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The crystalline silica respiratory hazard from rhyolitic lava dome eruptions in New Zealand's Taupo Volcanic Zone: A case study from the 1315 CE Kaharoa eruption



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ABSTRACT

The rhyolitic Kaharoa 1315 CE eruption was a complex, long-lived event from Tarawera volcano, New Zealand. Explosive phases were followed by around 5 years of lava dome extrusion and collapse which produced blockand-ash flows (BAF). Lava domes generate crystalline silica in the form of cristobalite, and rhyolitic magmas often contain quartz phenocrysts. Fine-grained ash containing crystalline silica can be formed through dome collapses or explosions, generating a respiratory health hazard for communities affected by ashfall. The aims of this study are to: i) determine whether the Kaharoa eruption dome-forming phase generated substantial quantities of crystalline silica and, therefore, to determine the potential for future dome-forming eruptions of Tarawera to do the same; ii) consider the potential hazard of the crystalline silica by studying the crystal habit and chemistry compared to other lava domes, globally; and iii) assess the particle size and crystalline silica content of the Kaharoa ash, to inform a respiratory hazard assessment.

Five co-BAF ash samples and one co-ignimbrite (explosive) ash sample from the Kaharoa pyroclastic deposits were analysed for health-pertinent factors: particle size distribution and crystalline silica content. Eight domerock samples were collected from the dome complex and associated BAF deposits and groundmass texture (especially forms of crystalline silica) and quantity of crystalline silica were assessed.

Cristobalite was present in the 4 ash samples analysed by X-ray diffraction (XRD; 1.3–3.7 wt%) as was quartz (5.7–12.5 wt%). For the 4 dome samples analysed by XRD, all samples contained quartz (4.1–10.4 wt%) and two contained significant quantities of cristobalite (24.7 and 27.3 wt%). Of the two dome samples with minimal cristobalite (visible as individual vapour-phase crystals by SEM but not quantifiable by XRD), one was from the non-devitrified dome carapace and the other was from the compacted interior but had not undergone devitrification. The two dome samples with substantial cristobalite were from dome interiors and were highly devitrified, with well-developed spherulitic textures. Using energy-dispersive X-ray spectroscopy, cristobalite in all samples contained minor aluminium, as has been seen for volcanic cristobalite from other lava domes, which may ameliorate its toxicity. By laser diffraction, the quantities of ash in the health pertinent size fractions varied, with a range of 1.3–8.1 vol% for particles of <4 μ m diameter and 1.7–15.6 vol% for particles of <10 μ m diameter, which is lower than measured in ash from large-scale dome collapse events at other volcanoes.

The findings suggest a potential for substantial crystalline silica to be formed in future Kaharoa-style eruptions, but that cristobalite generation is site-specific, depending on location within the dome and whether the dome remains sufficiently hot for spherulite formation and glass devitrification. Respiratory hazard will therefore vary depending on the collapse of (or explosions through) individual lobes – although all lava is expected to contain quartz phenocrysts – as well as the size and energy of those collapses, which will influence particle size and quantity of ash generated and dispersed.

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1. Introduction

In approximately 1315 CE, the rhyolitic Kaharoa eruption of Tarawera volcano, New Zealand, ended with a phase of summit lava dome growth and collapses that likely lasted several years. Dome collapses (gravitational failure of part, or all, of the dome) generated block-andash-flows (BAF) – a type of pyroclastic density current (PDC) – with related, lofting plumes then forming co-BAF ash deposits that drape the surrounding environment. Such co-BAF deposits, at other volcanoes, have been found to contain up to 23 wt% crystalline silica, predominantly as the polymorph cristobalite (e.g., Horwell et al., 2014; Horwell et al., 2010a). Volcanic domes act as 'incubators' for the formation of crystalline silica, by vapour-phase crystallization and devitrification of volcanic glass (Baxter et al., 1999; Horwell et al., 2013b; Schipper et al., 2020), which results in ash containing cristobalite upon collapse and fragmentation. Rhyolitic magmas will also frequently contain quartz as a primary phenocryst (i.e., a crystal derived from the magma).

For industrial exposures, cristobalite, quartz and the other common polymorph, tridymite, are classified as carcinogenic and can cause the fibrotic lung disease silicosis (International Agency for Research on Cancer, 1997). The hazard is understood to be a 'variable entity' (Donaldson and Borm, 1998), meaning that disease does not always result from substantial exposure. In volcanic environments, the pathogenicity of the crystalline silica polymorphs is unclear (Damby et al., 2018; Damby et al., 2016; Horwell and Baxter, 2006; Horwell et al., 2012), especially as no cases of chronic diseases, such as lung cancer, have been definitively linked to volcanic ash exposures (reviewed by Horwell and Baxter, 2006; Stewart et al., 2022).

There are several possible mechanisms that may reduce the capability for volcanic cristobalite to cause disease, one of which is that volcanic, and other forms of cristobalite, have Al and Na substituted into the silica crystalline structure (Damby et al., 2014; Horwell et al., 2012; Nattrass et al., 2015). Nattrass et al. (2017) showed that such structural substitutions may dampen the toxic potential of cristobalite *in vitro* (i.e., in experiments with cells). However, Damby et al. (2018) identified a biological mechanism through which volcanic cristobalite can induce inflammation and generation of reactive oxygen species, which may both be precursors to chronic disease. There is no evidence that volcanic quartz or tridymite toxicity is different from that in other settings or that their chemical structure is altered and, therefore, they must be assumed to be potentially pathogenic.

Until there is definitive evidence that volcanic cristobalite has a different pathogenic potential to the other forms of crystalline silica, a precautionary approach in public health and workplace management has been taken, which requires assessing the concentrations and hazard of all types of crystalline silica in volcanic ash, and dust created by quarrying of volcanic deposits (Damby et al., 2013). This hazard assessment includes the concentration of particulate that is of sufficiently small particle size to be inhaled. Different fractions have been defined, with <100 µm being equivalent to the 'inhalable' fraction of particles which can enter the upper respiratory tract, <10 µm being equivalent to the 'thoracic' fraction which penetrates beyond the larynx, and $< 4 \ \mu m$ being equivalent to the 'respirable' fraction which penetrates into the unciliated airways and alveoli. Sub-1 and $<2.5~\mu m$ are even finer particles which carry the highest risk of pathogenicity due to their ability to penetrate into the alveoli and, potentially, into the bloodstream where they can translocate from the lungs to other organs (Brown et al., 2013; Horwell, 2007; Horwell and Baxter, 2006). Ideally, the concentration of respirable crystalline silica is determined during a hazard assessment (e.g., Searl et al., 2002) but, for practical reasons, usually the concentrations of crystalline silica polymorphs and the concentrations of the inhalable fractions are determined separately.

