Bull Volcanol (2010) 72:1077–1092
DOI 10.1007/s00445-010-0382-7

RESEARCH ARTICLE

# Mineralogical analyses and in vitro screening tests for the rapid evaluation of the health hazard of volcanic ash at Rabaul volcano, Papua New Guinea

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Received: 9 November 2009 / Accepted: 4 June 2010 / Published online: 14 July 2010


**Abstract** The continuous ash and gas emissions from the Tavurvur cone in Rabaul caldera, Papua New Guinea, during 2007–08, raised concerns regarding how exposure would affect the respiratory health of nearby populations and impact on the environment. As part of a formal evaluation of the effects of volcanic emissions on public health, we investigated the potential health hazard of the ash using a suite of selected mineralogical analyses and in vitro toxicity screening tests. The trachy-andesitic ash comprised 2.1–6.7 vol.% respirable (sub-4 μm diameter) particles. The crystalline silica content was 1.9–5.0 wt.% cristobalite (in the bulk sample) with trace amounts of quartz and/or tridymite. Scanning electron microscopy showed that the ash particles were angular with sparse, fibre-like particles (~3–60 μm max. diameter) observed in some samples, which we confirmed to be $CaSO_4$ (gypsum, at <6 wt.% in the bulk samples) and not asbestiform fibres. The ash specific surface area was low (0.1–2.7 $m^2\ g^{-1}$). The leached solution from one of the ash samples was slightly acidic (pH 5.6), but did not contain high levels of toxic metals (such as F, Cu, Zn, Mn, As, Ni and Cd) when compared to previously tested volcanic ash leachates. Ash

Editorial responsibility: H. Delgado

**Electronic supplementary material** The online version of this article (doi:10.1007/s00445-010-0382-7) contains supplementary material, which is available to authorized users.

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samples generated potentially-harmful hydroxyl radicals through an iron-mediated catalytic reaction, in the range of 0.15–2.47 μmol $m^{-2}$ (after 30 min of reaction). However, measurement of particle oxidative capacity (potential oxidative stress reaction using ascorbic acid) and silica-like injury to red blood cells (erythrolysis assay, i.e. measurement of cell death) nevertheless revealed low biological reactivity. The findings suggest that acute exposure to the ash would have a limited potential to exacerbate pre-existing conditions such as asthma or chronic bronchitis, and the potential for chronic exposure leading to silicosis was low.

**Keywords** Public health · Hazard assessment · Rabaul · Volcanic ash · Multidisciplinary

## Introduction

Rabaul volcano, Papua New Guinea (PNG), entered a new eruptive phase in 1994 with a Plinian event involving simultaneous eruptions at Tavurvur and Vulcan vents, ending a period of repose dating from the 1940s. Since 1994, Tavurvur has shown intermittent eruptive activity. The most recent ash emission crisis began after a sub-Plinian event on 7th October 2006, with increased gas and ash emissions that became continuous during 2007–08. The severe air pollution caused by the particulate matter (PM) and gas raised concerns for the respiratory health of approximately 70,000 people living downwind of the volcano. Exposure to the plume occurred mainly during the dry season when prevailing winds blew the plume over occupied areas for 6 months of the year, before reversing direction in the wet season. We present the results of a rapid mineralogical investigation of the ash (incorporating grain size, bulk composition, particle morphology and composition, and crystalline silica content) to study its potential for causing acute and chronic adverse health effects on the respiratory system, and additional in vitro toxicity screening tests (surface hydroxyl radical generation, particle oxidative capacity and erythrocyte lysis assays) to assess its inflammatory potential in the lung.

Scientific knowledge about the effects of exposure to air pollution has increased exponentially in the last two decades, especially through research relevant to the health effects of airborne PM in urban and non-urban environments (WHO 2006). A limited number of studies have been undertaken during volcanic eruptions to determine the potential human respiratory health effects of the $PM_{10}$ fraction of ash (PM of aerodynamic diameter sub-10 μm), a key metric in air pollution monitoring (e.g. Choudhury et al. 1997). Volcanic emissions containing respirable sized ash particles (sub-4 μm diameter) have been found to provoke acute respiratory symptoms in both relatively healthy individuals (e.g. Popocatepetl, Mexico eruption in 1994–95; Rojas-Ramos et al. 2001) and those with pre-existing conditions such as chronic lung diseases (e.g. Mount St Helens, USA eruption in 1980; Bernstein et al. 1986), living in areas impacted by ash fall. During long-lived eruptions, exposure to repeatedly-raised concentrations of respirable crystalline silica (RCS) in some types of volcanic ash could potentially cause silicosis (a disabling fibrogenic lung disease), and an associated increase in the risk of lung cancer (IARC 1997; Dollberg et al. 1986; Yano et al. 1986). The fibrogenic properties of RCS (silicosis) and asbestos or asbestiform fibres (asbestosis) have been well recognised in industrial settings for many years, where mineral dusts are routinely analysed for the presence of RCS or fibres to meet occupational health and safety regulations.

Epidemiological surveys, toxicological studies and related ash analysis techniques, were slowly developed during landmark eruptions, such as Mount St Helens and the on going eruption at the Soufrière Hills volcano, Montserrat (as summarised by Horwell and Baxter 2006). Since then, the importance of having a rapid response to meet public health concerns during eruptions has become evident, and this paper defines a selected suite of mineralogical analyses and in vitro toxicity screening tests that can be used in a single comprehensive investigation of samples of ash to evaluate their health hazard.

### Geological setting

Rabaul caldera (688 m asl) is located on the northeastern tip of New Britain Island, PNG (Fig. 1). The latest of the 5–9 caldera forming eruptions occurred 1,400 years ago and breached the southeastern wall to form Blanche Bay (Heming 1974). At least eight intra-caldera eruptions have occurred since the breaching event (Nairn et al. 1995), which were predominantly basaltic and basaltic-andesitic cone building Strombolian eruptions with evidence of effusive and pyroclastic eruptions dating back to 1767 (McKee et al. 1985). Vulcan and Tavurvur (Fig. 1) have been the two most active centres over the last 130 years and erupted simultaneously during 1878, 1937–1943 and 1994 eruptive periods (Nairn et al. 1995).

It is estimated that around 70,000 people reside within a 15 km radius of Rabaul caldera (Smith 2001). During the 1994 eruption, ash deposits measured up to 800 mm (as compacted deposits) in Rabaul town and the combined weight of rain and ash caused many buildings to collapse, destroying large areas of the town (Blong 2003). Following the eruption, the provincial capital was moved from Rabaul to Kokopo, further along the coast (Blong and McKee 1995), but the harbour at Rabaul (the third largest in PNG) is vital to the economy of New Britain.

