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Lower crustal magmatic processes and andesite genesis at Shiveluch Volcano

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10 Abstract

The silicic melts that eventually erupt at arc volcanoes are cumulative products of crystallization and assimilation in the upper and lower crust. Yet, the storage conditions of magma in the lower crust are less well constrained than in the upper crust. In this study, we conduct and analyze hydrous piston cylinder experiments to determine the mid-to-lower crustal magma storage conditions of primitive melt at Shiveluch, an arc volcano located in
15 northern Kamchatka. The near-liquidus assemblage of amphibole and olivine, observed in mafic enclaves, empirically compared to experimental products requires storage of primitive magmas to pressures between 500 MPa and 1 GPa, temperatures from 1000-1100 °C, and high (≥ 7.2 wt%) H₂O contents. Compositions of glasses in our experiments also show that crystallization-driven differentiation in the lower crust cannot be the only process involved in the production of andesites at Shiveluch. By comparing synthetic and natural compositions of
20 amphibole we determine that anatexis of the lower crust is also likely to significantly contribute to produce andesitic melts at Shiveluch.

Introduction

The lower crust sets the stage for upper crustal magmatic processes and eruptions at arc volcanoes. Continued
25 addition of hot, primitive magma from the mantle to the bottom-most crust establishes a lower crustal “hot zone” where magmas evolve (e.g., Annen et al., 2006). Fractional crystallization of olivine, pyroxenes, feldspar, Fe-Ti oxides, and amphibole from primitive magmas in the lower crust can produce the relatively silicic melts that are stored and partially crystallized in the upper crust (e.g., Sisson et al., 2005; Blatter et al., 2013; Nandedkar et al., 2014; Blatter et al., 2017; Ulmer et al., 2018). Melting of surrounding lower crustal rocks can also produce

30 intermediate to silicic melts in greater volumes than fractional crystallization per unit mantle-derived basalt (e.g.,
Till et al., 2019). Some combination of both processes produces the silicic magmas that erupt at arc volcanoes.

Despite the importance of the lower crust to the trans-crustal magma system, pressures and temperatures of magma
storage are more commonly estimated for silicic magmas in the upper crust (see, for example, the overwhelmingly
35 shallow storage depths compiled for Cascades volcanoes by Wieser et al., 2023). Storage conditions provide
quantitative constraints on conceptual models of crustal structure. They can be directly compared to the depths of
earthquakes to relate chemical processes to earthquakes (e.g., Dayton et al., 2023) or compared to other geophysical
constraints on the current depths of magma storage (as done in Wieser et al., 2023). Storage conditions of magmas
in the upper crust have been assessed by application of rhyolite-MELTS (e.g., Gualda et al., 2012; Pamukcu et al.,
40 2015; Harmon et al., 2024), empirically calibrated mineral and melt thermobarometers (e.g., Putirka, 2008; Wieser
et al., 2022), analysis of volatiles in melt inclusions (e.g., Barth et al., 2024), and experimental determination of
phase diagrams (e.g., Hammer et al., 2002; Rutherford and Devine, 1996; Pichavant et al., 2002). Several factors
render the conditions of lower crustal magma storage challenging to estimate. For one, the signatures of lower
crustal processes can be difficult to isolate from the signatures of upper crustal processes in erupted silicic magmas
45 because they may be mixed away or because they are overprinted by diffusive re-equilibration. Moreover, the
stability of amphibole—hypothesized to crystallize in lower crustal zones (e.g., Davidson et al., 2013)—cannot be
predicted by rhyolite-MELTS, which inhibits its use in this scenario. These challenges limit the assessment of lower
crustal magma storage conditions.

50 In this study, we take an experimental approach to determine the mid-to-lower crustal magma storage conditions
of primitive melt at Shiveluch, an arc volcano located in northern Kamchatka. Shiveluch has had more VEI 4+
eruptions in the Holocene than any other volcano ([Global Volcanism Program, Smithsonian Institution](#)), and thus
it is particularly consequential to understand the magmatic processes occurring beneath it. The compositions of a
basalt and basaltic andesite hypothesized to reflect the compositions of magmas feeding the Shiveluch crustal
55 plumbing system are preserved in two tephra units (Volynets et al., 1997; Ponomareva et al., 2007).

In their study of mafic enclaves from Shiveluch, Goltz et al. (2020) identified a likely near-liquidus phase
assemblage of amphibole, olivine, and clinopyroxene. The mafic enclaves are basaltic to basaltic andesitic blebs of
magma sampled from within an andesitic host rock at Shiveluch. The enclaves are distinct from the two tephra
60 units described above but are hypothesized to be related via fractional crystallization (Goltz et al., 2020). The

enclaves' crenulate margins at the contact with the andesite suggest that they were still at least partially molten upon contact with the andesite. Models vary on how mafic enclaves are formed and preserved (e.g., Ruprecht et al., 2020), although, in general, they are taken as evidence of mingling between mafic and felsic magmas in the upper crust (i.e., as a result of mafic recharge or rejuvenation; Bacon, 1986). The enclaves reflect the composition of more primitive magmas associated with the Shiveluch system. Some enclaves contain very high Mg# (i.e., Fo>88) olivine, demonstrating that the enclaves preserve the mineral record of near-liquidus crystallization. Many enclaves contain amphibole and plagioclase that is complexly zoned, suggesting a protracted history of mixing and rejuvenation, potentially within the mid to lower crust; this line of evidence leads us to interpret the enclaves as representing a lower crustal, mushy "hot zone" (Annen et al., 2006).

Using mineral thermometry and hygrometry, Goltz et al. (2020) showed that magmas with water contents of at least 10 wt% were stored in the lower crust at ~1060°C and at a minimum of approximately 16 km depth (~460 MPa). The goal of this study is to experimentally reproduce the mineral assemblage found in these enclaves (i.e., olivine + amphibole ± clinopyroxene) to assess the lower crustal storage and differentiation conditions of Shiveluch mafic melts, with particular focus on the major and minor element chemistry of experimental amphibole. Here, we experimentally constrain the phase relations of the two different Shiveluch primitive magma compositions, hypothesized to be parental to erupted Shiveluch enclaves and andesites, at a range of water contents and temperatures at mid-to-lower crustal pressures (500 MPa and 1 GPa). The resulting experimental co-existing crystal assemblages, phase compositions, and stability are used to isolate pressures, temperatures, and water contents at which the near-liquidus assemblage of amphibole, olivine, and clinopyroxene is stable and, thus, determine the likely pressures and temperatures of primitive magmatic storage. Additionally, using the chemistry of synthetic glass and amphibole, we constrain the processes involved in producing intermediate magmas at Shiveluch.

Methods

Starting material synthesis and capsule Fe-saturation

Phase equilibrium crystallization experiments were conducted on starting compositions representative of the major element composition of tephra erupted at Shiveluch 3959 BP and 8363 BP (e.g., Ponomareva et al. 2015), or related to these compositions by fractional crystallization or olivine addition (**Table 1**). In total, eight synthetic mixes were used in this study, and their compositions (confirmed by and with uncertainties based on repeated electron probe

90 microanalysis of glassed mixes; see Supplementary Material for more information on mix preparation for these
analyses and potential sources of heterogeneity) are reported in **Table 1**. The eight mixes are related to one of two
tephra compositions proposed to represent the parental composition of magmas at Shiveluch (e.g., Volynets et al.,
1997; Goltz et al., 2020). The 3959 BP tephra major element composition is more magnesian and potassic than the
8363 tephra; thus, throughout this study, experiments done on mixes related to the 3959 BP tephra composition
95 will be referred to as “hi-K” and experiments conducted on mixes related to the 8363 BP tephra composition will
be referred to as “lo-K”. Instead of considering the phase relations resulting from experiments on each mix, in this
study, we group experimental results by the tephra to which the mix is related because they are a part of the same
chemical system. By conducting experiments on the tephra compositions and their evolved derivatives, we seek to
partially simulate the effects of equilibrium and fractional crystallization on phase equilibria and chemistry.

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We experimented on three mixes related to the hi-K tephra: two modeled after the tephra composition itself (from
Ponomareva et al., 2007; mix 60 and mix 70, where mix 60 was decarbonated and mix 70 was not) and one mix
representing a composition where olivine was added incrementally to bring the tephra composition into equilibrium
with Fo₉₂ olivine (composition from Gavrilenko et al., 2016; mix 53, which we term the hi-K tephra parent and
105 which was decarbonated). For the lo-K tephra, we conducted experiments on five starting mixes with three overall
target compositions: two mixes modeled on the tephra composition (from Ponomareva et al., 2007; mix 59 and mix
73, where mix 73 was not decarbonated), one mix modeled after a composition where olivine was iteratively added
to bring the tephra into equilibrium with Fo₉₂ olivine (assuming an Fe-Mg K_D of 0.3; mix 54, which we term the
lo-K tephra parent and which was decarbonated), and two mixes modeled after the glass composition from
110 experiment OD161 (Table 2), where Na₂O and K₂O were corrected for alkali loss to a fluid (as discussed further
below) using the batch crystallization equation, mineral-melt partition coefficients of Na and K for pyroxene and
olivine, the calculated proportions of pyroxene and olivine from mass balance, melt composition as analyzed by
EPMA, and a melt fraction of 81% (slightly different than our reported value of 83% because it used an earlier
version of the LIME algorithm; mixes 76 and 79, where mix 79 was not decarbonated).

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A subset of these experiments (F136, OD102, F163, F174, OD143, F137, OD109, and OD144; Table 2) were
previously published in Goltz et al. (2022). The phase proportions of these experiments have been recalculated
using the updated algorithm LIME as published in Prissel et al. (2023) and some are slightly different than those
reported in Goltz et al. (2022). The phase proportions—and particularly their uncertainties (reported in Table 3,

120 Supplementary Table 1, and Supplementary Table 2)—as published in this study are more robust and supersede
the calculated phase proportions from Goltz et al. (2022).