Rhyolitic eruptions are historically rare, providing few opportunities to assess the formation and prevalence of cristobalite, although the recent, volumetrically small eruptions of Chaitén and Puyehue-Cordón Caulle in Chile (in 2008 and 2011, respectively) indicate that pyroclastic material and lava domes/flows from rhyolitic eruptions can be cristobalite-rich (Horwell et al., 2010a; Schipper et al., 2015). In New Zealand, rhyolitic lava domes are scattered across the central Taupo Volcanic Zone (TVZ). Over the past 50,000 years, a total of sixteen dome-forming rhyolitic eruptions occurred from four caldera systems within the TVZ (Wilson et al., 2009). In the Okataina Volcanic Centre (north-central TVZ, to the east of Rotorua), rhyolitic domes have formed during five separate eruptions in the last ~22,000 years, forming two volcanic complexes: the Tarawera and Haroharo Volcanic Complexes. Both groups of domes erupted separate from aligned fissures controlled by the extensional rifting (Ashwell et al., 2018; Nairn, 1989; Rowland and Sibson, 2001; Smith et al., 2006).

In this study, we consider the crystalline silica hazard from the domes and associated co-BAF ash deposits formed over an estimated 5 years during the final phase of the 1315 CE Kaharoa eruption of Tarawera volcano, which is part of the Okataina Volcanic Centre (Sahetapy-Engel et al., 2014). There is archaeological and oral history evidence that Māori settlers arrived prior to the Kaharoa eruption, so they may have been adversely affected by the eruption (Ashwell et al., 2018; Lowe et al., 2000). Tarawera last erupted in 1886, with a basaltic but highly-explosive Plinian eruption blasting through the previous rhyolitic domes (including Kaharoa). There was no rhyolitic phase during the 1886 eruption, but the 25,000-year history of volcanism on the Tarawera and Haroharo Volcanic Complexes is overwhelmingly rhyolitic in composition, and all eruptions (except for in 1886) included effusive, rhyolitic lava-dome forming phases (see Sahetapy-Engel et al., 2014, their Table 1).

A future rhyolitic, Kaharoa-style eruption with dome-forming phases may present a substantial respirable crystalline silica hazard because of the potential for quartz to be present as a primary phenocryst and the potential for cristobalite and tridymite to form in the lava domes. In this study, we conduct a respiratory health hazard assessment, where we evaluate the characteristics of the eruptive deposits that could potentially cause respiratory harm, including a petrographic description of lava dome samples, in order to better understand the conditions for crystalline silica formation in the dome and the presence of quartz as a phenocryst. The aims of this study are to: i) determine whether and how the Kaharoa eruption dome-forming phase generated substantial quantities of crystalline silica and, therefore, to assess the potential for future dome-forming eruptions of Tarawera to do the same; ii) consider the potential hazard of the crystalline silica by studying its crystal habit and chemistry; iii) assess the particle size and crystalline silica content of the Kaharoa ash, to inform a respiratory hazard assessment. The findings of this study may inform the assessment of crystalline silica hazard at other rhyolitic dome-forming volcanoes, globally.

To address these aims, ash samples were obtained from both the co-BAF, BAF and co-ignimbrite deposits, collected from the medial stratigraphic sequence, and rock samples from the domes, collected in situ and from BAF deposits. Crystalline silica content was determined by Xray diffraction (XRD) for both ash and dome samples. Crystal morphology and chemistry in quartz and cristobalite were determined by scanning electron microscopy (SEM) with elemental analysis by energy dispersive X-ray spectroscopy (EDS). Ash particle size distributions were assessed by laser diffractometry.

2. The Kaharoa eruption domes and deposits

Nairn et al. (2004) define the final phase of the Kaharoa eruption (eruptive unit N in the stratigraphy, which included lava dome formation and BAFs) as the end of 13 more explosive episodes that included explosion breccias, Plinian, pumiceous PDC, and mild ash venting. These lasted a minimum of 12 days (up to the top of unit L) (Sahetapy-Engel et al., 2014, their Fig. 2 and Table 3), after which dome-forming and related activity dominated (units M and N). As stated above, these final 2 episodes may have lasted at least 5 years.

The effusion of domes in unit N included the Tarawera, Ruawahia,

Table 1

Ash sample and site descriptions.

| Sample Name | Original sample name | Site number | Source of ash | Site information and sample description |
|----------------|----------------------------|----------------|---|--|
| NZK_01 | K253_CH | K253 | Interpreted as co- BAF ash from a period of early Ruawahia dome growth and collapse, based on positioning of the deposit. | Crater Block Forest, 3 km from the present dome. Sample from unit N. |
| NZK_02 | K630_CH | K630 | Interpreted as pumiceous PDC (i. e., co-ignimbrite) ash from an explosive eruption from Ruawahia vent | Off Ngamotu Road. Sample of unit H ash to compare with co- BAF deposits. |
| NZK_03 | K46_CH | K46 | Interpreted as layer of slightly re-worked co-BAF wind-blown ash of Ruawahia BAF origin. Top of Kaharoa sequence.* | Ash Pit Road. 80 cm of aeolian ash deposit with re- worked bedding. White/grey at base grading up to yellow/brown. Sample from unit N. |
| NZK_04 | K99/32A (2) | K234 | Interpreted as the base of a Wahanga BAF deposit. | At the entrance road to a collapse gully. Lower 15 cm of 35 cm relatively fine- grained, inversely graded deposit. Sample from unit N. |
| NZK_05 | K99/16 (2) | K270 | Interpreted as Ruawahia co-BAF ash deposit. | Quarry on Ash Pit Road with BAF section – mainly rhyolite blocks with some fibrous pumice. Sample from unit N. Lower 50 cm of fine- grained, reverse graded base of BAF deposit overlying upper Kaharoa tenbra (unit L or K) |
| NZK_06 | K99/48 (2) | K253 | Interpreted as BAF deposit from a period of Ruawahia dome growth and collapse. | Crater Block Forest, 3 km from the present dome. Ashy matrix of middle BAF deposit (upper part of the lower BAF deposit). Sample from unit N. |

^{*} See Fig. 2 of Sahetapy-Engel et al. (2014). Site numbers were assigned by author SS and Ian Nairn (e.g., Nairn et al., 2001).

and Wahanga domes (with Crater Dome being extruded before the intervening explosive phase), and were accompanied by extensive BAFs, and associated co-BAF ashfall deposits (Cole, 1970b; Nairn et al., 2001). These rhyolite dome lavas vary from pumiceous blocks of dome carapace to devitrified, massive grey lava exposed by the 1886 craters, located in the dome cores. The dome rock samples in this study derive from the Ruawahia and Wahanga domes (Fig. 1), which were erupted within approximately a four-year period (Nairn et al., 2001). The ash samples studied are from co-BAF and BAF deposits from Ruawahia and Wahanga domes. These deposits, which consist of blocks of lava with an ash matrix, and ash layers, primarily occur on the NW, NE and SE slopes of the Kaharoa complex (Ashwell et al., 2018; Nairn et al., 2001)(Fig. 1).

The Ruawahia dome is a high silica (~76 wt% SiO₂), high crystallinity (up to 65 vol%) dome consisting of several separate flow lobes which overtopped the pyroclastic cone produced during the initial explosive phases of the Kaharoa eruption (Ashwell et al., 2018; Leonard et al., 2002). The interior of the dome, exposed in the 1886 crater, has a low to moderate porosity (9 to 33 vol%), weak flow banding and is mostly devitrified (Ashwell et al., 2018). Contrasting with this is non-devitrified dome carapace on the outer edge of the dome, where porosity is higher (35 to 70 vol%) and outcrops exhibit numerous breadcrust surfaces and undeformed spherical vesicles (Ashwell et al., 2018). The contrast in dome textures and porosity on Ruawahia has been interpreted as being due to compaction and shearing processes in the dome core (Ashwell et al., 2015).

