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SHORT SCIENTIFIC COMMUNICATION

Cristobalite in a rhyolitic lava dome: evolution of ash hazard

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Abstract Prolonged and heavy exposure to particles of respirable, crystalline silica-rich volcanic ash could potentially cause chronic, fibrotic disease, such as silicosis, in individuals living in areas of frequent ash fall. Here, we show that the rhyolitic ash erupted from Chaitén volcano, Chile, in its dome-forming phase, contains increased levels of the silica polymorph cristobalite, compared to its initial plinian eruption. Ash erupted during the initial, explosive phase (2–5 May 2008) contained approximately 2 wt.% cristobalite, whereas ash generated after dome growth began (from 21 May 2008) contains 13–19 wt.%. The work suggests that active obsidian domes crystallise substantial quantities of cristobalite on time-scales of days to months, probably through vapour-phase crystallisation on the walls of degassing pathways, rather than through spherulitic growth in glassy obsidian. The ash is fine-grained (9.7–17.7 vol.% <4 µm in diameter, the respirable range) and the particles are mostly angular. Sparse, fibre-like particles were confirmed to be feldspar or glass.

Keywords Rhyolite · Dome · Cristobalite · Ash · Health · Hazard · Obsidian

Introduction

Prolonged and heavy exposure to fine, crystalline silica-rich volcanic ash particles could potentially cause chronic, fibrotic disease, such as silicosis, in vulnerable individuals (Horwell and Baxter 2006). Cristobalite is the silica polymorph of prime concern as it may crystallise, post-extrusion, in volcanic lava domes, filling cracks and vesicles, so that it becomes a major mineral phase (up to 12 wt.%). This concern primarily relates to andesitic/dacitic eruptions where cristobalite crystallises in porphyritic domes by vapour-phase deposition and devitrification of glass (Baxter et al. 1999), although it may also be found as an alteration product in old volcanic edifices (Getahun et al. 1996). In rhyolitic, obsidian (glassy) domes, cristobalite is observed in spherulites which slowly nucleate from glass (Swanson et al. 1989; Watkins et al. 2009), but it is not known whether rapid, large-scale cristobalite formation is also possible through vapour-phase deposition in cracks, as with their andesitic/dacitic counterparts.

Rhyolitic eruptions are relatively rare, and the eruption of Chaitén volcano, Chile, (from 2 May 2008 to present) provides the first opportunity to determine whether active rhyolitic domes form substantial cristobalite and could therefore potentially pose a health hazard as in the andesitic eruption on Montserrat (Hincks et al. 2006; Horwell and Baxter 2006). Initial explosions, through a vent in an

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ancient (approximately 9.3 ka B.P. (Naranjo and Stern 2004)) rhyolitic lava dome, generated ash which fell across Patagonian Chile and Argentina with local towns being temporarily evacuated (e.g. Futaleufú) or abandoned (e.g. Chaitén village). By 21 May, lava dome growth had commenced and is ongoing (at time of press).

Sample collection

A suite of ash samples were collected, deposited from the initial explosive eruption (2–5 May 2008) and thereafter following collapses of the new dome (August 2008, January 2009 and February 2009; Fig. 1 and Table 1). All samples were dried in an oven at 80°C for at least 12 h. Samples were then sieved (Endecott stainless steel sieves) through 1- and 2-mm sieves to remove non-ash-grade particles. In all cases, there were no particles >1 mm in diameter.

Crystalline silica quantification

A key parameter of silica toxicity assessment, in both occupational and environmental settings, is the accurate quantification of the silica polymorphs present in the dust. For heterogeneous ash samples, this has been challenging (Baxter et al. 1999; Horwell et al. 2003), primarily because of the overlap in the major cristobalite and plagioclase feldspar peaks in the X-ray diffraction (XRD) pattern, but recent innovations in XRD methodology now allow rapid, accurate quantification (Le Blond et al. 2009).