Experiments were run water saturated, water undersaturated with no added CO₂, or water undersaturated with
mixed volatiles (i.e., H₂O and CO₂). Non-mixed volatile experiments were prepared by dehydrating and
125 decarbonating starting mixes and adding free water to the starting mix during capsule preparation, whereas mixed
volatile experiments were conducted on mixes with added gibbsite and which were not decarbonated. Mixed
volatile experiments had molar H₂O/CO₂ ranging from 2.30-2.77 and XH₂O (defined as H₂O/(H₂O+CO₂), all in
moles) of 0.70-0.73 (Table 1). Mixes were synthesized using a combination of SiO₂, TiO₂, Al₂O₃, Al(OH)₃ (mixed
volatile mixes only), MnO, MgO, Mg(OH)₂, CaSiO₃, Na₂CO₃, K₂CO₃, AlPO₄, FeO, Fe₂O₃, and Fe₀. Mass balance
130 results calculated using LIME (Prissel et al., 2023) show that some proportion of Na₂O added to our capsules was
lost during our experiments, likely to a fluid phase. The loss across all experiments varied from 1.2% to 57%. On
average, for saturated experiments, loss was 39 ± 11%; for mixed-volatile experiments, the average loss was 18 ±
6% (Table 2). The stability of phases in our experiments are self-consistent despite different degrees of alkali and
iron loss (see below), so the impact of alkali and iron loss on phase stability is minimal, though compositions of
135 phases (especially melt/glass) in the experiments are likely depleted in alkalis.

To prevent excessive iron loss, gold capsules were used in experiments run at or below 1100°C. For higher
temperature experiments, Fe-saturated gold-palladium (80:20) capsules were used. The capsules were saturated
140 using a method after Blatter et al. (2013). To saturate the Au₈₀Pd₂₀ capsules, the capsules were packed with and
surrounded by a 2:1 mixture by weight of magnetite and clear jewelry enamel in a large Pt crucible. The packed
crucible was suspended in a gas mixing furnace at 1100°C with a flow of CO₂-H₂ gas to control the f_{O₂} at NNO for
about a week, after which the crucible and capsules were cleaned by immersion and sonication in hydrofluoric acid
for 2-4 days. Success of the Fe-saturation procedure was confirmed by measurement of Fe in two saturated capsules
145 using EPMA. We analyzed 34 line-scans using a traditional background correction method (rather than the mean
atomic number correction used for our analyses of silicates) across the two capsules and found that the alloy was
Au₇₈Pd₁₉Fe₃ throughout, approximately consistent with values calculated using the equations and procedure of
Balta et al. (2011). For these analyses, we used the nominally iron-free Au₈₀Pd₂₀ tubing used to form the capsules
before iron saturation as a primary standard for gold and palladium and a National Bureau of Standards (NIST)
150 stainless steel standard (NBS160a) as the primary standard for iron. Success of the Fe-saturation of Au₈₀Pd₂₀

capsules was also evaluated using a mass balance calculation of Fe-loss for all experiments (see method in Prissel et al., 2023). The maximum Fe-loss observed in successful experiments was ~21%, but the average Fe-loss in the AuPd capsules was much more moderate in general, averaging 6% (Table 2). Some experiments show evidence for up to 17% Fe gain (**Table 2**). As experiments with varying degrees of Fe loss are self-consistent and Mg-Fe systematics vary consistently with decreasing temperature, we believe that neither Fe loss nor Fe gain substantially impacts our results and do not discuss this aspect further.

Experimental Procedures

Capsule Design

Experiments used a nested capsule design following Matjuschkin et al. (2015), although our design uses crushable MgO above and below the capsule. A Pt buffer capsule packed with 20-30 mg of a 5:1 molar mixture of Ni:NiO and an Au or Au₈₀Pd₂₀ sample capsule packed with 30 mg of the starting mix were surrounded with and separated by Al₂O₃ powder in a larger diameter gold or gold palladium outer capsule. For water saturated and water undersaturated experiments with no mixed volatiles, free water was added to all capsules (2 or 3 μ L in the Pt buffer capsule, 3 or 6 μ L in the sample capsule, and 10 or 20 μ L in the outer capsule). For mixed volatile experiments, 1 μ L of free water was only added to the Pt buffer capsule and outer capsule to mitigate water loss through diffusion and to equilibrate oxygen fugacity in the experiment with the buffer. After packing, all capsules were crimped straight across (Pt buffer capsule) or in a three-fin design (sample and outer capsules) and welded shut using a tungsten-inert gas micro-arc welding. Leaks were checked for by weighing, heating in a 149°C oven for 2 minutes, and reweighing the capsule three times. After showing no leaks, the outer capsule was compressed to a final height of 7-8.5 mm.

Piston Cylinder

Experiments were conducted using piston cylinder apparatuses at Washington University in St. Louis at either 1 GPa or 500 MPa using a 12.7 mm or 19.1 mm pressure vessel bore diameter, respectively, and details of the assembly are described in Goltz et al. (2022). In all experiments, capsules were surrounded by a pyrophyllite sleeve and other pieces within the graphite furnace were made of fired, crushable MgO. Experimental temperature ranged from 900 to 1205°C and experimental duration ranged from 12 to 52 hours (**Table 2**).

Experiments at 1 GPa were conducted using a barium carbonate pressure medium. The experiments were first pressurized to 1 GPa and then heated at 50°C/min to the target temperature, with a 6-minute dwell in the temperature ramp at 865°C. 500 MPa experiments were run using an assembly with a pyrex or fused silica glass sleeve separating the graphite furnace from the NaCl pressure medium. Pyrex sleeves were used for experiments at temperatures $\leq 1125^\circ\text{C}$, and fused silica glass sleeves were used at higher experimental temperatures. For all but two experiments (F174 and F175), samples were pressurized and then heated at 15°C/min to the target temperature with a 24-minute dwell at 600°C. F174 and F175 were pressurized and then heated at 50°C/min to the target temperature with a 6-minute dwell at 600°C. Details of the experimental calibration of these assemblies, including uncertainty on temperature, are given in the Supplementary Information.

Experimental Charge Evaluation

In all cases, experimental success was initially evaluated upon inspection of the quenched experimental charge. The outer capsule was punctured with a small drill-bit to confirm the presence of free water in the outer capsule. The outer capsule was then opened and experiments where the sample capsule had obviously leaked silicate material during the run or where the alumina in the outer capsule was densely recrystallized were considered failures and were not analyzed further. In all successful experiments, we also confirmed the presence of nickel metal and nickel oxide in the platinum capsule visually and by using a magnet. Experiments that appeared successful based on capsule evaluation were subjected to further analysis, and were disqualified from inclusion if crystals were strongly zoned in major elements consistent with the effects of Fe-loss, had a mineral-melt $\text{FeO}_{\text{tot}}\text{-MgO } K_D > 0.40$ for olivine, displayed open system behavior in the form of Fe-loss, or had a proportion of glass calculated by mass balance inconsistent with that of bracketing higher and lower temperature experiments. In this manuscript, we only report successful experiments.

Analytical Methods

The major element compositions of synthetic products were determined by electron probe microanalysis (EPMA). Analyses were performed on a JEOL JXA-8200 electron microprobe using five wavelength-dispersive spectrometers. The background correction method (using a mean atomic number background; Donovan and Tingle, 1996), analytical conditions, and analytical standards are identical to those described in Goltz et al. (2022). A time dependent intensity correction was applied to glass analyses in experiment F174; the details of that correction are described in Goltz et al. (2022).

Results

Approach to Equilibrium

While the long durations of our experiments and limited iron loss from our experimental charges encourage equilibrium, they are insufficient to demonstrate that equilibrium was achieved. Several aspects of our experimental charges are consistent with the achievement of equilibrium. First, phases in our experiments are relatively homogeneous. To analyse our experiments, we first crushed the experimental products to produce chips typically hundreds of microns in size. We then mounted three or more randomly selected chips in ~1/4" diameter brass rings. The chips were then imaged and analysed using EPMA, as described in Analytical Methods. Thus, our analyses are of phases from throughout the experimental charge. The phases are relatively homogenous, as exemplified by the relatively small standard deviation of phase compositions as determined from EPMA analysis (see also the lack of zoning in phases in Figure 1). Only one of our experiments, OD102, proves an exception to this: olivine in this experiment is normally zoned from core to rim (i.e., rims are lower in Mg#; Table 3, Supplementary Figure 1). Such normal zonation cannot be an effect of Fe-loss to the capsule, which would produce reverse zonation in the olivine. Because the cores constitute a relatively minor volumetric percentage of the charge as calculated by mass balance, the range in Mg# is restricted from core to rim (84 to 79; Table 3), and K_D^{Fe-Mg} is not abnormal, we do not exclude this experiment from our analysis. Secondly, there are consistent changes in phase assemblages and proportions with decreasing temperature. As evidenced in phase diagrams (Figure 2), phase boundaries are regular. Table 3 demonstrates that, as temperature decreases, for a given starting mixture, crystallinity increases (i.e., percent glass in the charge decreases). Between starting mixes, there is some minor variability in phase appearances. For example, an experiment conducted using mix #53 as a starting composition is saturated with amphibole at 1050°C (OD102; Table 2), while another experiment run at the same temperature but using mix #60 (related to mix #53 through the fractionation of olivine, see Methods) is not saturated with amphibole (F153; Table 2). However, for a given starting composition at a given water content, phase stability is self-consistent, suggesting attainment of equilibrium. Together, these factors suggest that equilibrium was attained in the experiments reported here.

General Observations

Observed phases in our experiments include olivine, clinopyroxene, orthopyroxene, amphibole, plagioclase, liquid (i.e., glass), and minor apatite (Table 2). As in Marxer et al. (2023), the lack of early crystallizing oxide minerals

could be related to the lack of Cr in our experimental starting mixes and a slightly lower oxygen fugacity of our experiments compared to others where oxide phases saturate at higher temperatures. Crystal size varies from ~1 μm to ~200 μm , with clinopyroxene and minor phases usually among the smallest analyzed phases and amphibole and plagioclase among the largest. Crystals appear unzoned in major elements (Figure 1), except in experiment OD102 where crystals are zoned from core to rim in Mg and Fe (Table 3). Glass in all experiments is vesicular, and glass in H_2O -saturated experiments at 1 GPa is also devitrified due to their high H_2O contents and difficulty quenching high pressure hydrous melts to glass (Gavrilenko et al., 2019).