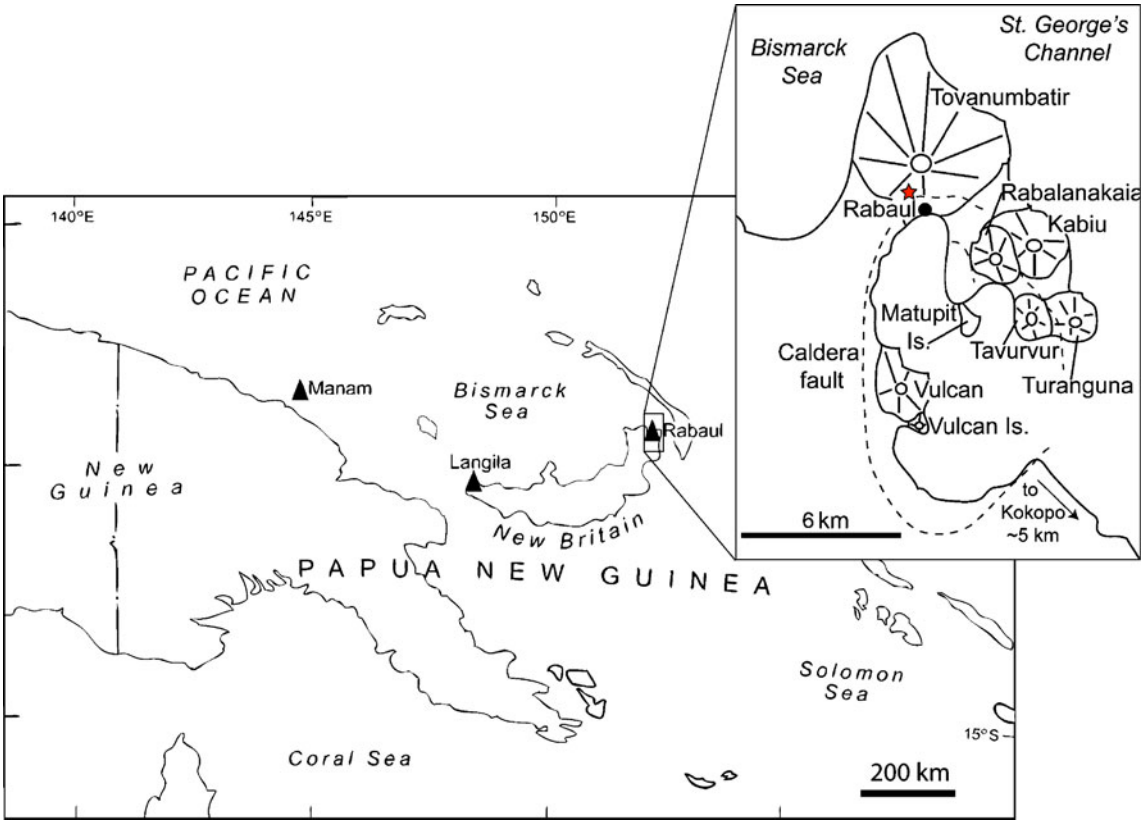


**Fig. 1** Map of PNG showing the location of the volcanoes and Rabaul caldera with the locations of the vents within the caldera (based on Greene et al. 1986; Heming 1974). The star indicates the location of RVO

Tephra composition

The basaltic and andesitic eruptions, which occur on average every 30–60 years (Patia 2004) from satellite vents such as Tavurvur, tend to erupt less than 0.1 $km^3$ (dry rock equivalent) of ash and lava (Cunningham et al. 2009a). The ash from both Vulcan and Tavurvur is characteristically water-modified (i.e. is fine grained, poorly vesiculated and angular; Nairn et al. 1989) and similarities between the bulk ash composition from Tavurvur and Vulcan suggest that both vents share the same magma chamber (Johnson et al. 1995; Roggensack et al. 1996). The composition of ejecta from Vulcan and Tavurvur did not alter significantly over the period 1878 to 1937–1994 and can be classified as generally andesitic to dacitic (~61–63 wt.% $SiO_2$), although there have been a few basaltic enclaves (Cunningham et al. 2009b). An increase in magma production (which resulted in a more frequently recharged magma chamber with less-differentiated melts), perhaps due to episodic faulting within the caldera, may have caused andesitic, as well as dacitic, magma production (Wood et al. 1995). Some information is available on the composition of ash from Tavurvur since 1994 (Cioni and Rosi, personal communication, July 2009): Cioni and Rosi sampled the sequences of ejecta material from Tavurvur (post 1994) and Vulcan (in 1994 only) in February 2002 and found no clear compositional changes with time, indicating that the magma had not altered substantially from the andesitic-dacitic ejecta sampled before 1994.

## Methods

We obtained samples of ash emitted from Tavurvur and Vulcan from the 1994 eruptions, and samples from subsequent eruptions at Tavurvur until April 2008. With the exception of Tav R2, R3, R4, R6 (collected fresh) and Tav 00 (collected after rainfall), samples were supplied by the Rabaul Volcano Observatory and little information was available on the state of the ash when it was collected, for example if was collected as a fresh deposit, or if it had been rained on (i.e. weathered). Table 1 summarises the details of the ash samples and analysis techniques used. Tav R2 was tested with all techniques as it represents a recent, well-sourced sample. For comparison, ash samples from Langila and Manam volcanoes (also in PNG; Fig. 1) were included in this study. Prior to analysis, all samples were dried in an oven (<90°C) for 24 h and sieved through 1 and 2 mm

**Table 1** Sample information and summary of the analytical techniques in this paper

| Sample Name | Volcano | Date erupted | Date collected | Location | Collected by | Analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Malvern | XRF | SEM-Raman | XRD | SSA | Surface reactivity | Leachate | Haemolysis |
| Lang L5 | Langila | 01/04/63 | 01/04/63 | 9.5 km from vent | Prof W Rose | √ | | √ | √ | | | | |
| Vul 94N | Vulcan | 19/09/94 | 09/94 | 2.5 km N of Vulcan | RVO | √ | √ | | √ | √ | √ | | |
| Vul 94S | Vulcan | 19/09/94 | 09/94 | 1 km S from base of Vulcan | RVO | √ | √ | | √ | | | | |
| Vul 94W | Vulcan | 19/09/94 | 09/94 | 1 km W from base of Vulcan | RVO | √ | √ | | | | | | |
| Tav 98a | Tavurvur | 13/05/98 | 13/05/98 | 2 km NW of Tavurvur | RVO | √ | | | | | | | |
| Tav 98b | Tavurvur | 12/06/98 | 12/06/98 | RVO ~6 km NW of Tavurvur | RVO | √ | | | | | | | |
| Tav 98c | Tavurvur | 17/07/98 | 17/07/98 | Matupit Island ~2 km from Tavurvur | BGS | √ | √ | | √ | | | | |
| Tav 98d | Tavurvur | 19/10/98 | 19/10/98 | Matupit Island ~2 km from Tavurvur | RVO | √ | √ | √ | √ | √ | √ | | |
| Man 98 | Manam | 01/11/98 | 01/11/98 | 4 km SW of Manam summit | RVO | √ | √ | | √ | √ | √ | | |
| Tav 99a | Tavurvur | 15/02/99 | 15/02/99 | RVO ~6 km NW of Tavurvur | RVO | √ | | | | | | | |
| Tav 99b | Tavurvur | 25/08/99 | 25/08/99 | RVO ~6 km NW of Tavurvur | RVO | √ | | | | | | | |
| Tav 00 | Tavurvur | 01/09/00 | 01/09/00 | Rabaul airport ~3 km from Tavurvur[a] | RVO | √ | √ | √ | √ | √ | √ | | |
| Tav 05 | Tavurvur | 05–06/10/05 | 05–06/10/05 | RVO ~6 km NW of Tavurvur | RVO | √ | √ | √ | √ | √ | √ | | |
| Lang 07 | Langila | 02/06/07 | 02/06/07 | 9.5 km NW from vent | RVO | √ | √ | √ | √ | √ | √ | | |
| Tav 07 | Tavurvur | 03/10/07 | 03/10/07 | RVO ~6 km NW of Tavurvur | RVO | √ | | | | | | | |
| Tav R2 | Tavurvur | 09/04/08 | 09/04/08 | 3–4 km from vent, collected on frangipani leaves[b] | Dr P Baxter | √ | √ | √ | √ | √ | √ | √ | √ |
| Tav R3 | Tavurvur | 09/04/08 | 09/04/08 | 3–4 km from vent, collected on frangipani leaves[b] | Dr P Baxter | √ | √ | √ | √ | | | | |
| Tav R4 | Tavurvur | 10/04/08 | 10/04/08 | At base of Tavurvur[b] | Dr P Baxter | √ | √ | | √ | √ | √ | | |
| Tav R6 | Tavurvur | 12/04/08 | 12/04/08 | At base of Tavurvur[b] | Dr P Baxter | √ | √ | | √ | | | | |

*RVO* Rabaul Volcano Observatory, *BGS* British Geological Survey, *Malvern* Malvern Mastersizer laser diffractometer, *XRF* X-ray fluorescence, *SEM-Raman* scanning electron microscopy with Raman spectroscopy, *XRD* X-ray diffraction, *SSA* BET specific surface area

[a] Rained on before collection

[b] Collected fresh

sieves to obtain the 'ash fraction' (<2 mm) and to remove large particles which could damage the particle size analyser. Full details of the methodologies are available as an Online Resource.

