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Storage conditions of Bezymianny Volcano parental magmas: results of phase equilibria experiments at 100 and 700 MPa

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Abstract The crystallization sequence of a basaltic andesite from Bezymianny Volcano, Kamchatka, Russia, was simulated experimentally at 100 and 700 MPa at various water activities (aH₂O) to investigate the compositional evolution of residual liquids. The temperature (T) range of the experiments was 950-1,150 °C, aH₂O varied between 0.1 and 1, and the log of oxygen fugacity (fO₂) varied between quartz-fayalite-magnetite (QFM) and QFM + 4.1. The comparison of the experimentally produced liquids and natural samples was used to constrain the pressure $(P)-T-aH_2O-fO_2$ conditions of the Bezymianny parental magma in the intra-crustal magma plumbing system. The phase equilibria constraints suggest that parental basaltic andesite magmas should contain ~2–2.5 wt% H₂O; they can be stored in upper crustal levels at a depth of ~ 15 km, and at this depth they start to crystallize at $\sim 1,110$ °C. The subsequent chemical evolution of this parental magma most probably proceeded as decompressional crystallization occurred during magma ascent. The final depths at which crystallization products

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accumulated prior to eruption are not well constrained experimentally but should not be shallower than 3–4 km because amphibole is present in natural magmas (>150 MPa). Thus, the major volume of Bezymianny andesites was produced in a mid-crustal magma chamber as a result of decompressional crystallization of parental basaltic andesites, accompanied by mixing with silicic products from the earlier stages of magma fractionation. In addition, these processes are complicated by the release of volatiles due to magma degassing, which occurs at various stages during magma ascent.

Keywords Bezymianny Volcano · Crystallization experiments · Phase equilibria · Magma storage

Introduction

The eruptive products of Bezymianny Volcano (Kliuchevskoi Group, Kamchatka, Russia) range in composition from basaltic andesite to dacite with predominant intermediate andesites, especially in the products of all historical eruptions (Gorshkov and Bogoyavlenskaya 1965; Kadik et al. 1986; Bogoyavlenskaya et al. 1991; Braitseva et al. 1991; Ozerov et al. 1997; Almeev et al. 2002). Although the basaltic source of Bezymianny Volcano is undoubted, no original Bezymianny basalts have been found to date, and the problem of identifying the parental magma composition and the conditions of its generation remains unresolved (Kadik et al. 1986). Despite smallscale variability, the Bezymianny rocks have strong geochemical affinities with high-magnesia and high-alumina basaltic lavas of the adjacent (~10 km) Kliuchevskoi Volcano. Ozerov et al. (1997) first suggested, and later Almeev et al. (2013a) confirmed, that the basalts of

Kliuchevskoi and andesites of Bezvmianny may represent a co-genetic calc-alkaline volcanic series of rocks, which despite their common (or very similar) mantle source(s), evolved along different paths controlled by their respective magma plumbing systems. According to Ozerov et al. (1997), a basaltic magma rich in Al₂O₃ and H₂O accumulated at upper crustal depths beneath Bezymianny. The basaltic magma was the product of differentiation and mixing of mantle-derived high-magnesia basalts. This hypothetical slightly evolved basaltic magma would be chemically similar to the basalt abundantly erupted at Kliuchevskoi parasitic cinder cones (Ozerov et al. 1997). In contrast to Kliuchevskoi Volcano, where such high-magnesia primary basaltic magmas were considered to differentiate as a result of polybaric decompression (Ariskin et al. 1995), the Bezymianny parental magmas were thought to have stagnated in a magma chamber(s) and/or slowly ascended and evolved under isobaric and H2O-saturated conditions (Ozerov et al. 1997).

Almeev et al. (2013a) speculated on the role of fractional crystallization processes in the Bezymianny magma reservoir(s) at different upper crustal levels based on the interpretation of the chemical fractionation trends defined by the eruptive products collected from recent and prehistoric eruptions. This study also demonstrated the role of magma mixing in the genesis of andesites from both historical and prehistoric Bezymianny eruptions (Almeev et al. 2013a). To test these models, experimental data relevant to the Bezymianny magma plumbing system are necessary, with accurately constrained intensive parameters of crystallization, especially P and aH₂O, which affect greatly the liquid lines of descent (LLDs) of the parental magma. The available experimental data sets are helpful for constraining the problems qualitatively, but they are not conclusive due to differences in starting composition and/ or experimental conditions (Moore and Carmichael 1998; Cottrell et al. 1999; Martel et al. 1999; Pichavant et al. 2002; Grove et al. 2003; Pichavant and Macdonald 2007; Botcharnikov et al. 2008a; Hamada and Fujii 2008). Our phase equilibria simulations (Almeev et al. 2013b) demonstrated that magma evolution along water-saturated isobaric cotectics (particularly at high P) proceeded without plagioclase (Plag) on the liquidus of basaltic andesite. However, Plag is the mineral phase which predominates amongst phenocrysts in natural samples. LLDs calculated at low P (below 50-100 MPa) were more satisfactory (with stable *Plag*) but could not reproduce the observed natural trends completely, mainly due to the lack of amphibole crystallization in the COMAGMAT program (Ariskin 1999) that was utilized in Almeev et al. (2013b).

The earlier experimental work on Bezymianny twopyroxene (2Px) and esite (Maksimov et al. 1978) was particularly useful for determining the pre-eruptive conditions of different types of evolved andesites. For example, for orthopyroxene (OPx)- and hornblende (Hbl)-bearing and esites, values of P > 300 MPa, $T \sim 930$ °C, and 5–6 wt% H₂O, and $P \ge$ 300–400 MPa, $T \sim$ 930 °C, and 6-7 wt% H₂O, respectively, were obtained. However, the crystallization conditions for 2Px andesite (P: 150-1 GPa, T: 1,000-1,150 °C, 1-3 wt% H₂O) have been only determined with very large uncertainty, especially with respect to P. In addition, the starting andesite investigated in Maksimov et al. (1978) is notably off the narrow trend defined by Bezymianny bulk rocks (Almeev 2005) and probably represents an extreme product of degassing-driven crystallization and/or Plag accumulation (it contains high Al₂O₃ and Na₂O and low FeO and TiO₂ at given SiO_2). As a result, the melt compositions produced in Maksimov et al. (1978) cannot be applied reliably to natural Bezymianny LLDs.

The major goals of our experimental study were (1) to identify the conditions of parental basaltic andesite multiple saturation (saturation with respect to clinopyroxene (Cpx) + Opx + Plag; (2) to produce LLDs by obtaining a set of experimental liquids equilibrated with all mineral assemblages representing the chemical trend defined by whole rock compositions; and (3) to constrain the conditions at which the different crystallization sequences found in different natural magma types could be reproduced (2Px)andesites, OPx-bearing andesites, Hbl-bearing andesites, and dacites). To achieve these goals, crystallization experiments were conducted to constrain the stability, composition and proportions of equilibrium phases in basaltic and site melt as a function of T and aH_2O . Two boundary pressure conditions (100 and 700 MPa) have been chosen. A pressure of 700 MPa (\sim 20–23 km) corresponds to the transition between upper and lower crust (20-30 km) above the Moho (30-40 km) beneath Kliuchevskoi Group volcanoes. The pressure of 100 MPa is close to the lowest pressure at which amphibole is stable (850-950 °C) in andesitic to rhyodacitic melts under H₂Osaturated conditions (Moore and Carmichael 1998; Cottrell et al. 1999; Sato et al. 1999). This pressure also corresponds to the average depth of the shallow-level magma reservoirs located at 1-1.5 and 7 km deep according to recent seismic investigations (Thelen et al. 2010), and to the pressure estimates (77–87 MPa) of the last H_2O-CO_2 equilibration event before eruption/degassing, a pressure which was deduced from the study of H_2O-CO_2 in Px- and Plag-hosted melt inclusions in andesites from the 2000-2007 eruptions (Shcherbakov et al. 2011). The total depth interval from 3 to 20 km covered by our experiments at 100-700 MPa probably brackets the full pathway of the intra-crustal evolution of the parental mantle derivatives (analogues of Kliuchevskoi magnesian and alumina-rich basalts) during their ascent to the surface with episodes of magma storage, stagnation and differentiation in intermediate and shallow magma chamber(s). Experiments under intermediate pressures (200 and 400 MPa) are in progress and will be presented elsewhere.

Experimental and analytical methods

Starting material

The starting material was a synthetic analogue of basaltic andesite (sample BA, Table 1) with a chemical composition at the mafic end of the evolutionary trend of the Bezymianny lavas; this was assumed to be the composition of a possible parental magma (Almeev et al. 2013a). The starting glass powder was prepared from a mixture of oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO) and carbonates (CaCO₃, Na₂CO₃, K₂CO₃) ground in a rotary mortar. The powder was melted for 2 h in a Pt crucible at 1,600 °C and 1 atm in air (log $fO_2 = -0.68$). This melt was quenched to a glass by placing the crucible into an H₂O bath. The glass was ground in an agate mortar and remelted for another 2 h to improve the homogeneity of the sample. The composition and homogeneity of the basaltic andesite glass was verified by electron microprobe. The glass was finally crushed in a mortar and sieved to grain sizes of <100 and $100-200 \mu m$. The two fractions were mixed together in a 50:50 proportion to minimize the free volume and, hence, the amount of atmospheric nitrogen in the experimental capsules.

Capsules

All experiments at temperatures higher than 1,040 °C were conducted using $Au_{80}Pd_{20}$ capsules (15 mm length, 2.8 mm internal diameter, 0.2 mm wall thickness), whereas all low *T* runs were conducted in Au capsules (of the same size). To minimize the loss of Fe in experiments at 700 MPa with low aH_2O , we used $Au_{80}Pd_{20}$ capsules presaturated with Fe following the procedure of Botcharnikov et al. (2008b). After the presaturation procedure, all glass remnants were mechanically removed from the capsules and the capsules were additionally cleaned in HF acid for 2 days. Although this procedure minimizes the risk of Fe loss, it does not completely avoid the problem, especially in samples with extremely low aH_2O or in nominally dry runs. In some high T and low aH_2O runs, we observed the opposite effect of Fe gain (runs AB15, AB19, AB25, AB30, see Δ Fe values in rel.% in Table 2). In general, to minimize the Fe-loss problem, run times were as short as possible and experimental products were mainly analysed from the central part of the sample (although no significant compositional differences as a function of location within a sample were detected). Although it was observed that Au capsules may absorb large amounts of Fe at low fO₂ (Ratajeski and Sisson 1999), we did not find significant Fe loss from our Au capsules in experiments conducted at 100 MPa. Hence, Au containers were not Fe presaturated prior to experiments. However, in our last low-T experiment conducted at 700 MPa, we observed Fe loss in Au capsules for runs AB86 and AB87, suggesting that P may facilitate the partitioning of Fe into an Au capsule even under oxidized conditions (Table 2).