Phase Relations

In this study, we conducted experiments at pressures of 500 MPa and 1 GPa and at temperatures ranging from 900-1205°C (Table 2; Figure 2). At 1 GPa, for mixes related to the hi-K tephra, we conducted experiments from 950-1175°C; at 500 MPa, experiments ranged in temperature from 950-1080°C. At 1 GPa, for mixes related to the lo-K tephra, we conducted experiments from 900-1125°C; at 500 MPa, experiments ranged in temperature from 955-1205°C. H_2O -saturated experiments have olivine as the liquidus phase, whereas the highest temperature runs in H_2O -undersaturated experiments contained ortho- and clino-pyroxene, consistent with a higher activity of SiO_2 in the melt favoring orthopyroxene over olivine crystallization (e.g., Sisson and Grove, 1993; Koch et al., 2025). Relatively higher temperature stability of plagioclase in H_2O -undersaturated experiments compared to H_2O -saturated runs is observed and was expected due to the suppression of plagioclase at high water contents (e.g., Sisson and Grove, 1993; Yoder and Tilley, 1962; Holloway and Burnham, 1972). Phase relations in all our experiments are tabulated in Table 2 and we present a phase diagram with our results in Figure 2.

H_2O -Saturated Experiments (Mixes 53, 54, 59, 60, 54, 59, and 76)

Olivine is the highest temperature crystallizing phase in H_2O -saturated experiments on the lo-K tephra starting compositions (Mixes 54, 59, and 76). In 1 GPa experiments on the lo-K tephra starting mix, clinopyroxene joins the equilibrium assemblage between 1075 and 1050°C. Between 1010 and 975°C at 1GPa, amphibole and orthopyroxene crystallize and olivine and clinopyroxene are no longer part of the crystallizing assemblage. Plagioclase crystallizes at temperatures below 925°C at 1GPa.

We did not determine the liquidus phase in H_2O -saturated experiments on the hi-K tephra starting compositions, but our highest temperature runs at 1050°C had equilibrium assemblages of olivine+clinopyroxene (mix 60) or

olivine+clinopyroxene+amphibole (mix 53). In both starting mixes at 1 GPa, amphibole is present below 1025°C. At 500 MPa, amphibole is in equilibrium with melts below 1000°C.

265 A key aspect of our results is the identification of a pressure-temperature condition—~1000°C and 1 GPa at water saturated conditions—that captures a peritectic reaction in progress to produce amphibole in both starting compositions. At this pressure-temperature condition, olivine, clinopyroxene, orthopyroxene, and amphibole co-exist before the full consumption of the olivine and pyroxene phases to produce amphibole in a peritectic reaction at lower temperatures (e.g., Blatter et al., 2017, 2023; Figure 2).

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The temperatures at which amphibole stabilizes in our water saturated experiments are likely minima. Excess fluids and subsequent alkali loss, which we observe in our experiments (see Methods) can impact the stability of amphibole. Mandler and Grove (2016) and Putak Juriček and Keppler (2023) show that the amphibole stability field in peridotite decreases in size with increasing water content as a result of alkali loss. In our experiments, it is more challenging to disentangle the impacts of alkali loss and increasing H₂O contents. Mixed volatile and H₂O-undersaturated experiments stabilize amphibole at higher temperatures than H₂O-saturated experiments at the same pressure (Figure 2 and Table 2). However, at lower water contents, amphibole stability occurs at higher crystallinity. Among lo-K starting compositions, amphibole comes in at 1000°C and 41% crystallization for H₂O-saturated experiments, 1060°C and 60% crystallization for H₂O-undersaturated conditions, and 1050°C and 54% crystallization for mixed-volatile experiments (Table 2). So, while amphibole comes in at lower T in H₂O-saturated experiments, it also comes in closer to the liquidus, assuming a constant rate of crystallization with respect to decreasing temperature. The lower temperature stability of amphibole for these experiments might thus be linked to the depressed liquidus in the H₂O saturated system, rather than to alkali loss. It is possible that, in the absence of alkali loss, amphibole may stabilize even closer to the liquidus, so our experiments can be taken as the minimum T stability of amphibole.

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H₂O-undersaturated, CO₂-free Experiments (Mixes 59 and 60; 1 GPa only)

Orthopyroxene+clinopyroxene±olivine are equilibrium phases in the highest temperature experiments at these conditions. Amphibole is observed in the 1060°C runs in both starting compositions (i.e., lo-K and hi-K tephra;

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mixes 59 and 60). Relative to H₂O-saturated experiments, amphibole joins the crystallizing assemblage at higher temperatures (and higher crystallinities; Table 2). Plagioclase was not observed.

H₂O-undersaturated, Mixed-Volatile Experiments (Mixes 70, 73, and 79)

Orthopyroxene±clinopyroxene are the equilibrium phases in the highest temperature experiments on mixed volatile
295 experiments. In experiments on the lo-K tephra starting composition (mixes 73 and 79), plagioclase joins the crystallizing assemblage between 1100 and 1025°C at 1 GPa or between 1205 and 1055°C at 500 MPa. At 1025 °C at 1 GPa, amphibole joins the equilibrium assemblage; amphibole is not observed in experiments with mixed-volatiles at 500 MPa.

Phase Chemistry

300 The average chemistry of mineral phases and glass in our experiments is summarized in **Table 3**.

Olivine

Olivine composition in our experiments ranges from Fo₇₆ to Fo₈₈ (**Table 3**). The Fe-Mg mineral-melt exchange coefficient (Fe-Mg K_D, calculated assuming all Fe is FeO) of olivine ranges from 0.25-0.35 (**Figure 3; Table 3**). The median Fe-Mg K_D is 0.29, consistent with other experimentally determined values (e.g., Roeder and Emslie,
305 1970). Olivine coexisting with amphibole ranged from Fo₇₇ to Fo₈₄.

Amphibole

Amphibole composition in our experiments ranges from Mg# 66 to 84 (where Mg# is calculated Mg/(Mg+Fe_{Tot}) all in moles), in Al₂O₃ from 11 to 16 wt%, and in TiO₂ from 1.1-3.7 wt% (**Figure 4; Table 3**). Amphibole in the mixed volatile experiments have high concentrations of TiO₂ relative to the water saturated experiments. The higher
310 titanium content of the amphiboles in equilibrium with lower H₂O content melts is consistent with lower hydroxyl occupancy in its O3 site (i.e., greater oxo component) due to the lower H₂O content of the equilibrium melts and assuming a constant partition coefficient of H between amphibole and melt. Hydrogen content in amphibole is negatively correlated with the sum of Ti, Fe³⁺, and ^{VI}Al in the amphibole, all of which balance the excess negative charge from the oxo component with excess positive charge in its octahedral sites, assuming no change in halogen

315 content (e.g., King et al., 1999; Oberti et al., 2007). Given the similar aluminum content of the amphiboles compared to others in this study and the similar experimental f_{O_2} (which should generate a similar Fe^{3+}/Fe^{2+} in the amphibole; e.g., King et al., 2000; Goltz et al., 2022), the potentially lower hydroxyl content of amphiboles in the lower H_2O content experiments would require more titanium for charge balance.

320 *Clinopyroxene*

Clinopyroxene composition ranges in Mg# from 75 to 87, and ranges in Al_2O_3 from 0.8 to 5.7 wt% (**Figure 5**). On average, clinopyroxene in mixed volatile experiments has higher Al_2O_3 than clinopyroxene in H_2O -saturated experiments. The Fe-Mg K_D for clinopyroxene ranges from 0.15 to 0.32, with a median value of 0.24 (**Figure 3**; assuming FeO_{Total}). The range of Fe-Mg K_D in our experiments is included within 2 standard deviations of the
325 average clinopyroxene-melt Fe-Mg K_D calculated in Putirka (2008) (0.28 ± 0.16).

Orthopyroxene

Orthopyroxene in our experiments is most commonly observed in mixed volatile experiments as a near-liquidus phase, usually with clinopyroxene. Its composition ranges from Mg# 61 to Mg# 87 (where Mg# is calculated $Mg/(Mg+Fe_{Total})$ all in moles; Figure 5; Table 3). Fe-Mg partitioning between orthopyroxene and melt (assuming
330 FeO_{Total}) ranges from 0.18 to 0.36 with a median value of 0.26 (**Figure 3**), all of which are within 2 s.d. of the average Fe-Mg K_D calculated by Putirka (2008) (0.29 ± 0.12).

Plagioclase

Plagioclase is present in seven of our experiments, six of which were run with mixed volatiles and one of which was run at H_2O -saturated conditions. The composition of the plagioclase ranged from An_{51} to An_{87} . The highest An
335 plagioclase in our experiments crystallized from the H_2O -saturated run, OD176, at our lowest experimental temperature, and is in equilibrium with amphibole of Mg# 66. Plagioclase with An_{52-54} is in equilibrium with amphibole (Mg# 67-69) in mixed volatile experiments.

Glass

Glasses generally decrease in CaO and FeO^{T} and increase in SiO_2 and K_2O with decreasing MgO, and there is significant overlap in the CaO, FeO^{T} , K_2O , and SiO_2 contents of glasses in mixed volatile, H_2O -undersaturated, and H_2O -saturated experiments (**Figure 6; Supplementary Figure 2**). In H_2O -saturated experiments, FeO^{T} appears to plateau until around 3wt% MgO, at which point amphibole crystallization drives a decrease in FeO^{T} , as has also been observed in other experimental studies (Andrys et al., 2024). In contrast, FeO^{T} consistently decreases in mixed-volatile experiments, even without the crystallization of amphibole or magnetite, due to crystallization of orthopyroxene high in FeO relative to the melt (Table 3); as a result, we do not discuss FeO^{T} as a good discriminant between melts with different volatile contents. On the other hand, glasses from amphibole-bearing H_2O -saturated experiments decrease in TiO_2 around 4 wt% MgO or lower; glasses from mixed volatile experiments maintain a constant TiO_2 with relatively low MgO and are higher in TiO_2 than glasses from H_2O -saturated experiments at the same MgO, regardless of the presence or absence of amphibole in the charge. Glasses in several mixed volatile experiments are lower in Al_2O_3 than H_2O -saturated experiments at the same MgO, which may be related to the presence of plagioclase in these experimental charges. Glasses in our H_2O -saturated experiments are low in alkalis relative to glasses from mixed volatile experiments, likely due to the preferential partitioning of these fluid-mobile elements into a free fluid phase.

