10	0 51 0 73	31 0 30 0	10.0
scoria	+	CC	07	V.U	7.1	7.0	I	(10.0)	1./	c0.0	0./1-0./2	07.0-4-0.70	C+.0-0C.0	0+.0-66.0	01.0-01.0	c/.0-+c.0	0.4.0-02.0	10.0
$\mathrm{K}08^{\mathrm{a}}$	43	57	25	8.7	6.5	3.1	Ι	(0.01)	1.7	0.03 - 0.04	0.64 - 0.72	0.25 - 0.33	0.43	0.39 - 0.40	0.17	0.55-0.78	0.20 - 0.42	0.01 - 0.03
K43	54	46	36	8.5	5.4	4.8	Ι	(0.05)	2.6	0.03	0.67 - 0.71	0.26 - 0.30	0.43 - 0.44	0.41 - 0.44	0.13 - 0.15	0.56 - 0.75	0.23 - 0.41	0.01
K47	51	49	34	7.3	5.5	4.1	I	(0.09)	2.7	0.03 - 0.04	0.68 - 0.72	0.25 - 0.29	0.43	0.41 - 0.44	0.12 - 0.15	0.63 - 0.76	0.22 - 0.35	0.01
$K41^{a}$	51	49	33	8.8	4.7	3.5	I	(0.14)	2.4	0.03	0.64 - 0.73	0.24 - 0.33	0.43 - 0.45	0.41 - 0.43	0.12 - 0.16	0.58 - 0.76	0.23 - 0.4	0.01
K50	64	36	42	9.8	6.7	3.6	I	(0.16)	2.5	0.04	0.59 - 0.71	0.26 - 0.37	0.42 - 0.45	0.39 - 0.44	0.11 - 0.19	0.55 - 0.64	0.34 - 0.43	0.01 - 0.02
Dacite																		
K1490	42	58	30	4.1	4.8	2.4	0.4	(0.03)	3.4	0.02 - 0.03	0.59 - 0.64	0.33 - 0.39	0.43 - 0.46	0.41 - 0.42	0.13 - 0.14	0.36 - 0.43	0.55 - 0.62	0.02
pumice																		
$KD13^{a}$	45	55	33	4.9	4.1	1.6	0.5	(0.02)	3.7	0.03	0.61 - 0.69	0.28 - 0.36	0.44 - 0.46	0.39 - 0.41	0.15	0.34 - 0.49	0.48 - 0.60	0.02 - 0.06
$KD05^{a}$	45	55	34	4.2	5.1	1.8	0.5	(0.03)	3.7	0.02 - 0.03	0.60 - 0.67	0.30 - 0.38	0.43 - 0.44	0.39 - 0.41	0.16 - 0.17	0.36 - 0.59	0.39 - 0.61	0.02 - 0.04
KD21	46	54	34	3.9	5.3	1.7	0.6	(0.05)	3.7	0.02 - 0.03	0.61 - 0.69	0.28 - 0.37	0.44	0.40 - 0.41	0.15 - 0.17	0.35 - 0.50	0.48 - 0.61	0.02 - 0.04
KD23	45	55	33	4. 4	4.9	1.5	0.6	(0.02)	3.5	0.01 - 0.03	0.60 - 0.65	0.34 - 0.37	0.41 - 0.43	0.40 - 0.42	0.15 - 0.17	0.33 - 0.48	0.49 - 0.61	0.03 - 0.06
KD25	$56^{\mathrm{b}}$	44	38	4.4	4.7	1.8	0.7	(0.01)	4.1	0.03	0.61 - 0.69	0.29-0.36	0.43-0.45	0.40	0.16 - 0.17	0.35-0.51	0.46-0.61	0.03-0.07
<sup>a</sup> Calculated <sup>b</sup> Total inclu	using solu ides 6.3 wt <sup>1</sup>	bility m % quar	tz. KI	of Mo 225 is	ore et the o	al. (1 nly se	998) umple	for wh	ich mass b	alance indic	ated quartz	content > 1	.0 wt%					



**Fig. 6.** Phase diagram for K1490 dacite under  $H_2O$ -saturated conditions. Experiments are given by *triangles* which point in the direction of approach to equilibrium. *Symbols* for mineral-in curves are as defined in Fig. 4 with the addition of quartz (*qtz*). The natural phase assemblage is stable in the *lightly shaded region* bounded by the quartz *curve*; Fe-Ti-oxide temperatures are shown by the *darker shading*, and the experimental matrix glass compositions closely match the natural compositions within the *diagonally hatched* region. *Dashed lines* are calculated  $H_2O$  solubilities using the algorithm of Moore et al. (1998) with composition and experimental conditions as model inputs. The volatile contents of glass inclusions obtained by Lowenstern (1993) are indicated at left

1912 magma in which amphibole has been recognized is the rhyolite dome extruded at the Novarupta vent after the explosive phases of 1912. Recent experimental work shows that the hornblende in the dome rhyolite is not in equilibrium with the surrounding melt over the experimental conditions required to reproduce the natural mineral and melt compositions (Coombs and Gardner 2001). Those authors concluded that the hornblende originated elsewhere, possibly in the intermediate magmas.

