The timing of compositionally-zoned magma reservoirs and mafic 'priming' weeks before the 1912 Novarupta-Katmai rhyolite eruption

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Abstract

The June, 6, 1912 eruption of more than 13 km³ of dense rock equivalent (DRE) magma at Novarupta vent, Alaska was the largest of the 20th century. It ejected >7 km³ of rhyolite, ~1.3 km³ of andesite and ~4.6 km³ of dacite. Early ideas about the origin of pyroclastic flows and magmatic differentiation (e.g., compositional zonation of reservoirs) were shaped by this eruption. Despite being well studied, the timing of events that led to the chemically and mineralogically zoned magma reservoir remain poorly known. Here we provide new insights using the textures and chemical compositions of plagioclase and orthopyroxene crystals and by reevaluating previous U-Th isotope data. Compositional zoning of the magma reservoir likely developed a few thousand years before the eruption by several additions of mafic magma below an extant silicic reservoir. Melt compositions calculated from Sr contents in plagioclase fill the compositional gap between 68 and 76% SiO₂ in whole pumice clasts, consistent with uninterrupted crystal growth from a continuum of liquids. Thus, our findings support a general model in which large volumes of crystal-poor rhyolite are related to intermediate magmas through gradual separation of melt from crystal-rich mush. The rhyolite is incubated by, but not mixed with, episodic recharge pulses of mafic magma that interact thermochemically with

the mush and intermediate magmas. Hot, Mg-, Ca-, and Al-rich mafic magma intruded into, and mixed with, deeper parts of the reservoir (andesite and dacite) multiple times. Modeling the relaxation of the Fe-Mg concentrations in orthopyroxene and Mg in plagioclase rims indicates that the final recharge event occurred just weeks prior to the eruption. Rapid addition of mass, volatiles, and heat from the recharge magma, perhaps aided by partial melting of cumulate mush below the andesite and dacite, pressurized the reservoir and likely propelled a ~10 km lateral dike that allowed the overlying rhyolite to reach the surface.

Key words: rhyolite, eruption, plagioclase, orthopyroxene, diffusion, chronology

1. Introduction

Knowledge of the processes that generate rhyolitic magma and drive its transport and eruption are paramount to understanding volcanic hazards as well as the evolution of earth's crust (Hildreth, 1981; Jellinek and DePaolo, 2003; Self and Blake, 2008; Castro and Dingwell, 2009; DeGruyter et al., 2016). A point in case is the 1912 Novarupta-Katmai eruption which has long propelled our understanding about how silicic pyroclastic deposits are produced (Hildreth and Fierstein, 2012). Moreover, the large range of magma compositions, and the chemical and mineralogical zonation of these deposits also fueled vigorous debate about the importance of crystallization-differentiation relative to assimilation and magma mixing (Fenner; 1926; Bowen, 1928). Modern field and geochemical data have since revealed that the rhyolite-dacite-andesite magmas were petrologically 'contiguous' (Hildreth, 1983; Hildreth and Fierstein, 2012)

and stored at shallow depths between 3 and 6 km below the former Katmai edifice (Coombs and Gardner, 2001; Hammer et al., 2002). However, the origin of the compositional zoning has been debated (Eichelberger et al., 2000) and the intersection of a rhyolitic dike with an andesitic-dacitic magma reservoir has been proposed (Eichelberger and Izbekov, 2000). More recently, short-lived U-series isotope data (Reagan et al., 2003; Turner et al., 2010) reveal that the Novarupta-Katmai reservoir was built progressively by episodic input of mafic magma such that the crustal residence time of the rhyolite may have exceeded that of the dacite and andesite by thousands of years.

How volcanic unrest manifests prior to a rhyolitic eruption and how eruptions are primed and triggered remain obscure, largely because there are few historical examples. Recent studies of the rhyolitic to rhyodacitic eruptions in Chile at Chaiten in 2008 and Cordon Caulle in 2011 indicate periods of pre-eruptive unrest as short as months to days and rapid transport rates (Castro and Dingwell, 2009; Jay et al., 2014). However, the precursory seismic and deformation signals and petrological characteristics are ambiguous as to the processes that lead to silicic eruptions (e.g., Singer et al., 2014). There is some information about the period of unrest prior to the Novarupta-Katmai eruption. Eyewitnesses reported feeling earthquakes 5 days before the eruption began. Moreover, Katmai volcano—10 km to the east—collapsed above the partially emptied magma reservoir leading to the hypothesis that transport of rhyolitic magma to the surface was by a lateral sill or dike (Hildreth and Fierstein, 2000; Pinel and Jaupart, 2004). We use the textures, major and trace element zoning of plagioclase and orthopyroxene crystals, and reevaluate existing geochemical and

U-series isotope data to address the questions of how and when the Novarupta magma reservoir became compositionally zoned. We integrate our results with recent modeling of the impacts that mafic recharge (DeGruyter et al., 2016) and volatile accumulation (Parmigiani et al., 2016) have on crystal-poor rhyolites, to discuss how the rhyolitic magma was propelled toward the surface leading to seismicity in June, 1912, and the timing of the primer for the seismicity and eruption.

2. Eruption chronology, petrological background, samples and methods

After five days of increasingly severe earthquakes, on June 6, 1912 magma spanning a remarkably diverse range of composition including crystal-poor high-silica rhyolite (76.5-77.8% SiO₂), and a continuum of crystal-rich dacite through andesite (57.9-68.6% SiO₂) began to erupt. The eruption occurred from the Novarupta vent in three plinian episodes that produced 17 km³ of fall deposits over 60 hours. The first comprised the plinian dispersal of 8.8 km³ of pyroclasts, starting with 2.3 km³ of DRE rhyolite, joined by an increasing amount of andesite and eventually dacite, together forming the zoned ignimbrite filling the Valley of Ten Thousand Smokes. The second episode comprised 3.4 km³ of DRE dacite with minor rhyolite and andesite, and a third episode deposited 2.6 km³ of DRE dacite joined by andesite and minor rhyolite. Altogether >7 km³ DRE of rhyolite, ~1.3 km³ of andesite and ~4.6 km³ of dacite were erupted during these three phases. A fourth episode comprised plugging of the vent by a small dacite dome and its explosive destruction (Adams et al., 2006). The Novarupta rhyolite dome, about 0.1% of the erupted volume, later filled this vent. Although eruption was through the Novarupta vent, the roof of the magma reservoir was ~10 km to the

east below Mount Katmai, which collapsed during episode 1 (Hildreth and Fierstein, 2000; 2012).