Finally, it should be noted that the analytical uncertainty of FeO determination by microprobe (5–6 rel.%, see also standard deviations in Supplementary Table) could also be responsible for 4–5 rel.% of Fe loss/gain. Therefore, experiments with a Δ Fe value below 5 rel.% can be considered as runs produced within experimental and analytical uncertainties (Table 2). Within the whole data set, only run AB63 exhibits serious problems with Fe loss along with a high (1.9) residual sum of squares (ΣR^2 , see Table 2).

Experimental technique

For each experiment, $0-5 \ \mu l$ of deionized H₂O and 40 mg of glass powder were loaded into Au, Au₈₀Pd₂₀, or Fe-

 Table 1
 Compositions of synthetic basaltic andesite (BA) starting material and natural Bezymianny basaltic andesites OB-19, OB-21, OB-35 (Almeev et al. 2013a)

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
BA	54.36	0.96	17.46	8.72	0.17	5.76	8.75	2.88	0.92	0.00
OB-19	53.17	1.12	17.54	9.26	0.17	5.81	8.78	3.03	0.94	0.17
OB-21	53.87	1.13	17.44	9.35	0.17	5.23	8.69	3.03	0.91	0.17
OB-35	53.15	1.04	18.26	9.04	0.16	5.13	9.00	3.16	0.89	0.18
Tephra glass	73.83	0.23	14.71	1.67	0.09	0.53	2.59	3.88	2.38	0.08

All analyses are 100 % normalized

Tephra glass composition is an average of 45 analyses provided by M. Portnyagin (unpublished data)

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Experimental run co	
Table 2	

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Run	Capsule	P (MPa)	T (°C)	Duration (hours)	XH ₂ O ^a	H ₂ O EPMA (wt%)	H ₂ O FTIR (wt%)	aH ₂ O ^b	AQFM intrinsic IHPV	$\begin{array}{c} \operatorname{Log} \\ fO_2 \\ (\mathrm{bar}) \end{array}$	ΔQFM	Fe ²⁺ / Fe ^{Tc}	Phase assemblages and proportions (when possible)	ΣR^2	Crystallization degree (%)	ΔFe (%)
AB15	Fe- AuPd	702	1,140	24	0	1.12		0.06	4.1	-6.9	1.7	0.75	Gl(64), Plag(23), Cpx(3), Opx(10)	0.24	36	Г
AB18	Fe- AuPd	702	1,140	24	0.3	2.00		0.15	4.1	-6.1	2.5	0.68	Gl(98), Opx(2)	1.12	5	8
AB19	AuPd	702	1,140	24	1	9.00		1	4.1	-4.5	4.1	0.47	Gl(100)	I	0	
AB25	Fe- AuPd	703	1,120	24	0.2	1.30		0.1	4.1	-6.9	1.9	0.73	Gl(56), Plag(27), Cpx(7), Opx(10)	0.30	44	6
AB35	AuPd	703	1,120	24	0.4	2.90		0.25	4.1	-5.9	2.9	0.62	Gl(97), Opx(3)	0.12	3	-2
AB27	Fe- AuPd	703	1,120	24	9.0	4.27		0.43	4.1	-5.4	3.4	0.58	<i>Gl</i> (100)	I	0	
AB11 ^d	Fe- AuPd	704	1,100	25	0	1.60		0.1	4.1	-6.9	2.1	0.70	Gl(28), Plag(42), Cpx(11), Opx(17), Mt(1), llm(1)	0.06	72	
AB12	Fe- AuPd	704	1,100	25	0.3	2.50		0.20	4.1	-6.3	2.7	0.64	Gl(63), Plag(21), Cpx(7), Opx(9), Mt(1)	0.04	37	
AB13	Fe- AuPd	704	1,100	25	9.0	3.80		0.37	4.1	-5.8	3.2	0.58	Gl(100), Mt(trace)	0.19	0	
AB26	Fe- AuPd	703	1,080	28	0.4	2.50		0.2	4.1	-6.6	2.7	0.64	Gl(57), Plag(22), Cpx(11), Opx(10), Mt(1)	0.08	43	б
AB30	Fe- AuPd	703	1,080	28	9.0	3.70		0.35	4.1	-6.1	3.2	0.59	Gl(93), Cpx(5), Opx(3)	0.58	L	~
AB34	AuPd	703	1,080	28	0.8	6.00		0.63	4.1	-5.6	3.7	0.52	Gl(100)	I	0	
AB32	AuPd	703	1,080	28	1	10.70		1.17	4.1	-5.1	4.2	0.46	Gl(100)	I	0	
AB20	Fe- AuPd	703	1,050	24	0.4	2.90		0.24	4.1	-6.8	2.9	0.61	Gl(52), Plag(23), Cpx(13), Opx(9), Mt(3)	0.03	48	8-
AB21	Fe- AuPd	703	1,050	24	0.6	3.40		0.30	4.1	-6.6	3.1	0.59	Gl(83), Plag(trace), Cpx(11), Opx(5), Mt(2)	0.14	17	
AB22	Fe- AuPd	703	1,050	24	0.8	3.70		0.33	4.1	-6.5	3.2	0.59	Gl(84), Cpx(11), Opx(3), Mt(2)	0.13	16	4
AB23	AuPd	703	1,050	24	1	8.54		06.0	4.1	-5.7	4.0	0.46	Gl(100), Mt(trace)	1.98	0	
AB86	Чu	701	066	96	0.5	5.21		0.51	3.3	-7.8	2.7	0.62	Gl(81), Cpx(8), Hbl(9), Mt(2)	0.27	19	-14
AB87	Чu	701	066	96	9.0	5.23		0.51	3.3	-7.8	2.7	0.62	Gl(79), Cpx(8), Hbl(12), Mt(1)	0.13	21	-10
AB90	Au	701	066	96	0.85	7.45		0.77	3.3	-7.5	3.1	0.58	Gl(90), Cpx(5), Hbl(3), Mr(2)	0.13	10	
AB89	Au	701	066	96	0.9	8.46		0.87	3.3	-7.4	3.2	0.57	Gl(94), Cpx(4), Mt(2)	0.08	9	4
AB91	Au	701	066	96	1	9.73		1.03	3.3	-7.2	3.3	0.55	Gl(98), Mt(2)	0.23	2	5
AB76	AuPd	104	1,150	10	0	0.27	0.29	0.01	3.3	-9.2	-0.4	0.87	Gl(93), Plag(7)	0.82	7	-8
AB77	AuPd	104	1,150	10	0.1	0.14	0.47	0.04	3.3	-8.4	0.4	0.83	Gl(92), Plag(8)	0.09	8	-3

1392

Table .	2 continue	þ														
Run	Capsule	P (MPa)	T (°C)	Duration (hours)	XH ₂ O ^a	H ₂ O EPMA (wt%)	H ₂ O FTIR (wt%)	aH2O ^b	AQFM intrinsic IHPV	Log <i>f</i> O ₂ (bar)	ΔQFM	${\rm Fe}^{2+/}$ ${\rm Fe}^{{\rm Tc}}$	Phase assemblages and proportions (when possible)	ΣR^2	Crystallization degree (%)	ΔFe (%)
AB78	AuPd	104	1,150	10	0.2	0.68	0.86	0.11	3.3	-7.4	1.4	0.76	Gl(99), Plag(1)	0.10	1	-2
AB67	AuPd	103	1,100	72	0	0.33		0.02	3.3	-9.6	-0.2	0.85	Gl(82), Ol(9), Plag(16), Opx(-7)	0.29	18	L
AB68	AuPd	103	1,100	72	0.3	0.54		0.05	3.3	-8.8	0.7	0.80	Gl(86), Ol(8), Plag(12), Opx(-6)	0.11	14	5
AB69	AuPd	103	1,100	72	0.6	0.84		0.10	3.3	-8.1	1.3	0.75	Gl(92), Ol(2), Plag(6)	0.29	8	-5
AB70	AuPd	103	1,100	72	0.8	1.89		0.40	3.3	-6.9	2.5	0.63	Gl(100)	I	0	
AB63	AuPd	102	1,075	72	0	0.70	0.30	0.02	3.3	-10.1	-0.3	0.86	Gl(48), Plag(34), Opx(18)	1.90	52	-27
AB64	AuPd	102	1,075	72	0.3	0.50	0.70	0.08	3.3	-8.7	1.1	0.77	Gl(72), Ol(6), Plag(21), Opx(1)	0.14	28	-3
AB65	AuPd	102	1,075	72	9.0	0.50	06.0	0.12	3.3	-8.3	1.4	0.74	Gl(83), Ol(4), Plag(13)	0.26	17	9-
AB66	AuPd	102	1,075	72	1	3.06	3.15	0.86	3.3	-6.6	3.2	0.57	Gl(100)	I	0	
AB71	Au	104	1,040	96	0.2	0.70		0.07	3.3	-9.2	1.0	0.76	Gl(37), Plag(39), Cpx(8), Opx(12), Mt(4)	0.05	63	
AB72	Au	104	1,040	96	0.4	1.50		0.27	3.3	-8.1	2.2	0.66	Gl(44), Plag(37), Cpx(7), Opx(8), Mt(4)	0.03	56	
AB73	Au	104	1,040	96	0.6	1.90		0.39	3.3	-7.8	2.5	0.62	Gl(65), Plag(21), Cpx(4), Opx(7), Mt(3)	0.04	35	
AB74	Au	104	1,040	96	0.8	2.20		0.49	3.3	-7.6	2.7	09.0	Gl(78), Ol(6), Plag(15), Cpx(3), Opx(-4), Mt(2)	0.02	22	
AB75	Au	104	1,040	96	1	3.10		0.82	3.3	-7.1	3.1	0.56	Gl(97), Ol(1), Mt(2)	0.04	3	
AB62	Au	102	1,000	120	0.7	1.61	1.59	0.28	3.3	-8.6	2.2	0.64	Gl(34), Plag(38), Cpx(12), Opx(10), Mt(6)	0.05	66	
AB60	Au	102	1,000	120	0.0	2.70	2.36	0.52	3.3	-8.1	2.7	0.58	Gl(45), Plag(31), Cpx(10), Opx(8), Mt(6)	0.03	55	
AB61	Au	102	1,000	120	1	3.00	2.86	0.75	3.3	-7.8	3.1	0.55	Gl(60), Plag(19), Cpx(10), Opx(6), Mt(5)	0.09	40	
AB54	Au	102	975	168	6.0	2.90		0.73	3.3	-8.2	3.0	0.54	Gl(44), Plag(31), Cpx(11), Opx(8), Mt(6)	0.09	55	
H ₂ O in {	glasses was	s determinec	l by FTIE	k in experin	tents AB6	0-AB66; AB	76-AB78 and	1 can be co	ompared to H	20 determin	led using th	ne "by d	ifference" method. Note, value	es of H ₂	O used in Figures a	nd in

calculations of $aH_{2}O$, fO_{2} and $Fe^{2+f}Fe^{T}$ are given using normal font (non-italic). ΔFe : Fe loss or gain (in relative percent) from the starting material based on the difference between the starting material and the calculated bulk composition of the experiment using mass balance calculations