Compositions of experimentally grown hornblende from andesite, dacite, and rhyolite starting materials are compared with the natural hornblende from the rhyolite dome and natural dacite (K1490) in Fig. 8. The natural dacite amphiboles are identical to those from the rhyolite dome, indicating a common source (Coombs and Gardner 2001). Relative to the natural crystals, experimental hornblendes grown in the andesite are richer in Al<sub>2</sub>O<sub>3</sub>; those grown in rhyolite experiments have lower Mg# (MgO/(MgO + FeO)). Many of the hornblende crystals produced in the dacite experiment KD02a are similar to the natural compositions (typically the cores of crystals), but the analyses also extend to higher Al<sub>2</sub>O<sub>3</sub> contents and greater Mg# (typically the rims). The



**Fig. 7.** Matrix glass compositions versus pressure in H<sub>2</sub>O-saturated dacite experiments at 850 and 880 °C. Shaded horizontal *bars* represent natural matrix glass compositions and  $\pm 1\sigma$  uncertainty. Analytical accuracy and *symbols* are as defined in Fig. 5. *Solid* (850 °C) and *dashed* (880 °C) *curves* are drawn through the data as a guide

zoned hornblendes are interpreted to reflect changing melt composition as plagioclase melted during the experiment and  $a_{SiO2}$  in the melt decreased. A more evolved matrix melt (i.e., greater  $a_{SiO2}$ ) than that of KD02a would crystallize hornblende containing less Al<sub>2</sub>O<sub>3</sub> and MgO (Johnson and Rutherford 1988). Thus, hornblende nearer the natural compositions may be produced at conditions where the matrix melt is slightly more evolved; at 850 °C, this requires lower P<sub>H2O</sub> (see Fig. 7).

Evidently, the natural hornblende crystals found in both K1490 dacite and the rhyolite dome formed in a magma with bulk composition similar to K1490 at  $P_{H2O}$ <150 MPa, possibly  $\sim 120$  MPa. However, the matrix glass in hornblende-bearing experiment KD02 (73.8 wt%  $SiO_2$ ) is significantly less evolved than both the natural dacite matrix glass (79.1 wt%) and the rhyolite matrix glass (78.4 wt%). At 850 °C, the natural dacite matrix glass is reproduced experimentally only at low  $P_{H2O}$  (25– 50 MPa), and amphibole is unstable below  $\sim 125$  MPa. One explanation is that the hornblende crystals present in tephra K1490 actually formed in a deeper portion of the ADC and then moved, perhaps syneruptively, into contact with the evolved matrix melt of K1490 relatively soon before quenching. Hornblende crystals which found their way into the dome almost certainly were late



**Fig. 8.** Experimental (*open symbols*) and natural (*closed symbols*) hornblende compositions. *R*, *D*, and *A* prefixes stand for rhyolite, dacite, and andesite, respectively. Natural compositions measured in K1490 (dacite) and DW17 (rhyolite; Coombs and Gardner 2001). Experimental conditions are indicated beside each cluster of points

additions to the rhyolite magma, originating in the ADC as suggested by Coombs and Gardner 2001.

#### $H_2O$ -undersaturated experiments: and esite

By adjusting the molecular proportions of CO<sub>2</sub> and H<sub>2</sub>O in the fluid phase and varying P<sub>TOT</sub> from 125 to 225 MPa, a range in mole fraction of H<sub>2</sub>O in the fluid phase ( $X_{H2O}^{fl}$ ) of 0.34 to 0.85 was investigated. Combinations of P<sub>TOT</sub> and  $X_{H2O}^{fl}$  were chosen to maintain P<sub>H2O</sub> near the values (75–100 MPa) which best reproduced the natural mineral and glass compositions in the H<sub>2</sub>O-saturated experiments.

The procedure of matching experimental glass and mineral compositions, phase abundances, and relative modes to the natural andesite, as described for H<sub>2</sub>O-saturated experiments, is again applied to the CO<sub>2</sub>bearing experiments, hereafter called "H<sub>2</sub>O-undersaturated". There is no correlation between  $P_{TOT}$  of the experiment and matrix glass composition for the undersaturated runs, as shown for several oxides in Fig. 9a, b. However,  $P_{H2O}$  and composition are correlated, and moreover, the undersaturated data plot on top of the H<sub>2</sub>O-saturated trend at the same P<sub>H2O</sub> values. Likewise, the composition of the most albitic feldspar in each experiment is correlated with  $P_{H2O}$  but not  $P_{TOT}$  (Fig. 9c). These observations suggest that H<sub>2</sub>O content rather than P<sub>TOT</sub> controls the crystallization sequence of K131D andesite for the range of conditions investigated. The experimental data of Figs. 5 and 9 indicate that the  $P_{H2O}$  of crystal-melt equilibration was at ~75 MPa. Unfortunately for the purpose of determining magma storage depth, it is impossible to uniquely determine  $P_{TOT}$  because there is no independent information about  $X_{H2O}^{H2O}$  in the natural system ( $P_{H2O} = X_{H2O}^{H2O} * P_{TOT}$ ).