## Morphological and compositional analyses

### *Bulk composition*

The bulk oxide composition of the ash samples was determined, which allowed us to identify the magma type being erupted, using a PANalytical Axios Advanced X-ray fluorescence (XRF) spectrometer at the Department of Geology, University of Leicester, UK.

### *Particle size*

The grain-size distribution (from 0.2–2,000 μm) was determined using a Malvern Mastersizer 2000 laser diffractometer with a Hydro MU attachment and ultrasonics, at the Department of Geography, University of Cambridge, UK (according to Horwell 2007).

### *Crystalline silica content*

X-ray diffraction (XRD) enables identification and quantification of crystalline components in a bulk, powdered sample. XRD data were collected using an Enraf-Nonius X-ray diffractometer with an INEL curved position-sensitive detector (PSD) at the NHM, UK. The Internal Attenuation Standard (IAS) method (Le Blond et al. 2009, see Online Resource) was used to quantify the weight percentage of cristobalite and quartz in the bulk Rabaul ash samples. Crystalline silica polymorphs have been singled out for quantification because they cause the fibrotic lung disease silicosis and are classed as human lung carcinogens (IARC 1997).

### *Particle morphology*

Scanning electron microscopy (SEM) was used to investigate particle morphology. Analysis was carried out using the Philips XL-30 field emission SEM at the Natural History Museum (NHM), London, UK), at 5 kV and 10 mm WD.

### *Particle composition*

A LEO 1455VP SEM with Oxford INCA energy dispersive X-ray analysis system (EDS) (at the NHM, UK) was used to determine the elemental composition of individual particles in the samples (15 kV, 500 nm spot size). SEM-Raman was also carried out on some of the ash samples (at Renishaw Plc, Gloucestershire, UK) to accurately identify the mineralogical composition of individual particles. Unlike SEM-EDX, SEM-Raman can distinguish between different polymorphs of the same mineral (e.g. between the silica polymorphs—quartz, cristobalite and tridymite).

Interaction between the volatile components and ash particles in the volcanic plume may lead to the deposition of more or less soluble compounds onto the ash surfaces (e.g. Witham et al. 2005). As a result, an array of elements, including known toxic metals such as Pb, As, Cd, Ni, Cr, Mn, V and Hg, can be released from the ash surface upon contact with water and with fluids found in the lung. Soluble Fe is also of interest, since Fe contributes to particle-induced formation of reactive oxygen species through the Fenton reaction (see toxicity testing below and e.g. Kelly 2003; Fubini et al. 1995). Leachate analysis was carried out, according to Witham et al. (2005). Fe, As, Cd, Co, Cr, Cu. Mn, Ni, Pb and Zn in the water extract from Tav R2 was measured by inductively coupled plasma—optical emission spectroscopy (ICP-OES) and fluoride by ion chromatography (IC) both at the University of York. Tav R2 was the only sample analysed (as it was collected relatively soon after the eruption and had not been rained on) to give an indication of the labile elements that may become leached from the ash surfaces and impact on health and the environment.

## Analyses testing for potential toxicity

### *Particle specific surface area and reactivity*

The specific surface area and surface reactivity of selected fine-grained samples were measured as proxies for particle toxicity potential within the lung. A Micromeritics TriStar 3000 Surface Area and Porosimetry Analyser in the Department of Chemistry, Durham University, UK was used to determine sample surface area. Prior to analysis, all samples were degassed (under $N_2$) at 150°C for at least 2 h (e.g. Gregg and Sing 1982).

Particle surface reactivity can be determined by the particles' ability to generate free or surface radicals (Fubini and Hubbard 2003; Fubini and Otero Arean 1999; Hardy and Aust 1995; Ghio et al. 1992). Fe-catalyzed free radical production is known to potentially contribute to both lung inflammation and carcinoma (Hardy and Aust 1995; Kane 1996). Recent work by Horwell et al. (2003a, 2007) has shown that certain volcanic ash samples generate abundant hydroxyl radicals in the presence of hydrogen peroxide (found naturally in the lung) via the Fenton reaction. Hydroxyl radical production is particularly evident in basaltic ash samples (Fe-rich), previously considered to have a low respiratory health hazard due to their low crystalline silica content (Horwell et al. 2007). Electron Paramagnetic Resonance (EPR) spectroscopy, in association with the 'spin trap' technique, was used to quantify the

amount of free radicals generated by the samples (Horwell et al. 2003a, 2007; Fubini et al. 1995, 2001; Shi et al. 1995). The method replicates the Fenton reaction that may occur in the lung and was undertaken at the Università degli Studi di Torino, Italy (following Horwell et al. 2003a, 2007; see Online Resource). The amount of removable ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$) Fe on the sample surfaces, which represents the Fe available for the Fenton reaction, was also measured following a method previously described (Horwell et al. 2003a, 2007; Hardy and Aust 1995, see Online Resource).

*Particle oxidative capacity*

Particle oxidative capacity is a measure of the potential oxidative stress induced by a sample of PM within the lung. The respiratory tract lining fluid is the first physical defence encountered by inhaled particles entering the respiratory system and is known to contain antioxidants such as ascorbate (van der Vleit et al. 1999; Skoza et al. 1983; Willis and Kratzing 1974). In healthy individuals, most endogenous antioxidants are induced in response to slight changes in cellular redox status as a result of particle interaction within the lung. Cellular redox state can be altered by the introduction of oxidising species (such as redox active transition metals; Mudway et al. 2004) adsorbed on the particle surface. The potential for inhaled particles to provoke oxidative injury within the lung is, therefore, predominantly controlled by the reaction of the antioxidant defences (pro-oxidant and pro-inflammatory responses; Ayres et al. 2008). The strength of an individual's antioxidant defence is also important, as asthma sufferers can have an enhanced sensitivity to air pollutants, due to their impaired antioxidant defences (Kelly et al. 1999; Li et al. 2003). The oxidative potential of ash particles can be quantified, and reactions likely to occur in vivo at the air-lung interface inferred, by monitoring the depletion of antioxidant during incubation of the ash sample with ascorbate over time (at 37°C, pH 7.4; Ayres et al. 2008). The oxidative capacity assay was carried out at King's College, London, in order to elucidate a more complete understanding of in vitro toxicity (see Online Resource).

*Erythrocyte lysis assay (haemolysis)*

Red blood cells (erythrocytes) transport oxygen in the blood and are at risk of oxidation injury from endogenous substances (e.g. hydrogen peroxide, produced in response to inflammation), or exogenous chemicals. The erythrocyte lysis assay has been used for over three decades to screen mineral dusts for silica-type toxicity, and was carried out at the Centre for Inflammation Research, University of Edinburgh, UK (following Clouter et al. 2001, see Online Resource).