Samples for this study were collected by Hildreth and Fierstein and chosen to represent the compositional range of the Novarupta magma reservoir and the duration of the 60 h eruption. The stratigraphic designation of layers from which each pumice or scoria clast was collected follows Fierstein and Hildreth (1992; Fig. 1). Sample K-1525 is a pumice block from the initial all-rhyolite ignimbrite contemporaneous with Fall Layer A deposited on day 1 of the eruption. Dacite pumice (K-1490) and andesite scoria (K-131-D) are from the compositionally heterogeneous ignimbrite also deposited on day 1. Dacite pumice (K-1267) comes from Fall layer F and andesite scoria (K-184) is from a scoria flow intercalated with Layer F, both deposited on day 3 of the eruption (Fig. 1). Novarupta dome rhyolite (K-224) was emplaced days to weeks (?) following the eruption. Dacite sample K-1490 and andesite sample K-131-d were also used as starting materials in the experiments of Hammer et al. (2002). The major element composition of these 6 samples is in Table 1, along with proportions of plagioclase crystals that we found to have reverse-zoned rims and/or cores observed in a single thin section from each hand sample. Although an exceptionally minor component of the eruption, Hildreth and Fierstein (2012) note that of 265 whole rocks analyzed, two clasts in layer G deposited near the end of the eruption and three enclaves in the Novarupta dome have lower SiO₂ (50.4-57.1% SiO₂, though the lowest SiO₂ sample is olivine accumulative) and are thus more mafic than the andesites described earlier.

134 The rhyolites contain 0.5–3 weight % of phenocrysts of plagioclase, quartz,
 135 orthopyroxene, Fe-Ti oxides, plus exceptionally rare hornblende and tiny (0.1
 136 mm) apatite, sulfide and zircon that occur as inclusions in other phases (Hildreth
 137 and Fierstein, 2012). Plagioclase (An_{25-29} ; Anorthite = molar $100 \times$
 138 $Ca/[Ca+Na+K]$) and orthopyroxene (En_{49-50} ; Enstatite = molar $100 \times$
 139 $Mg/[Mg+Fe+Ca]$) are nearly unzoned in the rhyolite (Hildreth, 1983; Avery,
 140 1992). In contrast, the andesites and dacites contain phenocrysts of plagioclase
 141 (25-30 weight %), orthopyroxene (1.5-4 weight %), clinopyroxene (1-8 weight
 142 %), Fe-Ti oxides, and rare hornblende (Hildreth and Fierstein, 2012). Plagioclase
 143 crystals in both the andesite and dacite clasts are variably zoned ranging mainly
 144 between An_{35} and An_{85} , many crystals contain reversely zoned rims, and sparse
 145 crystals with An_{90} cores occur in the andesite and in Novarupta dome (Avery,
 146 1992; Hildreth and Fierstein, 2012; this study). Figure 2 compares the range in
 147 core-to-rim zoning in anorthite of 101 crystals for which Avery (1992) collected
 148 reconnaissance electron microprobe data from rhyolitic, dacitic, and andesitic
 149 clasts in ash flow and fall deposits. Although plagioclase zoning is generally
 150 normal in the dacite, many irregularly, and reversely zoned crystals, some with
 151 internal dissolution surfaces, are found in the dacite and are more abundant in
 152 the andesite (Avery, 1992). Most pyroxene crystals in the andesite and dacite are
 153 normally zoned (Hildreth and Fierstein, 2012), but some increase in Mg and Al
 154 concentration from core to rim. A reconnaissance ion probe study by Shearer et
 155 al. (1991) found that these rims are depleted in rare earth elements (REE)
 156 relative to their cores and suggested immersion of these crystals into an Mg-rich,
 157 REE-poor melt shortly prior to eruption. Co-existing Fe-Ti oxide minerals in the
 158 rhyolites yield temperatures of 800-857 °C, and log fO_2 values of -13.5 to -12.0.

For the dacites, the ranges are 848-950 °C and -11.7 to -10.0, and in andesites are 952-990 °C and -9.2 to -10.1 (Hildreth, 1983; Hildreth and Fierstein, 2012). These data imply a thermal continuum across the compositional spectrum, despite a compositional gap between the rhyolite and dacite, and together with the experimental results argue for contiguity of magmas in the reservoir (Hildreth and Fierstein, 2012).

We measured core-to-rim compositional profiles of 61 plagioclase phenocrysts from the three magma types using electron probe micro-analysis (EPMA), and 102 single spots in 15 of these crystals using an ion microprobe (Methods in the Appendix; Supplementary Figure 1 and Tables 1 and 2). Following optical examination of thin sections, core-to-rim EPMA traverses were also measured in 10 orthopyroxene crystals in thin sections of two andesites and a dacite. The core-to-rim ranges in anorthite in the crystals in rhyolitic, dacitic, and andesitic clasts in the ignimbrite and fall deposits are illustrated in Figure 2 alongside those from Avery (1992). The high spatial resolution of our EPMA traverses (few micrometer spacing between hundreds of spots per crystal) reveal that about one third of all crystals in both the dacite and andesite clasts that would appear to be normally zoned if only measured at the core and rim, but they contain reverse zoning either in the crystal interiors, in the outermost 50-100 micrometers at the rim, or both (Supplementary Figure 1). Moreover, rim compositions are continuous from An₃₂ to An₇₁ across the spectrum of dacite and andesite clasts. Inherited xenocrysts with exceptionally high An content are rare (Fig. 2).

3. Evidence for mafic recharge recorded in plagioclase and orthopyroxene zoning

3.1 Plagioclase zoning patterns and textures

The rhyolite plagioclase phenocrysts are virtually unzoned (mainly An₂₅₋₂₉) as noted above, whereas those of the dacites and andesites show more complex textures, including dissolution surfaces and sieving. Most crystals in the dacite have compositions between An₃₅ and An₆₀; and those in the andesites are more calcic and between An₄₉ and An₈₀ (Fig. 2; Supplementary Fig. 1). One crystal that ranges between An₃₈ to An₅₄ in the andesite may have originally grown in the dacite and thus be inherited (Fig. 2). The nearly unzoned crystals with <An₃₀, typical of the rhyolite, are nowhere present in either the andesite or dacite (Fig. 2). Of 19 plagioclase crystals we measured in the two dacite pumice clasts, nearly half (9) contain reversely zoned rims (An-enrichment in the outermost 50 to 100 µm), and 6 have reverse zoning present in their interiors. A much larger proportion of the reversely zoned crystals occur in the later erupted of the two dacite samples (K-1267) deposited during episode 3 (Fig. 1; Table 1). Of the 20 crystals we measured in the two andesite clasts, half contain reversely zoned rims, whereas 7 contain reverse zoning in their interior (Fig. 2; Table 1; Supplementary Fig. 1).