Fig. 9a–c. Experimental matrix glass (a, b) and feldspar (c) compositions for H<sub>2</sub>O-saturated and H<sub>2</sub>O-undersaturated experiments at 960 °C. *Closed symbols* represent H<sub>2</sub>O saturated experiments; *open symbols* represent P<sub>TOT</sub> for fluid-saturated, CO<sub>2</sub>-bearing experiments; *crossed symbols* represent P<sub>H2O</sub> for these "undersaturated" experiments. *Dashed lines* connect P<sub>TOT</sub> to P<sub>H2O</sub> for given runs. Shaded horizontal *bar* represents natural compositions  $\pm 1\sigma$  uncertainty

Nonetheless, it is possible to place some constraints on  $P_{TOT}$  because feldspar composition is a function of both  $X_{H2O}^{fl}$  and  $P_{TOT}$ , as shown below.

# $H_2O$ -undersaturated experiments: dacite

Experiments on the dacite containing a mixed fluid phase produced trends qualitatively similar to the H<sub>2</sub>Oundersaturated andesite runs (Fig. 10). Matrix melts on an anhydrous basis matched the saturated matrix glass compositions, having the same P<sub>H2O</sub> regardless of P<sub>TOT</sub> or X<sub>H2O</sub><sup>fl</sup>. Minimum An contents also correlate with P<sub>H2O</sub> rather than P<sub>TOT</sub> (Fig. 10c). Plagioclase An content versus X<sub>H2O</sub><sup>fl</sup> is contoured for P<sub>TOT</sub> using all experimental data at 960 °C (andesite) and 850 °C (dacite) in Fig. 11. The slopes of the contour lines are approximate, and are similar to P<sub>TOT</sub> isograds determined for the Fish Canyon tuff (Johnson and Rutherford 1988) and Mt. St. Helens eruptives (Gardner et al. 1995).



Fig. 10. Experimental matrix glass (a, b) and feldspar (c) compositions for H<sub>2</sub>O-saturated and H<sub>2</sub>O-undersaturated experiments at 850 °C. *Symbols* are as defined in Fig. 9

# Discussion

# P<sub>TOT</sub> versus P<sub>H2O</sub>

Experiments with andesite at a given P<sub>TOT</sub> with differing H<sub>2</sub>O contents produced dramatically different crystallinities, for example, 3 wt% crystals in K33  $(X_{H2O}^{fl}=1.0)$  versus 58 wt% in K50  $(X_{H2O}^{fl}=0.34)$ , both at 220 MPa. Much of the difference is due to changing plagioclase abundance. Plagioclase is particularly affected by variable dissolved H<sub>2</sub>O because the highly polymerized structure of feldspar-forming components in the melt are susceptible to disruption by OH groups (Kushiro 1969). This was observed in experiments on the Mount St. Helens dacite at 220 MPa (Rutherford et al. 1985), where the plagioclase-in temperature increased more than 200 °C as  $X_{H20}^{ff}$ decreased from 1 to 0.1; the orthopyroxene-appearance temperature increased by less than 100 °C over this interval. These effects commonly give rise to changes in melt composition as P<sub>TOT</sub> increases at a given H<sub>2</sub>O content and temperature (e.g., Venezky and Rutherford 1997).

Less well understood are the slopes of the mineral-in curves in  $P_{TOT} - X_{H2O}^{fl}$  space for intermediate composi-

**Fig. 11.** Plagioclase compositions of experimental feldspars in andesite (**a**) and dacite (**b**) runs as a function of  $X_{H2O}^{ff}$ . Note difference in y-axis values. *Closed symbols* represent H<sub>2</sub>O-saturated experiments; *open symbols* are H<sub>2</sub>O-undersaturated runs. Horizontal shaded *bars* represent minimum An of plagioclase rims in natural samples. Solid and dashed *lines* are total pressure isograds



tion magmas, particularly when H<sub>2</sub>O content is held constant, as in the andesite experiments where the melts contain  $4.0 \pm 0.5$  wt% H<sub>2</sub>O. The last notable contributions are the work on Parícutin and Mt. Hood andesites by Eggler (1972) and Eggler and Burnham (1973). Experiments at higher P<sub>TOT</sub> than investigated here would be required to determine the positions and slopes of plagioclase, oxide, and pyroxene mineral-in curves. However, Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O variation with SiO<sub>2</sub> in the matrix glasses from the isobaric, isothermal, and undersaturated experiments demonstrate subtle differences in the liquid lines of descent, particularly at low  $P_{H2O}$ and high SiO<sub>2</sub> (Fig. 12). Early plagioclase crystallization in the H<sub>2</sub>O-undersaturated andesite experiments lowers  $Al_2O_3$  at a given SiO<sub>2</sub>, whereas the H<sub>2</sub>O-saturated isothermal series undergoes early (i.e., high P<sub>H2O</sub>) enrichment in Al<sub>2</sub>O<sub>3</sub> because plagioclase crystallization is suppressed. At lower P<sub>H2O</sub>, however, melt Al<sub>2</sub>O<sub>3</sub> decreases and  $K_2O$  increases rapidly with increasing SiO<sub>2</sub>, compared with the isobaric and H<sub>2</sub>O-undersaturated runs.