EPMA, electron probe microanalysis; FTIR, Fourier transform infrared spectroscopy; Gl, glass; Plag, plagioclase; Cpx, clinopyroxene; Opx, orthopyroxene; Ol, olivine; Hbl, hornblende; Mt, magnetite; Ilm, ilmenite; ΣR^2 : residual sum of squares

 a XH₂O: molar fraction of H₂O added in the capsule. Runs with XH₂O = 1 are H₂O-saturated experiments

^b aH₂O calculated from H₂O in the melt using a model of Burnham (1994); FW eight and k-factors are calculated following the method in Holloway and Blank (1994)

 $^{\rm c}~{\rm Fe}^{2+}/{\rm Fe}^{\rm T}$: calculated after Kress and Carmichael (1988), ${\rm Fe}^{\rm T}$ is total iron

^d Cpx was not measured in the AB11 run due to small crystal size. Its composition (see Supplementary Table) was estimated by mass balance, but not used in further consideration

presaturated Au₈₀Pd₂₀ capsules. aH_2O in the experiments was varied by adding different proportions of H₂O and CO₂ into the fluid phase (experiment AB76 at 1,150 °C and 100 MPa was run without any fluid, Table 2). Silver oxalate (up to 16 mg) was used as the CO_2 source. The experiments were performed over a T range of 975-1,150 °C at 100 MPa and of 990-1050 °C at 700 MPa using an internally heated pressure vessel (IHPV) pressurized with Ar as the pressure medium (IHPV without Shaw membrane). A detailed description of the apparatus is given elsewhere (Berndt et al. 2002). Total pressure was measured and recorded continuously with an uncertainty of about 1 MPa using a strain gauge manometer. The pressure varied by ≤ 5 MPa during the experiments. Temperature was measured with four unsheathed S-type (Pt-Pt₉₀Rh₁₀) thermocouples over a length of about 30 mm; T varied by <5 °C. The capsules were first brought to the desired pressure (100 or 700 MPa) and then heated isobarically from room temperature to experiment temperature with a ramp of 30 °C/min. Thus, samples were taken directly to the final experimental conditions without high-temperature annealing, and the overheating did not exceed 10 °C. The run duration varied with temperature; it was more than 120 h for runs at 1,000 and 975 °C, and in the range of 10-96 h for runs at 1,150 and 1,040 °C (Table 2). After the experiment, all capsules were rapidly quenched with a quench rate of about 150 °C/s which was sufficient to avoid quench effects.

According to the IHPV technique, variations in fluid phase H₂O/CO₂ ratio also result in variations of fO_2 in the system (e.g. see experimental approaches described in Scaillet et al. 1995, Botcharnikov et al. 2005, 2008a, b). The IHPV is pressurized with pure Ar gas containing only trace amounts of hydrogen. Within the sample capsule, the fH_2 is fixed due to an in-diffusion of hydrogen. This, in turn, controls the fO_2 inside the capsule through the equilibrium reaction of H₂O dissociation (H₂ + $\frac{1}{2}$ O₂ \leftrightarrow H₂O).

The set of 100 MPa experiments was conducted in an IHPV in which the intrinsic fO_2 of the vessel was determined using a NiPd solid sensor (Schuessler et al. 2008) to be 3.3 log units above the fO_2 of the QFM solid assemblage (hereafter labelled as QFM + 3.3) under H₂O-saturated conditions. The 700 MPa set of experiments was conducted in a different IHPV with high *T* furnace in which intrinsic fO_2 under H₂O-saturated conditions was determined to be QFM + 4.1 (unpublished data). For both cases, in capsules with lower aH_2O , redox conditions are more reduced than in the experiments at intrinsic fO_2 conditions with $aH_2O = 1$ (e.g. ~QFM in runs with ~0.4 wt% H₂O at 700 MPa). The fO_2 in the H₂O-undersaturated experiments was calculated using the relation: log $fO_2^{capsule} = \log fO_2$ (at $aH_2O = 1$) + 2log aH_2O (Scaillet

et al. 1995; Botcharnikov et al. 2005), where aH_2O was calculated from the model of Burnham (1994) (see details in Holloway and Blank 1994) based on the estimated concentrations of dissolved H_2O in a residual melt (Table 2). The overall error in the calculated fO_2 was estimated to be about ~0.2–0.3 log units (Scaillet et al. 1995; Botcharnikov et al. 2005). The fO_2 values (Table 2) were also used to calculate the ferric-ferrous ratio in residual melts according to the model of Kress and Carmichael (1991).

Analytical techniques

After completion of the experiments, the capsules were weighed to ensure that there had been no loss of H_2O and CO_2 at high *P* and *T*. No weight loss was observed in the experiments listed in Table 2. To check for the presence of excess fluid, the capsules were punctured and weighed following the weight loss method. However, the amounts of fluid measured were too low to allow the molar fraction of H_2O (XH₂O) of the fluid to be estimated accurately by this method.

The starting glass BA and the experimental products were analysed using a Cameca SX100 microprobe (University of Hannover), operated at an accelerating voltage of 15 kV and a 10 and 15 nA beam current for glass and mineral analyses, respectively. The beam was focused to 1 µm for crystalline phases and varied from focused to 10 um defocused for glass analysis depending on crystallinity of the investigated sample. Na and K were analysed first with counting times of 8 s. Counting time for other elements was 10 s. Standards used for calibrations were: Fe₂O₃, MgO, TiO₂, Al₂O₃, albite (Na), orthoclase (K), wollastonite (Si and Ca) and rhodochrosite (Mn). In the course of each microprobe session, analytical precision and accuracy was verified by measuring the Smithsonian Institution's VG-2 natural glass standard (Jarosewich et al. 1980).

Compositions of experimental minerals and glasses were used in a mass balance calculation to determine phase proportions (Stormer and Nicholls, 1978). Glass analyses were normalized to 100 % to exclude the H₂O dissolved in the quenched glasses. Calculated modes are given in Table 2 (wt%), together with the residual sum of squares to the fit (ΣR^2). Most fits were satisfying with $\Sigma R^2 < 0.3$ (Table 2). Fits for less-crystallized charges, especially for those with high *a*H₂O (and high *f*O₂), were poorer, perhaps due to high Fe³⁺ in the melt, the proportion of which was not accounted for in the mass balance calculation. All charges with an Fe-loss/gain problem also demonstrated poor fits. In run AB11, we were not able to identify high-Ca *Px* among the run products; however, its crystallization is expected according to phase boundaries on the phase diagram (see "700-MPa Experiments" section). Composition of the *Cpx* in run AB11 was calculated to obtain the best fit minimizing the ΣR^2 value.

Two methods were applied to determine H₂O concentrations in the experimental quenched glasses. For runs with medium-to-high crystal contents, the H₂O content of the experimental glasses was determined following the "by difference" method described in Devine et al. (1995) using a series of Mutnovsky basaltic glass standards (Shishkina et al. 2010) containing different H₂O contents (0-8 wt% H₂O). The obtained calibration lines, established for each microprobe session, were used to calculate the actual H₂O concentration of the individual sample (See Appendix Fig. A1 where an example of a calibration line is provided). The uncertainty ranged from ± 0.5 to 0.9 wt% H₂O. The highest errors are found in experiments with low melt fractions where glass analyses were only possible with a focused microprobe beam only. In experimental runs (AB76-78, AB64-AB66) with a large amount of glass (more than 70 vol%), melt H₂O contents were determined using conventional mid-infrared Fourier transform infrared (FTIR) spectroscopy. In a few charges (AB60-AB63), glass pools close to bubbles were also large enough to measure with FTIR. Spectra were collected in the mid-infrared (MIR) range with a Bruker IFS 88 FTIR spectrometer coupled to an A590 IR microscope. The spot size was $50 \times 50 \ \mu m$ for most samples. This relatively small aperture was necessary to select crystal-poor zones in the experimental products. The operating conditions for MIR were glow bar light source, KBr beam splitter, MCT (HgCdTe) detector, 4 cm^{-1} spectral resolution, 13,000 to 0 cm^{-1} spectral range, 50 scans accumulated per measurement. Doubly polished 60-80-µm-thick samples for MIR were prepared from the experimental products. Sample thickness was measured at 5 points using a digital micrometer with an estimated uncertainty of $\pm 0.3 \ \mu m$. Three measurements per sample were performed to account for possible variations in thickness due to polishing. For calculating H₂O content, glass density was estimated to be constant at 2,757 kg m⁻³. The H₂O contents for MIR measurements $(3,550 \text{ cm}^{-1})$ were calculated using a molar absorption coefficient of $68 \ \text{l} \ \text{cm}^{-1} \ \text{mol}^{-1}$ (Shishkina et al. 2010). Three to five single measurements were performed per sample, and different locations in the sample were chosen to check for homogeneity. The average values of such measurements are used to calculate the H₂O content of the glasses, with a standard deviation of 0.02 wt%.

Attainment of equilibrium

The experimental approach used in our study, i.e., crystallization using a powder of homogeneous glass and fluid, is believed to be the best way to achieve near-equilibrium conditions (e.g. Pichavant 1987; Holtz et al. 1992). High volatile diffusivity and mineral dissolution/crystallization processes in basaltic and andesitic systems ensure fast equilibration (Botcharnikov et al. 2008a, b). Freise et al. (2009) conducted time-dependent crystallization experiments at 200 MPa with a basaltic composition (slightly more alkali rich) using the same experimental approach (dry powdered glass + fluid) in the same temperature range and demonstrated that near-equilibrium conditions were attained in less than 2 h for a H₂O melt content of ~ 2 wt% and in about 3 h at nominally dry conditions. Although the composition investigated by Freise et al. (2009) is slightly different from our composition, the degree of polymerization is similar and the crystallization kinetics is not expected to differ significantly.

There are no textural observations in the experimental products that indicate disequilibrium features. Mineral phases are homogeneously distributed throughout the samples (Figs. 1, 2) and the minerals have idiomorphic shapes. The morphology of the crystals does not indicate any quench crystallization (except for a few H₂O-saturated experiments at 700 MPa, which are excluded from further interpretation). Mineral phases are also homogeneous in composition within the bounds of analytical uncertainty. Phase equilibria and chemical trends of experimentally produced glasses exhibit regularities consistent with results of H₂O-bearing experiments obtained in other studies. Mineral melt and mineral–mineral partitioning coefficients are in the range of literature data for most runs (Supplementary Table).

Experimental results

General remarks

The experimental conditions, run products and their compositions are summarized in Table 2 and Supplementary Table. The crystallizing phases identified are olivine (Ol), clinopyroxene (Cpx), orthopyroxene (Opx), plagioclase (Plag), hornblende (Hbl), magnetite (Mt) and ilmenite (Ilm) (Figs. 1, 2). Glass (Gl) was present in all experimental charges (Figs. 1, 2) and was successfully analysed even in runs with high crystallinity. In a few runs at 100 and 700 MPa, conditions above the liquidus were reached (Gl was the only experimental product). The presence of an H₂O–CO₂ fluid phase during experiments can be proved by the presence of abundant bubbles (Figs. 1, 2). The liquidus temperature was not bracketed systematically as a function of aH_2O , leading to some uncertainties especially in the ranges of very low H₂O concentrations at 100 MPa $(<0.25 \text{ wt\% H}_2\text{O})$ and 700 MPa $(<1 \text{ wt\% H}_2\text{O})$ and of very high H_2O concentrations at 700 MPa (>6 wt% H_2O).