Using the Internal Attenuation Standard (IAS) method of quantification with XRD-static Position Sensitive Detection (sPSD; see Supplementary Information and Le Blond et al. 2009), we find that ash erupted explosively contained little cristobalite (approximately 2 wt.% except one sample with 7.4 wt.%), whereas ash erupted following collapse of the new dome contained 13.9–19.0 wt.% cristobalite (Fig. 2 and Table 2). We hypothesise that the ash from the initial explosions was generated from fresh magma and/or conduit material with minor incorporation of the ancient dome, with cristobalite therefore being sourced from the altered conduit or ancient dome material. The high cristobalite content measured in the ash erupted following onset of new dome growth suggests that the rhyolitic dome formed cristobalite in substantial quantities. By mid-August 2008, 3 months after dome growth began, cristobalite content was already approximately 16 wt.% of the ash, indicating that cristobalite crystallisation is rapid. Quartz observed in the samples is likely to have a magmatic origin, with little variation amongst the samples (0.6–2.3 wt.%); tridymite was not identified.

For comparison, we also used the IAS XRD-sPSD method to test cristobalite contents in ash produced after two lava dome collapses, and a series of vulcanian explosions at the andesitic Soufrière Hills volcano, Montserrat. The dome-collapse samples contained 12–15 wt.% cristobalite, and the vulcanian explosion sample contained 8.6 wt.%, not dissimilar to Chai_02 (Table 2). Horwell et al. (2003) found that the respirable fractions of ash (<4 µm aerodynamic diameter), which can reach the alveolar region of the lung where pathogenic reactions would be triggered, were enriched in crystalline silica in comparison to the coarser fractions (e.g. for sample MRA5/6/99, 30% of <1 µm fraction (by number of particles) was crystalline silica compared with 10 num.% for the >4 µm fraction). The actual quantity of cristobalite in the respired ash may, therefore, be greater than the proportions from bulk samples reported here.

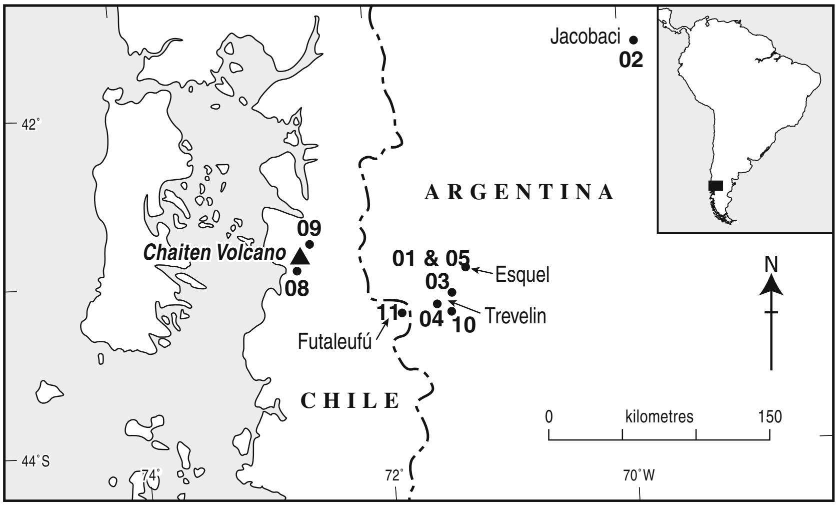

Fig. 1 Location of collection of samples in relation to Chaitén volcano

Table 1 Information on the samples

Sample number	Eruption date	Collection date	Location	Grid reference	Distance from volcano (km)	Contamination/ precipitation
Chai_01[a]	2 May 2008	8 May 2008	Esquel, Argentina	42°54′51″S 71°19′8″W	103	No
Chai_02[a]	2 May 2008	6 May 2008	Jacobacci, Argentina	41°33′31″S 69°52′87″W	307	No
Chai_03[a]	2 May 2008	8 May 2008	Trevelin, Argentina	43°04′37″S 71°27′46″W	80	No
Chai_04[a]	2 May 2008	8 May 2008	Trevelin, Argentina	43°08′21″S 71°34′03″W	80	No
Chai_05[b]	2 May 2008	10 May 2008	Esquel, Argentina	42°54′38.68″S 71°19′38.14″W	108	No
Chai_08[c]	13 Aug. 2008	13 Aug. 2008	Near Chaitén airport, Chile	42°55′63.7″S 72°41′80.10″W	12	No
Chai_09[d]	17,18 or 19 Jan. 2009	21 Jan. 2009	Near Chaitén village, Chile[f]	42°78′28.28″S 72°59′87.79″W	7	No
Chai_10[e]	19 Feb. 2009	21 Feb. 2009	Esquel region Argentina	43°11′23.26″S 71°28′19.40″W	103	?
Chai_11[c]	19 Feb. 2009	20 Feb. 2009	Futaleufú, Chile	43°11″06″S 71°52′10″W	75	No