All trends are essentially coincident in the range 67– 71 wt% SiO<sub>2</sub>, where the effect of  $P_{TOT}$  is to change the total amount crystallized and not the proportions of crystalline phases. For example, andesite experiments K43 and K50 were run at similar  $P_{H2O}$ , dissolved H<sub>2</sub>O content and temperature but differed in  $P_{TOT}$  by 150 MPa. Both experiments had plagioclase/ pyroxene ratios of ~2.5 but the run at higher  $P_{TOT}$ contained 10% more crystals (an increase in crystal content of 6.7% per 100 MPa of  $P_{TOT}$ ; Table 4). Comparison between dacite experiments KD05a and KD25, again at similar  $P_{H2O}$ , dissolved H<sub>2</sub>O contents and temperature but differing by 100 MPa in  $P_{TOT}$ , also shows that greater crystallization occurred in the higher-pressure experiment (Table 4). In this case, quartz and feldspar both contribute to the increased crystallinity, and the plagioclase/pyroxene ratio is elevated relative to the natural sample and KD05a. The divergence from natural phase proportions at  $P_{TOT} = 150$  MPa for this dacite bulk composition indicates that 150 MPa is greater than the natural equilibration pressure.

Fortuitously, the silicic dacite bulk composition  $(68\% \text{ SiO}_2)$  falls at the intersection of all three and esite matrix glass trends (Fig. 12b, d), and thus several experimental andesite matrix glasses are identical to the natural dacite bulk composition (e.g., K40, K36, K43, K49, K47, K44, K38; Tables 1, 3). These experiments span a range of P<sub>TOT</sub> (75-150 MPa) and  $X_{H2O}^{fl}$  (0.75–1.0). With increasing SiO<sub>2</sub>, the isothermal H<sub>2</sub>O-saturated liquid line of descent (LLD) at 960 °C is not contiguous with the dacite isothermal H<sub>2</sub>O-saturated LLD at 850 °C, principally because feldspar crystallization at low  $P_{\rm H2O}$  in andesite lowers the melt Al<sub>2</sub>O<sub>3</sub> content and drives up melt K<sub>2</sub>O. This is not surprising, given the observation of thermal gradation in intermediate compositions of 1912 products (Hildreth 1983). Rather, the isobaric H<sub>2</sub>O-saturated andesite trend at 100 MPa and, to a lesser extent, the H<sub>2</sub>Oundersaturated isothermal trend at 960 °C do retain higher melt Al<sub>2</sub>O<sub>3</sub> and produce LLDs which align with the dacite trends. Evidently, crystallization at lower T or lower H<sub>2</sub>O content (relative to the 960 °C H<sub>2</sub>O-saturated series) occurs without melt Al<sub>2</sub>O<sub>3</sub> enrichment caused by delayed feldspar crystallization. The experiments suggest that silicic dacite may be related to the andesite through fractional crystallization of the latter at H<sub>2</sub>O saturation by cooling and/or vertical advection under conditions of slight H<sub>2</sub>O undersaturation, but not by decompression of H2O-saturated melt.



**Fig. 12.** Representative oxide variation diagrams for experimental and natural matrix glass  $Al_2O_3$  (**a**, **b**) and  $K_2O$  (**c**, **d**) contents. **a**, **c** Microprobe analyses of experimental andesite (*open symbols*) and dacite (*closed symbols*) matrix glasses. Selected experiments are labeled individually. **b**, **d** Natural glasses and bulk compositions are shown in relation to trends of experimental glasses, drawn through data in **a** and **c**. *Solid curves* represent the isothermal series at the indicated temperature, *dashed curve* is the andesite isobaric series, and *dotted curves* are H<sub>2</sub>O-undersaturated experiments. Andesite and dacite data points and curves are labeled with A and D prefixes, respectively

# Pre-eruptive storage conditions: constraints from phase relations

The new constraints on the 1912 magma storage depths and temperatures are summarized graphically (Fig. 13) along with similarly obtained P-T relationships for the co-erupted rhyolite (Coombs and Gardner 2001). Fe-Tioxide thermometry and phase equilibria at H<sub>2</sub>O-saturated conditions indicate K131D andesite magma equilibration at 930–960 °C at NNO+1 and P = 100-75 MPa (see Fig. 4); K1490 dacite storage conditions were 850–880 °C,  $fO_2 = NNO + 1$ , and P = 50-25 MPa (Fig. 6). Assuming overburden density of  $2,700 \text{ kg m}^{-3}$ , these pressures correspond to 3.8-2.8 and 1.9-0.9 km depths for the andesite and dacite, respectively. If these extreme mafic and felsic compositions in the ADC are assumed to bracket the conditions of equilibration for all intermediate eruptives, then these values constrain the final pre-eruptive magma storage to a region of T-depth space wherein cooler, shallow dacite grades continuously to warmer, deeper andesite (Fig. 13).