Discussion

The primary goal of this study is to put constraints on the processes controlling the chemical evolution of the crustal magma system at Shiveluch Volcano, Kamchatka. We have conducted a suite of 47 high-pressure experiments on two primitive magmas erupted at Shiveluch and their derivatives. In order to draw conclusions, we directly compare the phase assemblages and phase compositions of our experiments to the whole rock compositions, phase assemblages, and phase compositions of basaltic tephra, mafic enclaves, and andesites erupted at Shiveluch. We find that the generation of andesites at Shiveluch requires some high-pressure differentiation of variably hydrated basalts in addition to other processes.

Conditions of Mid-to-Lower Crustal Storage at Shiveluch

Our approach in using experiments to constrain the conditions of mid to lower crustal crystallization at Shiveluch is similar to the approach used to determine the conditions of shallow intermediate magma storage prior to explosive eruptions at volcanoes like Mt. St. Helens, Pinatubo, Santorini, Volcan Colima, Mascota, and Novarupta

(e.g., Rutherford et al., 1985; Rutherford and Devine, 1996; Moore and Carmichael, 1998; Cottrell et al., 1999; Hammer et al., 2002; Prouteau and Scaillet, 2003). In those studies, P-T- X_{H_2O} space was mapped for erupted compositions. The likely P-T- X_{H_2O} of crystallization was determined by matching the observed phase assemblage in the erupted products to an area in the resulting phase diagram. Results were further refined and models given more complexity using phase chemistry, particularly of amphibole (e.g., Rutherford and Devine, 1988; Prouteau and Scaillet, 2003). These experiments were crucial, especially to relate the location of earthquakes to depths of shallow storage within the crust (e.g., Rutherford et al., 1985). Since then, the importance of lower crustal processes to volcanic behavior has been emphasized by models (e.g., Annen et al., 2006; Karakas et al., 2017; Glazner, 2021) and petrographic and geochemical observations (e.g., Davidson et al., 2007; Burns and de Silva, 2023). The lower crust is a fruitful area for study experimentally (e.g., Melekhova et al., 2015; Ulmer et al., 2018), and we explore lower crustal storage here in the context of Shiveluch, where mafic enclaves preserve near-liquidus phase assemblages and relatively undifferentiated magmatic compositions (Goltz et al., 2020). In the case of the Shiveluch mafic enclaves, the target mineral assemblage is amphibole + olivine $\pm$ cpx. This is the near-liquidus assemblage in mafic enclaves and tephra, and minerals are accordingly high Mg# ($Ol \geq Fo_{88}$, $Amph \geq Mg\# 70$, $Cpx Mg\# \geq 80$). In mafic enclaves, some amphibole with high Mg# (i.e., $Mg\# \geq 74$) is found as inclusions in high forsterite ($Fo > 88$) olivine (Goltz et al., 2020).

The target assemblage (amph+ol $\pm$ cpx) is relatively rare in the experimental literature. This may be partially related to the peritectic reaction of olivine $\pm$ pyroxenes to produce amphibole. Due to the peritectic reaction, inverse experiments (i.e., those where the peritectic liquid is used as the starting composition) may not crystallize the reactant mineral assemblage, meaning that even experiments conducted at relevant P-T conditions may not have the co-existing olivine and amphibole that we target here. We used a compilation of phase equilibrium experiments from Weber and Blundy (2024) to identify experiments containing equilibrium amphibole and olivine and compare them to our experimental products. The database of Weber and Blundy (2024) includes a summary of phase assemblages and published glass compositions normalized to 100. From a database of 2,546 experiments, only 74 experiments contain the key assemblage of amphibole + olivine (Supplementary Table 4). To these, we manually added published compositional information for cpx, ol, and amph where available; this compilation is available in Supplementary Table 4. Of the 74 experiments, 50% have plagioclase in their equilibrium assemblage, which is dissimilar to our target assemblage, and thus we do not discuss them further. All but one of the plagioclase-bearing experiments equilibrated at relatively low temperatures at or below 1000 °C and at or below 700 MPa. Of the 37 remaining plagioclase-free experiments, we exclude from discussion 10 additional experiments from Kelemen et

al. (1990) and 7 experiments from Helz (1976) because amphibole in those experiments was crystallized during the quench of the experiment. We also exclude an additional 6 experiments from Prouteau and Scaillet (2003); these experiments, designed to assess the equilibrium between dacite and peridotite, only achieved localized equilibrium, as evidenced by heterogeneity in crystal chemistry and the presence of reaction rims around olivine crystals.

The remaining 20 plagioclase-free experiments provide an interesting window to the factors controlling amphibole stability in hydrous melts (Figure 7; Table 4). For example, experiments at upper crustal pressures (i.e., ≤ 300 MPa) where high Mg# amphibole and olivine are in equilibrium with mafic melt are from a higher alkali region of compositional space (Na_2O of basaltic starting compositions ranges from 3.97 to 4.59 wt%; Barclay and Carmichael 2004; Moore and Carmichael, 1998); enrichment in alkalis promotes amphibole stability at higher temperatures (Wallace and Green, 1991; Mandler and Grove, 2016), which likely contributed to the near-liquidus amphibole crystallization in these experiments. At mid-crustal pressures (300–700 MPa), high oxygen fugacities (up to NNO + 5) increased the liquidus temperature of amphibole, allowing it to be in equilibrium with high Mg# olivine (e.g., Krawczynski et al., 2012; Melekhova et al., 2015). At higher pressures, the effect of H_2O content is evident; all experiments with amphibole at 1 GPa are H_2O saturated (likely water contents >10 wt%, and potentially up to 20 wt%; Mitchell et al., 2017), with the exception of experiment BM24 (Melekhova et al., 2015), which has a melt H_2O content of 9.3 wt%.

Our experiments—which show that amphibole and olivine are stable between 1000 and 1050°C at 1 GPa and H_2O saturated conditions (Table 2; Figure 7)—align well with the conditions of amphibole+olivine stability demonstrated in the literature, despite having different starting compositions and being run at a different oxygen fugacity. Taking into consideration our experimental results and published results from experiments with broadly similar bulk compositions, conducted at oxygen fugacities ranging C-COH to NNO+5.5 (Krawczynski et al., 2012; Melekhova et al., 2015; Ulmer et al., 2018), we bracket the conditions of high Mg# olivine and amphibole crystallization from mafic magmas at Shiveluch between 500 MPa and 1 GPa, and from 1000–1100 °C, with high (≥ 7.2 wt%) H_2O contents and at a range of oxygen fugacities. These conditions align with those estimated by microanalysis of minerals in mafic enclaves by Goltz et al. (2020).

The agreement between our experiments and results from the literature gives us confidence in and adds nuance to our results while exposing a fundamental problem with the experimental approach to creating new phase diagrams.

Namely, there is no way to predict the extent to which we can accurately extrapolate between phase diagrams with
430 multidimensional compositional differences in the presence of amphibole because of the inability of current models
to predict amphibole stability. A question we must address in coming years is: how similar is similar enough when
we consider the effect of variations in compositional space on phase stability and composition? A combination of
experimental and modeling efforts is required to constrain and fill gaps in the experimental literature through which
extrapolation cannot be done accurately.

435 **Processes Contributing to the Generation of Andesite at Shiveluch**

Below, we compare mineral and melt compositions in our experiments to those observed in natural samples to
elucidate the processes contributing to andesite genesis at Shiveluch.

Fractional Crystallization Plays a Role in Generating Andesite

The fractionation of phases crystallized in equilibrium with superhydrous magmas produces similar trends in major
440 element oxides defined by andesites and mafic enclaves (with a noticeable exception of Al_2O_3 , discussed below,
and the experiments having a slightly higher CaO content) extending to lower MgO (**Figure 6**). Specifically, we
find that glass compositions in H_2O -saturated experiments that bear amphibole best reproduce the chemical trends
in TiO_2 defined by whole rock compositions of andesites and mafic enclaves. While experiments reproduce the
observed decrease in TiO_2 with decreasing MgO, they extend the trend to lower MgO, and have limited overlap
445 with the compositions of natural samples. This may be related to a delay in amphibole saturation in the experiments
caused by alkali-loss to excess fluids (see Methods). In their study of mafic enclaves, Goltz et al. (2020) interpreted
decreases in whole-rock TiO_2 and CaO with decreasing MgO starting at MgO ~4 wt% as resulting from increased
amphibole fractionation leading to compatible behavior of TiO_2 .

450 Decreasing melt TiO_2 could be attributed to a change in the partitioning behavior of titanium between amphibole
and melt or to the fractionation of more amphibole relative to other phases. We calculated the partition coefficient
of titanium between amphibole and melt (D_{Ti}) for all amphibole-bearing experiments without normalizing
amphibole compositions to 100 (Figure 8). On average, the partition coefficient of titanium between amphibole
and melt in our experiments is 2.7 ± 0.7 , consistent with partition coefficients from Waters et al. (2021) and Andrys
455 et al. (2024). The partition coefficient is only weakly correlated with experimental temperature, as was also reported
in Ulmer et al. (2018). The lowest H_2O content experiments containing amphibole do have the highest titanium
content among amphiboles crystallized in this study by at least 1-2 weight percent (**Table 3; Figure 4b**), but the

amphibole-melt titanium partition coefficients (3.3 and 3.5) are within 2 standard deviations of the average value. To summarize, the decrease in titanium observed in H₂O-saturated experiments containing amphibole is not associated with changes to the amphibole-melt titanium partition coefficient as a function of temperature (**Figure 8**). The trend in decreasing titanium observed in natural whole rock compositions thus indicates a necessary increase of amphibole percent in fractionated solids (see Figure 8b), in the absence of titanium-rich phases like ilmenite or Ti-rich magnetite, for which there is no petrographic evidence for early crystallization (Goltz et al., 2020).

The high proportion of amphibole in H₂O-saturated experiments causes experimental glasses in these experiments to decrease in TiO₂ with decreasing Mg#, as has also been proposed in Waters et al. (2021), Andrys et al. (2024), Nandedkar et al. (2014), Ulmer et al. (2018), and Marxer et al. (2022,2023). The titanium content of the melt is negatively correlated with the percent of amphibole in the experiment among amphibole-bearing experiments (**Figure 8**). The implication of this finding is that the titanium content of a melt in equilibrium with a high proportion of amphibole will decrease. In our experiments, such high proportions of amphibole (i.e., >>20%) only crystallize in experiments with very high (i.e., ≥10 wt%) H₂O contents, which indicates the importance of superhydrous melts in the liquid line of descent and the production of andesite at Shiveluch.