Fig. 1 Scanning electron microscope images of selected run products obtained in crystallization experiments at 100 MPa in the temperature range of 1,150-975 °C and with melt water contents from 0.3 to

3 wt% H₂O. Phase abbreviations—Gl glass, Plag plagioclase, Cpx clinopyroxene, Opx orthopyroxene, Ol olivine, Hbl hornblende, Mt magnetite



Fig. 2 Scanning electron microscope images of selected run products obtained in crystallization experiments at 700 MPa in the temperature range of 1,120–990 °C and with melt water contents from 1.3 to 7.6 wt% H_2O

However, such conditions are assumed to be irrelevant for natural Bezymianny magmas. Thus, interpolation of the liquidus and low-T phase boundaries based on our

experimental data set seems to be sufficient to bracket the mineral crystallization sequences and intervals of coexisting minerals in basaltic andesite melts from Bezymianny. The position of the solidus curve is more uncertain and should be considered with caution. As discussed above, fO_2 varies as a function of aH2O. The fO2 at given melt H2O content is given in Table 2 and is indicated in Figs 3a and 4a at the top of each plot. In the 100-MPa experiments, the full range of redox conditions exists between QFM-0.3 (0.3 wt% H₂O) and QFM + 3.1 (\sim 3 wt% H₂O), whereas in 700 MPa experiments, redox conditions range between QFM + 1.85 (1.3 wt% H₂O) and QFM + 4 (\sim 8.5 wt% H₂O). The most relevant interval of experimentally investigated redox conditions is within the range of 1-4 wt% H₂O (QFM + 1.5 to QFM + 3.3) which is the assumed range of redox conditions prevailing in subduction zone magma chambers (Gill 1981). Thus, when interpreting a phase diagram such as those shown in Figs. 3 and 4, one should keep in mind that crystallization sequences are affected not only by changing melt H₂O concentrations, but also by changing fO_2 . It should be noted that this observation is of particular importance for oxide stabilities (e.g. Mt and Ilm); the Mt stability increase is not only caused by silicate crystallization suppression as a result of increasing aH_2O , but also by increasing fO_2 . In Figs. 3b and 4b, the stability fields of different phase assemblages are superimposed along with degrees of crystallization indicative of the ability of the magma to erupt.

Phase relations

100 MPa experiments

Plag is the liquidus phase of basaltic andesite at 100 MPa at all melt H₂O concentrations (Fig. 3). At H₂O-saturated conditions, the liquidus temperature was not bracketed, and at 1,040 °C, melt coexists with Plag, Mt, and Ol. With temperature decrease, Plag crystallization is followed by Ol, Opx and Cpx. The Ol crystallization interval is restricted around \sim 40 °C; it disappears as the result of a peritectic reaction involving Opx formation. This reaction is completed at T below 1,075 °C at low H₂O concentrations and below ~1,025 °C in H₂O-saturated conditions. *Mt* joins silicate phases below 1,075 °C under dry conditions and at 1,050 °C under H_2O -saturated conditions. Cpx is the latest phase to crystallize in basaltic andesite at 100 MPa. The stability field of andesitic liquids equilibrated with a Plag + Cpx + Opx + Mt mineral assemblage (see also Fig. 3b) is the domain in which the phase assemblage of the natural 2Pxandesites is reproduced (Almeev et al. 2013a). At 975 °C, a successful run was obtained only at nearly H2O-saturated conditions (2.9 wt% H₂O) and all other runs with initial low XH₂O in the fluid experienced nearly complete crystallization (>90 %). Although these experiments are not used for further interpretations due to the potential problem of not attaining full equilibrium and the extremely small size of experimental phases (<1-2 µm), they are helpful to constrain the position of the basaltic andesite H2O-saturated solidus which is probably between 975 and 950 °C at conditions close to H₂O saturation. Thus, the experiments at 100 MPa suggest that andesitic melts saturated with a mineral assemblage analogous to Bezymianny 2Px andesites can be experimentally simulated from basaltic andesite parental magma within the T interval of 1,040–975 °C in the range of 0.5–3 wt% H_2O in the melt (Fig. 3b). However, it should be stressed that these experimental runs reach 50-70 % crystallization (Figs. 1, 3b, 5a), indicating high magma crystallinity and limiting the potential of such magma derivatives to be stored at 100 MPa lithostatic pressure and to erupt from such levels. It is also emphasized that phenocryst abundance in natural Bezymianny lavas has never exceeded 25 % (see Figs. 5, 6, and also Table 1 in Almeev et al. 2013a).

700 MPa experiments

At 700 MPa, mineral stability fields were investigated in melts containing up to $\sim 10 \text{ wt\% H}_2\text{O}$ (Fig. 4). Neither the dry liquidus nor the H₂O-saturated liquidus (+solidus) were reached at the investigated temperatures. The sequence of silicate mineral appearance is similar up to 1,050 °C at all investigated melt H₂O contents: Opx crystallizes first, then Cpx joins Opx, and finally Plag crystallizes together with Cpx + Opx. Ol was never observed at 700 MPa. At low H₂O contents (<2.5 wt%), Mt is the last phase to crystallize (Ilm was also observed in one run). Mt stability increases with increasing aH_2O (and fO_2), similar to the 100 MPa runs, and Mt is the liquidus phase in melts with about 4 wt% H₂O. At the lowest investigated temperature of 990 °C, Hbl crystallization is observed in runs with intermediate melt H₂O content. However, in experiments with high H₂O contents (9–10 wt%), *Hbl* is not stable at 990 °C, and only $Mt \pm Cpx$ are present as solid phases. In the 1,050-990 °C temperature interval, Opx stability seems to be controlled by peritectic reaction; it is not observed among the crystallizing minerals. Thus, six isothermal experimental series obtained in the range of 1-10 wt% H₂O were sufficient to bracket the region where and esitic liquid is saturated with the Plag + Cpx + Opx + Mt mineral assemblage: 1–2.5 wt% H₂O at 1,110 °C to 2.5-4.5 wt% H₂O at 1,050 °C (grey field in Fig. 4b). The mineral stability in the region below 1,050 °C is more problematic to elucidate and needs to be confirmed by additional experiments (e.g. at 1,020 °C to accurately constrain the *Opx* out curve).

Crystallinity

The melt fraction decreases and the proportion of solid phase increases with decreasing H_2O contents in the melt at all investigated temperatures (Fig. 5a, b; Table 2), and with



Fig. 3 a Phase relationships in Bezymianny basaltic andesite as a function of melt water content and temperature at 100 MPa. The change of redox conditions in IHPV with increasing aH_2O (melt H_2O) is shown by vertical arrows. The approximate location of the solidus is indicated by the *dashed line*. The inferred curve for H_2O saturation is shown as a *dotted near-vertical line*. Amount of crystallization (Table 2) for each run is given by a small italic numbers. Run AB63 (1,075 °C, 0.3 wt% H_2O) is shown in Fig. 3a with a "?" due to significant Fe loss (27 %, Table 2) and should be considered with caution. For example, the lack of *Ol* crystallization observed in this run could be related to the Fe loss and the change of bulk composition

decreasing temperature (at a given H_2O in the melt). At lower temperatures (e.g. 1,040 °C at 100 MPa and 1,050 °C at 700 MPa), the crystallinity increases up to ~60–50 wt% within relative variations of H₂O contents of

after 3 days of experimental treatment. **b** Phase boundaries of coexisting $Ol + Plag \pm Mt$, Ol + Plag + Cpx + Opx + Mt, and Plag + Cpx + Opx + Mt mineral assemblages (*shaded fields*) at 100 MPa with superimposed isocrystallinity curves derived from the experiments (*dotted lines*). Note that the 100-MPa experimental mineral assemblage corresponding to natural 2Px andesite is generally characterized by moderate-to-high crystallinity (>20 %). Olbearing 2Px andesites with crystallinity below 20 % can be produced at 100 MPa in a narrow range of experimental conditions: 1,030–1,040 °C, 2.5–3 wt% H₂O

2.5 wt% H₂O at 100 MPa and \sim 5 wt% H₂O at 700 MPa (Fig. 5a, b). In the presence of \sim 2 wt% H₂O, \sim 50 % crystallinity may be reached in the temperature drop of 40 °C at 100 MPa and 20 °C at 700 MPa.

Fig. 4 a Phase relationships in Bezymianny basaltic andesite as a function of melt water content and temperature at 700 MPa. The change of redox conditions in IHPV with increasing aH_2O (melt H₂O) is shown by vertical arrows. The approximate location of the solidus is indicated by the dashed line. The inferred curve for H₂O saturation is shown as a *dotted* near-vertical line. Amount of crystallization (Table 2) for each run is given by a small italic number. b Phase boundaries of coexisting Plag + Cpx + Opx + Mt and Cpx + Hbl + Mt mineral assemblages (shaded fields) at 700 MPa with superimposed isocrystallinity curves derived from the experiments (dotted lines). Note that the 700-MPa experimental mineral assemblage corresponding to natural 2Px andesite is generally characterized by moderate-tohigh crystallinity (>20 %)



Since both, temperature and aH_2O affect crystallinity (Fig. 5a, b), in a strict sense, it is necessary to compare the evolution of the modal proportions during cooling, using runs with the same aH_2O (e.g. $aH_2O = 0$: dry conditions or $aH_2O = 1$: H₂O-saturated conditions). Therefore, in Fig. 5c, d, comparison of the modal proportions of mineral and liquid phases is given for experiments with close values of the aH_2O (these experiments are connected by grey dashed lines in Fig. 5a, b). As one can see from Fig. 5c, d, there is no significant change of the mineral proportions: *Plag* is always the prevailing mineral in the solid phase, the proportions of *Cpx* and *Opx* are very similar, and the proportion of *Mt* and, if present, *Ol* are the lowest. The proportion of the liquid phase in the presence of $Plag + Cpx + Opx \pm Mt \pm Ol$ mineral association in our experiments is significantly lower than that observed in natural andesites (see phase proportions in natural basaltic andesite and 2Px andesite to the right of the plot Fig. 5c, d plots). Comparison of the mineral proportions in the solid phase (when the proportion of the liquid phase is subtracted from the system) demonstrates that (1) the effect of H₂O on mineral proportion is insignificant in the range of $aH_2O = 0$ to ~ 0.5, with a small decrease of *Plag* proportion in the range of aH_2O from 0.5 to ~ 0.8 (Fig. 6a), and (2) the proportion of the mafic minerals and *Mt* (if present) in our crystallization experiments (Fig. 6a, b) is higher than that observed in natural lavas (Fig. 6c).