Wahanga dome, to the east of Ruawahia, likewise shows a denser, devitrified interior (with porosity ranging from 13 to 27 vol%, with an average of 19 %), which is surrounded by a more vesicular and undevitrified carapace (with porosity ranges from 34 to 37 vol%, with an average of 36 %). The dome interior is also exposed by the 1886 eruption, although the fissure only cuts through the outer edge of Wahanga, rather than through the centre (as at Ruawahia dome). Wahanga dome is considered "Tapu" (or sacred) by the Ngāti Rangitihi Iwi (who are the kaitiaki, or guardians, of Tarawera), so fieldwork on Wahanga dome was minimised to respect this status and the porosity data cited for Wahanga are from previously unpublished work (by author PA).

Early extrusion of lava dome lobes and spines was accompanied by gravitational collapse events (of the dome lobes/spines) which exposed the hot, pressurised interior of the dome. This resulted in re-vesiculation and cracking of the hot and pressurised interior and accompanying explosive decompression events (Ashwell et al., 2018; Fink and Kieffer, 1993). The resulting BAF deposits contain ash and lava blocks. The blocks show the same variation in porosity and facies as is observed in situ on the dome, showing that the BAF material is sourced from both the dome exterior and interior (Ashwell et al., 2018). The presence of non-deformed, vesicular lava that outcrops on the margins of Ruawahia dome indicates that small explosive collapse events occurred after the dome front had stopped moving (Ashwell et al., 2018). This suggests that the threat of an explosive dome collapse could exist beyond the period of active lava dome extrusion.

Regarding crystalline silica in the Tarawera Volcanic Complex, Cole (1970a) identified quartz, cristobalite and tridymite in the lavas. Quartz was identified as a phenocryst, while cristobalite was found within spherulites. Tridymite was identified as euhedral prismatic crystals, with wedge-shaped twinning, lining or filling vesicles in spherulitic rhyolite. Cole interpreted the tridymite to have been formed during reheating of the rhyolite by the 1886 basaltic intrusion.

Leonard et al. (2002) state that the Kaharoa rhyolites contain 5-17 vol% quartz. Farther north from Tarawera, in the Haroharo Volcanic Complex (HVC; still within the Okataina Volcanic Centre), several rhyolitic eruptions have occurred in the past 10 ka (Rotoma episode, 9.5 ka; Mamaku episode, 8.1 ka; Whakatane episode 5.6 ka). Smith et al. (2006) found that the Rotoma lavas contained up to 6 % quartz (based on our re-calculation of modal mineral percentages with average total crystal content of ~14 % in the lavas and pumices), up to 4 % in the Mamaku lavas and 8 % in the Whakatane lavas. The Rotoiti eruption in the HVC, which occurred around 50 ka, contained 5-10 % quartz (Smith et al., 2010). In the Taupo Volcanic Centre, the Oruanui eruption rhyolites (26.5 ka) are estimated to contain up to 2 % quartz (re-calculated from modal percentages with 5-10 wt% crystal content) (Wilson et al., 2006). However, quartz is not found ubiquitously in the New Zealand rhyolites. Little to no quartz has been found in the post-Oruanui (26.5 ka) eruptions of the Taupo Volcanic Centre (Ewart, 1963; Sutton et al., 2000). It should be noted that the above papers may have included all polymorphs of crystalline silica in their quartz calculations, depending on the identification and quantification methods used.

3. Methodology

3.1. Sample sourcing

Ash samples were either collected from field deposits by author CH



Fig. 1. Map of the Tarawera Volcanic Complex including the Kaharoa eruption lava domes (Tarawera, Ruawahia, and Wahanga), pyroclastic deposits and collection locations (stars) of samples used for this study. The map area is shown in the rectangle within the Taupo Volcanic Zone (denoted by dotted line) in the inset. Note that locations starting with K correspond to site numbers given in Tables 1 and 2. Samples of both ash and dome rock were collected at sites K253 (NZK_01, NZK_06, L1.12, L1.18), K630 (NZK_02, SS1) and K270 (NZK_05, SS4).

(as labelled in original sample names in Table 1), in February 2001, or were donated from the archives of GNS, New Zealand. All ash samples are interpreted to be derived from the Ruawahia dome, due to the samples' locations relative to the dome, except for NZK_04 which is from Wahanga dome. All ash samples are from co-BAF or BAF deposits (unit N), except for NZK_02 which is interpreted to be ash derived from a pyroclastic density current (i.e., co-ignimbrite ash from unit H) derived from an explosion through a pre-Kaharoa dome. Up to 100 g was collected or donated for each sample.

Dome rocks were collected by authors PA and SS, from the domes themselves and from BAF deposits, and are described in Table 2. Samples RW1.12, TP4.3, WH1.3, TP5.10, L1.12 and L1.18 were provided by author PA and are all derived from the Ruawahia or Wahanga domes (erupted during episode N). Samples SS1 and SS4 were provided by author SS. Sample SS1 is from unit H, to provide a comparison with ash sample NZK_02 and to give an example of the pre-unit N phase.

Site numbers correspond with Table 1 and were assigned by SS and Ian Nairn (e.g., Nairn et al., 2001).

3.2. Sample preparation

To prepare the ash samples for analysis, samples were weighed and then dried in an oven, in glass bowls, at 80–90 °C overnight and then weighed again. The samples were then sieved (Endecott stainless steel) into fractions of >2 mm, 1–2 mm and < 1 mm, and the weights of the sieved fractions recorded. The >2 mm fraction was not used in analyses, as it is larger than the defined size of volcanic ash (Rose and Durant, 2009). The dome rock was cut into thin sections and diamond polished.

3.3. Porosity and crystallinity measurements

Small (2.5 cm diameter and 5 to 10 cm length) cores were taken from dome samples RW1.12, TP4.3, WH1.3, TP5.10, L1.12 and L1.18, from which open porosity measurements were determined via a Quantachrome Ultrapycnometer 1000 with nitrogen gas. All mentions of porosity (including in Section 1) refer to measurements of open porosity. Visual estimates of area % for crystallinity and glass by light microscopy were performed on thin sections of RW1.12, L1.12 and L1.18. The porosity and crystallinity assessments are presented in Table 2 alongside sample information.