## Results

### Bulk composition

The ash samples ranged from basaltic, basaltic-andesite to trachy-andesite (i.e. mafic to intermediate; Table 2, Fig. 2). The Tavurvur samples were all trachy-andesitic with the exception of Tav 00 which appeared more mafic. XRF data show that this sample had elevated Ca and S (as CaO and $SO_3$) and this sample was rained on before collection.

### Particle size

The data are presented as cumulative volume percentages, according to health-pertinent size fractions (from Horwell 2007). In general, the Tavurvur samples were fairly similar in size distribution (Table 3). The proportion of particles sub-4 μm in diameter varied from 4.5–6.5 vol.%, which may be due to a number of factors including eruptive behaviour (explosivity, plume dynamics, magma composition) but also location of sample collection with respect to the volcano (i.e. distance from vent).

The samples from Manam and Langila were generally coarser than those from Tavurvur and have 3.3 and 3.5 vol.% sub-4 μm, respectively. The Manam and Langila samples were also more basaltic than the Tavurvur/Vulcan samples (Fig. 2) and their coarseness probably reflects a more effusive eruption style. Tav R2, R3, R4 and R6 were almost identical in terms of quantity of respirable particulate although Tav R2 and R3 had a higher proportion of material sub-63 μm in diameter, compared with R4 and R6.

Most of the Tavurvur samples had a similar grain size distribution to ash samples measured from the 1997 explosive eruptions of the Soufrière Hills, Montserrat (andesitic, Vulcanian explosion) and at Tungurahua, Ecuador (andesitic, Strombolian-Vulcanian) (Horwell 2007), which is in keeping both with their andesitic composition (Fig. 2) and with the mildly-explosive nature of the eruptions (VEI 2–3). The more basaltic samples from Manam and Langila were similar in vol.% distribution to that found for other basaltic eruptions such as the 1976 eruption of Fuego, Guatemala (basaltic, sub-Plinian) and from Mt. Etna, Italy (basaltic, Strombolian), although these eruptions were unusually explosive (VEI 3–4) (Horwell 2007).

### Crystalline silica content

Table 2 gives the quantification results for the crystalline silica polymorph cristobalite. Both tridymite (which had an

**Table 2** Results from the IAS method for quantifying the cristobalite phases within the volcanic ash samples (the error is estimated at 1–3 wt.%), results of the BET analysis to determine the specific surface area (SSA) and results of the XRF analysis for the bulk ash samples (wt.%)

| Sample Name | XRD | SSA | | XRF | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cristobalite (wt.%) | ($m^2\ g^{-1}$) | Error +/− $m^2\ g^{-1}$ | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | LOI | Total |
| Vul 94N | 2.27 | 2.7 | 0.0034 | 61.21 | 0.85 | 15.29 | 6.29 | 0.16 | 1.90 | 4.64 | 4.37 | 2.38 | 0.32 | 0.18 | 2.35 | 99.83 |
| Vul 94S | 2.67 | – | – | 61.94 | 0.89 | 15.39 | 6.25 | 0.16 | 1.78 | 4.22 | 4.42 | 2.47 | 0.35 | 0.02 | 1.96 | 99.87 |
| Vul 94W | 1.19 | – | – | 61.45 | 0.89 | 15.46 | 6.38 | 0.16 | 1.89 | 4.64 | 4.49 | 2.38 | 0.36 | 0.02 | 1.60 | 99.72 |
| Tav 98c | 4.60 | – | – | 60.34 | 0.86 | 15.90 | 6.84 | 0.16 | 2.59 | 5.88 | 4.29 | 2.16 | 0.32 | 0.17 | 0.47 | 99.99 |
| Tav 98d | 5.01 | 0.5 | 0.0009 | 60.59 | 0.90 | 15.58 | 6.61 | 0.16 | 2.48 | 5.14 | 4.48 | 2.37 | 0.34 | 0.09 | 0.64 | 99.37 |
| Man 98 | 1.93 | 0.2 | 0.0001 | 51.25 | 0.35 | 15.93 | 9.90 | 0.16 | 7.75 | 11.42 | 2.50 | 0.68 | 0.12 | 0.05 | 0.64 | 99.29 |
| Tav 00 | 1.96 | 2.0 | 0.0033 | 54.28 | 0.81 | 14.61 | 6.73 | 0.13 | 2.48 | 6.31 | 3.22 | 1.67 | 0.24 | 2.62 | −0.02 | 99.45 |
| Tav 05 | 2.40 | 0.2 | 0.0006 | 62.28 | 0.90 | 15.81 | 6.43 | 0.16 | 1.90 | 4.72 | 4.67 | 2.50 | 0.33 | 0.01 | 6.34 | 99.87 |
| Lang 07 | 2.42 | 0.5 | 0.0013 | 55.89 | 0.55 | 17.00 | 9.36 | 0.18 | 3.46 | 8.00 | 2.96 | 1.76 | 0.21 | 0.14 | 0.17 | 99.81 |
| Tav R2 | 2.04 | 0.6 | 0.0012 | 61.76 | 0.88 | 15.78 | 6.40 | 0.16 | 1.89 | 4.83 | 4.66 | 2.49 | 0.35 | 0.08 | 0.29 | 99.72 |
| Tav R3 | 2.37 | – | – | 61.77 | 0.89 | 15.79 | 6.50 | 0.16 | 1.94 | 4.86 | 4.62 | 2.46 | 0.34 | 0.08 | 0.44 | 99.74 |
| Tav R4 | 2.53 | 0.3 | 0.0025 | 61.26 | 0.90 | 15.74 | 6.81 | 0.17 | 2.11 | 5.18 | 4.56 | 2.38 | 0.36 | 0.01 | 0.32 | 99.64 |
| Tav R6 | 3.06 | – | – | 61.44 | 0.90 | 15.77 | 6.68 | 0.16 | 2.12 | 5.03 | 4.59 | 2.40 | 0.35 | 0.08 | 0.17 | 99.87 |

identifiable peak, just above background level) and quartz were too scarce to be quantified. Samples from 2005 onwards were relatively similar with cristobalite values between 2–3 wt.%. The greatest cristobalite concentrations were in the 1998 samples (4.6–5.0 wt.%).

The new Internal Attenuation Standard (IAS) method (Le Blond et al. 2009) of crystalline silica quantification for volcanic ash samples has been tested successfully on ash samples from the Soufrière Hills volcano, Montserrat, Chaitén volcano, Chile (Horwell et al. 2010a), and Vesuvius, Italy (Horwell et al. 2010b). Ash from these volcanoes had cristobalite contents ranging from <2 to ~18 wt.% in the bulk samples. It should be noted that results presented here, and in Horwell et al. papers, were for wt.% of crystalline silica polymorphs in the bulk ash sample and not sub-4 or sub-10 μmPM fractions in which crystalline silica minerals may be further concentrated (Horwell et al. 2003b).