Crustal Melting Also Contributes to the Generation of Andesites at Shiveluch

Although glasses in H₂O-saturated experiments reproduce the trend of decreasing TiO₂ observed in natural samples, glasses are much higher in Al₂O₃ than natural andesites and are slightly higher in CaO (**Figure 6**). The enrichment of Al₂O₃ in glass synthesized from hydrous, high pressure experiments relative to andesites and dacites has been observed by others (e.g., Marxer et al., 2022; Marxer et al., 2023; Blatter et al., 2013; Blatter et al., 2017; Blatter et al., 2023) and is caused by the suppression of plagioclase at high H₂O contents (Sisson and Grove, 1993). While hydrous crystallization of basalt at upper crustal pressures (i.e., 100-200 MPa) produces glasses more similar in Al₂O₃ to natural andesites and dacites (e.g., Barclay and Carmichael, 2004; Rutherford et al., 1985; McCanta et al., 2007), these experiments do not produce the high Mg# amphibole and olivine assemblage from lower alkali content basalt that we observe in mafic enclaves, and thus this mechanism cannot work alone to produce intermediate arc lavas.

Others have invoked mixing in the upper and lower crust, crustal melting, and polybaric crystallization pathways to reconcile the high Al₂O₃ experimental melts with relatively low Al₂O₃ whole rock compositions, with various

implications for crustal growth and delamination (Blatter et al., 2017; Rezeau et al., 2021; Marxer et al., 2022; Marxer et al., 2023; Blatter et al., 2023; Andrys et al., 2024). The compositions of amphibole in mafic enclaves and experiments can help refine this list of hypotheses.

Generally, we find that the compositions of minerals in our experiments are similar to compositions observed in mafic enclaves (Figure 5). An important exception is the composition of amphiboles. At Mg# greater than ~70, amphiboles in Shiveluch mafic enclaves seem to define two groups: one with relatively high Al₂O₃ (11-12wt%) and one with relatively low Al₂O₃ (<10 wt%) (Figure 4). The groups converge at lower Mg# and higher Al₂O₃. At these Mg#, amphiboles in our experiments only overlap with the higher Al₂O₃ group. Similarly low Al₂O₃, high Mg# amphiboles have also been observed at Mt. Shasta (Krawczynski, 2011), Ciomadul (Cserep et al., 2023), Buldir (Waters et al., 2021), and Mt. Pinatubo (Bernard et al., 1996; Rutherford and Devine, 1996).

In the mafic enclaves, low Al₂O₃, high Mg# amphiboles are observed in a variety of contexts. In addition to being observed at the rims of amphiboles with relatively high Al₂O₃, they are found in complex zoning relationships with higher Al₂O₃, high Mg# amphiboles (Figure 9). In Figure 9, high Mg#, low Al₂O₃ amphiboles are both in the core and at the rim of amphibole phenocrysts with higher Al₂O₃. The petrologic context of the low Al₂O₃ amphiboles is key to their interpretation, as we will expand upon below.

One possibility to produce the low Al₂O₃, high Mg# amphiboles is polybaric crystallization of basalt. The Al-Tschermak's exchange in amphibole is widely recognized as a thermodynamic barometer for relatively silicic melts (Blundy and Holland, 1990). For less silicic melts, ^{VI}Al of amphibole has been empirically calibrated as a barometer (e.g., Ridolfi et al., 2010; Larocque and Canil, 2010; Krawczynski et al., 2012). Generally, amphibole crystallized at lower pressure should have lower ^{VI}Al than an amphibole crystallized at higher pressures from a melt of identical composition. A few observations suggest that lower pressure crystallization alone cannot explain the high Mg#, low Al₂O₃ amphiboles in the mafic enclaves. First, there is extremely limited overlap between the composition of amphiboles in the experimental literature—including experiments run at relatively low and high pressures and at a range of starting compositions—and the low Al₂O₃, high Mg# amphiboles we observe (Figure 4a). Excepting experiments from Nandedkar et al. (2014, 2016) which contain extremely MnO-rich amphiboles (i.e., 0.8-3.4 wt%; for context, typical amphiboles in our database have 0.1-0.4 wt% MnO), experiments closest in composition to the group of low Al₂O₃, high Mg# amphiboles that we observe in the mafic enclaves were done at low pressures (~200 MPa) with a dacitic starting composition, and are relatively crystalline (Scaillet and Evans, 1999). Second, the

observation of high Mg#, low Al₂O₃ amphiboles in the cores of some otherwise relatively high Al₂O₃ amphiboles (Figure 9) shows that a population of low Al₂O₃ amphiboles may have crystallized before high Al₂O₃ amphibole (though alternative explanations for this observation are possible; see below). If the aluminum content of the amphiboles was strictly related to pressure, this would require low and then subsequent high pressure crystallization of amphibole, which is unlikely, given the neutral to positive buoyancy of magma in the crust.

The low Al₂O₃, high Mg# cores thus require a more nuanced explanation beyond polybaric crystallization. One alternative interpretation of the low Al₂O₃, high Mg# cores is that they formed during magmatic ascent. This interpretation rests on the interpretation of the texture of the low Al₂O₃, high Mg# amphibole cores as resorbed and is supported by the similarity in Al₂O₃ of cores to amphibole rims, which may have feasibly crystallized at lower pressures. In this scenario, interconnected embayments in 3D would have connected the amphibole to the equilibrium melt. This is not our preferred explanation, however, because if this were the dominant mechanism for producing this population of amphibole cores, then the cores should be similar not only in Al₂O₃ but also in Mg# to rims; this is not always the case, as evidenced by the difference in Mg# between cores and rims in Figure 9a.

If the cores are indeed resorbed, another interpretation may be that the low Al₂O₃, high Mg# cores are xenocrystic and inherited from a metasomatized ultramafic lithology. Amphibole in subarc, metasomatized ultramafic lithologies tends to be low in Al₂O₃ and high in Mg# (e.g., Prouteau et al., 2001; Cserép et al., 2023); indeed, high Mg#, low Al₂O₃ amphiboles have been observed in upper mantle xenoliths from Shiveluch (Bryant et al., 2007). It is possible that the low Al₂O₃, high Mg# cores that we observe in the enclaves are relict from these upper mantle lithologies or perhaps formed as a consequence of melt-peridotite interaction in the uppermost mantle.

Both of these hypotheses to explain the low Al₂O₃, high Mg# amphibole cores rely on the interpretation of the cores' texture as indicative of resorption. This is not necessarily the case. Primary growth textures run the gamut from euhedral to relatively wormy because of skeletal or dendritic growth patterns caused by high degrees of undercooling or, potentially, low magmatic H₂O contents (e.g., Welsch et al., 2013; Erdmann et al., 2014; Shea and Hammer, 2013; Masotta et al., 2019). Thus, the wormy textures of low Al₂O₃, high Mg# cores could be related to a period of primary dendritic growth, rather than to secondary resorption.

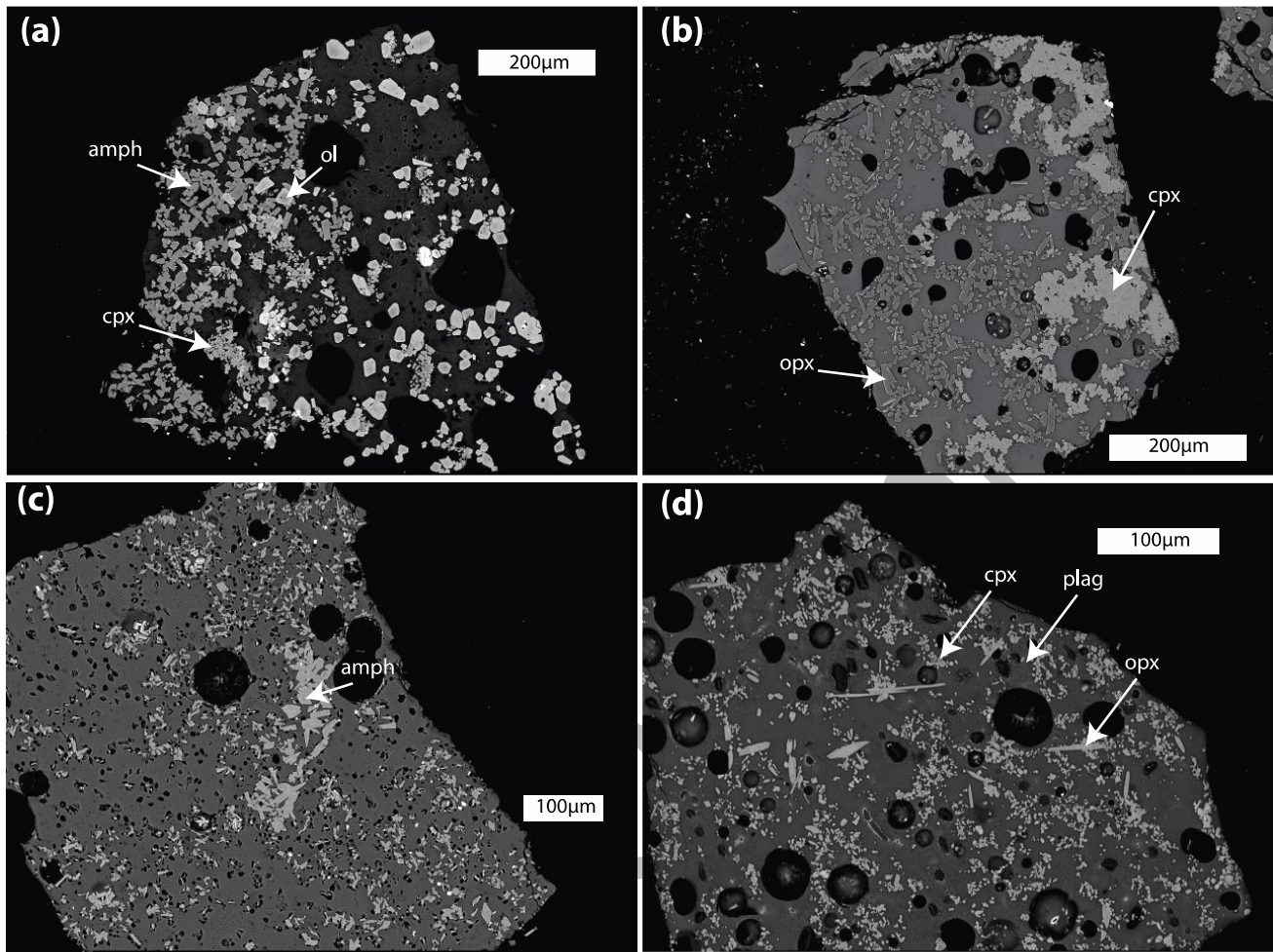
Our preferred mechanism interprets the low Al₂O₃, high Mg# as resulting from primary crystallization from a relatively SiO₂-rich, metaluminous magma. Low Al₂O₃ amphiboles are correspondingly high in SiO₂ to fill the