3.4. Scanning electron microscopy

Scanning electron microscopy with backscattered electrons (SEM-BSE) was used to image the morphology and investigate the chemistry of the crystalline silica in the thin sections from the eight samples of dome rock. Previous work has determined two key diagnostic methods for identifying cristobalite by textural observations and chemical analysis by Electron Probe Micro Analysis (EPMA), Raman spectroscopy and SEM. Using textural observations, large ($\sim 20 \ \mu m$ or larger) patches of cristobalite have a characteristic 'fish-scale' cracking which forms during the displacive transition from β to α cristobalite (Carpenter et al., 1998; Damby et al., 2014; Horwell et al., 2012; Horwell et al., 2013b). Using chemical analysis, Horwell et al. (2012) first showed that minor aluminium (Al) and sodium (Na) are present as structural substitutions of Al^{3+} and Na^+ for Si^{4+} in the crystal lattice in volcanic cristobalite (< 3 wt% Al by EPMA). This amount of Al is readily detectable by SEM-EDS, even though the Al peak may be poorly resolved, making it a reliable identifier to distinguish volcanic cristobalite from quartz where diagnostic 'fish-scale' cracking is not visible, for example due to the size of the crystal. Al and Na in volcanic cristobalite have since been measured in several studies (Damby, 2012; Horwell et al., 2013b; Schipper et al., 2015; Schipper et al., 2020) and in non-volcanic cristobalite (Nattrass et al., 2017; Nattrass et al., 2015) and it has become a reliable diagnostic tool.

Diamond polished, carbon coated thin sections were imaged using a Hitachi SU-70 field emission scanning electron microscope equipped with an Oxford Instruments INCA MicroAnalysis system for energy-dispersive X-ray spectroscopy (EDS) (Department of Physics, Durham University) at 15 kV and \sim 15 mm working distance. EDS point analysis was used to qualitatively determine the elemental composition (and, hence, inference of any structural substitutions) of the crystalline silica. EDS mapping was used to look at elemental distributions in the groundmass.

Table 2

Dome rock sample and site descriptions.

| Sample name | Dome | Sample collection location | Sample description |
|----------------|----------|--|--|
| RW1.12 | Ruawahia | Ruawahia dome, interior | Sample collected from exposed Ruawahia interior, close (0.5 m) to intrusion of 1886 basalt dyke. ~30 area % crystals (quartz, plagioclase and biotite), ~40 area % brown spherulites, ~20 area % glass and with low perceptive (0.0%) |
| TP4.3 | Ruawahia | Ruawahia dome, interior | Sample collected from the centre of the exposed interior of Ruawahia dome, with a porosity of ~20 %. |
| WH1.3 | Wahanga | Wahanga dome, interior/ carapace | Sample collected from Wahanga dome exposed in 1886 fissure; considered to be close to transition from carapace to interior. Porosity of 26 %. Glassy appearance. |
| TP5.10 | Wahanga | Wahanga dome, interior | Sample collected from centre of 1886 fissure cutting through Wahanga dome, and is part of the dome interior with a porosity of |
| L1.12 | Ruawahia | Site K253 | ~14 %. Devitrified appearance. Block from BAF deposit; textures of sample correspond to the interior of Ruawahia dome, with low porosity (~15 % porosity). No devitrification, with weak flow banding in glass from faint relict vesicles. Approx. 40 % area crystals (quartz, plagioclase, biotite and opaques) and 55 % area glass. Interpreted as having been ejected |
| L1.18 | Ruawahia | Site K253 | prior to devirtincation onset. Block from BAF deposit; textures of sample correspond to outcrops observed on the edge of Ruawahia dome, with no devirtification, and strong flow banding shown in flattened and aligned vesicles. Approx. 25 area % crystals (quartz, plagioclase, biotite and opaques), ~35 area % glass and ~ 40 % |
| SS1 | Ruawahia | Site K630 | porosity. A high porosity clast of dome material from unit H which is a pumiceous PDC deposit erupted before the main dome-forming phase; see NZK_02 for the fine ash- |
| SS4 | Ruawahia | Site K270 | fall equivalent. A breadcrust bomb from the BAF deposit at Ash Pit Road quarry (see NZK_05 ash sample). Representative of the early lava dome in Ruawahia crater that largely collapsed to form BAF deposits. |

3.5. X-ray diffraction

The abundance of crystalline silica as quartz, cristobalite and tridymite was quantified in four samples of volcanic ash (NZK_01, NZK_02, NZK_05 and NZK_06) and four samples of dome rock (RW1.12, TP4.3, WH1.3 and TP5.10) by XRD on a Bruker D8 Advance (Department of Chemistry, Durham University) using a parallel beam with fixed incidence angle ($6^{\circ} \theta$) and moving detector over the range 7–90° 2 θ (0.07° 2 θ step size) with CuKa radiation. Crystalline silica quantifications followed the Internal Attenuation Standard (IAS) method of Le Blond et al. (2009). This method allows for quantification of single phases without determination of bulk mineralogy. All samples were first finely-ground using an agate pestle and mortar. In-house standards for quartz, cristobalite, plagioclase (labradorite) and zinc oxide (the IAS) were analysed in duplicate for use in peak stripping and phase quantification. Crystalline silica data are the average of two separate quantifications. IAS technique error was determined to be +/-3 wt% (Le Blond et al., 2009).

3.6. Laser diffraction

Particle size distributions of the <1 mm ash fractions were determined by laser diffractometry, using a Beckman Coulter LS 13–320 Particle Size Analyser (Department of Geography, Durham University), with Fraunhofer optical model. The particles were first suspended in water, and ultrasonics used to aid aggregate dispersion. The data presented are the average of three runs. Only sub-1 mm particles were measured using the laser diffractometer to avoid damaging the instrument. The data were subsequently rescaled to incorporate the 1–2 mm fraction of the ash using the fraction weights measured after sieving, resulting in particle size distributions of 0.02–2000 μ m.

4. Results and discussion

4.1. Crystalline silica morphology and chemistry

SEM-BSE imaging of dome rock thin sections showed similar textures in six of the samples (SS1, SS4, L1.12, L1.18, TP4.3 and WH1.3). These samples were predominately composed of vesicles (some of which were stretched; SS4, TP4.3, WH1.3), supported by glassy groundmass containing phenocrysts and, in the one sample from unit H, microlites (SS1) (Fig. 2). The glass in all samples was pristine (not devitrified). These six samples likely represent the textures of the dome material close to the time of extrusion, due to their relative lack of compaction and complete lack of devitrification.

Embedded within the glass of these six samples were large (up to 500 µm) crystals, which appear darker grey by SEM-BSE. SEM-EDS analysis showed that these crystals were pure SiO₂ (Fig. 2A,B and Fig. 3A), which we interpret to be quartz. The quartz crystals are rounded and embayed, with some minor cracking (Fig. 2A,B), and are likely primary phenocrysts (which ascended with the lava, as also documented in Soufrière Hills, Montserrat dome rock; see Fig. 1A, Horwell et al., 2013b). As noted in Section 2, previous authors have identified quartz from New Zealand rhyolitic eruptions as part of the phenocryst assemblage. Whilst it is possible for quartz to form as a secondary phase in dome rock, via devitrification (Horwell et al., 2013b and demonstrated experimentally by Lofgren, 1971), previous textural descriptions (holes in the crystals, missing groundmass/diktytaxitic textures) related to secondary quartz in dome lavas at Soufrière Hills have indicated that extensive volatile flux or hydrothermal fluids may be required, which result in promotion of a reconstructive phase change from devitrification-generated cristobalite to quartz (see Fig. 1F in Horwell et al., 2013b). Such textures are not observed in these six pristine Kaharoa samples.