The storage region is further limited by ancillary observations. Limited melt-inclusion H<sub>2</sub>O content data from other 1912 dacite pumices (Lowenstern 1993) indicate minimum entrapment pressure of 50 MPa, supporting the low-temperature/higher-pressure end of the experimentally defined dacite storage region. Whereas two Fe-Ti-oxide pairs yielded temperatures for K131D and esite of  $\sim 960$  °C, the only experiment which closely reproduced the natural andesite glass and phase proportions (especially plagioclase/pyroxene ratio) was run at 930 °C (K08a; Table 4). The cooler temperature corresponds to slightly deeper storage at  $\sim 4$  km, and these are the provisionally preferred storage conditions for the mafic andesite under H<sub>2</sub>O-saturated conditions. The vertical dimension of the ADC body or plexus of bodies which erupted may have been as little as 0.9 km or as much as 1.9 km, depending on the depth of the most mafic andesite. The radii of cylinders which would contain the 5.5-km<sup>3</sup> volume of erupted ADC magma, given these vertical heights, are 1.4 and 0.96 km, respectively. The aspect ratios (diameter/height) of such bodies are 3.1 and 1.0, indicating that if ADC magma occupied a compact stratified reservoir, its shape would be sill-like to equant. If the total volume of ADC magma including unerupted cumulate mush were significantly greater than 5.5 km<sup>3</sup>, the aspect ratio of the storage reservoir would be commensurately increased.

The range of 1912 rhyolite equilibration depths is large (40 to 100 MPa) because a variety of  $P_{H2O}$ -T combinations experimentally reproduced the natural crystallinity, phase assemblage, and mineral

Fig. 13. Summary of experimental constraints on magma storage conditions **a** prior to the 1912 eruption from this study and Coombs and Gardner (2001), and **b** in comparison with a model suggested by Hildreth and Fierstein (2000). See text for explanation



compositions. The rhyolite Fe-Ti oxides record a range of pre-eruption temperatures (800 to 850 °C) and, because the liquid composition is invariant, pressure is constrained to vary accordingly.

# Depth constraints for ADC magmas

Previous descriptions of thermal structure of the 1912 magma storage region based on Fe-Ti-oxide thermometry underscore the continuity of rhyolite and ADC temperatures (Fig. 2; Hildreth 1983). This continuum has been cited in support of a single, zoned magma chamber (Hildreth and Fierstein 2000) and/or close physical proximity of magma bodies. Experiments have confirmed these analytically derived temperature ranges. Significant contributions of the experimental studies are the pairings of temperature values with  $P_{TOT}$  under H<sub>2</sub>O-saturated conditions (Fig. 13). Thermal and pressure (depth) continuity between the rhyolite and (H<sub>2</sub>Osaturated) ADC occurs only at the high-T end of the rhyolite range – that is, if the temperature of the rhyolite was  $\sim$ 850 °C, then it could form the upper layer of a single, vertically stratified chamber, as proposed by Hildreth and Fierstein (2000). The top of the chamber would have been very shallow, just 0.9 km below the surface. Problems with this model are that (1) the measured volatile contents of melt inclusions in the rhyolite require entrapment at a minimum pressure of 100 MPa. corresponding to a depth of 3.8 km; at 100 MPa the rhyolite is positioned at the deep end of the ADC range, and cannot overlie the ADC if the latter magmas were  $H_2O$ -saturated; and (2) high  $P_{H2O}$  is required by the rhyolite melt composition and low Fe-Ti-oxide temperatures (800 °C), as explained above.

The present experiments also demonstrated the possibility that ADC magmas were fluid undersaturated or saturated with a CO<sub>2</sub>-bearing fluid phase. Mineral and melt compositions of these magmas are produced in mixed volatile conditions, and  $P_{H2O}$  rather than  $P_{TOT}$  is