Further observations that provide evidence for exceptionally mafic melt in the system include: (1) many plagioclase crystals in the dacite contain calcic zones of An₈₀ or greater, and greater than An₈₄ in the andesites, and (2) crystals in andesite scoria and Novarupta dome lava with calcic An₈₇₋₉₄ sieve-textured cores overgrown by ~50 µm wide normally-zoned rims of lower An. Similar

observations by Avery (1992; Fig. 2) and Hildreth and Fierstein (2012) indicate that such crystals in the scoria and pumice clasts are not unusual and that inherited xenocrysts of plagioclase are rare, except in the Novarupta rhyolite dome lava. The observation that the different rocks contain different clusters of plagioclase compositions shows that the chemical zoning of the eruption is the result of the coexistence of melts of different compositions, rather than simple bulk-mixing of minerals and melts from a silicic and mafic end member (e.g., Costa and Singer 2002; Hildreth and Fierstein, 2012). Many crystals have one or more dissolution surfaces that truncate underlying zones and which are associated with abrupt rim-ward excursions to more An-rich plagioclase. These are interpreted as thermal-chemical fluctuations due to the arrival of melts of different composition, temperature and/or water content. (Tsuchiyama, 1985; Singer et al., 1995). Moreover, the observation that reverse zoning is common not only at the rims of many crystals in the andesite and dacite, but is also within their interiors, argues for multiple thermal and compositional oscillations in the melts that were in contact with these crystals as they grew (c.f., Hammer et al., 2002). We infer that development of the chemical and mineralogical zonation of the eruption, particularly within the andesite-dacite compositional continuum, reflects repetitive influx of mafic melts into the base of the reservoir.

In contrast, crystals in the Novarupta rhyolite dome lava exhibit the entire spectrum of compositions and textures just described, likely due to syn-eruptive mingling of the various magmas with the final batch of erupted rhyolite (Hildreth and Fierstein, 2012).

The concentrations of trace elements (e.g., Mg, Sr, Ba, Ti, REE) in plagioclase generally show a limited variation: a typical An_{29-27} crystal in rhyolite contains 79-65 ppm Mg, 616-560 ppm Sr, and 6.6 to 5.6 ppm La, and is identical to one crystal from Novarupta dome lava. Here we focus on the Sr and Mg concentrations to track the mixing and time of arrival of mafic magmas (e.g., Druitt et al., 2012). The An_{34-74} crystals in the dacites contain 130 to 210 ppm Mg, with the exception of 3 spots that have > 300 ppm Mg in sieve-textured cores (Fig. 3; An_{44-54}). The crystals in the andesites (An_{48-79}) contain 200 to 280 ppm Mg, except for a remarkable group of rim analyses (An_{51} , An_{68} , and An_{68-72}) and two cores (An_{82-84}) that have Mg concentrations extending to nearly 600 ppm Mg (Fig. 3). Many crystals from the Novarupta dome rhyolite are similar to those in the andesite and dacite with some exceptionally high Ca and Mg cores (Fig. 3; Supplementary Fig. 1). The observation that the high An plagioclase rims and some cores have high Mg concentrations is further chemical and textural evidence for the repetitive influx of mafic melts right up to the onset of the eruption. Other trace elements such as Ce, and Ba are consistent with the relations described above: high An domains within crystals, including An-rich rims have lower Ce and Ba concentrations than those with lower An content. This shows that the high An and Mg zones grew from a more mafic magma, rather than resulting from a period of rapid crystal growth which would have also increased the concentrations of other incompatible elements such as Ba and Ce (e.g., Singer et al., 1995). It also shows that the low Mg of some high-An cores might be the result of diffusion re-equilibration, since slower diffusing elements like Ce and Ba also have retained their original concentrations (Fig. 3).

3. 2 Orthopyroxene zoning patterns and compositions

The orthopyroxene textures and compositions also record multiple arrivals of mafic melts at various times during growth of the crystals. The andesites and dacites contain rare 150 to 200 μm -long euhedral orthopyroxene crystals with 10 to 50 μm -wide rims that have Mg#s (= molar $100 \times \text{Mg}/[\text{Mg}+\text{Fe}]$) of 67 to 74 which is up to 14% (relative) higher than the crystal interiors (Fig. 5). Moreover, Al_2O_3 typically increases with Mg# in all crystals except for one which has the opposite relation (Fig. 5). The shifts in Al_2O_3 concentration occur abruptly, over only 3-4 μm , whereas the shifts in Mg# are broader, and occur over 8-20 μm (Fig. 5). This likely reflects that Al_2O_3 , which is far more immobile relative to faster diffusing Mg-Fe (Allan et al., 2013), records rapid growth of the rims, and that the Mg# profiles have been broadened by diffusion following rim growth.

We interpret the high-An, high-Mg rims on a large proportion of plagioclase crystals in the dacite and andesite to reflect immersion of these crystals in a more CaO and MgO rich melt. Moreover, the interior zones of high An content indicate that many crystals record multiple mixing events, some having recorded the overall development of chemical zoning within the eruption. Similarly, we interpret the high-Mg and -Al rims on some orthopyroxene crystals to reflect exposure of these crystals in melt with higher MgO and Al_2O_3 than the melt from which the crystal interiors grew (cf., Shearer et al., 1991). Orthopyroxene in a glomerocryst that also contains magnetite and clinopyroxene (Fig. 5) is interpreted to have grown at least twice during exposure to high-MgO melt and may reflect repeated interaction of mafic melts with crystal-rich mush near the floor or margin of the magma reservoir.