Fig. 5 Variations of crystal content (vs. melt H₂O) and phase proportions (vs. temperature) in experiments at 100 MPa (**a**, **c**) and 700 MPa (**b**, **d**). In (**a**) and (**b**) isotherms are connected by *solid lines*; stars represent runs where simultaneous crystallization of *Plag* + *Cp*- $x + Opx \pm Mt \pm Ol$ was observed. In (**a**) and (**b**), *grey dotted lines* connect runs shown in (**c**) and (**d**), respectively: these experiments are

In general, only two experiments, AB74 (100 MPa, 1,040 °C, 2.2 wt% H₂O) and AB21 (700 MPa, 1,050 °C, 3.4 wt% H₂O), exhibit both crystallinities and phase assemblage similar to natural Bezymianny 2Px andesites (black and white stars located in the field of natural compositions in Fig. 5a, b). However, the proportion of *Plag* in the AB21 700-MPa run is very low (<1 %, Table 2) and the $P-T-aH_2O$ conditions of this run cannot be considered as pre-eruptive conditions. In contrast, the AB74 100-MPa run with 2.2 wt% H₂O (Table 2) demonstrates mineral proportions similar to those in basaltic andesite OB-19 (see run AB74 with $aH_2O = 0.5$ in Fig. 6a). Only the mode of experimental Mt is nearly 30 % higher than that observed in natural lavas. However, the high proportion of Mt in experiments did not result in the TiO₂ depletion trend required to better fit the experimental observations to the natural data (see below).



used to demonstrate the change of crystal proportions with temperature across a very narrow range of aH_2O (0.1–0.2). In (c) and (d), to the right of the main plots, mineral proportions in natural basaltic andesite and 2Px and esite (Almeev et al. 2013a) are shown for comparison

Mineral compositions

In Fig. 7a-e, experiments produced at 100 (filled symbols) and 700 MPa (open symbols) at different temperatures (symbols connected by line) are shown to illustrate the change of mineral compositions: anorthite content An (mol%) in Plag, Fig. 7a; mg# numbers (mg# = Mg/ (Mg + Fe), molar) in Cpx and Opx, Fig. 7b, c; forsterite content Fo (mol%) in Ol, Fig. 7d; and ülvospinel component (X^{USP}) in *Mt*, Fig. 7e) as a function of melt H₂O contents and redox conditions. For comparison with natural Bezymianny Volcano minerals, histograms of the phenocryst core compositions from 2Px and esites are shown along the vertical axis of each plot. For both pressures, experiments contoured by grey fields represent runs where simultaneous crystallization of Plag + Cpx + Op $x \pm Ol \pm Mt$ was observed. Figure 7f demonstrates

Fig. 6 Variations of mineral proportions in solid phase (a) at constant temperature 1040 and 1000 °C as a function of melt H₂O at 100 MPa; (b) at nearly constant aH₂O (~0.1–0.2) as a function of temperature at 700 MPa; (c) in natural basaltic andesite OB-19 and 2Px andesite OB-9 (Almeev et al. 2013a). See text for more details



compositions of coexisting *Hbl* and *Cpx* produced at 700 MPa and 900 $^{\circ}$ C and illustrates the potential crystallization conditions of the *Hbl-Cpx*-bearing xenoliths.

Plagioclase

At both pressures investigated, the An in *Plag* increases strongly with an increase in melt H₂O and temperature (Fig. 7a). However, at 700 MPa, *Plag* has a systematically more albitic composition, indicating the well-known opposite effects of *P* and H₂O on *Plag* composition. At constant H₂O, as *P* increases from 100 to 700 MPa, An content decreases by up to ~20 mol% An (~3.3 mol% An decrease per 100 MPa; e.g. compare 100- and 700-MPa isotherms at 1,100 °C and 1 wt% H₂O, Fig. 7a). Assuming that the effect of H₂O on *Plag* composition is similar at both pressures (slopes of isotherms at both pressures are nearly identical in Fig. 7a), the similar absolute change (increase) up to ~20 mol% of the An in *Plag* can be obtained by adding 2 wt% H₂O (~10 mol% An increase per 1 wt% H₂O; e.g., compare 100-MPa isotherms at 1,100 or 1,040 °C) in the melt. Our data demonstrate that the addition of 0.33 wt% H₂O to the system and the *P* drop of 100 MPa may compensate each other; indeed no change in *Plag* composition seems to be observed. However, both *P* drop and H₂O addition affect the temperature stability of *Plag*, and the effect of H₂O (~36 °C *T* drop in the presence of 0.33 wt% H₂O, Almeev et al. 2012) is much stronger than that of pressure (~5–7 °C per 100 MPa, Ariskin 1999) which will result in different degrees of undercooling: an "An-compensation" effect should not be expected in this case.

The experimentally produced *Plags* represent only a minor number of natural *Plag* composition possibilities. As one can see from Fig. 7a, natural *Plags* demonstrate a bimodal distribution (Almeev et al. 2013a), and the largest maximum (An85–90) was observed in our experiments at



Fig. 7 Compositions of synthetic *Plag* (a), *Cpx* (b), *Opx* (c), *Ol* (d), *Mt* (e) and *Hbl* (f) produced in experiments with basaltic andesite at 100 (*filled symbols*) and 700 MPa (*open symbols*). Experiments produced at the same temperature are connected by lines. *Grey fields* with dashed contour enclose experimental runs where simultaneous crystallization of *Plag* + *Cpx* + *Opx* \pm *Ol* \pm *Mt* was observed. On

each diagram the histograms of natural core mineral compositions from 2Px and sites are provided along the vertical axis for comparison. In (a) to (e) mineral compositions are plotted versus melt H₂O. Experimental *Hbl* compositions observed only at 700 MPa and 990 °C are plotted versus mg# of the coexisting *Cpx*. See text for more details

neither 100 nor 700 MPa. However, *Plag* synthesized at 700 MPa is closer to the second natural maximum (An55–60). Thus, our new experimental data demonstrate that *Plag* with composition An55–60 is the product of hydrous fractionation at depths of more than 3–4 km,

under pressure >150 MPa. The high-Ca *Plag* (An85-90) abundantly observed in basaltic andesites and 2Px andesites is the product of shallow-level fractionation (<100 MPa), which possibly proceeds under H₂O-saturated conditions.



✓ Fig. 8 Compositions of experimental melts produced at 100 MPa (black squares: 1,040 °C; black crosses: 1,000 °C; black triangle: 975 °C) and 700 MPa (open squares: 1140-1050 °C) and coexisting with the $Plag + Cpx + Opx \pm Mt$ mineral assemblage, in comparison with natural Bezymianny Volcano lavas (grey circles, Almeev et al. 2013a). Glasses saturated with Cpx + Hbl + Mt at 700 MPa and 990 °C are shown by open crosses. The silicic tephra glass composition (provided by M. Portnyagin) is shown as representative of the final evolutionary stage of Bezymianny melt evolution (grey triangle). Also shown are glass matrix (grey crosses) and glass inclusion (grey diamonds) compositions (Shcherbakov et al. 2011). To clarify the Al₂O₃-SiO₂ and FeO-SiO₂ plots, the 700-MPa glasses produced at similar (close) temperatures are enclosed by ovals and 100-MPa glasses obtained from experiments conducted at the same temperature are connected by lines. In addition, on these plots, the dashed line demonstrates the possible evolution of the 100 MPa $Plag + Cpx + Opx \pm Mt$ -saturated melts with constant aH_2O (0.1, 0.4 and 1). Numbers near 100-MPa runs on selected plots indicate melt H₂O contents. Natural lavas from prehistoric (pre-Bezymianny stage) and historical (Bezymianny stage) eruptions are discriminated by dark and light grey circles respectively

Pyroxenes

There is a strong positive effect of H₂O on mg# at constant temperatures observed in experimental Cpx and Opx (Fig. 7b,c) at both pressures as a direct consequence of the different redox conditions maintained in runs with different aH₂O (see the experimental IHPV technique above). In more oxidized conditions, pyroxenes crystallize from more magnesian melts due to the higher proportion of the melt Fe^{3+} . This is an experimental artefact which should not be generalized to crystallization in natural magma chambers which is believed to proceed under fO_2 buffered conditions (e.g. \sim NNO (nickel-nickel oxide) in island arcs, Gill 1981). Nevertheless, it is possible to observe relative changes by comparing experimental runs at different pressures and similar temperatures and melt H_2O (and fO_2 , e.g., in Fig. 7b-e, see grey arrows, indicating redox conditions relative to the QFM buffer). For example, the mg# of both Cpx and Opx at given H_2O are notably higher in low P 100-MPa runs. This can be explained by the more iron-rich (and hence less mg#) compositions of coexisting 700-MPa liquids caused by suppression of Mt and high proportion of *Plag* crystallization at this pressure (see Fig. 8a-h).

Experimental *Cpxs* are found within the range of natural compositions: similar to *Plag*, their mg# is bimodally distributed (Almeev et al. 2013a). A more magnesian mode (mg# \sim 77–80) is found in 100-MPa *Cpx*, whereas 700-MPa *Cpx* is closer to the low magnesian mode (mg# \sim 70) of natural *Cpx* compositions. Although there is a good fit between mg# numbers of experimental and natural *Cpx* (Fig. 7b), it should be noted that the experimental *Cpxs* (especially those produced at 700 MPa) are slightly but systematically lower in SiO₂ and CaO contents.

In contrast to Cpx, experimental Opx are generally more magnesian than the natural low-Ca pyroxene (Fig. 7c). Only high T and low H₂O runs exhibit Opx which are similar to the most magnesian natural Opx with mg# ~75–80. It is not clear from Fig. 7c, whether simply increasing the P (e.g. >700 MPa) will allow a natural low magnesian Opx (mg# ~60–70) to be reproduced. Perhaps similar Opx compositions can also crystallize at lower P (100 MPa <P <700 MPa), at T between 1,120 and 1,040 °C and melt H₂O <2 wt% H₂O (Fig. 7c).

Olivines

Crystallization of *Ol* is only observed in our 100-MPa runs. These low *P* experimental *Ol* compositions demonstrate a good fit (Fig. 7d) with *Ol* from natural 2*Px* andesites where *Ol* is usually a rare phase (Almeev et al. 2013a). It is also clear that at this low *P*, *Ol* may precipitate simultaneously with *Plag* + *Cpx* + *Opx* only below 1,075 °C and only from andesitic melts with more than 1.5 wt% H₂O (note the grey field which encloses the run exhibiting the *Plag* + *Cpx* + *Opx* \pm *Ol* \pm *Mt* mineral association). To reproduce less magnesian *Ol* from 2*Px* andesites (or from basaltic andesite in which *Ol* exhibits an Fo ~74 mode, Almeev et al. 2013a, b) pressures higher than 100 MPa (but lower than 700 MPa) may need to be utilized.