550 tetrahedrally-coordinated site in the amphibole structure (i.e., T site; Hawthorne and Oberti, 2007) and so may be more likely to crystallize from a relatively high SiO₂ melt. The low Al₂O₃ of a metaluminous magma (relative to the peraluminous intermediate melts produced via fractional crystallization of basalt) may encourage crystallization of a relatively low Al₂O₃ amphibole, even at high pressures (e.g., Putirka, 2016; Krawczynski et al., 2012; Larocque and Canil, 2010). Intermediate (i.e., relatively high SiO₂, potentially dacitic), metaluminous magmas could be
555 produced via peritectic melting of an existing assemblage of 2-pyroxenes+amphibole±plagioclase (Blatter et al., 2017) in the mid-to-lower crust. While there is no robust regional seismic model of the crust underlying Shiveluch, a study of the more southerly Klyushevskoy group volcanoes shows that the lowermost 10 km of the crust is basaltic (Fedotov et al., 2010). If this crustal structure extends below Shiveluch, it is possible that the mafic lower crust could melt to produce lower Al₂O₃, higher SiO₂ magmas, a process that does not require the presence of garnet
560 (Blatter et al., 2017). Subsequent mixing with basalt (as proposed in Blatter et al., 2023) is a mechanism that could produce both low Al₂O₃, high Mg# amphibole and metaluminous andesite at Shiveluch. While we cannot discount the possibility that all low-Al₂O₃, high Mg# amphibole cores are amphibole xenocrysts, our preferred explanation involves crustal melting and primary crystallization, which can account for both the chemistry of the amphibole and generate metaluminous magmas. This hypothetical mechanism to produce low Al₂O₃, high Mg# amphibole
565 and metaluminous intermediate melts may be tested in the future by microanalyzing trace elements in high Mg# amphibole with variable Al₂O₃ and with further experimentation.

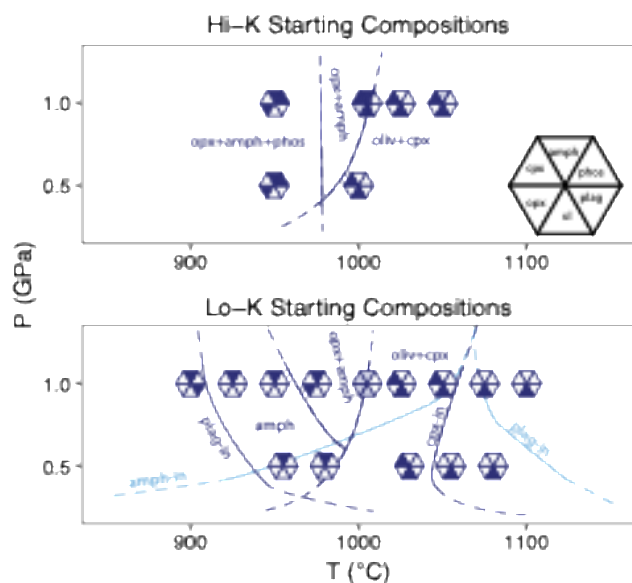
Conclusions

Our experiments show that mid-to-lower crustal differentiation of a hydrous basalt is required to reproduce the near
570 liquidus phase assemblage of amphibole+olivine±clinopyroxene observed in mafic enclaves at Shiveluch. We find that primitive magmas likely equilibrated with the observed near-liquidus assemblage between 500 MPa and 1 GPa, and from 1000-1100 °C, with high (≥7.2 wt%) H₂O contents, consistent with mineral geobarometry and thermometry (Goltz et al., 2020). However, this process cannot produce the metaluminous andesite erupted at Shiveluch and a group of low Al₂O₃, high Mg# amphibole alone. Using experimental data from the literature, we
575 suggest that crystallization of and mixing of basalt with a hydrous dacite produced by melting of existing crust is also a key process in andesite production.

Figures and their captions



580 **Figure 1.** Back-scattered electron images of experiments (a) F136, (b) OD153, (c) F243, and (d) F242. Note frothy and vesiculated glass in water saturated experiments (a and c) as compared to glass in mixed volatile experiments (b and d). Phase abbreviations used throughout this text and tables (see also Table 2): ol=olivine, opx=orthopyroxene, cpx=clinopyroxene, plag=plagioclase, amph=amphibole, ap=apatite, g=glass.



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Figure 2. Diagrams summarizing the stability of phases in our experiments on hi-K and lo-K related starting compositions. Hexagons and dark blue lines show the stability of phases in H₂O-saturated experiments; phase boundaries in light blue show the stability of phases in mixed volatile experiments (hexagons not pictured). Filled wedges correspond to stability of phases, as represented in the legend in the upper diagram. At 1000°C and 1 GPa in the lo-K starting composition, we represent the results of experiments F137, OD166, and OD109 with a single hexagon. These experiments differ in the starting mix used and in temperature (a difference of 10°C), and contain some combination of olivine, orthopyroxene, clinopyroxene, and amphibole, which we notate with the partially filled hexagons. The discrepancies between these three experiments indicate our proximity to a point in P-T space where all four phases co-exist before the olivine and pyroxenes are fully consumed to produce amphibole via peritectic reaction. At 1000°C and 1 GPa in the hi-K starting compositions, we summarize the results of experiments F136 and F163, which differ in starting mix and in temperature by 10°C, where one contains orthopyroxene and the other does not. This P/T condition also represents a point of multiple saturation prior to the consumption of pyroxenes and olivine to produce amphibole via peritectic reaction. At 1050°C and 1 GPa in the hi-K starting compositions, we summarize experiments OD102 and F153 with a single hexagon. These experiments differ in starting mix, and only one contains minor (i.e., 4%) amphibole, which we indicate with the partially filled amphibole hexagon wedge.

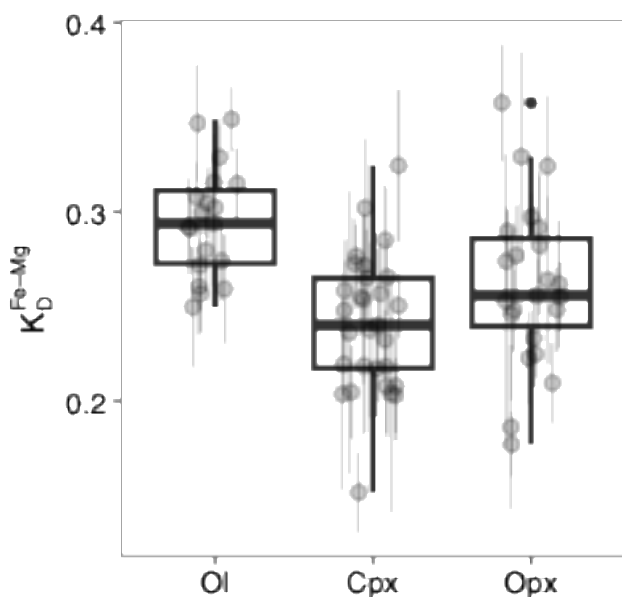


Figure 3. Mineral-melt Fe-Mg K_D for olivine, clinopyroxene, and orthopyroxene. Pale black points are average
605 distribution coefficients for individual experiments; error bars are calculated by analytically propagating standard
deviations of the average FeO and MgO of mineral and melt. Jitter around the x-axis is introduced for clarity only.
Box and whisker plots show the median (central thick black line), interquartile range (top and bottom of the box),
and range of K_D for all experiments.

