

Electronic Supplementary Material

Analytical methods

XRF: whole-rock major elements

Internal standards WS-E (Whin Sill Dolerite) and OU-3 were analysed repeatedly throughout analytical batches. Approximate 2 standard deviation (2sd) analytical precisions are <2 relative % for all elements, excepting those with concentrations <0.5 wt. %, for the 22 replicate analyses of each standard. High accuracy is indicated by the close agreement (generally within ~1 % offset) between average values for the standard analyses and recommended values for each element. Similar values (within ~2 % offset) were calculated from the difference between duplicate analyses of samples. The XRF standard data are available in Conway (2016).

Solution ICP-MS: whole-rock trace elements

International standard BCR-2 was analysed throughout analysis sessions to monitor the precision and accuracy of data. Approximate 2sd analytical precisions calculated from 18 analyses of BCR-2 are <13 relative % for all elements (most are ~8–10 %) except Nb (~24 %). Analyses of BCR-2 are accurate to within 5 % of preferred values for all elements (most are within 1–2 %), except Cr, U (~6 %), Cu (~18 %) and Ni (~30 %). The bulk powder (TPI) of a single large clast from Taupo ignimbrite was used as an additional secondary standard throughout analysis sessions. From replicate analyses of TPI, most trace element analyses are precise to ± 5 –10 %. Separate dilutions of same unknown sample powders were also analysed to monitor accuracy of the analyses as well as the reliability of the sample preparation procedure and homogeneity of powders. Values of ≤ 5 –10 % offset were recorded for all elements from analyses of duplicate digestions. Full standard data are presented in Conway (2016).

EPMA: mineral and glass major elements

Calibration and secondary standards were analysed as unknowns to monitor instrumental drift and precision and accuracy of the measurements throughout analytical sessions. All standard

data are presented in Conway (2016). Values of approximate 2sd precisions measured from repeated analysis of glass standard VG-568 are within 1–5 relative % for major element oxides SiO_2 , Al_2O_3 and K_2O , and ~ 14 % for Na_2O . Analyses are accurate to ≤ 2 % for SiO_2 , Al_2O_3 and K_2O , and to 4 % for Na_2O of the preferred values of the standard. The level of analytical precision and accuracy is comparable to that obtained using a 10 μm spot (Barker, 2015) and indicates that using a spot size of 5 μm does not result in significant alkali loss under the analytical conditions used. Values for precision and accuracy are high for other (minor) element oxides with concentrations < 1 wt. %. Approximate 2sd analytical precision from repeated analysis of mineral standards are generally 1–7 relative % for major element oxides with concentrations > 0.5 wt. %. Analyses of the standards are accurate to within 5 % of the preferred values for those major element oxides.

Laser ablation ICP-MS: glass trace elements

Data was processed using the LaserTRAM software developed at Oregon State University (Loewen, 2013). The software was used to select a 20 second background interval and a ~ 20 second ablation interval for each analysis. The software corrected for the background and normalised the count rates for each element over the ablation interval to the concentration of ^{29}Si as determined by EPMA for the sample. The selected ablation interval was divided into 5 subintervals of equal duration using the software and background-corrected counts recorded in each of these were binned before calculating normalised ratios for each subinterval. Final normalised ratios for each sample are the median value of the normalised ratios calculated for each subinterval. Trace element abundances were then calculated using the known concentrations in the bracketing standard (GSD-1G). BHVO-2G and BCR-2G were analysed as secondary standards. Because the analysis session was intended as a preliminary exercise for collecting trace element data for Ruapehu glasses, only 2 spots on each standard, and 11 spots on samples were analysed. Analyses of standards were generally accurate to within 15 % of reference values, and mostly < 5 % for the light rare earth elements and elements of interest for the purposes of this study (Rb, Sr, Zr, Ba). Exceptions to these values were calculated for Tm and Hf in BCR-2G and Cs, Eu and Lu in BHVO-2G. The standards data are given in Conway (2016).

Mineral chemistry

Te Herenga Formation

The mineral assemblage of the 200–150 ka basaltic-andesites is dominated by subhedral pyroxene phenocrysts and glomerocrysts that range in size up to 14 mm and are readily visible in hand specimen. Orthopyroxene phenocrysts exhibit minimal compositional zonation ($\sim\text{Mg}_{\#70}$) but commonly have resorbed edges that are overgrown by coronas of orthopyroxene with $\text{Mg}_{\#55-60}$ than the cores. Clinopyroxene often displays complex multiple zoning outward of resorbed or mottled cores. Rims are typically more magnesian ($\text{Mg}_{\#75-80}$) than cores ($\text{Mg}_{\#70}$). Plagioclase phenocryst interiors are invariably sieved and often resorbed, whereas the outer $<200\ \mu\text{m}$ display faint cyclic zoning towards sub- or euhedral rims that are generally less calcic than the cores. Plagioclase crystals typically record more complex growth histories than pyroxene and olivine phenocrysts. Within CC348, the least evolved and oldest precisely dated Ruapehu sample collected in this study, olivine is relatively common as 100–500 μm -wide rounded crystals (either isolated or within clots) that display a gradual decrease from $\text{Mg}_{\#70-80}$ in cores towards $\text{Mg}_{\#<70}$ in rims. The rims are often resorbed (wavy) and overgrown by orthopyroxene with similar compositions to groundmass pyroxene ($\text{Mg}_{\#70}$).

Mangawhero Formation

Within the geochemically diverse Mangawhero Formation, the crystal-specific aspect of this study was restricted to lavas of the Mangaehuehu and Te Kohatu packages erupted during the early stage (50–35 ka).