Titanomagnetite

Similar to pyroxenes, the change of redox conditions driven by the change of aH_2O in our runs resulted in compositional changes of the experimental Mt. The X^{USP} in Mt decreases with increasing melt H_2O contents and fO_2 (Fig. 7e). Although the mode of natural $Mt X^{\text{USP}} = 0.33$ is not observed in our runs, experimental Mts retain their natural counterparts ($X^{\text{USP}} \sim 0.1$ to 0.25). It should be stressed, however, that most experimental Mts are produced at more oxidized conditions (>QFM + 2) than was estimated for natural Mt from Mt-Ilm oxy-barometry (\sim QFM + 0.7–QFM + 1.7, Almeev et al. 2013a).

Hornblende

Three experimental amphiboles produced in runs at 700 MPa, 990 °C and 5.21, 5.23 and 7.5 wt% H₂O are large euhedral unzoned calcic amphiboles, which according to the classification of Leake et al. (2004) can be named ferri-tschermakites. Similar to pyroxenes, there is an increase in mg# in transition from 5.2 to 7.5 wt% H₂O, which is related to the change of redox conditions (see Table 2 for fO_2 values).

In Fig. 7f, *Hbl* mg# is plotted versus *Cpx* mg# for both experimental and natural coexisting pairs. Natural pairs represent the Hbl and Cpx from Hbl-CPx xenoliths (cumulates?) found abundantly in Hbl andesites of the Plotina Dome on the southern slope of the Bezymianny Volcano (Almeev et al. 2013a). The chemical analyses were obtained from samples taken in the vicinity of the mineral grains, under the assumption that the grains may represent coexisting (cotectic) compositions. In addition, histograms of core analyses of Hbl xenocryst and Cpx phenocryst core analyses from basaltic andesite OB-21 (Table 1, see also Almeev et al. 2013a) are also provided along the appropriate axis. In general, our experimental amphiboles produced in runs with $\sim 5 \text{ wt\% H}_2\text{O}$ (AB86 and AB87) correspond well to the Hbl from natural samples (both, basaltic andesite OB-21 and Hbl-CPx xenolith). The experimental Cpx in these runs also matches to the natural Cpx from basaltic andesite OB-21, but is less magnesian than Cpx from Hbl-Cpx xenoliths. As was shown above, crystallization of the more magnesian Cpx from the same basaltic andesite parent may occur at lower pressure. This suggests that crystallization of a natural Hbl-Cpx assemblage might have occurred at different depths within the magma chamber in the case of basaltic andesite OB-21 versus *Hbl-Cpx* xenoliths (\sim 700 and <700 MPa, respectively). On the other hand, crystallization of an Hbl-Cpx xenolith assemblage might have proceeded at the same pressure of 700 MPa, but in the presence of higher H₂O in the melt, at conditions similar to the AB90 run with 7.45 wt% H₂O (Fig. 7f). The mg# number of the experimental Cpx produced in this experiment is similar to Cpx from Hbl-Cpx xenoliths; however, the Hbl is more magnesian. Thus, in both cases, the effect of P (aH_2O and fO_2) on Hbl composition needs to be studied more systematically.

Glass compositions

The major element variations in glass compositions produced at 100 and 700 MPa (Supplementary Table) are shown in Fig. 8a-h along with compositions of natural Bezymianny lavas (Almeev et al. 2013a). Only experimental glasses saturated with $Plag + Cpx + Opx \pm Mt$ and with Cpx + Hbl + Mt are shown for clarity and considered in further discussion (see also Figs. 1, 2). In addition, the average of 45 tephra glass analyses (M. Portnyagin, personal communication), and the compositions of glass groundmass (grey crosses) and Px melt inclusions (grey diamonds) in andesites from 2000 to 2007 eruptions (Shcherbakov et al. 2011) are shown to provide a reference for the final stages of melt evolution reached in the natural system. The rhyodacitic to rhyolitic average tephra glass (grey triangle in Fig. 8) is located exactly on the silica-rich trend defined by Bezymianny bulk rocks (taking into account a slight bending of the Bezymianny trend, e.g., in Na₂O (Fig. 8e) and Al₂O₃ (Fig. 8c) due to more sodic *Plag* crystallization during final stages) and demonstrate significantly less scatter (note the error bars of the average tephra composition) than the compositional field of glass inclusions and groundmass glasses. This probably indicates that the efficient cooling rates of the naturally quenched samples avoid sample compositional modification in comparison with slow cooling (interstitial melts) or post-entrapment processes (glass inclusions).

The composition of all 100 (black symbols) and some of the 700-MPa (open symbols) glasses saturated with $Plag + Cpx + Opx \pm Mt$ resembles the natural trend of lavas (grey circles) with respect to most major oxides except for TiO₂ (Fig. 8d). A remarkable agreement is observed for all glasses produced at 100 MPa with respect to FeO (Fig. 8a), MgO (Fig. 8b), CaO (Fig. 8g) and K₂O (Fig. 8f). A good agreement is observed for Al_2O_3 (Fig. 8c) and Na₂O (Fig. 8e). The CaO concentration in 700-MPa glasses is close to that observed in Bezymianny bulk rock, but at this pressure, the K₂O concentration is slightly higher and the MgO slightly lower at any given SiO₂. In only one run, with 2.9 wt% H₂O in the melt synthesized at 1,050 °C and 700 MPa, do Al₂O₃ and FeO concentrations fall within the variation of natural compositions. The second 700-MPa run performed at 1,050 °C but with slightly higher melt H₂O content (3.4 wt% H₂O) is more Al₂O₃ rich and FeO depleted. In contrast, all low H₂O (1-2.5 wt%) high T (1,080-1,140 °C) 700-MPa melts contain lower Al_2O_3 and higher FeO (Fig. 8).

In the case of the samples containing Cpx + Hbl + Mt, produced in low-*T* and H₂O-rich runs at 700 MPa, the residual liquids follow the trend of Bezymianny rocks for some major elements; they, however, have low FeO and high Al₂O₃ due to the high aH_2O which causes a strong suppression of *Plag* crystallization (see open crosses in Fig. 8).

Discussion

Evolution of andesitic and dacitic liquids under hydrous conditions at 100 and 700 MPa

These experimentally produced liquids exhibit the systematic variations expected for melts fractionating along $Plag + Cpx + Opx \pm Mt$ cotectic(s) under hydrous conditions. The 100-MPa experimental melts demonstrate strong SiO₂ enrichment indicating that fractionation of an anhydrous mineral assemblage at low pressures under hydrous conditions (1.5–3 wt% H₂O, 0.3 <*a*H₂O <1) results in the formation of andesitic to dacitic melts with

55–66 wt% SiO₂. *Mt* fractionation plays a key role in developing calc-alkaline melt affinity at low pressures (e.g. compare *Mt*-containing and *Mt*-free 100- and 700-MPa glasses in Fig. 8h). However, observations of the natural system indicate that extensive amphibole fractionation does occur in the magma chamber of Bezymianny. Thus, although fractionation of amphibole is not required to produce liquids with chemical compositions close to the natural andesites and some less-evolved dacites, the presence of *Hbl* in the natural lavas indicates that a pressure above 100 MPa is more realistic for the magma storage depth beneath Bezymianny.

With increasing pressure, the likelihood of hydrous melts to be silica rich along $Plag + Cpx + Opx \pm Mt$ cotectics diminishes due to the depression of Mt stability at higher pressures (see Figs. 3, 4). Mt-free 700-MPa melts produced at 1,120-1,140 °C show an FeO enrichment trend with a lack of (or a weak) silica increase. The appearance of Mt below 1,120 °C in melts containing 1-3 wt% H₂O influences the FeO concentration of the residual melts, but it does not result in any silica enrichment, because the Mt proportion remains low and the melt crystallinity is high (up to 50 % in the run AB20 at 1,050 °C and 2.9 wt% H_2O , Table 2; Fig. 5d). Higher aH_2O at 700 MPa could result in an increased Mt proportion. However, Plag crystallization is strongly depressed at such high aH₂O conditions (melt H₂O >3.5 wt%) and Plag + Cpx + Opx $\pm Mt$ saturation is not attained in a realistic temperature range estimated from results of phenocryst geothermobarometry (1,130–1,050 °C, Almeev et al. 2013a). Thus, at 700 MPa, it is probably not possible to produce the liquid composition found on the natural Bezymianny trend and saturated with minerals observed in the natural basaltic andesite (Almeev et al. 2013a). As was mentioned, this AB20 run with $Plag + Cpx + Opx \pm Mt$ (Fig. 2) has a glass composition which does locate on the natural Bezymianny trend (Fig. 8), but it has a crystal content of 48 % which is too high to represent the Bezymianny parental magma stored at 700 MPa. The AB12 and AB26 runs (1,100 and 1,080 °C, respectively) have lower crystallinity (37 and 42 %, respectively) and may represent still eruptible magma. However, residual liquids in these runs are notably off the Bezymianny trend.

The difference in MgO and K₂O contents of residual melts produced at 100 and 700 MPa is in agreement with differences in degrees of crystallization of melts produced at hydrous conditions and different aH_2O (e.g. Botcharnikov et al. 2008b). Due to the differences in the extent of crystallization, the "extent of incompatibility" of K₂O in *dry* and *hydrous* melts differs for the same parental composition and the enrichment factor drops from ~6 in the dry system up to ~2.5 in H₂O-saturated melts. Melts obtained at 700 MPa contain higher K₂O and lower MgO than melts obtained at 100 MPa at comparable temperature and H₂O melt concentration (but with different aH₂O), indicating that the extent of crystallization is higher in 700-MPa runs. It should be noted, however, that runs at 990 °C, 700 MPa and 1,000 °C, 100 MPa cannot be compared due to the large differences in H₂O melt concentrations.

The Na₂O contents in the 100-MPa residual melts increase with increasing SiO₂ along the Bezymianny trend in most experimental runs except for two low aH_2O (<0.3) runs produced at 1,040 and 1,000 °C with 0.7 and 1.6 wt% H₂O, respectively. These two glasses have lower Na₂O at a given SiO₂ than do glasses produced with higher H₂O contents in the melts. This can be used to bracket the aH_2O in natural amphibole-free andesitic and dacitic magmas (with SiO₂ up to 65 wt%). Following the natural trend defined by lava composition (a proxy of LLD), the aH_2O of magmas stored at 100 MPa should not be lower than 0.4.