Samples supplied by:

[a] SEGEMAR, Argentina (Patricia Sruoga)

[b] Local government offices in Esquel, Argentina (Veronica Botto)

[c] SERNAGEOMIN, Chile (Luis Lara)

[d] Costanza Bonadonna, Université de Genève

[e] Gustavo Villarosa, Universidad Nacional del Comahue, Argentina

[f] Chai_09 specific location: beginning of the Sendero Muichinmahuida trail leading to the Muichinmahuida Glacier

Morphology, grain size and composition

Grain size analysis (using the methodology of Horwell 2007 on the Malvern Mastersizer 2000 with Hydro MU attachment at the Department of Geography, Cambridge University, UK) confirmed that the Chaitén samples have abundant respirable material (8.8–17.7 vol.% <4 µm diameter; Table 2) with sample Chai_09 being particularly fine. Horwell (2007) noted that ash generated in dome-collapse eruptions seems to be as fine, if not more so, than ash generated in plinian explosive eruption columns. X-ray fluorescence (XRF; PANalytical Axios Advanced XRF spectrometer at the Department of Geology, University of Leicester, UK) confirmed that all Chaitén samples are rhyolitic (72.6–74.9 wt.% SiO_2).

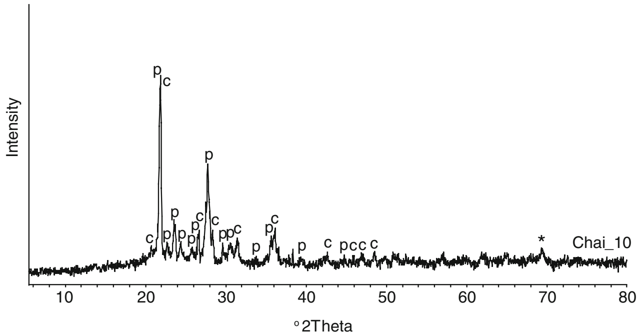

Fig. 2 X-ray diffraction pattern for Chai_10, with the main peaks for cristobalite (*c*) and plagioclase feldspar (*p*, labradorite) labelled. The peak labelled by *asterisk* is a detector glitch (artefact from a damaged channel in this particular detector)

Field emission scanning electron microscopy (FE-SEM; Philips XL-30 at the Natural History Museum, London, UK) observations confirmed that the general morphology of the ash was similar to previously observed volcanic ash samples (as discussed in Horwell and Baxter 2006). The ash particles are angular, with fractured surfaces, being composed of glass and fragmented crystals. Figure 3a shows a typical view of very fine-grained particles in sample Chai_04. Many of the particles are <1 µm in diameter. In addition to the angular particles, we occasionally observed fibre-like particles (e.g. Fig. 3b). The dimensions of these particles conform to the WHO definition for fibres (>5 µm length, <3 µm diameter with 3:1 aspect ratio; World Health Organisation 1986), but they are needle-like (acicular) single crystals rather than bundles of fibres which separate into individual fibrils (asbestiform or fibrous habit). The largest needle imaged was approximately 15 µm along the longest axis, and the smallest was approximately 2 µm. The short axis was usually between <0.2 and 0.8 µm in diameter. Most of the fibre-like particles were lath-shaped with occasional, longer, cylindrical particles. The samples did vary in the number of fibre-like particles that could be found by SEM. It was easiest to locate the needles in Chai_08 sample, although they were still scarce. Elemental analysis (SEM-energy dispersive spectroscopy (EDS) on a LEO 1455VP with EDS Oxford Inca software at NHM, London, UK) showed that the majority were composed of Si>Al>Na, K

Table 2 Quantification of crystalline silica by the Internal Attenuation Standard method with X-ray diffraction with static position sensitive detection and grain size results from Malvern Mastersizer analyses (average of three tests)