the dominant factor controlling crystallization sequence and the liquid line of descent.  $P_{H2O}$  is determined by the  $H_2O$  concentration of the fluid phase ( $X_{H2O}^{fl}$ ) and  $P_{TOT}$ , and their relationships to plagioclase phenocryst rim composition can be used to place limits on either parameter if the other one can be evaluated independently. Thus, we can take two approaches to comparing  $H_2O$ undersaturated experimental results to the storage model proposed by Hildreth and Fierstein (2000) using Fig. 11. The first is to assume a minimum likely value of  $X_{H2O}^{\ \ fl}$  and find the corresponding  $P_{TOT}$  which satisfies the natural plagioclase composition constraint. The smallest value of  $X_{H2O}^{fl}$  determined for intermediate arc magmas is 0.4 (Mount St. Helens Wn tephra; Gardner et al. 1995). Most of the analyzed erupted magmas are volatile saturated with  $X_{H2O}^{ff} = 0.6$  (Gardner et al. 1995; Moore and Carmichael 1998). For the present purpose, we assume that 0.5 is a reasonable minimum value for Katmai ADC magmas. In this case, the natural andesite plagioclase composition would be produced at  $\sim$ 150 MPa or 5.7 km depth; the dacite would reside at  $\sim$ 130 MPa or 4.9 km (scatter in the experimental feldspar data is the chief source of uncertainty, and  $X_{H2O}^{ff}$ values are estimated to be accurate to within  $\pm 0.05$  for the andesite and  $\pm 0.10$  for the dacite). Given the minimum estimate of  $X_{H2O}^{fl}$ , the upward evolution in bulk composition of ADC magmas would be preserved, the dacite storage depth would be pushed below that of the deepest conceivable rhyolite, and the temperature contiguity from rhyolite through the ADC would correspond to continuous pressure increase.

The second approach to evaluating the vertically stratified model is to solve for the values of  $X_{H2O}^{fl}$  which correspond to the model depths of Hildreth and Fierstein (2000), and then evaluate their likelihood in the context of similar volcanic systems for which  $X_{H2O}^{fl}$  is known. The proposed top of the ADC at 4 km corresponds to 106 MPa and  $X_{H2O}^{fl}$ =0.88 for the dacite; the bottom of the erupted magma at 4.5 km corresponds to 120 MPa and  $X_{H2O}^{fl}$ =0.72 for the andesite. These values of the second secon

ues of  $X_{H2O}^{fl}$  are about halfway between the estimated minimum reasonable value and the maximum at 1.0.

### Origin and storage of rhyolite

The connection between ADC magmas and the rhyolite is fundamental to an understanding of the eruption mechanism and the unusual plumbing at Katmai-Novarupta. Several lines of evidence indicate that the rhyolite magma was saturated with an H<sub>2</sub>O-rich volatile phase during the crystallization interval in which quartz and plagioclase phenocrysts formed. Glass-inclusion CO<sub>2</sub> concentrations were below the minimum detection limit (50 ppm). Many glass inclusions contained vapor bubbles (fluid inclusions), some of which were exceptionally rich in Cu. In addition, the concentrations of volatile elements (S and Cu) in the matrix glass, relative to glass inclusions, are too low to have resulted from simple fractionation of phenocryst phases in the rhyolite. These observations suggest that volatiles partitioned into at least one fluid phase and were subsequently removed from the system by syneruptive degassing (Westrich et al. 1991). Furthermore, experiments at H<sub>2</sub>O-saturated conditions reproduce the mineral and melt compositions for a 50 °C range in temperature (Coombs and Gardner 2001). There appears to be no evidence in the rhyolite of an origin at depth >4 km (100 MPa), as suggested by Eichelberger and Izbekov (2000), i.e., crystals preserved are all in equilibrium with the low-pressure melt, and none contain high-pressure melt inclusions. Furthermore, the bulk composition projected into the H<sub>2</sub>O-saturated haplogranite ternary system (quartz<sub>35</sub> albite<sub>49</sub> orthoclase<sub>16</sub>; method of Cashman and Blundy 2000) lies on a low-P<sub>H2O</sub> (~200 MPa) cotectic. An H<sub>2</sub>O-rich partial (minimum) melt originating at significantly greater depth would crystallize during ascent to 200 MPa unless it was significantly H<sub>2</sub>O-undersaturated to start with. The very low crystal content of the erupted rhyolite would require near-complete separation of precipitating crystals to achieve the final bulk composition.

An alternative possibility is that  $H_2O$ -poor rhyolite separated from a deep source region and only began to crystallize near the surface, possibly just after the point of volatile saturation, when melt devolatilization could begin to cause crystallization of anhydrous phases. Crystals preserve evidence of fluid saturation and contain 4 wt% H<sub>2</sub>O because these would have been the ambient conditions during their formation, which postdates the melt accumulation and separation from a source region.

A constraint on the duration of the crystallization interval is suggested by the morphology of quartz crystals in the 1912 rhyolite, in that the faceted bipyramidal euhedra are inconsistent with rapid growth. Laboratory crystallization experiments with rhyolite melts demonstrate that over short time scales (days–weeks), quartz requires very large effective undercoolings (100s of °C)

to nucleate (Fenn 1977; Swanson 1977; Naney and Swanson 1980). Subsequent growth appears to be limited by volume diffusion in the melt so that pristine facets rarely form. Instead, crystals are anhedral and are commonly intergrown with feldspars, which nucleate at smaller degrees of undercooling (Swanson 1977). Observations of related systems suggest that nucleation may occur at small undercoolings ( $\Delta T$ ) if very long induction times are available (Kirkpatrick 1981; Deubener 2000). Subsequent growth at small undercooling would promote interface-reaction-limited growth, development of facets, and the quartz morphologies observed in the 1912 rhyolite (Swanson and Fenn 1986). Thus, in the absence of new quartz nucleation and growth data, the crystal morphologies alone support a long-term storage model over rapid, synascent crystallization. The hypothesis of a deep rhyolite origin distinct from the ADC is not supported by current data and requires further study.