Plag stability is known to be strongly dependent on the H₂O content in the melt (Sisson and Grove 1993). Under dry or at low aH₂O conditions, the Plag primary phase volume proportions are enhanced, which, in turn, results in strong Al₂O₃ depletion and FeO enrichment in the residual melts. In contrast, high aH₂O delays the onset of Plag crystallization, resulting in alumina enrichment. In addition, the proportion of Fe-Mg-bearing silicates in the crystalline assemblage is higher and the appearance of Fe-Ti oxides occurs at higher temperature, which results in FeO depletion in the coexisting melt. Our 100-MPa experiments confirm these observations since glasses with different aH₂O can be used to trace the above-mentioned systematics (Fig. 8). For clarity, the experimental melts produced at 1,040 and 1,000 °C are connected with thin dashed lines in Fig. 8, and H₂O concentrations are shown for each experiment. In addition, possible trends at constant aH_2O (0.1, 0.4 and 1) are shown by dotted lines. It is obvious from Fig. 8 that at any given SiO₂, increasing aH₂O may drive the LLD towards Al₂O₃-rich and FeOpoor compositions. These diagrams can be used to bracket the aH_2O in the natural andesitic and dacitic magmas, which vary between 0.3 (1.7 wt% at 100 MPa, Table 2) and 0.6 (2.7 wt% at 100 MPa, Table 2). All lower or higher aH₂O will drive the residual melt compositions saturated with $Plag + Cpx + Opx \pm Mt$ at 100 MPa away from the trend defined by the bulk rock compositions of Bezymianny (Fig. 8).

How far is the natural trend of Bezymianny bulk rocks from real LLDs?

The natural Bezymianny rocks define a common single trend of silica enrichment which approaches the compositions of melt inclusions and the tephra glass compositions from historical eruptions (Fig. 8). Nearly all the liquid compositions estimated from the bulk rock and mineral compositions (Table 1 in Almeev et al. 2013a) follow the Bezymianny trend defined by whole-rock compositions (Fig. 5 in Almeev et al. 2013a). The andesitic and dacitic liquids experimentally produced at 100 MPa (especially those with 1.7–2.7 wt% H₂O) are also located within natural compositions, except for TiO₂ (see discussion in 4.3). This allows us to assume that the unique linear evolutionary trends of the Bezymianny lavas may represent the LLD.

Almeev et al. (2013a) demonstrated that the natural trend defined by Bezymianny bulk rocks is a result of fractional crystallization and magma mixing. Evidence for both mechanisms can be found in mismatches of lava and phenocryst chemical compositions (chemical disequilibrium, e.g. Sakuyama, 1981). The two mixing components are (1) less-differentiated parental basaltic andesite and primitive andesites, and (2) highly differentiated dacitic (and rhyodacitic) melts/magmas. The silica-rich component may have originated through fractionation at the earliest stages of magma chamber formation (volcanic products with ages 10 ka and older), or may represent the products of in situ crystallization (Langmuir, 1989) or of boundary-layer fractionation (Nielsen and Delong, 1992; Kuritani, 1998). Our experiments at 100 MPa demonstrate that liquids saturated with an anhydrous mineral assem- $(Plag + Cpx + Opx \pm Mt)$ blage cotectics without amphibole) may define the LLD which reproduces the evolutionary path followed by the natural bulk rocks for most elements. This strengthens the conclusion made in Almeev et al. (2013a) that the "magma-mixing" trend and the "fractional crystallization" trend follow similar paths and cannot be resolved using major elements, since magma mixing results in a reworking of melt fractions and magma portions which themselves have an original "cotectic" nature. Magma mixing shrinks the space of compositional variations through time: all products of historical and recent eruptions have a significantly narrower compositional range (Braitseva et al. 1991; Turner et al. 2013) than those observed in samples covering the whole history of magma chamber evolution including pre-Bezymianny (dark grey circles in Fig. 8) and Bezymianny (light grey circles in Fig. 8) stages (Almeev et al. 2013a). Thus, magma mixing appears as an additional complexity of crystallization history and is responsible for linear major element variations in binary diagrams.

Magma mixing, however, does not completely wipe out all chemical systematics and characteristics of fractional crystallization processes. For example, in the SiO₂–MgO diagram, a concave chemical trend (dark grey circles) is observed for lavas with a "crystallization" signature (similar to the Ni vs. Rb plot, Fig. 12 in Almeev et al. 2013a). These samples are also more Na rich (Fig. 8 and also see Fig. 12 in Almeev et al. 2013a) and the slight offset of our experimental liquids towards samples with a "magma-mixing" signature (light grey circles) is mainly caused by the initial Na₂O content of our starting basaltic andesite, which is slightly too low (probably due to a loss of Na during glass synthesis). Finally, variations in Al₂O₃ are mostly controlled by the stability and proportion of Plag in cotectic associations which, in turn, is a function of aH₂O prevailing in magmatic melts (Sisson and Grove, 1993). Although high/low proportions of *Plag* caused by crystal accumulation cannot be completely ruled out, the lack of an Eu anomaly and the calculated Plag proportions and crystal contents of the studied andesites (Almeev et al. 2013a) indicate that crystal fractionation is not sufficient to explain the scatter in Al₂O₃ concentrations seen in Fig. 8. H₂O degassing, resulting in extensive Plag crystallization and accumulation, is an additional factor which may explain the scatter of Al₂O₃ in natural compositions.

Behaviour of TiO_2 in bulk rocks and experimental melts

The Bezymianny lavas are strongly depleted in TiO₂ and V, which is interpreted as a result of Mt fractionation in the early evolutionary stages of the parental basaltic magma (Almeev et al. 2013a). Mt fractionation has also been recorded in the trace element contents of fractionated *Plag* and amphiboles (Almeev et al. 2013a). Mt fractionation (Osborn, 1959; Kadik et al. 1986) is believed to be the most important factor controlling the calc-alkaline chemistry of Bezymianny melts, driving them towards silica-rich compositions at nearly constant FeO/MgO (Fig. 8h). The major problem in the experimental results is that Mt fractionation (occurring with Pl + Cpx + Opx) does not lead to strong TiO_2 depletion as it is observed in the natural LLD. Instead, with progressive crystallization, experimental liquids show TiO₂ enrichment in the early fractionation stage, followed by constant behaviour and then finally depletion in dacitic and rhyodacitic melts. In a few 700-MPa H₂Orich and *Plag*-free experiments, we observed melt TiO₂ contents similar to the natural compositions (e.g. AB22, Table 2). Low TiO_2 contents in residual melts is caused by the high proportion of Px and Mt in the solid assemblage $(\sim 10 \% Mt, Fig. 6)$. However, the lack of *Plag* drives the melts to Al₂O₃-rich compositions inconsistent with the Bezymianny trend.

Thus, the studied low-pressure and H_2O -saturated conditions do not sufficiently enhance *Mt* fractionation, and melt evolution along *Mt*-bearing cotectics under the investigated conditions does not result in strong TiO₂ depletion. Two hypotheses can explain this discrepancy between the experimental and the natural compositional trends: (1) TiO_2 depletion observed in the bulk rock is not controlled by the LLD but is completely modified by the subsequent magma mixing, and (2) TiO_2 depletion observed in the bulk rock is controlled by the LLD, but experimental conditions and factors investigated in this study are not relevant and other conditions should be considered.

The major problem of the first hypothesis is that it assumes a magma-mixing mechanism that affects almost exclusively TiO₂; however, the behaviour of many other major and trace elements (except for Ni, Cr, and Mg) can readily be explained by fractional crystallization processes. On the other hand, if TiO₂ is controlled by fractionation processes, a physical process should be assumed to selectively and systematically extract TiO₂ (e.g. sinking *Mt* crystals) which also appears unrealistic. We believe that before speculating on complex dynamic processes in the magma chambers, additional experimental work has to be performed to explore the possible role of other thermodynamic parameters and mineral associations.

In the current study, we observed Hbl crystallization at 700 MPa and 990 °C in association with Cpx and Mt. No *Plag* crystallized at such high aH_2O (5–7 wt% H_2O). Nevertheless, the chemical trend defined by Cpx + Hbl + Mt fractionation is nearly identical to the trend of Bezymianny lavas with respect to all major elements, except for Al₂O₃ (open crosses highlighted by black arrow in Fig. 8). The Al_2O_3 content in these liquids increases due to the lack of Plag. It is clear that new experiments should mainly focus on Hbl stability (together with Plag) at intermediate pressures, between pressures utilized in this study. Bezymianny Hbl contains up to 2.5 wt% of TiO₂, the proportion of Hbl is expected to be high (30-50 % in solid phase, Table 2; see also (Barclay and Carmichael 2004), and together with *Mt* the presence of Hbl should increase the TiO₂ concentration in the solid assemblage.

Melt evolution within mineral component space

Figures 9 and 10 show the compositional variations of 100 and 700 MPa liquids saturated with Plag + Cp $x + Opx \pm Mt$ projected onto pseudo-ternary diagrams (see Tormey et al. 1987; Grove 1993 for details of recalculations). The discussion of the influence of H₂O on saturation and reaction boundaries and directions of liquid evolution during crystallization along mineral cotectics can be found in Sisson and Grove (1993), Grove et al. (2003) and Botcharnikov et al. (2008b). In Fig. 9, experimental glasses produced in this study (black and open squares represent 100 and 700 MPa, respectively) are compared with 200 MPa Ol + Plag + Cpx (black solid lines) and Plag + Cpx + Opx (black solid lines and grey diamonds) saturation boundaries obtained under H₂O-saturated conditions (Grove et al. 2003). Also shown are H₂O-undersaturated liquids in equilibrium with $Plag + Cpx + Opx \pm Mt$ in Unzen andesite produced at 200 MPa (grey crosses in Fig. 9; Botcharnikov et al. 2008a) and in synthetic island arc high-magnesium basalt (HMB) produced at 700 MPa (grey dots in Fig. 9; Hamada and Fujii 2008).

As illustrated in the Cpx-Qtz (quartz)-Ol diagram (Fig. 9a), the compositional range of the Ol-free H₂Oundersaturated melts obtained in this study is located close to the compositional field of melts saturated with Ol + Plag + Cpx determined at 200 MPa under H₂Osaturated conditions (Grove et al. 2003). Similar to systematics observed for dry (Tormey et al. 1987) and H₂Osaturated (Sisson and Grove 1993; Grove et al. 2003) systems, our hydrous 100 and 700 MPa liquids are shifted towards the Qtz apex on the projection in Fig. 9a with a compositional trend nearly parallel to the Cpx-Qtz sideline of the diagram. In Fig. 9a, high pressure 700-MPa Bezymianny melts (this study and Hamada and Fujii, 2008) are shifted away from the Cpx-Qtz sideline towards Ol-rich compositions, indicating expansion of the Cpx primary phase volume with pressure. In Fig. 9b, the liquids are below the Ol + Plag + Cpx cotectic of Grove et al. (2003), indicating that *Plag* saturation occurs earlier in the Bezymianny experiments due to the lower aH_2O at higher pressure. In contrast to the relatively good alignment of the cotectic composition positions constructed for H2O-saturated conditions (Sisson and Grove 1993; Grove et al. 2003), the scatter in the position of the 700 MPa (also 100 MPa, see below) Bezymianny liquids saturated with the same solid composition $(Plag + Cpx + Opx \pm Mt)$ can be directly related to differences in prevailing aH_2O . In addition to the sensitivity (Tormey et al. 1987; Grove et al. 2003) of phase relations in pseudoternary diagrams to both bulk composition and pressure (see e.g. the shift of Ol + Plag + Cpx cotectics observed for two different compositions in Fig. 9a and Fig. 9 in Grove et al. 2003), the presence of different amounts of H_2O (aH_2O) also affects the cotectic position within the mineral compositional space. This is illustrated by the results of our experiments at 100 MPa where $Plag + Cpx + Opx \pm Mt$ saturated melts were produced in the range of $0.1 < aH_2O < 1$ at 975, 1,000 and 1,040 °C (Figs. 6c, 9b).