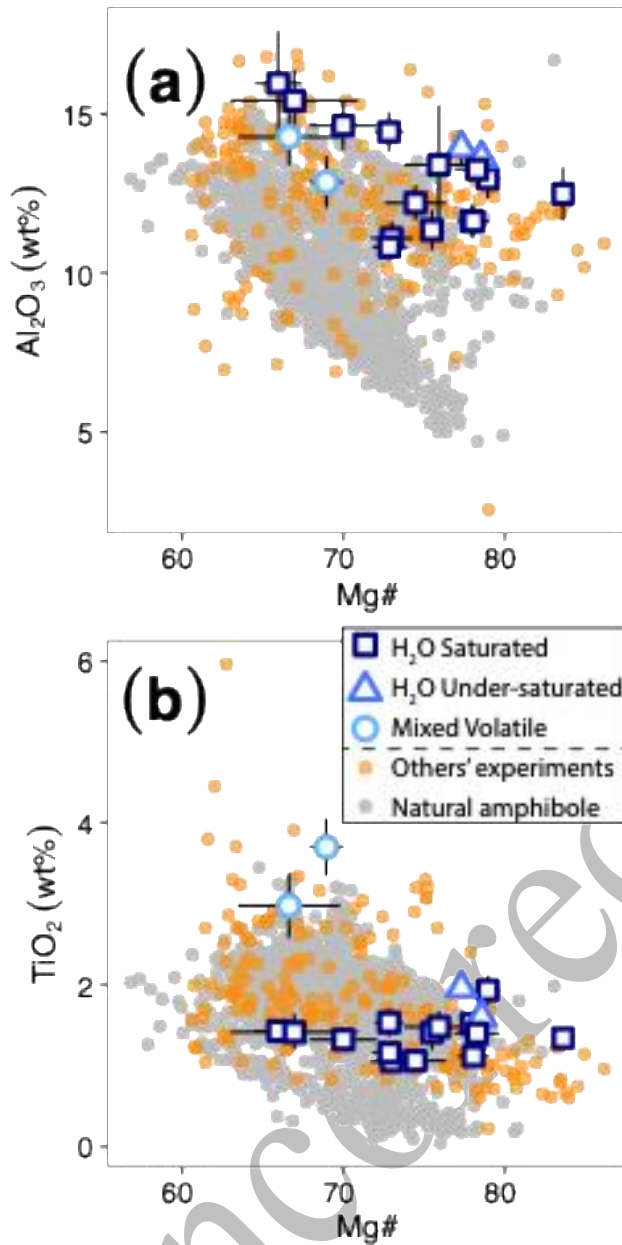
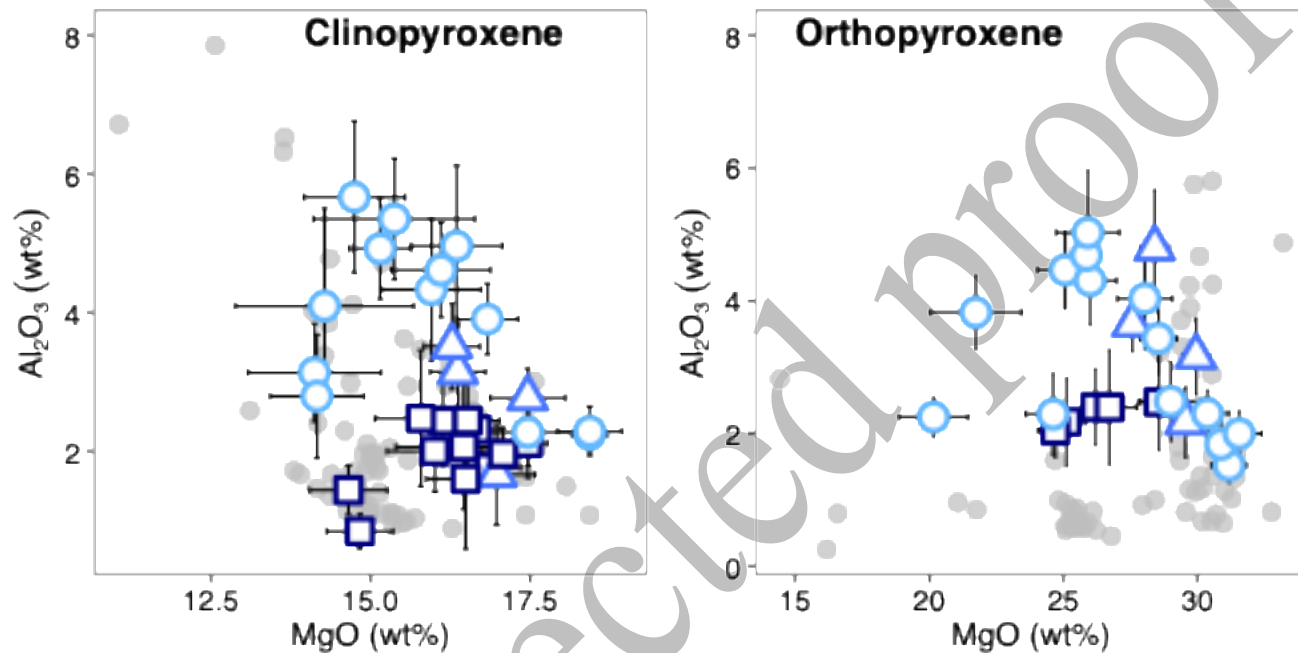


Figure 4. Mg# versus (a) Al₂O₃ and (b) TiO₂ of amphibole in our experiments (blue squares, triangles, and circles), experiments from the literature (orange circles), and in Shiveluch mafic enclaves (grey points). Error bars are 1 standard deviation. The shape and color of our experimental points correspond to the volatile condition of the experiment, as per the legend. Experimental data is from Andujar et al. (2017), Barclay and Carmichael (2004), Beermann et al. (2017), Blatter et al. (2017, 2023), Botcharnikov et al. (2008), DeAngelis et al. (2020), Feig et al.

615 (2010), Freise et al. (2009), Grove et al. (1997, 2003), Helz (1976), Holtz et al. (2005), Kawamoto (1996), Krawczynski et al. (2012), Müntener et al. (2001), Martel et al. (1999), Marxer et al. (2021, 2023), Melekhova et al. (2015), Moore et al. (1998), Nandedkar (2014, 2016), Pichavant et al. (2002, 2018), Prouteau and Scaillet (2003), Prouteau et al. (1999), Rutherford and Devine (2003), Scaillet and Evans (1999), Sisson et al. (1993, 2005), and Ulmer et al. (2018).



620 **Figure 5.** MgO vs Al_2O_3 of clinopyroxene and orthopyroxene in mafic enclaves (grey points) and experiments (blue points). Colors are as in Figure 4. Error bars are 1 standard deviation.

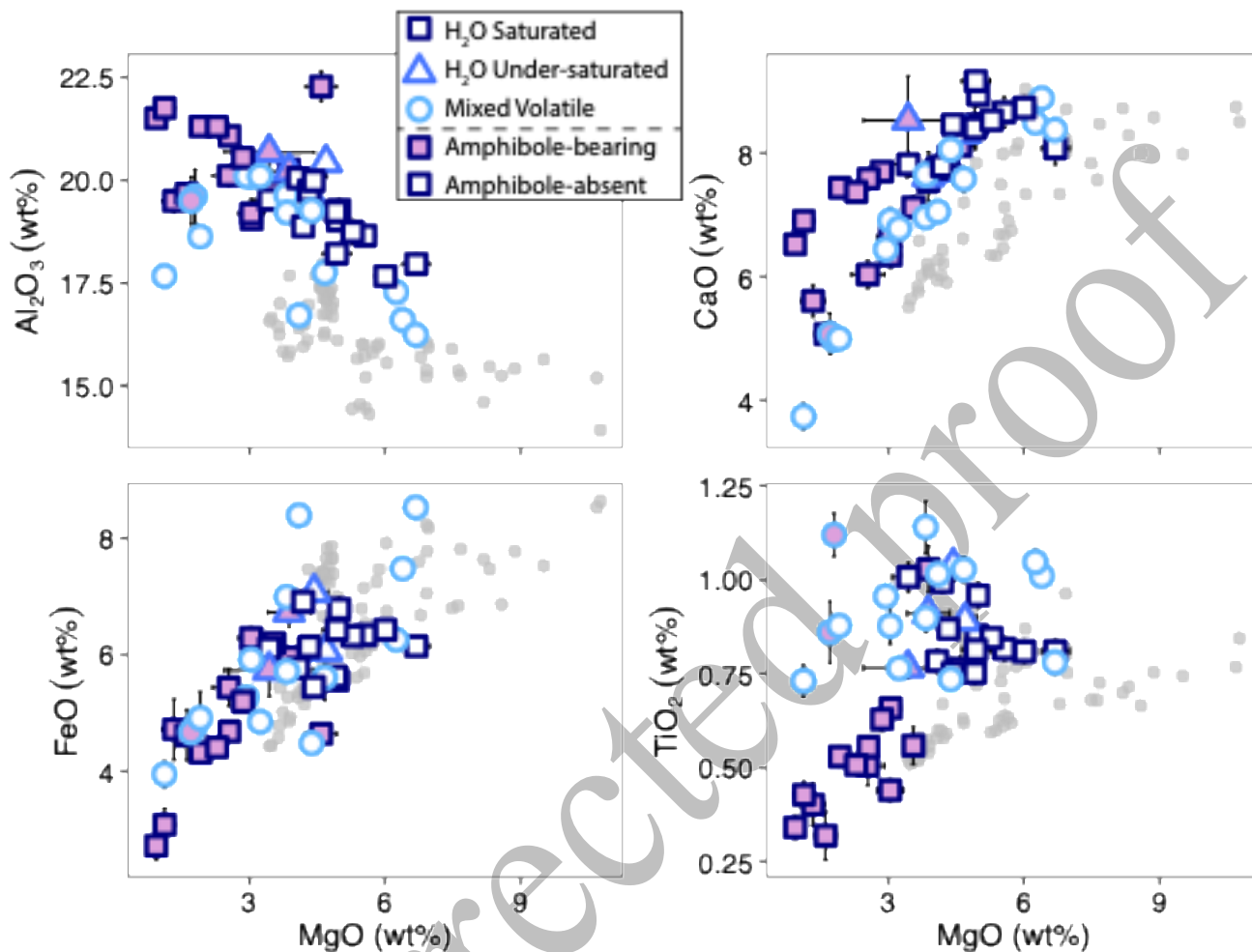


Figure 6. Compositional variation diagrams of experimental glasses and natural samples from Shiveluch. The color and shape of open shapes refers to the volatile content of the experiment containing that amphibole: dark blue squares are water saturated, periwinkle triangles are water undersaturated, and light blue circles are mixed volatiles. Points filled with pink represent experimental glasses in equilibrium with amphibole. Grey points are whole rock compositions of tephra, mafic enclaves, and andesites erupted from Shiveluch from Ponomareva et al. (2007), Goltz et al. (2020), Gorbach and Portnyagin (2011), Hochstaedter et al. (1996), Ishikawa et al. (2001), and Ferlito (2011).