3.4 Calculated melt compositions

More quantitative insight into the melt that these crystals grew from can be obtained using An- and temperature-dependent plagioclase partition coefficients (Bindeman et al., 1998). Using the Mg and Sr compositional relations we find that the An₂₅₋₂₉ crystals in the rhyolites are in equilibrium with melt equivalent to the whole-rock compositions (Fig. 4). Moreover, most of the volume of the crystals in the andesites and dacites are in equilibrium with melts lower in MgO and Sr than the whole rocks. Assuming that Sr concentration in the plagioclase has not been modified by diffusion we find that these calculated melts fill in the compositional gap between the rhyolite and the dacite indicating that most plagioclase grew from a continuous spectrum of melt compositions. This is consistent with plagioclase-hosted melt inclusions in dacite and andesite that contain much higher SiO₂ (72-75%) and lower MgO (0.25-0.48%) than the whole-rocks (Lowenstern, 1993). Moreover, a continuum of melts that link the rhyolite to the dacite parallels the continuous T-fO₂ spectrum recorded in oxide minerals (Hildreth, 1983) implying petrogenetic continuity among all the erupted materials via dominantly crystal-liquid fractionation processes.

However, a subset of our analyses, from within the rims and cores of a few plagioclase crystals in the andesite and dacite, are in equilibrium with melts that are much richer in MgO and Sr than the andesite (Fig. 4). These calculated mafic melts are similar in composition to some rare late-erupted basaltic andesite scoria clasts. We use these high Mg and Ca rims plus the orthopyroxene zoning in the next section to put constraints on the time of arrival of the last mafic melt

into the silicic reservoir. Finally, we also find that many calculated melt compositions in equilibrium with plagioclase record hybrid compositions formed during mixing between the basaltic andesite recharge magma, and melts initially comprising the andesite and dacite (Fig. 4).

4. Timing of the development of chemical zonation and last mafic recharge

Previous timescales for the assembly of the Novarupta-Katmai magma reservoir were proposed from U-Th-Ra isotope disequilibrium (Reagan et al., 2003; Turner et al., 2010). The 1912 rhyolites have higher ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios than the andesites and dacites leading to the hypothesis that the rhyolite was generated 50-200 kyr earlier than the andesite or dacite (Turner et al., 2010). However, the local eruptive record includes little rhyolite, thus Hildreth and Fierstein (2012) prefer more recent remelting of a late Pleistocene pluton that may have fed a small rhyolite eruption at Katmai volcano at 22.5 ka. The rhyolites and most dacites have a narrow range of ($^{226}\text{Ra}/^{230}\text{Th}$) activity of 1.00 ± 0.04 that are in secular equilibrium. However, two of the rare, late-erupted, basaltic to basaltic andesitic scoria clasts have large Th-excess with ($^{230}\text{Th}/^{238}\text{U}$) of 1.023 and 1.054, and ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios of 1.09 and 1.21 (Turner et al., 2010). Interestingly, the andesites, including samples equivalent to those studied here, are near U-Th secular equilibrium, but have a wide range of Ra disequilibrium with ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios ranging from 1.07 to 2.52, the latter being by far the highest value measured in the Aleutian-Alaskan arc (Turner et al., 2010; George et al., 2003). ^{226}Ra has a half-life of 1600 years. Assuming the ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratio of 2.52 represents the maximum attainable in this subduction zone, we infer that this disequilibrium was

generated recently and has not been modified by radioactive decay. Using 2.52 as an initial ($^{226}\text{Ra}/^{230}\text{Th}$) ratio, it would take 3400 to 7800 years for ^{226}Ra to decay to the levels measured by Turner et al. (2010) in the basalt and basaltic andesite scoria clasts. That these earlier and more recent additions involved different batches of mafic magma is also underscored by $^{87}\text{Sr}/^{86}\text{Sr}$ contrasts between the basalt-basaltic andesite scoria (0.70339-0.70349), and the more radiogenic andesites (0.70358-0.70374), respectively (Turner et al., 2010; Hildreth and Fierstein, 2012). Regardless of when and how the rhyolite formed, these observations imply that arrival of a variety of mafic magmas into the reservoir below the rhyolite, and that development of the chemical and mineralogical zoning of the erupted magma, were underway a few thousand years before the eruption and continued, possibly with the addition of exceptionally ^{226}Ra -rich melt, until very shortly prior to the eruption.

Experiments aimed at reproducing thin plagioclase rims due to magma mixing imply crystal growth rates of between 4×10^{-10} and 60×10^{-10} cm/s (Larsen, 2005), suggesting that the ~ 100 μm -wide rims on reversely zoned Novarupta-Katmai plagioclase crystals could have formed in less than a month. Our results indicate that many of the plagioclase and orthopyroxene crystals erupted in the andesite, plus several in the later-erupted dacite, grew rims while immersed in a basaltic andesite magma poorer in SiO_2 (and other incompatible elements like Ce and Ba) and richer in CaO, MgO, Al_2O_3 , and Sr than the host magma (Figs. 4 and 6).

4. 1 Time scales from plagioclase and orthopyroxene chemical zoning

To further refine when the last mafic recharge occurred relative to the eruption we use diffusion chronometry of Mg in plagioclase and Mg-Fe interdiffusion in orthopyroxene. The orthopyroxene crystals were modeled at the two-oxide temperatures of their host magmas, using an initial sharp profile and a constant composition at the boundaries (Modeling methods are in the Appendix). We constructed ten diffusion models of Mg# profiles in nine orthopyroxene crystals. We found durations for re-equilibration of the rims prior to eruption that range between 1 and 14 weeks, with an average of 6 ± 4 weeks ($\pm 1\sigma$; Table 2) using the diffusion coefficient reported in Allan et al (2013). Using a more recent calibration of Dohmen et al (in press) we would obtain time scales a factor of two longer. The compositional shifts between the rims and the interiors of the crystals were assumed to be an infinitely sharp step function, and thus our times between rim growth and eruption are likely to be maximums.

The plagioclase zoning styles and wide spacing between ion microprobe analyses preclude detailed modeling of the trace element compositional profiles. Many plagioclase crystals have rims that grew from higher Mg and Ca melts (Fig. 4), and their concentrations are not in equilibrium with their crystal interiors or intermediate zones that grew from more silicic melts (Fig. 3). Given this observation we calculated maximum survival times separating the growth of the high-An and Mg rims from the eruption. We used the measured profiles as initial conditions and allowed the rim and adjacent zones to re-equilibrate until they were out of the measured values. Two such models for two andesite crystals indicate that the high Mg rims could not have survived for more than 100 days at

the temperature of the andesite (Fig. 3). Such short periods also validate our assumption that Sr concentration has not been affected by diffusion.