Whilst some of the vesicles were empty or had fragmented particles in them, some samples (and especially SS1 which was from unit H) had small ($<20 \mu m$) crystals protruding from some vesicles (shown for SS1 in Fig. 2C,D). Crystal morphology was difficult to discern in thin section, but some crystals appeared euhedral and SEM-EDS confirmed that these were likely to be cristobalite, due to the presence of small Al peaks in addition to Si and O (see Fig. 3B and Section 3.4). These crystals would have been likely formed by vapour-phase deposition, as documented at other dome-forming volcanoes (Damby, 2012; Horwell et al., 2013b; Schipper et al., 2015). Potassium feldspar crystals were also present in some vesicles (data not shown). Feldspar has been previously found as a vapour-phase mineral in dome lava vesicles and vapour-phase cristobalite is sometimes seen protruding from a bed of smaller vapour-phase feldspar crystals (Horwell et al., 2013b; Schipper et al., 2020).

The two other dome-rock samples – RW1.12 (Ruawahia) and TP5.10 (Wahanga) – have very different micro-textures from the other six samples observed by SEM, but are very similar to each other, and both have low porosity (9 and 14 vol%, respectively; Table 2). Quartz

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Fig. 2. SEM-BSE images of non-devitrified dome rock samples. Note differing scale bars on the images. A) Sample SS1 (from unit H) is highly vesicular, with large, embayed quartz crystals (as confirmed by SEM-EDS, see Fig. 3B)(see centre of image). The image shows some vesicles are filled with vapour-phase crystals (denoted by orange arrow), others appear to have broken particles inside (denoted by blue arrow), and others are empty. B) Sample TP4.3 (from unit N) is also vesicular, though denser, with many stretched vesicles. Quartz phenocrysts are common (as in the centre of image). As with sample SS1, vesicles either contain vapour-phase deposits, broken particles, or are empty. C) Zoomed image of SS1 showing a vapour-phase cristobalite crystal (centre of image, confirmed as cristobalite by EDS analysis, see Fig. 3B for example) and microlite textures in the glass. D) Higher resolution image of sample SS1 showing another vapour-phase cristobalite crystal in a vesicle. Note that the vesicle has a fractured wall. Small particles can be seen in a neighbouring pore. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

phenocrysts were present (e.g., Fig. 4B) but appeared less embayed than for the other six samples. Whilst the groundmass is porous in places (as can be seen in Fig. 4D,F), it is not clear if these spaces are original vesicles, due to their non-distinct shape. It is possible that the original porosity has been over-printed by compaction and then post-compaction corrosion of the groundmass by hot fluids or vapours (Horwell et al., 2013b; Schipper et al., 2015). Alternatively, or additionally, the spaces could be miarolitic cavities resulting from the volume change upon crystallization from glass, as described by Lofgren (1971), or may be the result of gas-driven filter pressing, where over-pressurised vapoursaturated melt is forced out from between microlite crystal boundaries, into vesicles, leaving behind diktytaxitic textures (interstitial cavities around plagioclase feldspar laths)(Kushnir et al., 2016).

Regarding identification of cristobalite in samples RW1.12 and TP5.10, three textures were associated with the presence of cristobalite: spherulites, tuffisite veins and groundmass. These are described below.

At low magnification, the groundmass of sample TP5.10 is organised into irregular-shaped patches (Fig. 4A,B) of up to 300 μ m diameter, surrounded by 'channels' which are sometimes infilled with vapourphase cristobalite (Fig. 4C). These pore-filling minerals could be the result of gas-driven filter pressing, as described by Kushnir et al. (2016). Sample RW1.12 displayed the same textures, but the patches were more corroded/diktytaxitic. Fig. 4A shows how the patches, themselves, sometimes appear to be organised around a central point. Fig. 4B, to the lower right of the quartz crystal, and the patches with linear textures in Fig. 5, show that the textures radiate outwards from central points in the patches. These features are, therefore, interpreted to be microspherulites, potentially with 'bow-tie' or 'orb' textures (Granasy et al., 2005; Lofgren, 1971), although we have not found similar textures in the volcanic literature with which to confirm this. However, this interpretation is in agreement with previous documentation that the Kaharoa dome interiors are spherulitic (Cole, 1970a; Cole, 1970b), as exposed by the 1886 Tarawera eruption craters.

At higher magnification (Fig. 5A) with SEM-BSE, the spherulitic patches have a speckled/dendritic texture (depending on orientation) of lighter grey material amongst darker grey material. The texture could be described as granophyric, although the term usually applies to threads of quartz in a base of feldspar (Lofgren, 1971) whereas, here, we believe the lighter grey 'threads' are potassium feldspar or feldspathic glass (Damby, 2012), and the darker grey base is cristobalite (since phases with higher mean atomic numbers appear brighter by BSE imaging). However, we were unable to differentiate the phases by semi-



Fig. 3. SEM-BSE images showing location of EDS point analysis (top) and accompanying EDS spectra (bottom). A) Large, embayed crystal from sample SS1. The spectrum shows only Si (right hand) and O (left hand) peaks and is interpreted as quartz. B) A small crystal inside a vesicle in sample SS1. The spectrum shows a dominant Si peak (to the right) with a small Al peak adjacent, to the left, which is typical of volcanic cristobalite (and O to the far left). C) A large patch with 'fish-scale' cracking from sample TP5.10 showing Al and Na peaks, in addition to Si and O, which are a key indicator of volcanic cristobalite. The C peak to the farthest left in both images is from the carbon coating on the thin section. Note differing scale bars on SEM-BSE images.

quantitative elemental mapping (SEM-EDS; Fig. 5B) at the scale of the texture. Such textures have previously been documented by Gardner et al. (2012), Damby (2012) and Castro et al. (2008).

Fig. 4E shows that there are areas (in both samples, but shown here for TP5.10) where large pores have been partially filled with vapourphase minerals, growing from the pore walls. Much of the infill is cristobalite (darker grey colouring and laminar or fan-shaped morphology, but without the wedge-shaped twinning typical of tridymite) but there are also 'sprays' of iron oxides (bright, white areas) and some potassium feldspar. Amongst the crystals are angular fragments; a highmagnification view of these (Fig. 4F) shows that these are composed of a mixture of phases resembling the surrounding groundmass, including the speckled texture of the spherulitic glass. The number and dense packing of these particles indicate that they were likely not formed during thin sectioning. This texture is interpreted to be a tuffisite (ash-filled crack that forms in and around volcanic conduits and domes; Gardner et al., 2018; Sparks, 1997; Wadsworth et al., 2022), similar to those observed in other lava dome samples (e.g., Kendrick et al., 2016).

Larger (>50 μ m), dark grey patches within the groundmass (in Figs. 3C, 4D and 5A) were confirmed as cristobalite by textural identification of fish-scale cracking and elemental analysis showing Si, O & Al (with some Na; Fig. 3C), as has been previously observed at other dome-forming volcanoes (Damby, 2012; Horwell et al., 2013b; Martel et al., 2021; Schipper et al., 2015). Due to the lack of original vesicles and loss of groundmass, there is insufficient context to determine if this cristobalite is due to vapour-phase growth or complete devitrification of glass.