Sample	Cristobalite (wt.%)	Quartz (wt.%)	<4 μm material (cumulative vol.%)	<10 μm material (cumulative vol.%)
Chai_01	2.2	0.7	9.71	20.23
Chai_02	7.4	1.9	10.73	21.60
Chai_03	2.8	0.6	11.93	24.35
Chai_04	2.4	0.8	8.73	18.13
Chai_05	2.8	0.6	10.32	21.39
Chai_08	16.2	2.3	11.39	21.66
Chai_09	13.9	1.4	17.65	39.63
Chai_10	19.0	2.0	12.68	26.43
Chai_11	17.1	1.2	11.07	24.78
Mon5/6/99[a]	15.2	1.2	10.70[b]	23.10[b]
Mon12/7/03[a]	11.9	1.6	11.47[b]	22.49[b]
MonExp[a]	8.6	0.9	5.90[b]	13.40[b]

XRD errors are ±3 wt.%

[a] Bulk ash samples from the Soufrière Hills volcano, Montserrat. *Mon5/6/99* erupted in a dome-collapse event on 5 June 1999. *Mon12/7/03* erupted in a dome-collapse event on 12 July 2003. *MonExp* is a composite of vulcanian explosion ash deposits erupted between 25 Sep. 1997–6 Oct. 1997

[b] Data from Horwell (2007)

and Ca, indicating that they are glass or feldspars (Fig. 3b inset; in this spectrum the Al peak is relatively large, indicating a feldspar; other needles produced spectra with reduced Al and raised K, which is interpreted here, and in the SEM-EDS spectra of Horwell et al. (2003), as volcanic glass).

Discussion

The similarity in cristobalite content of the Chaitén and the Soufrière Hills dome-collapse ash suggests that the mechanism of cristobalite formation may be similar. This is backed up by visual observations of the Chaitén obsidian which is glassy, crystal-poor, vesicle free and fractured (Luis Lara, SERNAGEOMIN, personal communication), indicating that cristobalite generation through vapour-phase deposition on the walls of degassing pathways is a viable mechanism and that spherulitic formation, for the bulk of the cristobalite, is unlikely.

Recently, Reich et al. (2009) suggested that cristobalite nano-fibres, which they observed by transmission electron microscopy in the Chaitén explosive ash, may be formed through high-temperature vapour-phase reactions in the explosion column. Reich et al. did not quantify the nano-fibres, but here, we did not observe any nano-fibres (by FE-SEM), and the micro-fibres observed were not cristobalite and were sparse. We suggest an alternative mechanism for cristobalite nano-fibre formation, through break up of small spherulites in the ancient dome during the initial explosions in May 2009. Within spherulites, cristobalite grows as axiolitic intergrowths with feldspar, thereby forming acicular structures on fragmentation.

There is some concern as to whether single, acicular crystals and fibre-like particles pose a similar hazard to asbestos fibres. The fibre-like particles observed here, and in Reich et al., are not asbestos minerals (they do not contain any Mg or Fe). Fibre dimension, biopersistence (bio-solubility and breakability) and composition are key factors in determining fibre pulmonary pathogenicity. In

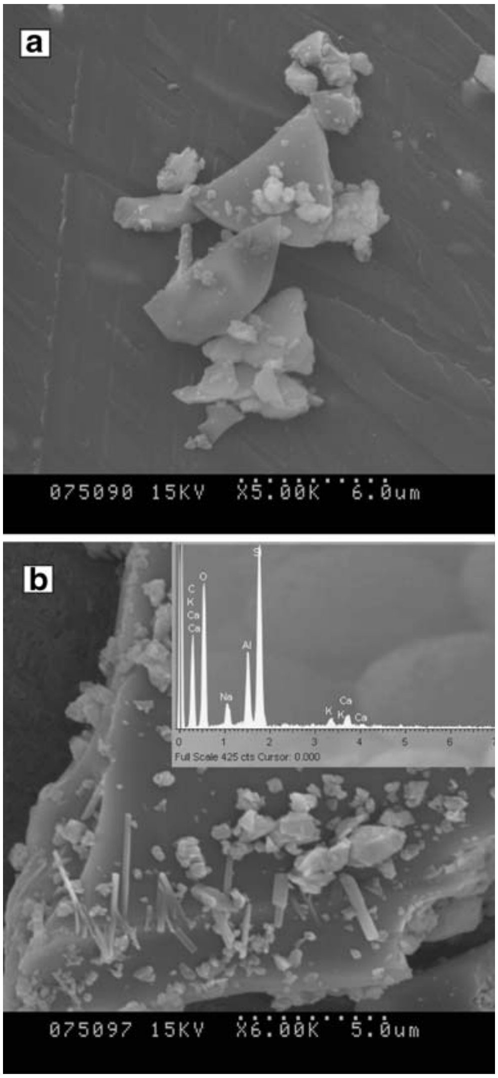

Fig. 3 Scanning electron microscopy (SEM) images of (**a**) Chai_04 showing a typical view of fine-grained and larger particles. (**b**) Fibre-like ash particles sitting on a larger ash particle in sample Chai_08. *Inset*: SEM-energy dispersive spectroscopy spectrum of elemental composition of a typical Chai_08 fibre-like particle