## Particle morphology

The general morphology of the ash was fine grained, poorly vesiculated, generally angular and similar to many other volcanic ash samples (e.g. Horwell and Baxter 2006; Horwell et al. 2003b), but in several samples, including those from Manam and Langila, we found micron-sized, fibre-like particles (Fig. 3a). We know of only three previous investigations that have identified fibrous-looking material in freshly erupted volcanic ash: (1) nano-sized cristobalite fibres from Chaitén, Chile in May 2008 (Reich et al. 2009); 2) plagioclase/glass micro-fibres also from Chaitén, Chile (Horwell et al. 2010a) and 3) gypsum micro-fibres in ash erupted from Halema`uma`u Crater, Kīlauea Volcano, Hawai'i in March-April 2008 (Horwell et al. 2008). Fibres have also been observed previously in airborne particulate samples generated as basaltic lava enters sea water at Kīlauea, Hawai'i (Kullman et al. 1994) and in core samples extracted from hydrothermally-altered lavas beneath Kīlauea (Bargar et al. 1995). SEM images (Fig. 3a and b) show ash-sized blocky particles, fibre-like particles and numerous particles sub-4 μm (i.e. respirable). The largest fibre-like particle imaged was ~60 μm along the longest axis (in Lang 07) and the smallest axis was ~4 μm in length. The short axis was usually between <1 μm and 3 μm diameter. The aspect ratio of these fibre-like particles conforms to the WHO definition for fibres (WHO 1986) used by regulatory authorities in their classification and measurement of asbestos fibres, but we established that these needle-shaped particles cannot be described as asbestiform, used to describe minerals in which fibres have a high tensile strength and flexibility, and are insoluble in the lung. Here we found that the fibre-like particles were easily broken with light milling and were too short to

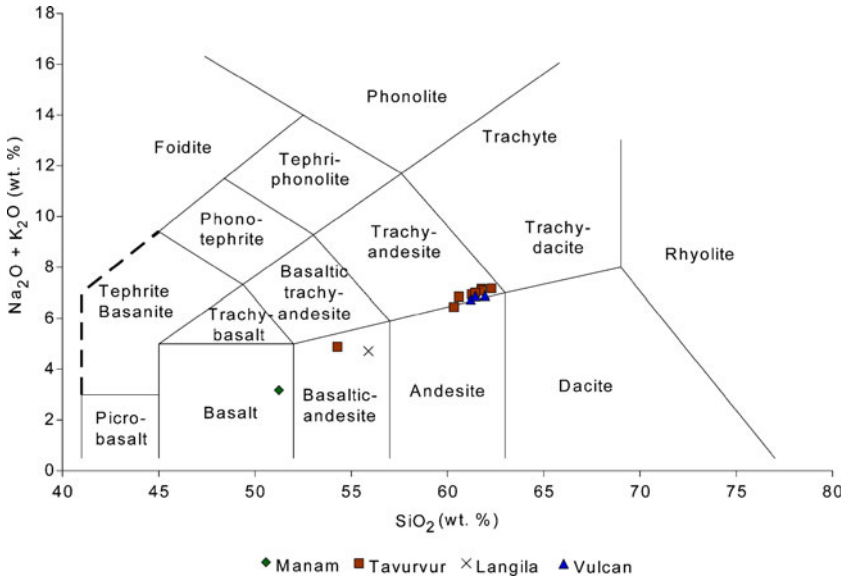


**Fig. 2** Results from XRF analyses of volcanic ash samples, on a TAS (total alkali versus silica content, after Le Bas and Streckeisen 1991) plot

display flexible morphology. They also did not display the 'fibril' (i.e. composite) morphology typical of tremolite (Skinner et al. 1988).

The samples did vary in the number of fibre-like particles that could be found and analysed under the SEM. In general, it was much easier to locate the fibre-like particles in more recent samples, for example Tav R2 and R3 and Lang 07. Samples R4 and R6 had fewer fibre-like particles than R2 and R3 samples. Overall, however, fibre-like particles were rare (~5% of all SEM field of view images taken contained one or more fibres).

## Particle composition

The MDHS (1998) 'Guidance on the discrimination between fibre types in samples of airborne dust on filters during SEM' advises that, "*Gypsum and anhydrite needles can resemble amphibole asbestos morphologically; they are distinguished easily by their EDXA* [EDX] *spectra which contain calcium and sulphur (sometimes with a little aluminium) in contrast to elements in the amphiboles*". In this study, when the fibre-like particles were probed by SEM-EDX, the X-ray spectra, in most cases, had two peaks (Ca and S) (Fig. 3c and d), roughly of equal size (reflecting the atomic formula $CaSO_4(.H_2O)$ for gypsum/anhydrite). Elemental mapping was carried out on a fibre in the Tav R2 sample. The Si seen in Fig. 4d is markedly reduced in comparison to the surrounding silicate particles and we attribute the presence of Si to smaller particles adhering to the fibre-like particle, as seen in the backscatter (BSE) image (Fig. 4a).

Mineralogical analysis by SEM-Raman further confirmed that these Ca-S fibre-like particles were either gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$) or hemi-hydrite (a gypsum and anhydrite-hybrid). We were unable to identify the exact composition for some fibre-like particles; as some would yield a gypsum spectrum lacking OH spectral peaks at ~3,500 $cm^{-1}$ (Fig. 5), which may be indicative of hemi-hydrite. Tav 00 contained ash-sized blocks of anhydrite. Here, SEM-Raman spectra were clearly identifiable as anhydrite and it may be that the Raman spectrometer was unable to obtain such clear spectra for much smaller fibre-like particles. Alternatively, the fibre-like particles are likely to have formed very rapidly and may not sustain the exact crystalline morphology of a well-formed crystal, hence giving less-defined Raman spectra.

## Leachate analysis

The ash leachate analysis (Table 4) gave concentrations of As, Mn, Co, Ni, Cu, Zn and Cd ranging from 0.023 to 10.25 mg $kg^{-1}$. Fe was below the detection limit (~0.1 mg $kg^{-1}$) and the ash leachate was slightly acidic (pH of 5.6).

## Particle specific surface area and reactivity

The measured specific surface area ranged from 0.2 $m^2 g^{-1}$ to 2.7 $m^2$ $g^{-1}$ (Table 2) which is within the range expected for volcanic ash samples (e.g. 0.2–1.8 $m^2$ $g^{-1}$, $n$=12; Horwell et al. 2007 and 0.2–6.9 $m^2$ $g^{-1}$, $n$=5; Horwell et al. 2010b), but is low when compared to known toxic powders, for example, Min-U-Sil 5 quartz standard (U.S. Silica, Berkeley Spring plant) which has a surface area of 5.2 $m^2$ $g^{-1}$.

All samples generated hydroxyl radicals and showed similar reactivity over the duration of the experiment (see Fig. S1, Online Resource). The only exceptions are Vulcan and Tav 00, which generated comparatively fewer hydroxyl radicals. Previous studies have shown that fresh dusts are

**Table 3** Results in cumulative vol.% from the Malvern Mastersizer 2000. Results are an average from three runs. The potential health effects (Horwell et al. 2007) are defined below

| Particle size (μm) | Sample name Lang L5 | Vul 94N | Vul 94S | Vul 94W | Tav 98a | Tav 98b | Tav 98c | Tav 98d | Man 98 | Tav 99a | Tav 99b | Tav 00 | Tav 05 | Lang 07 | Tav 07 | Tav R2 | Tav R3 | Tav R4 | Tav R6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sub-4 | 6.2 | 6.5 | 4.7 | 5.6 | 6.6 | 5.4 | 5.2 | 6.5 | 3.3 | 2.1 | 4.3 | 4.5 | 5.2 | 3.5 | 5.2 | 4.7 | 4.3 | 4.5 | 4.2 |
| sub-10 | 13.6 | 13.6 | 10.6 | 11.8 | 15.2 | 12.6 | 11.6 | 15.0 | 7.3 | 4.3 | 10.0 | 11.9 | 11.6 | 8.6 | 12.8 | 10.7 | 10.1 | 10.7 | 10.1 |
| sub-15 | 18.8 | 18.7 | 14.7 | 16.1 | 20.9 | 17.7 | 16.8 | 21.5 | 10.7 | 6.3 | 14.0 | 18.7 | 16.5 | 12.9 | 18.9 | 15.6 | 15.0 | 14.9 | 14.3 |
| sub-63 | 47.8 | 47.7 | 36.5 | 40.8 | 48.4 | 41.1 | 46.8 | 51.7 | 34.3 | 23.5 | 32.3 | 50.7 | 44.0 | 41.3 | 49.7 | 45.6 | 45.4 | 33.0 | 38.3 |