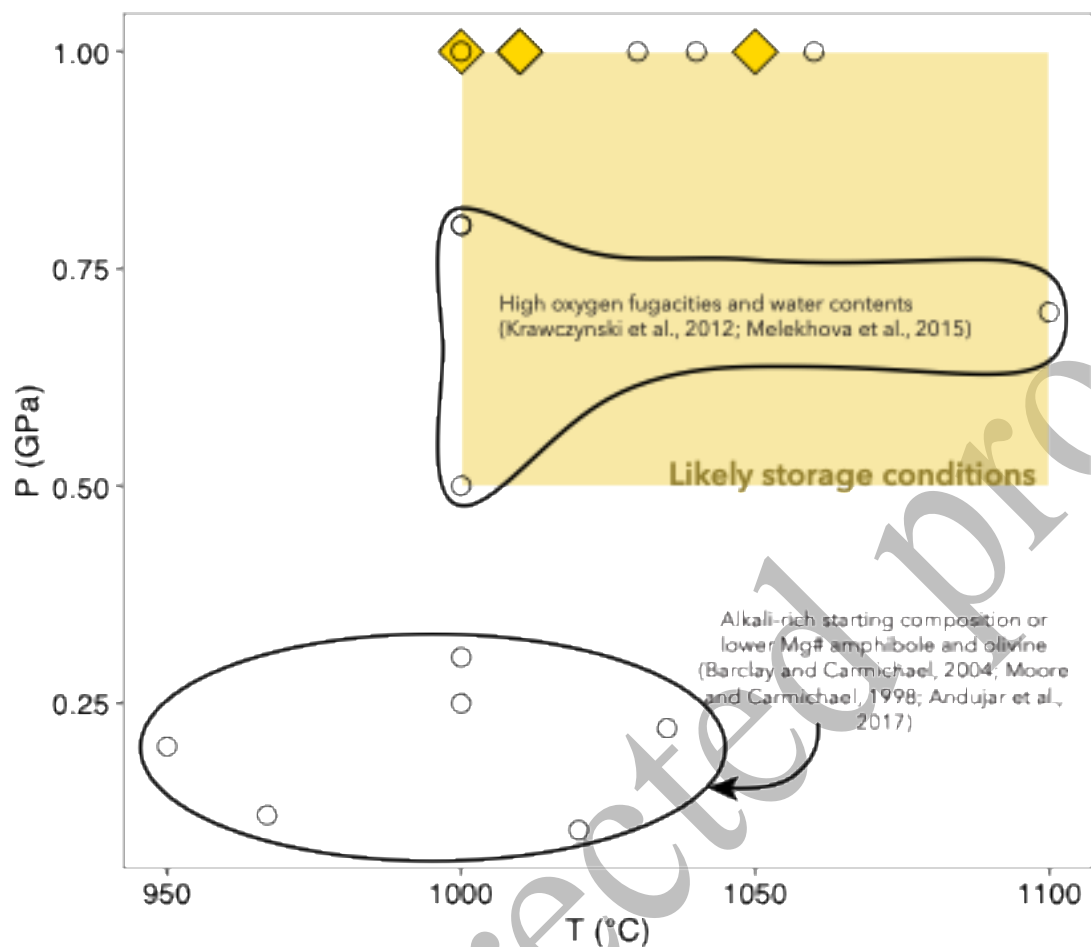


Figure 7. Pressure and temperature conditions of experiments with amphibole and olivine from this study (yellow diamonds) and the literature (open black circles). See Table 4 for more details on compiled amphibole- and olivine-bearing experiments from the literature.

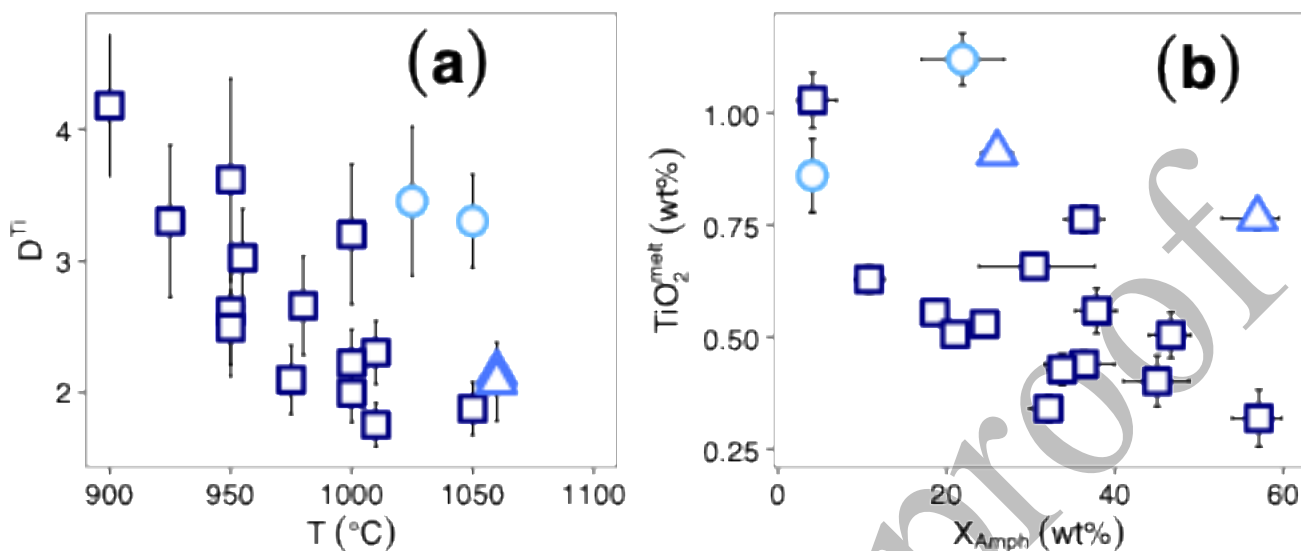


Figure 8. (a) Titanium partitioning between amphibole and melt (D_{Ti}) as a function of temperature. (b) Titanium content of experimental melt (TiO_{melt}) as a function of the proportion of amphibole in the experiment (X_{amph}). Colors and symbols are as in Figure 4.

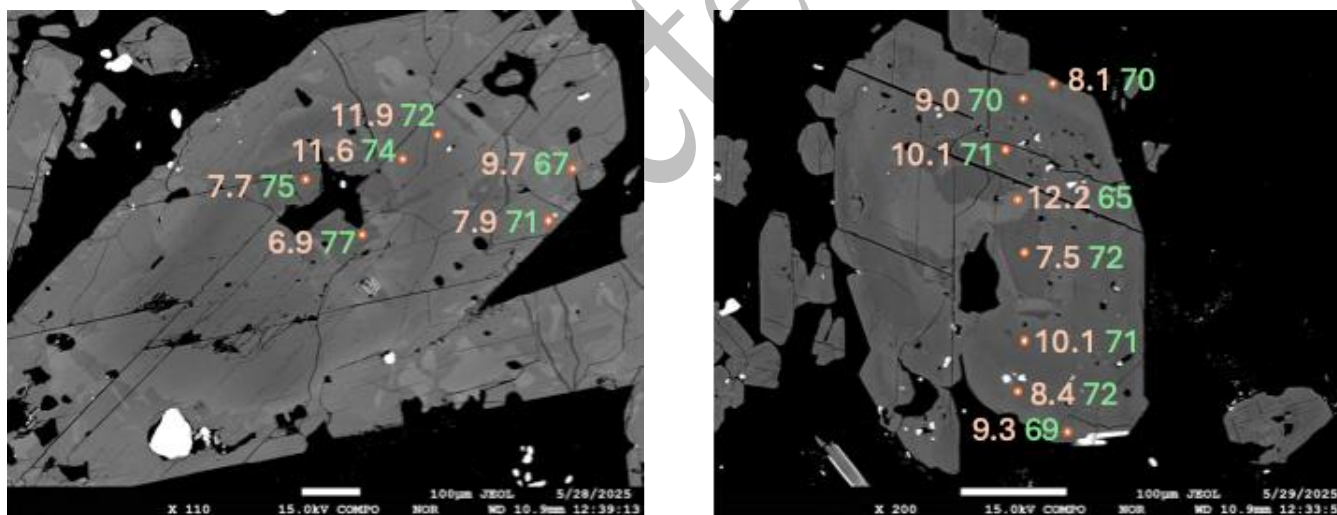


Figure 9. Back-scatter electron (BSE) images of amphiboles from samples 17-15f and 17-02B of Goltz et al. (2020). The aluminum content and Mg# of the analyzed points (shown as white points with orange stroke) is shown in orange and green text, respectively. Images and data were collected at Carnegie Science; see supplementary information for details on microprobe analyses and Supplementary Table 6 for complete microprobe data.

Table Captions (tables attached as .xlsx files to submission)

Table 1. Average compositions of experimental starting materials from repeated electron microprobe analysis and natural tephros from Ponomareva et al. (2007) in oxide wt%. Sigma is the 1 standard deviation of the number of analyses. XH_2O and $\text{H}_2\text{O}/\text{CO}_2$ are calculated from quantity of carbonates, and hydroxides added to starting mixture in moles. H_2O in wt% is calculated from the quantity of hydroxides added to the starting mixture when all volatile and major elements are normalized to 100.

Table 2. Experimental run conditions. Phase proportions (in parentheses) were determined using the MATLAB program LIME (Prissel et al., 2023), and uncertainties can be found in Table 3 and Supplementary Tables 1 and 2. Fe loss was determined using the method presented in Prissel et al. (2023), and sodium loss to fluid was determined by comparing the composition calculated using the LIME best estimate with the bulk composition.

Table 3. Compositions and proportions of synthetic phases in oxide wt%. Glass compositions are reported normalized to 100 with the un-normalized total. Numbers in italics are the 1 standard deviation of repeated analyses. Iron is reported as total iron as ferrous (FeO_T). Mg# is calculated as $\text{Mg}/(\text{Mg}+\text{FeTotal})$. Phase proportions are given as the best fitting phase abundance and the difference between the fit and the 25th and 75th percentiles of the probability density function output by LIME (-25% and +75%, respectively). Reporting error in this way reflects the asymmetry of the LIME algorithm's output; see Prissel et al. (2023) for more details on the best practices on reporting phase proportions.

Table 4. Details of experiments with equilibrium amphibole + olivine from the compilation of Weber and Blundy (2024).

Supplementary Table Captions (submitted as .xlsx files and in GitHub)

Supplementary Table 1. Computer-readable datatable, including key compositional and run information. Columns 6-12 are “factor” columns where “1” indicates the phase is present and “0” indicates its absence. Data in this sheet is formatted to be easily compatible with the Weber and Blundy (2024) data scheme.

Supplementary Table 2. Expanded, computer-readable version of Table 2, including uncertainties on phase proportions.

Supplementary Table 3. Computer-readable version of Table 3.

Supplementary Table 4. Weber and Blundy (2024) experimental database filtered for experiments containing olivine and amphibole. The database includes information about the experimental run and the source of the compiled experiment in addition to the composition of glass. To this information, we added the compositions of amphibole, olivine, and clinopyroxene, where available.

675 Supplementary Table 5. Weber and Blundy (2024) experimental database filtered for experiments containing olivine and amphibole, without plagioclase.

Supplementary Table 6. Complete EPMA analyses of points presented in Figure 9. Methods are given in Supplementary Information, Methods, and Figures document.

680 **Author contributions**

A.E.G. conducted and analyzed experiments, synthesized data, compiled relevant literature data, and wrote and edited this manuscript. M.J.K. initially conceptualized this study, aided in data analysis, and edited the manuscript.

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Data availability

Computer-readable data for this manuscript is freely available [at this GitHub repository](#).

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