Two plagioclase crystals (one from dacite and another from andesite; Fig. 3) also have high-An cores but their Mg concentrations have already been, or are close to being, equilibrated. Whereas the core of one of these crystals is in equilibrium with the host andesite magma, the other crystal is more complicated but the mantle of An₅₂ plagioclase could be in equilibrium with the Mg and Sr of an andesitic composition (Fig. 3). Notwithstanding these complexities, given the crystal sizes and temperatures of interest, we calculate that minimum equilibration times for the mantle or core of these crystals are between 100 and 400 years depending on how significant diffusion in multiple dimensions was (e.g., Costa et al., 2003; Longpre et al., 2014). These equilibration times are consistent with the high-Ca cores being related to older mafic magmas present in the magma reservoir, perhaps those with ²²⁶Ra activities that had decayed toward secular equilibrium over hundreds to thousands of years prior to the eruption. A single An₈₃₋₈₆ crystal in the Novarupta rhyolite dome, likely inherited from the andesite, still preserves a high-Mg concentration and thus has not been re-equilibrated by diffusion (Fig. 3). It is unclear what the relevant temperature would be to calculate such re-equilibration, and the presence of a sieved crystal core makes it unsuitable for simple diffusion modeling, but this crystal records a short time of residence at high temperature.

The variability of the (²³⁸U/²³⁰Th) and especially the (²²⁶Ra/²³⁰Th) activity ratios in the basaltic to andesitic clasts argues for accumulation and mixing of several

mafic recharge magmas at various depths in the deep crust (Hildreth and Fierstein, 2012). During at least the last ~7800 years (period required to explain the range of ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios) many batches of these mafic andesite magmas rose out of the deep crust to recharge the Novarupta magma reservoir, producing in the andesite and dacite high-An and high-Mg cores in some plagioclase and orthopyroxene, as well as the dissolution surfaces within many plagioclase crystals. The most recent batch of this mafic recharge magma promoted mixing of Mg-rich melts with the andesite within weeks prior to the 1912 eruption. From this last recharge magma, which may be the source of the distinctively elevated ^{226}Ra disequilibrium in parts of the system, the high-An and high-Mg rims grew on plagioclase and orthopyroxene, respectively. Both the earlier, and the latest, mixing events were spatially restricted within the zoned magma reservoir such that not every plagioclase or orthopyroxene crystal in the andesite or dacite were chemically or thermally affected (Fig. 6).

5. Implications for reservoir response, dike initiation, and eruption

Concentrations of H_2O , CO_2 , Cu and S in melt inclusions led Lowenstern (1993) to conclude that the pre-eruptive magma reservoir was saturated with an excess volatile phase. The effects of adding mafic magma to the base of zoned silicic magma reservoirs suggest that volatile addition from the recharge melt is important in pressurizing the reservoir (Folch and Marti, 1998; Wark et al., 2007; Parmigiani, 2016). At ~100 MPa, the heat carried by recharge magma may also promote buoyant rise of plumes, volatile exsolution and pressurization (Turner and Campbell, 1986; Snyder, 2000). But, perhaps a more effective way to pressurize the rhyolite involves the interaction between recharge magma and

crystal-rich cumulates at the base of the reservoir through the addition of mass, volatiles, and sufficient heat to partially melt cumulate mush (e.g., Wolf et al., 2015; DeGruyter et al., 2016; Parmigiani et al., 2016). The increase in volume associated with partial melting helps expel melts of andesitic composition and volatiles upward, and enhances mixing of these melts with extant magma within localized domains above the cumulate mush (DeGruyter et al., 2016). Moreover, fluid dynamic models indicate that bubbles ascend significantly more rapidly through crystal-rich mush than crystal-poor melt, thus volatiles are likely to accumulate rapidly within the viscous, crystal-poor, capping rhyolitic melt (Parmigiani et al., 2016).

Although banded pumice with streaks of andesite or more rarely dacite against rhyolite occur throughout deposits from the 1912 eruption, several observations, including sharp contacts, xenocrysts that are neither resorbed or reacted, and the absence of hybrid magma compositions between 68 and 76% SiO₂, argue that mingling of andesite and dacite with the rhyolite was largely syn-eruptive (Hildreth and Fierstein, 2012). Thus, if the contiguous single reservoir model of Hammer et al. (2002) and Hildreth and Fierstein (2012) is correct, the low density of the volatile-saturated rhyolite, and its high viscosity of $\sim 10^6$ Pa•s, were sufficient to prohibit convection and mixing with the underlying dacitic and andesitic magmas within the pre-eruptive reservoir. Moreover, the dearth of reverse zoning or dissolution textures in plagioclase in the rhyolite (Fig. 2) argue that heat supplied by recharge magmas was absorbed mainly by the andesite and dacite and did not reach the rhyolite.

457 Many zoned silicic eruptions produce progressively more mafic magma with
458 time, likely reflecting the reverse order emptying of a gravitationally stable
459 stratified magma reservoir. Such zoning could be the result of crystal
460 fractionation and melt mixing (Druitt and Bacon, 1989) even if it involved some
461 mafic intrusions (Sisson and Bacon, 1999), or simply a reflection of the bulk-
462 mixing between a silicic and a mafic end-member (e.g., Costa and Singer, 2002).
463 For the case of the Novarupta eruption, the chemical stratification was likely
464 developed by a combination of crystallization, melt extraction and progressive
465 mixing of melts within a compositional and temperature gradient field. The near
466 continuum of calculated melt compositions from which plagioclase grew, despite
467 the compositional gap between the dacite and rhyolite whole pumice
468 compositions (Fig. 4b & c), is consistent with extraction and hybridization of
469 melts via partial melting of crystal-rich cumulates during recharge events (e.g.,
470 Deering et al., 2011; 2016). The compositional zoning developed *before* the last
471 intrusive event. However, the eruption sequence at Novarupta was rhyolite, a
472 tiny amount of dacite, followed by large proportions of andesite then dacite,
473 which according to our density calculations based on bulk-rock and crystal
474 content of the magmas, would not be gravitationally stable. If the pre-eruptive
475 reservoir was a single contiguous zoned body as envisioned by Hildreth and
476 Fierstein (2012), and our interpretations that compositional zoning developed
477 through recharge at the base of the body, including a final recharge event that
478 primed the eruption, are correct, there are at least a couple of possible
479 explanations for the enigmatic sequence of materials erupted. One is that the
480 final mafic recharge may have been volatile-rich, buoyant, and thus vigorous
481 enough to disperse andesitic magma from the base of the reservoir through most

of the overlying dacite (e.g., Turner and Campbell, 1986) such that a tiny amount of dacite but much larger volume of andesite followed the rhyolite to the surface. Another possibility is that the ascent of hot, volatile and ^{226}Ra -rich, mafic magma into crystal-rich cumulates induced partial melting that released new volatile-rich andesitic melt into the overlying melt-rich layer of andesite. The effects would be to expand the andesite layer, destabilize its temperature structure, promote convective overturn or plume rise that penetrated through the overlying dacite layer and concentrated volatiles within the high viscosity crystal-poor rhyolitic cap (Parmigiani et al., 2016). Each of these processes may have contributed to pressurizing the rhyolitic melt (Fig. 6).