Toward a unified magma storage model

Excepting the possibility of a deep rhyolite source, three possible pre-eruption magma storage reservoirs are consistent with the new observations (Fig. 14, modified from Fig. 3 of Coombs and Gardner 2001). If rhyolite and ADC magmas are all saturated with an H<sub>2</sub>O-rich phase, then the experimental equilibrium conditions of matrix melts preclude the placement of rhyolite above the ADC in a vertically stratified stack, simply because the most silicic dacite equilibrated at lower  $P_{H2O}$  than the rhyolite. Instead, rhyolite may be situated either (1) near or encircling the ADC at approximately the level of the ADC beneath Mt. Katmai, or (2) elsewhere in the region at the same depth, possibly beneath the Novarupta vent. Although the former model (Fig. 14a) supports the idea of intermediate magmas as a heat source keeping rhyolite nearly aphyric, it is not necessarily consistent with the proposed petrogenetic link between the ADC and rhyolite. It is difficult to envision a melt percolation process which would segregate relatively low-density matrix melt from the ADC mush cleanly (without incorporating ADC phenocrysts), efficiently (generating 7.5 km<sup>3</sup> homogeneous rhyolite), and *later*ally (rather than vertically).

The second model (Fig. 14b) specifies no petrogenetic link between rhyolite and the ADC, does not provide a heat source for the rhyolite, and does not explain why ADC magma became involved in an eruption 10 km away which began solely with rhyolite. The decreasing fumarolic activity at Novarupta (Hildreth 1983; Keith 1991), lack of hornfelsed lithic "septa" in pyroclastic deposits (Hildreth 1987), shallow conductive heat flow observations in the vent region (Ballard et al. 1991), and absence of present-day shallow crustal seismicity at Novarupta (Hildreth and Fierstein 2000) are cited as arguments against this model. However, the experimentally determined phase relations and likelihood of





b. all magmas H<sub>2</sub>O-saturated, separate storage



**Fig. 14a–c.** Model storage reservoir geometries for rhyolite and ADC magmas which are consistent with experimental phase-equilibria data, modified from Coombs and Gardner (2001). See text for explanation

 $H_2O$  saturation of at least the silicic extreme of the ADC (Lowenstern 1993) are consistent with such a pre-eruptive magma configuration.

The final proposed model (Fig. 14c), essentially a revision of Hildreth and Fierstein (2000), restores the mafic-felsic stratigraphy by requiring H<sub>2</sub>O undersaturation of the ADC magmas. A possible scenario involves  $CO_2$ ,  $SO_2$  and other volatiles so that magmas are fluid saturated, as it is highly improbable that intermediate magma as shallow as 4.5 km would *not* contain sufficient volatiles for saturation (Johnson et al. 1994; Wallace et al. 1999). An apparent inconsistency is whether an  $H_2O$ -saturated rhyolite (with no detectable  $CO_2$  in glass inclusions) could arise from, and remain in contact with H<sub>2</sub>O-undersaturated ADC magma. One possibility is that the rhyolite was expelled from the ADC residue well before eruption and underwent degassing of the CO<sub>2</sub>bearing gas phase. Subsequent nominal crystallization would create H<sub>2</sub>O-rich vapor. This model shares with the previous one the unanswered question of why magma vented 10 km from its reservoir.

The compositional gap between rhyolite and bulk dacite has been presented as another objection to the idea of a single, zoned magma body feeding the 1912 eruption (Eichelberger and Izbekov 2000). Clearly the matrix glasses of the ADC magmas are a ready source of highly evolved melt (Fig. 12). The process of separating this melt from a crystal-rich ADC mush (Sisson and Bacon 1999) and then keeping it well-stirred, perhaps in a separately convecting layer (Fridrich and Mahood 1987), presents fluid dynamical difficulties.

Magma interaction and disequilibrium features

Much of the foregoing discussion rests on the premise that magma storage conditions may be gleaned from erupted materials because minerals, melts, and fluids were in local chemical and thermal equilibrium immediately before eruption and quench. Our conclusions about P<sub>TOT</sub> and P<sub>H2O</sub> are particularly dependent upon interpretations of matrix glass composition as an indicator of changes in crystallinity and mineral mode. This is founded on the idea that melts homogenize and equilibrate with crystal rims relatively rapidly because of high component mobility, particularly in hydrous melts. However, there are also abundant data for magma interactions leading to disequilibrium assemblages over a range of time scales leading up to the 1912 eruption. Several observations described separately in sections above may in aggregate lend insight into storage issues as well as eruption dynamics.