In general, our 100 MPa hydrous liquids systematically vary in the compositional space in comparison with the melts produced at 200 MPa at H₂O-saturated (aH₂O = 1, Grove et al. 2003) and H₂O-undersaturated conditions (aH₂O < 1, Botcharnikov et al. 2008a). In Fig. 9a, saturation boundaries at 200 MPa (aH₂O \leq 1) and 100 MPa (0.1 < aH₂O < 1) are systematically displaced from the *Ol* apex towards the dry 1 atm boundary (not shown, from Tormey et al. 1987). The same observation can be made if

[Cpx]

1040/1.9

1040/1.5

975/2.9

10 011.0.01 0.0.0.9

50 Otz

0.5

all.0.

Plag

200MPa, aH2O=1

(Grove et al., 2003)

Æ

Natural compositions:

Experimental liquids:

Cpx+Hbl+Mt saturated

100/2 5 1140/1.12

1080.2 5

Plag+Cp

Cox+Om



Fig. 9 Compositions of 100-MPa and 700-MPa Plag + Cp $x + Opx \pm Mt$ -saturated melts projected on ternary base through one of the apices (labelled in brackets) in the basalt tetrahedron: (a) Olivine (Ol)-Clinopyroxene (Cpx)-Quartz (Qtz) projected from plagioclase (Plag), (b) Ol-Plag-Qtz projected from Cpx, and (c) Cpx-Plag-Qtz projected from Ol. Projections on (b) and (c) show only the upper half of the triangles, from 50 % Ol-50 % Qtz to 100 % Plag and 50 % Cpx-50 % Qtz to 100 % Plag, respectively. All recalculations were performed

the cotectic compositions are projected onto the Plag-Ol-Otz diagram (Fig. 9b) with a shift towards the Plag-Otz sideline with increasing aH_2O . A similar behaviour is also observed in the projection from Ol (Fig. 9c): the increase in aH₂O drives the cotectic melt composition saturated with $Plag + Cpx + Opx \pm Mt$ away from the Cpx apex towards the *Plag-Qtz* sideline of the pseudoternary plot. It should be noted that the grey lines drawn in Fig. 9 only highlight the compositional range of melts saturated with $Plag + Cpx + Opx \pm Mt$ with similar aH_2O ; they are not strictly cotectic lines for any given aH₂O at 100 MPa. A similar *a*H₂O effect is expected at higher pressures (e.g. according to the method used by Tormey et al. (1987) and Grove (1993). Experimental liquids from the literature are shown to denote the position of melts saturated with $Plag + Cpx + Opx \pm Mt$ at different conditions: 200 MPa H₂O-saturated (Grove et al. 2003), 200 MPa H₂O-undersaturated (Botcharnikov et al. 2008a) and 700 MPa H₂O-undersaturated (Hamada and Fujii 2008). The silicic tephra glass composition (provided by M. Portnyagin) is shown as representative of the final evolutionary stage of Bezymianny melt evolution (grey triangle)

300 and 500 MPa), but knowledge about the positions of the cotectic compositions as a function of aH₂O is not available. Thus. the locations of Plag + Cp $x + Opx \pm Mt$ -saturated melts within pseudoternary projections make it difficult to interpret the natural rock systems as long as the effects of P and aH_2O are not clearly quantified. The analysis of LLDs defined by the natural bulk rock compositions can be performed only for suites for which independent P and aH_2O estimates are available.

Taking these limitations into account, we tried to apply our experimental data to Bezymianny andesites whose compositions were also converted to mineral components



Fig. 10 Compositions of 100 MPa and 700 MPa Plag + Cpx + $Opx \pm Mt$ -saturated melts and comparison with natural Bezymianny Volcano lavas (Almeev et al. 2013a) projected onto pseudoternary plots: (a) Ol-Cpx-Qtz projected from Plag, (b) Ol-

according to the scheme presented in Tormey et al. (1987) and Grove (1993). Our first attempt to interpret the Bezymianny LLD, utilized pseudoternary diagrams with melt evolution along consequently evolving mineral cotectics (Almeev et al. 2013a), allowed us to discriminate two major lava composition groups that were previously distinguished using some trace and major elements (Fig. 12 in Almeev et al. 2013a). These two groups are determined to be pre-Bezymianny lavas with "crystallization" and Bezymianny-stage lavas with "magma-mixing" signatures (in Fig. 8 dark and light grey circles, respectively). On the ternary diagrams, the trend defined by pre-Bezymianny lavas is composed of a group of "liquids" with the highest



Plag-Qtz projected from *Cpx* and (c) *Cpx-Plag-Qtz* projected from *Ol*. HMB-HAB Kliuchevskoi: high-magnesia (HMB) to high-alumina (HAB) basalts of the Kliuchevskoi Volcano (Almeev et al. 2013a)

proportion of *Plag* and *Qtz* components at any fixed *Cpx* and/or *Ol*, all of which follow the silica enrichment trend towards tephra glass shown by solid triangles in Figs. 9 and 10. This trend (shaded grey in Fig. 10; see also Fig. 13 in Almeev et al. 2013a) was interpreted to represent the LLD close to the real Bezymianny magmatic liquid evolutionary path, which passes through the set of mineral cotectics $Plag + Cpx + Opx \pm Mt \rightarrow Plag + Opx + Hbl + Mt \rightarrow Plag + Hbl + Mt$. The Bezymianny lavas from recent and historical eruptions were interpreted to represent magmas which formed as a result of mixing between less-differentiated basaltic andesite or andesite magmas and evolved silicic melts of fractionated products from the mafic magmas in the



Fig. 11 Phase relations in Bezymianny parental melt interpolated onto P-T diagrams with fixed melt H₂O content (1, 2 and 3 wt%). At about 500 MPa, 1,110 °C and 2 wt% H₂O in the melt, Bezymianny parental melt is close to saturation in *Plag*, *Opx* and *Cpx*

previous stages. Our new experimental data allow us to suggest an alternative interpretation for the origin of lavas with a "magma-mixing" signature.

As one can see in Fig. 10, pre-Bezymianny lavas tend to be placed at the $Plag + Cpx + Opx \pm Mt$ saturation boundary produced at the highest melt aH_2O (Figs. 10b, c) and 100-200-MPa pressures. In contrast, all the Bezymianny stage lavas which have been interpreted to be a result of magma-mixing plot in the region of the hydrous $(0.1 < aH_2O < 0.9), 100 \text{ MPa } Plag + Cpx + Opx \pm Mt$ saturated cotectic. It should be noted that the natural lavas (e.g. 2Px andesites, Opx-bearing andesites, and Hbl-bearing andesites) tend to cross the cotectic lines at constant aH₂O. This possibly indicates magma degassing resulting in Plag oversaturation and extensive crystallization and eventually in depletion of the *Plag* component in liquids by fractionation (Figs. 7c, 10b). In this sense, the 2Px and esite may not represent the equilibrium differentiation product of the parental basaltic andesite magma. In contrast to this scenario, the magmas may be formed by a more complex but probably more realistic process involving the combined effects of magma crystallization and magma degassing during ascent. In addition, Fig. 10a also indicates the importance of decompression during magma evolution. The LLD defined by the Bezymianny basaltic andesite was probably under elevated pressures (see constraints below). Starting at high pressure, this magma should cross several levels of neutral buoyancy during its ascent to reach a shallow magma chamber filled with silica-rich magmas similar to those observed in the tephra glasses.

Constraints on magma storage conditions of Bezymianny parental basaltic andesite

The phase relations experimentally determined at 100 and 700 MPa were used to constrain P-T diagrams for the starting basaltic andesite with constant initial H₂O content in the system. Mineral crystallization temperatures were interpolated using mineral crystallization temperatures constrained at 100 MPa and 700 MPa for three cases with different initial H₂O concentrations in the melt: 1, 2 and 3 wt%. The obtained diagrams (Fig. 11) demonstrate the role of pressure in changing phase stabilities in basaltic andesite with different initial H₂O contents. Although the linear approximation of phase boundaries is not absolutely correct since H₂O may affect the curvatures of mineral-in boundaries, we do not expect large deviations, and any estimation of multiple saturation conditions gives the maximum estimates of P-T conditions. The Ol phase boundaries are not shown in Fig. 11 since this phase was not observed at 700 MPa. However, potentially its stability field can be bracketed considering that (1) there is an incongruent reaction of Ol with melt and Opx in the 100-MPa experiments which defines the low-T stability boundary, and (2) Ol is not the liquidus phase and probably crystallizes after *Plag*, at least, especially at low pressures. Thus, the Ol stability field can be placed between the Plag and Opx boundaries. On the other hand, although Ol is present in natural basaltic andesites, its abundance is low and may indicate that magma evolved along (or at least close to) the Ol-Opx reaction boundary and Ol should

disappear. Thus, Ol may belong to the phase assemblage during basaltic andesite crystallization under certain conditions, but Ol may be absent under slightly different conditions. More importantly, high- and low-Ca pyroxenes and *Plag* should be present on or near the liquidus of the parental basaltic andesite; since all of these minerals are found in the rock as phenocrysts. As we can see in Fig. 11, the conditions of Plag + Cpx + Opx saturation when all three minerals are near liquidus can only be reached in a pressure interval between 500 and 550 MPa at 1,110–1,115 °C in a system with 2–2.5 wt% initial H_2O . These conditions give the maximum pressure estimate for basaltic andesite crystallization and constrain the initial conditions of Bezymianny primary magma stored at about 15 km depth in the intra-crustal magma chamber.

Conclusions

New experiments performed at various aH_2O conditions and at 100 and 700 MPa using Bezymianny basaltic andesite as a starting material allowed us to bracket the possible storage conditions of Bezvmianny parental magma. This magma was most probably located in the upper crust at depths of ~ 15 km (pressure interval between 500 and 550 MPa) at 1,110-1,115 °C. The parental magma should have contained $\sim 2 \text{ wt\%}$ initial H_2O in order to have been saturated with Plag + Cp $x + Opx \pm Ol \pm Mt$, a typical mineral assemblage of basaltic andesites and their evolutionary products mainly composed of 2Px and esites. The subsequent evolution of this parental magma occurred during magma ascent in the course of decompressional crystallization. The final depth of crystallization product accumulation prior to eruption is not well constrained but should not be shallower than 3 km (100 MPa) because amphibole is present in the natural mineral assemblage. The major volume of Bezymianny andesites was produced in the mid-crustal magma chamber as a result of decompressional crystallization of parental basaltic andesites, accompanied by mixing with silicic products from earlier stages. These processes were complicated by the release of volatiles due to magma degassing that occurred at various stages during magma ascent.

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