A rise in overpressure of ~ 10 MPa or more as a result of mafic recharge and volatile accumulation in the rhyolite (e.g., Parmigiani et al., 2016; DeGruyter et al., 2016) in May, 1912 may have become sufficient by June 1 to fracture wall rock (Jellinek and DePaolo, 2003), nucleate earthquakes (Castro and Dingwell, 2009) at the top of the shallow reservoir along planes of weakness in flat-lying Mesozoic sediments (Hildreth and Fierstein, 2000), and propel a lateral dike (Fig. 6). Pinel and Jaupart (2004) show that the path and shape of this dike are strongly influenced by the load of the Katmai edifice that was at least 700 meters higher than the Novarupta vent prior to eruption and locally neutralized the regional northwest-southeast direction of maximum compression. The reduction in lithostatic pressure by ~ 25 MPa as the magma transited westward away from Katmai allowed the dike to propagate rapidly and to curve until reaching subvertical northwest-oriented joints of the Naknek Formation where vertical

ascent occurred, consistent with the northwest-southeast orientation of fissures intersecting Novarupta vent deposits (Wallman et al., 1990).

Conclusions

The Novarupta-Katmai example illustrates that strong compositional zoning may develop in response to multiple inputs of mafic magma, over thousands of years, into the deepest portions of magma reservoirs that incubate large volumes of crystal-poor rhyolite. Moreover, our findings indicate that:

- Repeated mafic recharge is largely cryptic in expression, evinced mainly by:
 - (1) reversely zoned rims and interiors of many, but not all, plagioclase and orthopyroxene crystals in andesitic-to-dacitic portions of the magma reservoir, and (2) a few basaltic to andesitic clasts in erupted materials that have large contrasts in ^{226}Ra disequilibrium, and therefore pre-eruptive residence times, within the reservoir.
- The reservoir was destabilized by addition of mafic recharge magma shortly prior to the 1912 eruption. Diffusion chronometry of Mg—an element that diffuses faster than others—in the rims of plagioclase and orthopyroxene crystals in the andesite and dacite indicates that the eruption-priming recharge event occurred at most weeks prior to the eruption.
- Pressurization of large, shallow, silicic magma reservoirs in response to deep mafic recharge can be quite rapid. In the case of the Novarupta-Katmai reservoir, the priming recharge event added mass, volatiles, and heat to the andesite and dacite. Although volatiles from the final mafic recharge magma may have accumulated in the rhyolite, for reasons that remain unclear, this recharge event did not thermally impact the rhyolite enough to significantly

affect plagioclase-melt equilibria or to promote mixing of rhyolite and dacite prior to eruption.

- The volatile-saturated pre-eruptive state of the Novarupta rhyolite implies a high rate of mafic recharge was necessary to prime the reservoir, pressurize it, and force dike ascent, since bubble-rich magmas have greater compressibility than their volatile-undersaturated counterparts.

Numerical simulations of highly-crystalline magmas or crystal mushes (e.g., Dufek and Bachman, 2010) predict the evolution of compositional gaps similar to the one observed in Novarupta tephra. Major and trace element zoning in plagioclase and orthopyroxene—common phases in many compositionally zoned eruptions—offer powerful, yet underutilized means to bridge these gaps between mafic and silicic magmas. Moreover, zoning in these minerals reveals the potentially brief time scales of recharge processes that may be responsible for unrest and the triggering of eruptions at many volcanoes.

Appendix: Analytical and Modeling Methods

EPMA analyses

Major and minor elements in plagioclase were analyzed with a Cameca SX-50 electron microprobe at the University of Lausanne at 15 nA beam current and 15 keV accelerating voltage, with a counting peak time of 20 s for Al $K\alpha$, Si $K\alpha$, Ca $K\alpha$, Na $K\alpha$, Fe $K\alpha$, Mg $K\alpha$, and K $K\alpha$. Backgrounds were measured on either side of peak for one-half peak counting times. Linear traverses were performed with approximately 4 micrometers spacing between individual spot analyses and with an estimated beam diameter of 1-2 micrometers. Major and minor element compositions of orthopyroxene were determined using a JEOL JXA 8530-F Field

Emission Electron Probe Microanalyzer (FEG-EPMA) located at the Facility for Analysis, Characterisation, Testing and Simulation at Nanyang Technological University, Singapore. Point analyses were acquired using a focused beam, 20 nA beam current and 15 keV accelerating voltage. Results were quantified using well-characterized natural and synthetic calibration standards and a modified ZAF matrix correction procedure (Armstrong, 1988). Counting times were 20 seconds for Si $\text{K}\alpha$, Mg $\text{K}\alpha$, and Fe $\text{K}\alpha$, and 40 seconds for Ca $\text{K}\alpha$, Al $\text{K}\alpha$, Mn $\text{K}\alpha$, Ti $\text{K}\alpha$, Na $\text{K}\alpha$, and Cr $\text{K}\alpha$. Background intensity was calibrated based on mean atomic number and continuum absorption was corrected for (Donovan and Tingle, 1996). Oxygen was calculated by cation stoichiometry and included in the matrix correction. An interference correction was applied to Fe for interference by Mn (Donovan et al., 1993), and an absorption correction was applied for carbon coating applied to both standard and sample for electrical conductivity. Analytical uncertainty at the 99% confidence level was less than 1% of all reported values and detection limits ranged from 70 ppm for Ca to 420 ppm for Ti. As a quality check, analyses with totals outside the range 98-102 wt% were omitted.

Effects of signal convolution on orthopyroxene traverses

To evaluate the effects convolution of x-ray signal between adjacent EPMA point analyses, we performed simulations of 10,000 electron trajectories in a representative orthopyroxene matrix with a 10 nm carbon coating 100nm beam diameter using Casino version 2.42 (Drouin et al., 2007). After correction for absorption, >90% of all measured characteristic x-ray intensities were generated within a radial distance of 420 nm from beam center and >99% of measured

intensities were generated within a radial distance of 1310 nm, 1070 nm, 1300 nm, 860 nm, 930 nm, 1320 nm, and 1160 nm from beam center for Si, Ti, Al, Fe, Mn, Mg, and Ca, respectively. Thus, only very slight analytical overlap between adjacent EPMA point analyses would exist at 1 μ m spacing. This effect is negligible given that the lengths and magnitude of the chemical gradients that we evaluated were many times greater.