Samples RW1.12 and TP5.10 are the only two samples to display spherulitic and highly devitrified textures. As will be seen in Section 4.2, these are also the two samples with substantial cristobalite contents (Table 3). Spherulitic textures have been shown to develop on a timescale of weeks to months at, or just under, glass transition temperatures (Befus et al., 2015; von Aulock et al., 2013). Therefore, if portions of the dome cool very quickly (or collapse very soon after emplacement), devitrification and spherulite textures will not develop. We therefore suggest that these two samples were exposed to prolonged high temperatures in the core of the dome, allowing substantial cristobalite formation through glass devitrification and spherulite formation.

To note, both samples were situated very close to the intrusion of the 1886 basaltic dyke (Fig. 1): RW1.12 was within a few metres in the

Ruawahia dome and TP5.10 was likely within 10s of metres, based on where the dyke is preserved in the Wahanga crater. Previous work has shown that temperatures at the dyke were sufficiently hot to remelt the rhyolite immediately adjacent (within \sim 1 m) to the dyke (Kennedy et al., 2010; Schauroth et al., 2016). However, Cole (1970a) observed that tridymite was present in Kaharoa dome lavas which had been reheated by the 1886 dyke. We did not observe tridymite in our devitrified samples (by SEM or by XRD; see Section 4.2), so we infer that the formation of spherulites happened within the Kaharoa eruption and not as a result of later reheating. In support of this, there are many other examples of rhyolitic spherulitic domes around the world which formed without a later dyke intrusion (e.g., Gardener et al. 2012), although these tend to be obsidian domes, which the Kaharoa domes are not.

4.2. Crystalline silica abundance

Crystalline silica was quantifiable in all the ash and dome samples analysed, in the form of quartz and/or cristobalite (Table 3). No tridymite was measured in any sample. The amount of quartz was within a similar range for both ash and dome samples, ranging from 5.7 to 12.5 wt% in the ash samples and 4.1–10.4 wt% in the dome samples, which is in line with the quantities found by Leonard et al. (2002)(5–17 vol%). The amount of cristobalite in dome rock was essentially binary: either below quantifiable or ~ 25 wt% (24.7 wt% for RW1.12; 27.3 wt% for TP5.10). In the dome samples with below-detection quantities of cristobalite, the amount of quartz was also less; with the low number of samples analysed, we were not able to discern a reason for this.

The ash samples contained 1.3–3.7 wt% cristobalite. Overall, the two cristobalite-rich dome rock samples had the most total crystalline silica – 32.4 and 37.7 wt%, versus 8.6–14.1 wt% in the ash samples. There have not been many rhyolitic eruptions in recent years where quantification of crystalline silica has been conducted, but dome-collapse ash from the 2008 eruption of Chaitén (Chile) contained 14–19 wt% cristobalite and only 1–2 wt% quartz (Horwell et al., 2010a).

Presuming that the co-BAF/BAF ash was derived solely from dome rock, rather than also including contributions from magmatic explosions (which are not known to have occurred after dome growth onset), the ash samples from these co-BAF/BAF deposits (NZK_01, 05–06) indicate that little cristobalite was generated within these particular dome



Fig. 4. SEM-BSE images of cristobalite-rich dome rock samples. Note various scale bars in different images. A) Low magnification image of sample TP5.10 showing distinct patches of groundmass characterised by radial, linear or speckled devitrification textures (dependent on orientation of growth axes)(also observed in sample RW1.12). B) A quartz phenocryst (labelled Qtz) embedded within the devitrified groundmass of sample TP5.10. C) The pathways between some devitrified patches are filled with vapour-phase cristobalite (shown here for sample TP5.10 with label 'Cri' and 'fish-scale' cracking). D) Large patches of 'fish-scale' cristobalite are seen in the groundmass of sample RW1.12 (with label 'Cri'; also observed in sample TP5.10). E) Image of a pore infilled with vapour-phase crystals (sample TP5.10). Bright areas are iron oxides. Amongst the crystals are fragmented particles. F) A high-magnification image of the fragmented particles (sample TP5.10) shows that they are composed of the surrounding groundmass, with discernible spherulitic textures (i.e., those observed in images A–C) in some larger (>10 μm) particles.

segments prior to their collapse. Dome-block samples L1.12 and L1.18 were collected from the same BAF deposit as NZK_06 (and are part of the same section as the co-BAF deposit where NZK_01 was sampled). Although crystalline silica content was not analysed in these blocks by XRD, SEM observations of thin sections (Section 3.1) showed that they were not devitrified and were cristobalite-poor. Based on the porosity data (Table 2), L1.12 (15 vol% porosity) was from the Ruawahia interior whereas L1.18 (40 vol% porosity) was from the carapace. Therefore, we can conclude that these co-BAF/BAF ash samples were all derived from dome collapses where the dome interior had not yet devitrified (i.e., a short duration between extrusion and collapse) and/or from the carapace, where temperatures were too cool for cristobalite to form. A short interval between extrusion and collapse may possibly be due to a rapid extrusion rate resulting in unstable lobes (as argued for the Soufrière

Hills volcano, Montserrat in Horwell et al., 2014).

The fact that ash sample NZK_02 (interpreted as being generated in an explosion prior to the unit N co-BAF ash) contains a similar amount of cristobalite to NZK_01 and twice as much as NZK_05 and 06 suggests that these explosions may have disrupted and incorporated parts of a preexisting dome (or shallow conduit plug). Dome rock sample SS1 was collected from the same location (from the PDC deposit rather than the co-ignimbrite ash deposit); SEM observations (Section 4.1; Fig. 2) confirm that this block has the textures of a vesicular dome rock, including some vapour-phase cristobalite. This lends weight to the suggestion that there were previous domes present.

Higher cristobalite contents of ash than observed in this study could potentially be found in co-BAF ash if a dome collapse occurred after a prolonged period of dome growth and stability, thereby allowing time



Fig. 5. A) SEM-BSE image and B) overlain, composite EDS elemental map of an area of sample TP5.10. Gold = Si; Pink = K, Al, Si; Blue = Na, Al, Si. The Si-rich gold areas correspond with patches of 'fish-scale' cristobalite (to the right and bottom of the image) and the prevalence of cristobalite throughout the devitrification patches. The pink areas are interpreted as either K-rich glass or feldspar. The blue areas are interpreted to be either residual Na-rich glass or vapour-phase feldspar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Weight percentage of crystalline silica phases cristobalite and quartz in Kaharoa ash (NZK samples) and dome rock samples. BLQ indicates below the limit of quantification by the XRD-IAS method (< 1 wt%).

| Sample name | Cristobalite (wt %) | Quartz (wt %) | Total crystalline silica (wt %) |
|----------------|------------------------|------------------|------------------------------------|
| Ash | 0.7 | 0.5 | 10.0 |
| NZK_01 | 3./ | 9.5 | 13.2 |
| NZK_02 | 3.2 | 5.7 | 9.0 |
| NZK_05 | 1.6 | 12.5 | 14.1 |
| NZK_06 | 1.3 | 7.4 | 8.6 |
| Dome rock | | | |
| RW1.12 | 24.7 | 7.7 | 32.4 |
| TP4.3 | BLQ | 5.2 | 5.2 |
| TP5.10 | 27.3 | 10.4 | 37.7 |
| WH1.3 | BLQ | 4.1 | 4.1 |

for devitrification in the dome interior. This is substantiated by the abundant cristobalite in dome blocks RW1.12 and TP5.10 (24.7 and 27.3 wt%, respectively), both highly devitrified dome interior samples. The other two samples (TP4.3 and WH1.3, from Ruawahia and Wahanga domes, respectively) had undetectable quantities of cristobalite because they were not devitrified. The range in cristobalite quantities in the Kaharoa dome rock (0–27 wt%) reflects the full range of cristobalite values observed in the lava of other dome-forming volcanoes (Boudon et al., 2015; Damby, 2012; Horwell et al., 2023).