| Particle size (μm) | Potential health effects |
|---|---|
| sub-4 | 'Respirable' fraction—can enter the alveoli where chronic disease could occur with long-term exposure |
| sub-10 | 'Thoracic' fraction—can enter past the bronchus, where bronchitis, asthma and other acute diseases may be triggered in susceptible people |
| sub-15 | Can enter the throat, causing rhinitis, laryngitis and irritation |

more bio-reactive when compared to their weathered equivalents (e.g. Fubini 1998; Castranova et al. 1996; Vallyathan et al. 1995; Fubini et al. 1990), and although the state of Vulcan is unknown, Tav 00 was collected after rainfall which may explain the reduced surface reactivity. There were no consistent differences in the kinetics, except for Tav R4, which showed a linear increase of radical yield.

Comparable amounts of Fe ions in both oxidation states were extracted from the surface of the ash samples. As expected from the silicic composition of the samples (Fig. 2), all Tavurvur samples displayed relatively low Fe release in comparison to the basaltic Manam sample (see Fig. S2, Online Resource). The only exception is Langila which, along with Manam, had raised $Fe_2O_3$ content (from XRF analysis, Table 2) as would be expected for a more mafic sample, but the Langila sample does not seem to have a commensurate amount of available Fe for reaction.

Some samples of ash with little removable Fe are capable of generating plentiful radicals. With respect to previously published results, Fig. 6 compares PNG samples with four samples of volcanic ash previously analysed by Horwell et al. (2007). Here, these samples were re-analysed, and both new and old data compare well. Figure 6a shows that the Etna ash (basaltic) is capable of generating more radicals, and has more available Fe, than any of the PNG samples. Another basaltic sample (Cerro Negro) is very similar to the basaltic Manam sample. The Tavurvur trachy-andesitic samples all compare well with the andesitic Soufrière Hills, Montserrat and Pinatubo samples. The capacity of samples of similar Fe availability to generate a range of radical quantities is due to the fact that an excess of Fe in certain coordination states at the surface can, in fact, reduce the reactivity of a particle (Horwell et al. 2007; Fubini et al. 2001), suggesting that the ability to generate radicals depends on the presence of isolated Fe ions adhered to the surface.

## Particle oxidative capacity

The oxidation kinetics of re-suspended samples was calculated as nmol $L^{-1}$ of ascorbate oxidised $sec^{-1}$ (see Fig. S3, Online Resource). A 1-way ANOVA (Tukey) test was performed on the data to determine the significance ($p<0.05$). No significant increase in ascorbate oxidation was observed when Tav R2 was present in the incubation. Both positive and negative controls displayed expected outcomes during the experiment and a comparison can be seen for particles collected on London roadsides (Urban $PM_{10}$a and b).

## Erythrocyte lysis assay (haemolysis)

Once surface area is taken into account it can be seen that, per unit surface area, the ash samples induced significantly

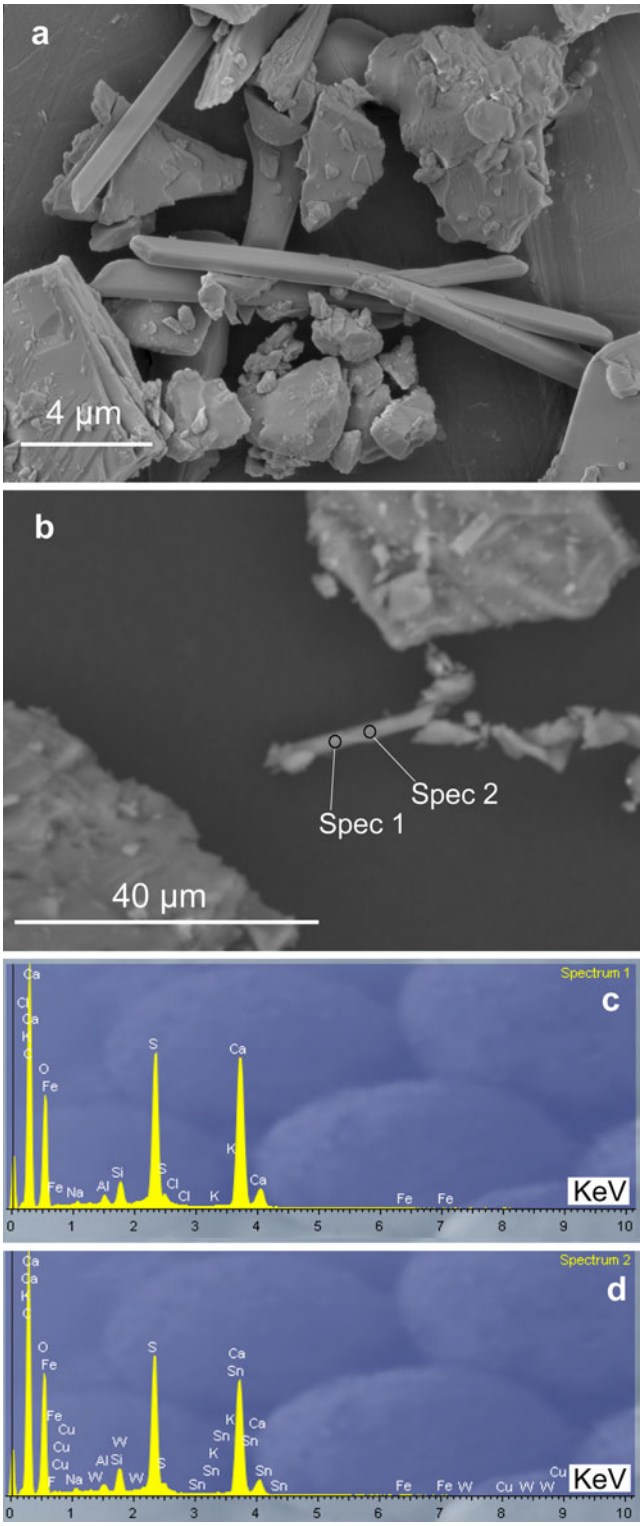


**Fig. 3** **a**) SEM SE image of fibre-like particles in Tav R2, **b**) SEM BSE image of Tav R3 sample, **c**) X-ray analysis spectrum 1, **d**) X-ray analysis spectrum 2. Location of both spectra are labelled in 3(b)

more haemolysis than low-toxicity $TiO_2$ polymorphs (rutile and anatase) but are still much less toxic to red blood cells than the positive control DQ12 quartz standard (Table 4). Although surface area normalised results are revealing about the relative harmfulness, exposure measurements (to meet health and safety legislation) are based on the mass metric and, on this basis, the ash is much less harmful than DQ12 quartz. It should be recognised, however, that volcanic ash is a mixed dust containing diluted concentrations of potentially-toxic minerals, so its toxicity is unlikely to match a pure standard.

## Discussion

The Rabaul ash contains fairly low amounts of sub-10 μm PM, in comparison to ash from other andesitic volcanoes (Horwell 2007), in keeping with the mild explosive nature of the eruptions. The amount of respirable (sub-4 μm) material is also low, typically just less than half of the sub-10 μmPM fraction (Horwell et al. 2010a; Horwell 2007), but the *number* of small particles in this fraction will be very high. On a by-weight or by-count basis the hazard will ultimately depend upon the actual individual's exposure.