SIMS analyses

Trace and minor element analyses plagioclase were performed at the University of Edinburgh with a Cameca IMS-4f ion microprobe with a 0 primary beam of net impact energy of 15 keV (10.7 keV primary and 4.5 keV secondary) and an operating current of 5 to 8 nA. The secondary ion accelerating voltage was 4500 keV. Only ions with energies falling between 55 and 95 eV (75 ± 20 eV) were analyzed to reduce molecular ion interferences. Beam diameter ranged between 15 to 30 μ m. The following isotopes were measured: ^{26}Mg , ^{30}Si , ^{41}K , ^{42}Ca , ^{56}Fe , ^{139}La , plus mass 60 for CaO overlap on Fe and mass 130.5 to monitor the background. The concentrations were obtained by normalization of mass ^{30}Si to the silica values obtained by electron microprobe analyses. The SRM-610 glass standard was used as a monitor of day-to-day changes in instrumental conditions (the nominal concentrations for SRM-610 are provided in Hinton, 1995). The ion yields for plagioclase relative to SRM-610 were determined with Lake County (LC) plagioclase, an alkali feldspar SHF1 (AF), and Corning glass (CG). The 2 sigma precision for most elements is under 5% relative. Only La is in some cases slightly above 10%.

606 *Modeling of Fe-Mg in orthopyroxene*

607 For the initial conditions we used homogeneous concentrations at each side of
 608 the gradient and assumed an extremely sharp (< 1 micrometer) transition zone
 609 between the two (Fig 3). This same condition has been used in other works (e.g.
 610 Allan et al. 2013) and is justified by the much shorter zoning of Al vs Fe-Mg (Fig.
 611 3), in accordance with the much slower expected diffusivity of Al. The conditions
 612 at the boundary taken as constant, although this doesn't influence the results
 613 given the short compositional gradients. We modeled the diffusion between the
 614 zones using the following analytical solution:

615

$$X_{Mg}(x, t) = X_{Mg}^{left} + \frac{X_{Mg}^{left} + X_{Mg}^{right}}{2} \left[1 + \operatorname{erf} \left(\frac{x}{\sqrt{tD}} \right) \right]$$

616

617 where the diffusion coefficient D is given by:

$$D_{Fe-Mg}^{opx} = \exp \left(-6.77 - 5.99X_{Mg} - \frac{240000}{RT} \right) \times \left(\frac{fO_2(sample)}{fO_2(IW\ buffer)} \right)^{\frac{1}{6}}$$

618

619 (Ganguly and Tazzoli, 1994) to correct for oxygen fugacity (Allan et al., 2013).

620 We assume that the initial profiles were abrupt, rim-ward step function

621 increases in X_{Mg} . This assumption allows to center the X_{Mg}^{left} and X_{Mg}^{right} terms of

622 the diffusion equation on the position of the initial step function increase in X_{Mg} .

623

624 The diffusion coefficient D was calculated using X_{Mg} half way between X_{Mg}^{left} and

625 X_{Mg}^{right} . The temperature and oxygen fugacity for each diffusion calculation are

626 estimated from the two-oxide thermometry in Hildreth (1983) of 980 °C and

$\log fO_2 = -9.5$ and 940°C $\log fO_2 = -10.5$ for the andesite and dacite-hosted crystals, respectively. This 1-D modeling approach is justified because the rims zones are thin relative to the size of the crystals (Allan et al., 2013). Adding an additional uncertainty of $\pm 25^\circ\text{C}$ in the temperature estimates and the corresponding change in fO_2 (Hildreth, 1983) for the host melt increases the uncertainty of the calculated timescales by at most a few days to 4 weeks. Using the diffusion coefficient of Fe-Mg in opx determined by Dohmen et al. (in press) our time scales would at most be a factor of two longer, because the Allan et al. (2013) and Dohmen et al (in press) datasets nearly overlap at the T- fO_2 conditions of the Novarupta dacite and andesite.

Modeling of Mg in plagioclase

We used the diffusion coefficient of Van Orman et al (2014) which depends on temperature and An content, together with the partition coefficient data of Bindeman et al (2008). The approach to equilibrium and diffusion equation was the same as that of Costa et al. (2003). We could not fit in detail the compositional profiles because of lack of spatial resolution from the ion microprobe data. Instead we created two end member models that give first order constraints on the time scales: (1) for crystals that had a high An and Mg rim we used as initial concentration the same as measured and we let it diffuse with the adjacent zones until the concentrations went out of the measured values and we recorded the time as maximum, and (2) for the high An crystal interiors we calculated how long it would take to reequilibrate the cores starting from liquids with similar compositions to the basaltic andesite inclusions. These are in principle minimum times because some of the crystal cores are completely

equilibrated. However, we used only 1 dimensional models and the effect of 3 dimensions on such large amount of reequilibration may be important (e.g., Longpre et al., 2014) so the diffusion times are approximate. These models are first order estimates and thus not precise, but a temperature uncertainty of ± 25 °C changes the times by a factor of two.

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Figure 1. Schematic diagram of relations among the 1912 pyroclastic deposits summarizing ignimbrite facies and time-equivalent fall deposits (Layers A through H). Rhyolite is abbreviated, rhy. Thicknesses not to scale; vertical dimension scaled to depict time equivalence. Positions of samples for this study are noted. VFI=Valley filling ignimbrite; HEPI=High energy proximal ignimbrite; PDC=pyroclastic density current deposit; BRU, block-rich flow units that dominate small-volume Package 9. Modified from Hildreth and Fierstien (2012).

Figure 2. Rank-order plot of range of anorthite zoning in plagioclase from samples of rhyolitic, dacitic, and andesitic clasts in pyroclastic flow and fall deposits. Ordering from left to right is based on the rim composition in the three magma types. Grey bars are EPMA data from Avery et al. (1992), red bars are EPMA data of this study. Many crystals that reveal only normal zoning on the basis of reconnaissance data in fact contain reverse zones in either the core, rim, or both as indicated. Crystals from which SIMS trace element data were measured are denoted with a red star and those for which Mg diffusion models were constructed are denoted *m*.