In general, lava domes exhibit higher porosity in the carapaces and lower porosity in the interiors (e.g., Dadd, 1992; Fink et al., 1992), a pattern also observed at Tarawera (Cole, 1970a; Ashwell et al., 2018). The two dome samples with undetectable cristobalite (TP4.3 and WH1.3) have 20 and 26 vol% porosity, respectively (Table 2). Although WH1.3 was collected from the Wahanga dome interior, it was sampled from a location close to the carapace. TP4.3 was collected from the Ruawahia dome interior but is not devitrified. Conversely, the two samples with substantial cristobalite (RW1.12 and TP5.10) have 9 and 14 vol% porosity, respectively, and were collected near the core of the domes. This localization of the low-porosity, cristobalite-rich samples in the compacted dome interior supports the theory that thermodynamic conditions in the interior were appropriate for cristobalite formation (Horwell et al., 2013b; Kushnir et al., 2016). The lack of cristobalite in high-porosity TP4.3 may result from the adjacent portion of the dome collapsing, thereby exposing and cooling this interior segment, before devitrification occurred. Similar to WP1.3, TP4.3 may also have been located some distance from the most interior part of the dome. In addition to potentially cooling more quickly to below optimal spherulite formation temperatures, it is possible that these 'distal' dome segments were (partially) isolated from circulating gases and vapours that can

promote cristobalite formation/deposition. This may happen by restriction of permeable networks by interior compaction and fracture healing (Ashwell et al., 2015; Cabrera et al., 2011), filling and closure of cracks with sintered pyroclastic material (i.e., tuffisites, see Section 4.1), and/or growth of vapour-phase crystals within vesicles, which may reduce permeability (Boudon et al., 2015; Horwell et al., 2013b). Evidence of vapour-phase crystallization was seen in some dome rock samples (see Section 4.1).

Given that the quartz in the samples is likely magmatic in origin, rather than from alteration of glass or cristobalite in the domes (see Section 4.1), the variation in quartz concentrations in the ash (7.4-12.5 wt% in unit N samples) suggests that there were variations in the crystal content throughout the episode which formed unit N and/or that there was physical fractionation in the BAFs and co-BAF plumes, resulting in variability of the componentry in the final ash deposits, as previously observed in Soufrière Hills ash deposits (Horwell et al., 2001). Although these lava samples are from two different domes, so some variation in magmatic composition and/or crystallization histories might be expected, Nairn et al. (2001) conducted X-ray fluorescence (XRF; major elements) on samples from the Ruawahia and Wahanga domes and found SiO₂ concentrations of 77 wt% and 76 % (whole rock; recalculated to 100 % for loss on ignition), respectively, indicating no substantial difference in magmatic composition. Leonard et al. (2002) measured bulk compositions of Kaharoa ash and dome rock by XRF and found the SiO₂ content of dome rock (whole rock) to be 75-76 wt% (5 samples) and ash to be 73-75 wt% (3 samples), suggesting some minor fractionation as the ash dispersed, although the dome origins for the samples are not described.

The total crystalline silica content of the ash and dome samples with almost 40 wt% in one dome sample - indicates that future Kaharoastyle rhyolitic eruptions in New Zealand have the potential to produce ash containing large quantities of total crystalline silica. If dome collapses happen soon (within days) after lava emplacement, then quantities of cristobalite are likely to be low, as discussed, but fractured quartz phenocrysts may pose a considerable hazard given that quartz does not contain the same structural impurities as cristobalite (Deer et al., 1996; Horwell et al., 2012) that may mitigate toxicity. This was evidenced for Kaharoa quartz, which was pure SiO₂ by SEM-EDS (see Section 4.1, Fig. 2A for an example). Quartz is only found in substantial concentrations in some highly silicic (rhyolitic) eruptions (and note that it was not abundant in the Chaitén eruption ash; Horwell et al., 2010a), so is not usually considered as a respiratory hazard in most eruptions. However, as discussed in Section 2, quartz is ubiquitous in the Okataina Volcanic Centre rhyolitic eruptions.

4.3. Particle size analysis

The particle size data are shown as cumulative volume percent (vol

%) of health-pertinent fractions, in Table 4, in accordance with previous studies (e.g., Damby et al., 2017; Horwell et al., 2013a; Horwell et al., 2023). The particle size distributions varied amongst the six ash samples. The sub-4 μ m fraction ranged from 1.3 to 8.1 vol% and the sub-10 μ m fraction ranged from 1.7 to 15.6 vol%. Sample NZK_01 (co-BAF sample) was particularly fine grained, containing 53.8 vol% sub-100 μ m particles compared to 20.7–40.4 vol% for the other samples.

These samples are coarser when compared with the particle size distributions measured for samples from some other dome-collapse eruptions, globally. For example, ash from dome collapses at Chaitén volcano (2008, rhyolitic eruption) contained 18–40 vol% sub-10 μ m material (Horwell et al., 2010a), ash from Soufrière Hills collapses (1999 and 2003, andesitic eruptions) contained ~23 vol% sub-10 μ m material (Horwell, 2007) and ash from Merapi (1998, basaltic andesite) contained 27 vol% sub-10 μ m material (Horwell, 2007). The comparatively low concentrations of sub-10 μ m particles in the Kaharoa samples could be a function of distance from vent or plume dispersal axis (Bonadonna et al., 2005) or be related to the size of the collapse events, whereby the energy involved in the collapses was insufficient to pulverise the dome rock into finer material (Damby, 2012). However, all the collapses were sufficiently large to generate substantial ash deposits that were retained in the stratigraphy of our sample locations.

It is notable that there is no clear difference between the particle size distributions of the ash sample from the co-ignimbrite deposit (NZK_02) and the co-BAF and BAF samples, except NZK_01 which was substantially finer than the other samples. This also indicates that all of these events were relatively small, low energy events. Vulcanian explosions at Soufrière Hills volcano generally generated less respirable ash than dome collapse events (Horwell, 2007; Horwell et al., 2003).

One concern with analysing ash that was not collected at the time of deposition is that erosional processes (wind and water) can winnow fine ash, leaving a non-representative particle size distribution. Several studies have shown that there is a strong linear relationship between the smaller health-pertinent size fractions (e.g., quantity of sub-10 μ m material vs. quantity of sub-4 μ m material, which approximates a 2:1 ratio) in pristine ash samples, and a polynomial relationship between the larger and smaller health-relevant fractions (e.g., sub-63 μ m and sub-4 μ m) (Hillman et al., 2012; Horwell, 2007; Horwell et al., 2013a supp. Matt.; Horwell et al., 2010b). For the <10 vs. <4 μ m relationship, a deviation from the 2:1 ratio, might indicate a change from the original particle distribution.