addition, biopersistence is affected by the ability of the particles to break longitudinally into fibrils. There is no evidence of fibril formation in the Chaitén ash, with fibre shape indicating transverse breakage giving brittle particles which are more easily cleared by macrophages (Zoltai 1981). No data exist on the toxicity of volcanic glass, feldspar or cristobalite fibres, so we cannot rule out that these fibres may be harmful, but the scarcity of the individual fibre-like particles means that they are unlikely to increase the potential respiratory hazard of the ash.

Summary

The presence of elevated levels of respirable crystalline silica in the form of cristobalite in the dome-related samples from Chaitén volcano indicates that the potential health hazard of the ash from Chaitén volcano increased as the eruption switched style from explosive to dome growth and collapse. The findings justify the air monitoring effort (set up by public health officials in Chile and Argentina in 2009) to assess exposure to ash in the population at risk from ash fallout whilst the eruption continues. Together with the fact that the ash contains significant levels of respirable material, exposure assessment of the local population is vital so that the hazard can be considered with respect to the duration and extent of exposure of populations to these particles.

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References

Baxter PJ, Bonadonna C, Dupree R, Hards VL, Kohn SC, Murphy MD, Nichols A, Nicholson RA, Norton G, Searl A, Sparks RSJ, Vickers BP (1999) Cristobalite in volcanic ash of the Soufriere Hills Volcano, Montserrat, British West Indies. Science 283:1142–1145

Getahun A, Reed MH, Symonds R (1996) Mount St. Augustine volcano fumarole wall rock alteration: mineralogy, zoning, composition and numerical models of its formation process. J Volcanol Geotherm Res 71:73–107

Hincks TK, Aspinall WP, Baxter PJ, Searl A, Sparks RSJ, Woo G (2006) Long term exposure to respirable volcanic ash on Montserrat: a time series simulation. Bull Volcanol 68:266–284

Horwell CJ (2007) Grain size analysis of volcanic ash for the rapid assessment of respiratory health hazard. J Environ Monit 9:1107–1115

Horwell CJ, Baxter PJ (2006) The respiratory health hazards of volcanic ash: a review for volcanic risk mitigation. Bull Volcanol 69:1–24

Horwell CJ, Sparks RSJ, Brewer TS, Llewellin EW, Williamson BJ (2003) The characterisation of respirable volcanic ash from the Soufriere Hills Volcano, Montserrat, with implications for health hazard. Bull Volcanol 65:346–362

Le Blond JS, Cressey G, Horwell CJ, Williamson BJ (2009) A rapid method for quantifying single mineral phases in heterogeneous natural dust using X-ray diffraction. Powd Diffr 24:17–23

Naranjo JA, Stern CR (2004) Holocene tephrochronology of the southernmost part (42°30′-45°S) of the Andean Southern Volcanic Zone. Rev Geol Chile 31:225–240

Reich M, Zúñiga A, Amigo A, Vargas G, Morata D, Palacios C, Parada MA, Garreaud RD (2009) Formation of cristobalite nanofibers during explosive volcanic eruptions. Geology 37:435–438

Swanson SE, Naney MT, Westrich HR, Eichelberger JC (1989) Crystallization history of Obsidian Dome, Inyo Domes, California. Bull Volcanol 51:161–176

Watkins J, Manga M, Huber C, Martin M (2009) Diffusion-controlled spherulite growth in obsidian inferred from H_2O concentration profiles. Contrib Mineral Petrol 157:163–172

World Health Organisation (1986) Asbestos and other natural mineral fibres: environmental health criteria 53. World Health Organisation, Geneva

Zoltai T (1981) Amphibole asbestos mineralogy. Mineral Soc Am Rev Mineralogy 9A:237–278