Figure 3. Nomarski differential interference microscopy contrast (NDIC) images and zoning profiles of representative plagioclase crystals. Location of EMPA traverses (An content, red line) and SIMS spots are overlain on the NDIC images. Arrows show dissolution surfaces. Concentration-distance profiles of An (red dots) and various trace elements with $\pm 1\sigma$ uncertainties (Scale for Sr and Ba is 0-800 ppm; for Ce 0-8 ppm). **A.** For K-131-D plag 3 (andesite host) blue curves are diffusion models for the high An rim after 100, 200, and 300 days at 980 °C. The initial and equilibrium curves for these diffusion models are also illustrated.

Figure 3. (continued) B. For crystal K-131-D plag 4 (andesite host) two models were calculated, one for the equilibration of the core (red curves) after 10, 110, and 310 years, and another for the rim (blue curves) after 100, 200, and 300 days.

Figure 3. (continued) C. For crystal K-1490 plag 4 (dacite host) we only calculated the percentage of re-equilibration (87%) starting from the shown initial and equilibrium concentrations because of the large degree of re-equilibration and effects of 3 dimensional diffusion. We obtain times ranging from 100 to 300 years using the models of Longpre et al. (2014) for a similar crystal, temperature and crystal sizes (their Fig. 14).

Figure 3. (continued) D. For crystal K-224 (inherited crystal in Novarupta rhyolite dome lava) a time could not be calculated because Mg concentrations are high and the profile has only 3 analyses. We show three equilibration curves for conditions of melt and temperature of the andesite, dacite, and rhyolite (details in methods and supplemental materials).

Figure 4. Melt compositions (red dots) calculated by inversion of plagioclase trace element compositions. **A.** MgO and Sr melt contents calculated using the plagioclase-melt partition coefficients of Bindeman et al. (1998). The temperatures used in these calculations, 980 °C for andesite, 940 °C for dacite, and 840 °C for rhyolite, are based on iron-titanium oxide thermometry typical of each magma composition (Hildreth, 1983). The calculated melts are compared to the composition of 265 whole-rock samples (open blue squares) spanning the 1912 eruption (Hildreth and Fierstein, 2012). Four late-erupted mafic clasts are shown as filled purple squares between 310 and 360 ppm Sr and 4.0 to 5.6 % MgO. The calculated MgO_{melt} and Sr_{melt} values from the rims or cores of five plagioclase crystals encompass the composition of the four mafic clasts and extend the range of MgO and Sr of the whole rock array to more mafic magma compositions. **B, C.** Use of calculated Sr_{melt} contents from plagioclase permits estimating the SiO_2 content of the magma from which the calcic high Mg and Sr rims or cores in plagioclase grew.

Figure 5. Compositional profiles of Mg# (red dots and line) and Al_2O_3 (black dots and line) measured by electron probe in orthopyroxene crystals shown in backscattered electron images below from Novarupta andesite and dacite. Fe-Mg diffusion models described in the text show: assumed initial position of the boundary between the core and rim (red dotted lines), and the model target curves (blue) chosen to best match the measured Mg# profile. Note that we used very sharp initial profiles for the models of Fe-Mg and thus, if there is a contribution of growth zoning, we are actually overestimating the time scales.

Figure 6. Summary model of plagioclase and orthopyroxene growth, magmatic processes, and their timescales within the single compositionally-zoned Novarupta-Katmai magma reservoir envisioned by Hildreth and Fierstein (2012).

Figure 1

Figure 2

Figure 3A

Figure 3B

Figure 3C

Dacite K-1490 plag 4

Figure 3D

Novarupta rhyolite K-224 plag 1

Inherited crystal with An_{57} core with 392 ppm Mg

Mg diffusion to equilibrium concentrations

- if in andesite host melt
- if in dacite host melt
- - - if in rhyolite host melt

• measured Mg concentration

Figure 4

Figure 5

Figure 6

Table 1

Sequence in eruption	1	2	3	4	5	6
Sample	K-1525	K-1490	K-131-d-r	K-1267-g	K-184	*K-224
SiO ₂	77.19	67.72	58.72	65.52	59.47	76.52
TiO ₂	0.18	0.57	0.72	0.67	0.72	0.21
Al ₂ O ₃	12.28	15.10	16.86	15.69	16.77	12.5
FeO*	1.30	4.37	7.08	5.07	6.81	1.53
MnO	0.05	0.10	0.14	0.11	0.12	0.07
MgO	0.19	1.59	3.71	1.95	3.56	0.34
CaO	0.87	3.91	7.44	4.56	7.03	1.16
Na ₂ O	4.32	4.08	3.49	4.08	3.63	4.32
K ₂ O	3.17	2.03	1.31	1.78	1.35	2.94
P ₂ O ₅	0.05	0.13	0.12	0.16	0.15	0.02
LOI	2.52	1.61	~	1.94	~	~
Original Total	96.51	97.65	97.63	97.13	99.70	99.7
# plag xtals analyzed	8	9	7	10	13	14
# plag with calcic rims	0	2	5	7	5	3
# plag reverse zones in core	0	5	1	6	6	2
reverse zoned opx?	0	0	1	3	6	0

*sample is identical to RLS-214 in Hildreth and Fierstein (2012).

The # of crystals listed with reverse zones are from surveys of a single thin section of each sample. rim-to-core profiles of anorthite content for each crystal analyzed are in Supplementary Fig. 1.

Table 2. Mixing-to-eruption times obtained by diffusion modeling of Fe-Mg in Novarupta orthopyroxene

Sample	Layer	crystal #	T °C	logfO ₂	Time (weeks)
K-131 Andesite	A	opx 3	980	-9.5	6.4
K-184 Andesite	F	opx 1	980	-9.5	8.0
K-184 Andesite	F	opx 2	980	-9.5	0.8
K-184 Andesite	F	opx 3	980	-9.5	3.6
K-184 Andesite	F	opx 4	980	-9.5	3.2
K-184 Andesite	F	opx 5	980	-9.5	14.4
K-184 Andesite	F	opx 6	980	-9.5	0.8
K-1267 Dacite	F	opx 2a	940	-10.5	7.2
K-1267 Dacite	F	opx 2b	940	-10.5	6.8
K-1267 Dacite	F	opx 3a	940	-10.5	10.8
				Average	6.4
				±1σ	4.4

Layer A is episode 1 ignimbrite, F is episode 3 fall deposit (from Fierstein and Hildreth (1992). Temperature and logfO₂ are estimates from two oxide thermometry (Hildreth, 1983).