- 1. Quartz is observed in the natural andesite. This phase is not in equilibrium with the matrix melt, and must have formed elsewhere. Rhyolite-dacite syneruptive mixing is observed in mingled pumice blocks (Hildreth 1983). The puzzling aspect is that quartz is present in trace quantity only in the most silicic intermediate magma (having escaped observation for many years), and even in the rhyolite constitutes only ~1 vol% of the magma.
- 2. Titanomagnetite grains in contact with ilmenite in the natural andesite are compositionally zoned. The increase in  $TiO_2$  toward the contact may represent an arrested process of chemical equilibration following a heating event.
- 3. Several "outlier" Fe-Ti-oxide pairs found in natural dacite record much higher temperatures than the majority of pairs (Fig. 2). These grains may have arrived from a hotter environment shortly before or during eruption.
- 4. Phase proportions of andesite phenocrysts are matched experimentally at 930 °C, not at 960 °C as indicated by Fe–Ti–oxide thermometry. Melt may have equilibrated at 930 °C and subsequently experienced a rise in temperature caused, for example, by convection within the ADC.
- 5. Hornblende from the rhyolite dome is identical in composition to hornblende found in silica-rich dacite (K1490) and experimentally produced in dacite at

*relatively high*  $P_{H2O}$ . Natural matrix melts in both magmas indicate low  $P_{H2O}$  at last equilibration. Hornblende formed in 850° dacite at high  $P_{H2O}$  must have been mixed into low  $P_{H2O}$  magmas shortly (< one week) before eruption or else they would have begun to react with the melt to form anhydrous phases (Rutherford, unpublished data).

These features fall into two categories: redistribution of crystals (1, 3, 5), and evidence for thermal excursion(s) (2, 4). Given the rapid rate of thermal diffusion relative to chemical diffusive processes (e.g., coupled cation exchange, mineral-melt cation exchange, melt homogenization, and crystal nucleation, growth, and dissolution), both categories of disequilibrium features must arise from kinetically limited mass transport. Quartz in contact with intermediate SiO<sub>2</sub> melt will eventually dissolve and TiO<sub>2</sub> gradients in titanomagnetite will relax, but the time scales of these processes are probably quite different. Despite high melt viscosities which impair porous flow, crystal settling, and bulk convection, crystals ( $\pm$  melts) apparently can depart from their formation environments. An important question arising from this study is understanding the mechanisms by which mineral phases are transported between melts. If volumetrically scarce phases are found outside their stability fields (as in 1, 3, and 5 above), then what about transport of major phases not so easily tracked? Adjacent crystals in pumice may have only a brief shared history in their local chemical environments (e.g., Tepley et al. 1999; Harms and Schmincke 2000). Transfer of crystals between melts may partly explain the large overlap in ADC phase compositions (Hildreth 1983).

The disequilibrium features may also reveal the timing of magma mingling and/or heating if the rates of dissolution and reaction caused by changes in temperature or  $P_{H2O}$  are well known. For example, incorporation of quartz into andesite without sign of chemical reaction probably occurs over very short time scales (hours) prior to or during eruption, and may be facilitated by the process of magma withdrawal. Disequilibrium features demonstrating a thermal excursion (2 and 4 above) may record heating which occurred up to several days preceding eruption. This could be caused by introduction of new, hotter material or internal mixing with a warmer portion of the pile.

#### Summary

New experimental data place constraints on the proposed magma storage models. Intermediate magmas erupted in 1912 from Novarupta may have been stored 2–4 km below the summit of Mt. Katmai if they were *undersaturated* with respect to H<sub>2</sub>O, either because a vapor phase did not exist or because CO<sub>2</sub> was a significant component of the vapor phase. In this instance, the end-member andesite would have last equilibrated at 930 °C, 75 MPa,

and  $X_{H2O}^{fl} = 0.7$ , whereas the end-member dacite equilibrated at 850 °C, 50 MPa, and  $X_{H2O}^{fl} = 0.9$ . These data are consistent with a model of magma storage proposed by Hildreth and Fierstein (2000) in which a single reservoir consisting of a compositionally zoned stack of intermediate magma underlay and supplied a separately mixed rhyolite magma body.

The ADC natural phase compositions and modes are also recreated experimentally under H<sub>2</sub>O-*saturated* conditions. The equilibration pressures in this case are lower (andesite: 75–100 MPa; dacite: 25–50 MPa) and, in fact, coincide with the equilibration pressure range occupied by the rhyolite (40–100 MPa). The rhyolite and ADC storage zones cannot occupy the same horizontal *and* vertical position prior to the 1912 eruption. Therefore, an equally valid case may be made, on phaseequilibria grounds, for laterally separated storage of these magmas at similar depths, as suggested by Coombs and Gardner (2001).

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