Mangaehuehu package

Orthopyroxene and clinopyroxene phenocrysts and glomerocrysts dominate the mineral assemblage of lavas of this eruptive package. Accumulations of subhedral, unzoned and compositionally identical orthopyroxene form clusters $\leq 1.5\ \text{mm}$ across within Mangaehuehu package lavas. These clots commonly contain glass (which has often partially crystallised to form plagioclase) along grain boundaries, as well as symplectite veins and pools (up to 300 μm -wide accumulations) of Fe-Ti oxide phases (magnetite). Outermost rims that are in

contact with groundmass have $<5\text{ }\mu\text{m}$ -thick reaction coronas composed of prismatic orthopyroxene with lower $\text{Mg}\#_{60-70}$. Crystal shapes range from euhedral to resorbed and rounded, with common examples of mechanical breakage. The most conspicuous crystal type is reverse-zoned orthopyroxene, which comprises $\sim 8\text{--}17\%$ of the total phenocryst proportion. This crystal type exhibits rounded and unzoned cores with $\sim\text{Mg}\#_{70}$. Crystals display sharp transitions over $5\text{--}10\text{ }\mu\text{m}$ to dark rims with $\text{Mg}\#_{85-90}$. The outer rims are generally euhedral, and average rim width varies between samples from $22\text{--}54\text{ }\mu\text{m}$ with widest rims observed in lavas with highest whole-rock $\text{Mg}\#$. Outermost crystal margins typically have $<5\text{ }\mu\text{m}$ -wide reaction coronas composed of orthopyroxene with similar $\text{Mg}\#$ values to the associated groundmass microcrystals ($\sim\text{Mg}\#_{70}$). Reverse zoned orthopyroxene are present both as individual grains and within clusters. For clustered crystals, only the outermost grain edges that are in contact with groundmass have Mg -rich rims and rim width varies between adjacent crystals. Many individual crystals display broken edges along which there are thin orthopyroxene coronas but no high- Mg rims.

Clinopyroxene phenocrysts are subordinate in abundance compared to orthopyroxene and generally exhibit multiple compositional zones outward of resorbed or mottled cores with spongy textures. Core compositions range from $\text{Mg}\#_{65-85}$; rim compositions lie within this range also. Clinopyroxene rarely ($<5\%$ proportion of clinopyroxene) exhibit the strong reverse zoning displayed commonly by orthopyroxene: rounded cores ($\text{Mg}\#_{70}$) are sharply overgrown by BSE-dark rims ($\text{Mg}\#_{88}$) and the outermost edges are composed of orthopyroxene coronas.

Plagioclase phenocrysts generally lack the intensely sieved and cored interiors that are characteristic of plagioclase crystals within Te Herenga Formation lava flows. They are characterised by cyclic zoning in the outer half of the crystal area and outer rims define sub-euhedral forms. Compositions dominantly lie between An_{50-60} , with rare calcic zones of An_{80} .

Interiors of olivine ($\text{Mg}\#_{78-84}$) are unzoned or normally zoned toward grain edges that are strongly resorbed and overgrown by clusters of coalescing orthopyroxene crystals.

Symplectite veins and $50\text{--}80\text{ }\mu\text{m}$ -wide patches of Fe-Ti oxide mineral phases are common at the interface between resorbed olivine and outer pyroxene crystals.

Te Kohatu package

As with Mangaehuehu package andesites, reverse-zoned orthopyroxenes (and minor clinopyroxenes) are present within Te Kohatu dacites, although in lower abundances (~7 % of total phenocryst proportion) compared to the andesites. Mg-rich rims (Mg_{#82-88}) have sharp boundaries with rounded cores (Mg_{#70-76}) and are overgrown by an outermost <5 µm-thick euhedral rim with compositions equivalent to groundmass pyroxene microcrystals (Mg_{#60-70}). Unzoned orthopyroxene phenocrysts (Mg_{#60-70}) are present as sub- to euhedral grains as well as anhedral and broken crystals within the dacites. Clinopyroxene are generally sub- to euhedral and exhibit multiple compositional zoning patterns. Plagioclase phenocrysts display a range of complexly zoned types, often comprising sieved or spongy cores that have been resorbed and overgrown by multiple zones and subhedral rims. Anorthite contents range from 45–65 mol. %, and rims generally display less calcic compositions than cores. Rare euhedral apatite crystals (100–200 µm-long) are present along pyroxene rims within glomerocryst clusters. Relict amphibole grains are identified based on their characteristic diamond-shaped cross-sectional forms but have been completely replaced by symplectite intergrowths of orthopyroxene + plagioclase + Fe-Ti oxides ± apatite ± minor glass. Clusters of crystals comprised of orthopyroxene, clinopyroxene, plagioclase and Fe-Ti oxides form clots up to 12 mm-wide within Te Kohatu dacite lavas. Interstitial glass is preserved between these phases within pockets that are not in immediate contact with groundmass.

Whakapapa Formation

Euhedral and subhedral grains of unzoned orthopyroxene with compositions of Mg_{#65-70} are the dominant crystal type within Whakapapa Formation lavas. Rare glomerocrysts of anhedral and unzoned orthopyroxene with Mg_{#65-70} occur within the lavas. Reverse zoned types with rim compositions of Mg_{#78-84} were observed in basaltic-andesite lava sample CC281 (~12 % of total phenocryst proportion) and rarely (<5 % phenocrysts) in samples CC193, CC260 and CC335. Clinopyroxene dominantly exhibits mottled cores, similar to those in the older formations. Resorbed olivine cores (Mg_{#70-75}) are overgrown by orthopyroxene (Mg_{#60-72}), and the boundary between olivine and orthopyroxene is often marked by magnetite symplectites. Plagioclase phenocrysts display resorbed cores that are often spongy or sieved. Outer zones of crystals exhibit fine-scale cyclic zoning (An₆₀₋₉₀) toward subhedral or euhedral rims.