Fig. 6 shows four correlations of different size fractions. The smallest fractions (<10 vs. <4 or < 2.5 μ m) have strong linear correlations (R² = 0.99 for both), as is expected from these fractions, which are closely related in mass and dispersion characteristics. The ~2:1 relationship is observed for the <10 vs. <4 μ m linear regression (slope of 0.49), indicating that the size distributions of the ash samples may not have changed since deposition. However, a polynomial fit for both the <100

Table 4

Cumulative volume percent (vol%) of respiratory health-pertinent size fractions for ash samples. Data are the average of three analyses, with standard deviations in round brackets.

| Sample name | Deposit type | $<1\ \mu m$ | <2.5 μm | $<4\ \mu m$ | ${<}10\;\mu m$ | <100 µm |
|----------------|-------------------|---------------|---------------|---------------|----------------|----------------|
| NZK_01 | Co-BAF | 1.9 (0.04) | 5.4 (0.13) | 8.1 (0.18) | 15.6 (0.32) | 53.8 (1.62) |
| NZK_02 | Co- ignimbrite | 1.5 (0.03) | 3.5 (0.05) | 4.9 (0.07) | 9.5 (0.14) | 40.4 (0.49) |
| NZK_03 | Co-BAF | 0.6 (0.11) | 1.1 (0.06) | 1.3 (0.06) | 1.7 (0.05) | 22.2 (4.41) |
| NZK_04 | BAF | 0.8 (0.08) | 2.2 (0.29) | 3.2 (0.44) | 6.1 (0.88) | 20.7 (3.09) |
| NZK_05 | Co-BAF | 0.8 | 2.3 | 3.4 (0.26) | 6.5 (0.50) | 24.0 |
| NZK_06 | BAF | 0.8 (0.02) | 2.1 (0.07) | 3.1 (0.09) | 5.8 (0.91) | 23.0 (0.17) |

vs. <4 and < 10 μ m fractions results in R² = 1 only when sample NZK_03 is excluded, which sits notably below the best fit curve (at ~1.5 vol% for sub-4 and 10 μ m compared to ~3 vol% and 6 vol%, respectively, for the other samples with similar quantities of sub-100 μ m material; samples NZK_04–06, as plotted in Fig. 6), indicating this sample may have lost fines. Sample NZK_03 had the lowest amount of sub-4, 2.5 and 10 μ m material but this did not adversely affect the linear relationships. The cumulative particle size distributions indicate that sample NZK_03 is depleted in particles under ~400 μ m compared to the other samples (not shown). Field observations (Table 1) indicated that this sample was likely a reworked deposit, and this is corroborated by the particle size data. The other five ash samples appear not to have undergone any reworking or winnowing since their deposition, so their particle size distributions are unlikely to have been altered and the data are, therefore, reliable.

5. Implications of hazard assessment and conclusions

This is the first study to investigate the crystalline silica respiratory hazard from a dome-forming eruption in New Zealand. The investigation focused on the rhyolitic lava domes generated during the 1315 CE Kaharoa eruptions of Tarawera volcano and involved a detailed petrological investigation to understand the formation mechanisms of the crystalline silica which, in turn, influences the respiratory hazard.

We found that quartz is abundant as a magmatic phenocryst, and substantial cristobalite was found as a secondary phase, only in devitrified samples. No tridymite was identified. In the two devitrified dome samples, more than 30 wt% crystalline silica (quartz and cristobalite combined) was found, representing a substantial hazard for local communities if this part of the dome had collapsed at the time (or any time after). As with all recent studies conducted on volcanic cristobalite (and some on other sources of cristobalite, e.g., diatomaceous earth; Nattrass et al., 2015), the cristobalite was found to contain structural substitutions of Al and Na (Horwell et al., 2012). Although Nattrass et al. (2017) were able to show that such structural substitutions did reduce the toxicity of synthetic cristobalite in *in vitro* laboratory experiments, we cannot be sure that this transfers to human exposures, and further work is required before this could be factored into a health impact assessment (Mueller et al., 2020).

The location of lava within the dome structure plays a fundamental role in the presence and quantity of cristobalite at Tarawera, with some of the comparatively dense, compacted lava samples from closest to the core of the Ruawahia and Wahanga domes containing abundant cristobalite (up to \sim 27 wt%), created via devitrification, vapour-phase deposition and spherulite formation, whereas the less dense, non-devitrified lava located closer to the carapace contains little to no cristobalite. Cristobalite is also not present in non-devitrified dome core samples; we interpret that this is likely due to rapid cooling of this dense dome portion, possibly due to collapse of an adjacent dome lobe, preventing devitrification. We also interpret that the ash analysed for this study was derived predominantly from the collapse of non-devitrified dome lobes, given the low concentrations of cristobalite in the samples.

The results indicate that future Tarawera dome forming eruptions would be capable of forming substantial cristobalite (as also seen at other dome-forming volcanoes) and, with the addition of considerable magmatic quartz (which is unusual with less silicic eruptions, generally), such rhyolitic dome-forming eruptions could present a substantial respiratory hazard. The hazard, itself, depends on whether and which dome portions are disrupted and, hence, whether crystalline-silica rich ash is generated, as well as how much respirable-sized material is produced (see below). Partial dome collapses of carapace and other material close to the dome exterior, or of young lobes, may result in BAFs and co-BAF plumes with relatively low crystalline silica contents (as seen in this study). Explosive magmatic eruptions which disrupt an existing dome (and dilute the amount of crystalline silica due to the fresh magma component) may also result in low crystalline silica contents, as



Fig. 6. Comparison of particle size data for Kaharoa ash samples. Note that NZK_03 data are not included in the fits for <100 vs. <4 µm and <100 vs. <10 µm fractions and are plotted separately.

hypothesised for the co-ignimbrite ash sample analysed here. However, large or wholesale collapses which remove devitrified dome-core material may result in fine-grained (respirable) ash deposits that are far richer in crystalline silica than seen in this study.

The amount of respirable (sub-4 μm) material found in the ash deposits is not as high as in some dome-collapse ash, globally, perhaps indicating that the collapses which formed them were relatively small/low-energy events, but experiences from around the world indicate that more respirable material is a possibility, especially from larger collapses. However, if a future Kaharoa-style eruption generated similar sized events, the respiratory health risk would likely be confined to those living closest to the eruption and the risk would depend on frequency of dome collapses and ash generation. Real-time air quality monitoring of the fine particle fractions (usually sub-10 μm and sub-2.5 μm) would provide a first step towards the assessment of health risk to these communities, as well as frequent assessments of crystalline silica concentrations in the ash.

To summarise, a future rhyolitic eruption of the Tarawera Volcanic Complex is likely to generate crystalline silica-rich ash. Magmatic explosive ash, and ash from the collapse of non-devitrified dome portions will contain quartz, and dome-collapse ash from devitrified portions will likely include substantial quantities of additional cristobalite. This information may inform disaster management planning, including efforts to monitor air quality and crystalline silica concentrations in the ash, and the need for further respiratory health risk assessments.

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CRediT authorship contribution statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The varied data in this paper are not easily uploadable to an online repository so will be made available on request to the corresponding author.

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