The next most important consideration is the RCS content (1–5 wt.% measured in bulk samples). The presence of cristobalite in the Rabaul ash may be related to crystallisation from hydrothermal fluids and the incorporation of hydrothermally-altered rock. The lack of quartz is expected from descriptions of the petrology of the andesitic products at Rabaul (Wood et al. 1995). Although the RCS content is low in comparison to exposure in occupational studies of workers who develop silicosis, it is nevertheless of concern when exposure continues for up to 24 h a day for 6 months of the year. Although the risk of silicosis contraction may be relatively low, the population exposed to ash from Rabaul contains sick adults and children who may be more susceptible to the dust than healthy adults. One other important consideration is the adverse impact that prolonged exposure to high levels of ash containing RCS might have on this population with its high prevalence of tuberculosis. RCS is known to increase the risk of developing tuberculosis in occupationally exposed groups in mining and to exacerbate its clinical course (teWaterNaude et al. 2006; Hnizdo and Murray 1998).

The low bio-reactivity of the ash in the erythrocyte lysis test, however, suggests that the cristobalite may be less reactive when other mineral or metal phases are present, as found in previous studies. Vallyathan et al. (1984) observed a modest haemolytic reaction when testing Mt St Helens ash, and Cullen et al. (2002) found a low reaction in ash from the Soufrière Hills volcano, Montserrat despite the high cristobalite content. In the latter, the cristobalite

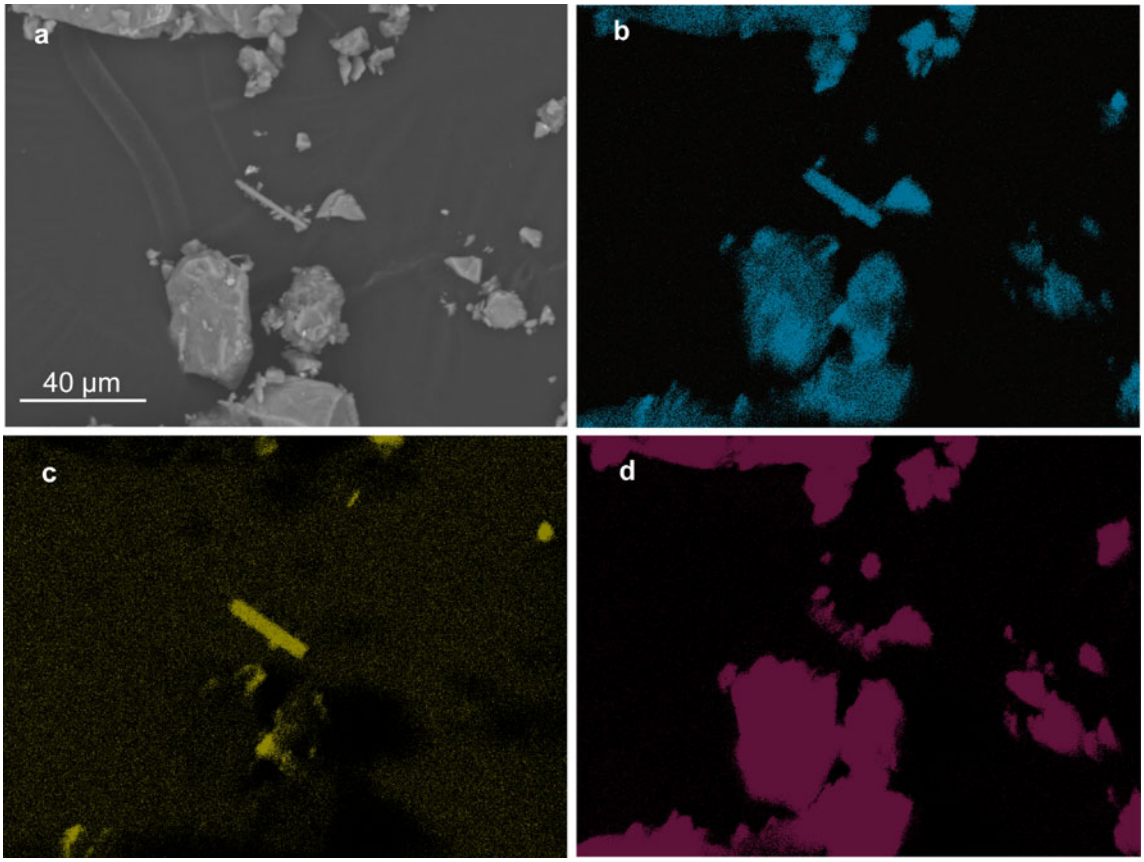


**Fig. 4** **a**) SEM BSE image of Tav R2, which shows a typical fibre-like particle in the centre. **b**), **c**) and **d**) are EDX maps of Ca, S and Si (respectively) within (**a**)

concentration was much higher than that found here (12–15 wt.% of the bulk ash, Horwell et al. 2010a) and would normally present a significant potential to cause fibrotic disease in the absence of other minerals or metals that may markedly reduce its bio-reactivity.

The oxidative capacity assay found that the Tavurvur ash did not oxidise ascorbate, an assay that simulates the effects of PM on the lining fluid of the lung and the potential of PM to trigger acute symptoms, such as asthma. The apparent differences in results among the hydroxyl radical, oxidative capacity and haemolysis experiments reflect the different mechanisms of toxicity in the lung that the tests are replicating, as they follow different oxidative pathways and involve different cell processes. Therefore, a negative result in one test does not preclude the possibility of toxicity via a different mechanism.

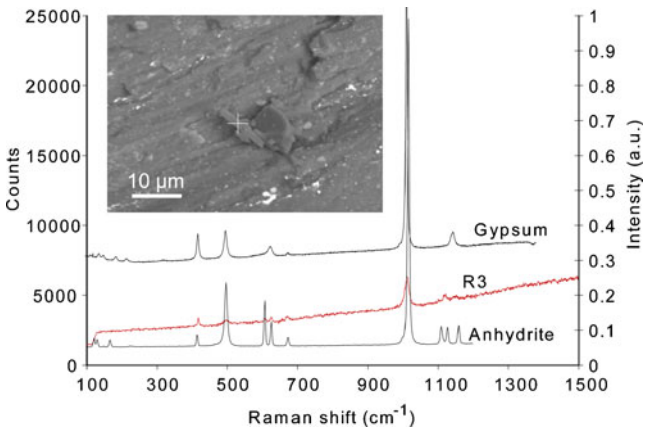


**Fig. 5** SEM BSE image of a fibre-like particle in Tav R3 inset with Raman spectrum, plus library spectra for gypsum and anhydrite (Handbook of Minerals Raman Spectra 2008)

An unknown factor, which could affect sample bio-reactivity of the older samples (all but R2-R6 and Tav 00), was their state prior to collection. If samples were collected from exposed sections in the field, years after eruption (rather than collected fresh), they may have been weathered, inducing oxidation and removal of Fe, which could reduce hydroxyl radical generation capacity. For example, Horwell et al. (2003a) studied a sample of 'mixed' ash from a section deposited between 1995–2000 at the Soufrière Hills volcano, Montserrat. This aged sample displayed substantially reduced hydroxyl radical generation capacity in comparison to fresh samples analysed. Similar results have been observed for older samples at Vesuvius volcano (Horwell et al. 2010b). There was, however, no major difference between the surface reactivity results for the

**Table 4** Erythrocyte Lysis Assay results (average% haemolysis) and the results of the leachate analysis for Tav R2

| Sample | Haemolysis | | | Leachate analysis | |
|---|---|---|---|---|---|
| | Mean% haemolysis[a] | BET $m^2$ $g^{-1}$ | Haemolysis (% haemolysis per unit surface area) | Element | mg $kg^{-1}$ |
| Negative Control | 0.00 | – | 0.00 | Fe | <0.1 |
| Rutile | 1.07 | 27.5 | 0.04 | As | 0.15 |
| Anatase | 3.05 | 258.0 | 0.01 | Cd | 0.023 |
| DQ12 quartz | 32.29 | 10.1 | 3.20 | Co | 0.05 |
| Tav R2 | 0.71 | 0.6 | 1.20 | Cr | <0.05 |
| Triton X | 100.00 | – | 100.00 | Cu | 1.5 |
| | | | | Mn | 10.2 |
| | | | | Ni | 0.075 |
| | | | | Pb | <0.05 |
| | | | | Zn | 2.85 |
| | | | | F | 21.8 |

[a] average from three runs

Rabaul R-type samples, known to be fresh, and the rest of the sample suite. It could be reasoned that the fine portion of the ash may be under-represented if the ash has been efficiently weathered. This theory could be tested by additional analysis of freshly deposited ash as the eruption continues.

The analysis of both fresh and aged samples during health hazard assessment is important as we must assess both the immediate hazard from the ashfall, the potential effects of long-term exposure to aged ash through re-suspension processes and the effects of exposure to older deposits through quarrying or agricultural processes.

The fibre-like particles observed in the Tavurvur samples raised our immediate concern that they could resemble asbestos minerals. Compositional analysis of the micron-sized fibre-like particles in this study, however, showed that they were gypsum/anhydrite/hemi-hydrite and *not* a variety of asbestos (fibrous silicates). Gypsum needles are unlikely to be pathogenic in the lungs, as gypsum has a short half-life (estimated at minutes) due its high solubility (US Department of Heath and Human Service 2006; Hoskins 2001). Epidemiological studies of workers exposed to pure-phase gypsum dust have not found evidence of lung fibrosis or pneumoconiosis (e.g. Burilkov and Michailova-Dotschewa 1990; Einbrodt 1988; Oakes et al. 1982). The fibre-like particles identified in Rabaul ash therefore can be assumed to be relatively harmless. Further testing to ensure their solubility would include incubating samples in water, HCl and simulated lung fluid solutions at different pH levels, to replicate conditions within the lung and macrophage cells.

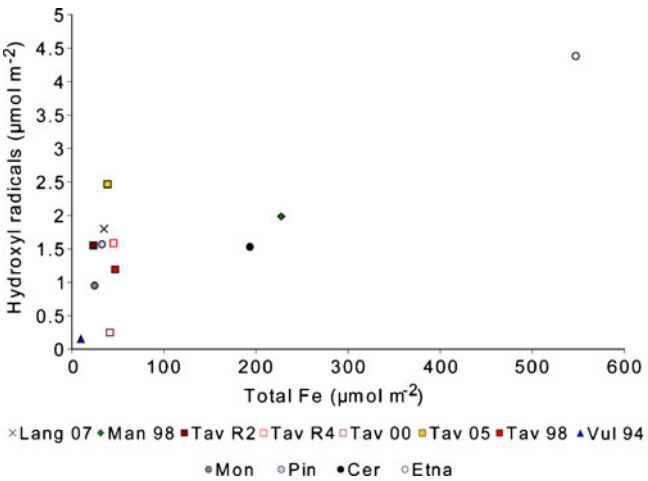


**Fig. 6** Amount of hydroxyl radicals generated after 30 min from the start of incubation versus total amount of iron extracted by chelators after 7 days for the PNG samples and four samples previously used by Horwell et al. 2007. Mon = Soufrière Hills, Montserrat (5/6/99); Pin = Pinatubo (1991); Cer = Cerro Negro (1995); Etna = Mt. Etna, Sicily (2002)

$CaSO_4$ is commonly found in acidic volcanic environments, formed as a secondary mineral phase by leaching of volcanic rock and is often precipitated around volcanic fumaroles (Africano and Bernard 2000). Gypsum, and other hydrothermal alteration minerals, may be incorporated into volcanic products through; 1) mechanical stripping from hydrothermally altered country rocks by ascending magma, steam or water, 2) sea water-magma interactions, 3) mechanical incorporation from aquifers or surface water into plume, 4) direct precipitation from volcanic fluids (Ohba and Nakagawa 2003). Risacher and Alonso (2001) also recognised high $CaSO_4$ in the leachate analysis of the ash from eruptions at Lascar volcano, Chile and attributed this finding to entrainment of ancient sedimentary evaporite-type deposits during the eruption.

The presence of substantial quantities of blocky anhydrite in Tav 00 (observed by SEM) is corroborated by the XRF data for this sample (Fig. 2), which appeared more mafic than the other Rabaul samples. If this additional

anhydrite were removed from the sample, we would expect composition to be in keeping with the other Rabaul samples.

The ash from Rabaul readily leached F, Cu, Zn, Mn, As, Ni and Cd upon mixing with water and their concentrations were not exceptional when compared to ash from other volcanoes (Witham et al. 2005 and references within). The concentrations of toxic metals in ash leachates are not often measured and vary for different volcanoes and eruption style (e.g. Cronin and Sharp 2002; Armienta et al. 1998; Cronin et al. 1997; Varekamp et al. 1984; Hinkley and Smith 1982; Smith et al. 1982; Fruchter et al. 1980). In vivo studies suggest that transition metals, including Fe, Cu and Ni, in respirable aerosols play a role in inflammatory response of the lung tissues (e.g. Rice et al. 2001), but epidemiological studies have not found any evidence of an association with adverse health outcomes that are substantially greater than for PM (e.g. Heal et al. 2009). The oxidative potential of the respirable ash fraction may also be enhanced by the presence of these metals in water-soluble forms, but we found that the Rabaul ash had a low oxidative capacity. Both As and Cd absorbed by inhalation are classified as human carcinogens (IARC 1980, 1993), thus could possibly contribute to the health hazard posed by volcanic ash. The slightly acidic pH of the leachate is due to $H_2SO_4$ and HCl adsorbed onto the ash surfaces (e.g. Hinkley and Smith 1982), which could add to the irritant effect of fine ash on the airways and provoke acute respiratory symptoms.

### Future hazard

Over geological history, Rabaul caldera has erupted magma of compositions ranging from basaltic to rhyolitic but the samples analysed for this study all display similar trachy-andesitic compositions. Samples from Manam and Langila volcanoes were more mafic. It is assumed that, providing there is no significant change in eruptive style at Rabaul, the characteristics of the ash particles will not vary considerably. A change in eruptive type, however, should be followed by re-sampling and re-evaluation in case its characteristics, as described here, alter. Future eruptions could switch to basaltic or rhyolitic magma compositions due to large-scale injection of basic magma, magma mixing and fractional crystallisation.

Rhyolitic eruptions at Rabaul are rare and an eruption of this type would likely be on a much larger, and more explosive, scale than recent eruptions (1994–present day). During such an eruption, we might expect generation of more fine-grained ash due to the explosivity of the eruption. We would not necessarily expect to see more cristobalite or gypsum fibres, but expect quartz phenocrysts to be present (Wood et al. 1995). It is also likely that surface reactivity (i.e. hydroxyl radical generation) would not increase and might even decrease due to the reduction in iron from rhyolitic magmas. Ash generation might be far greater than recent eruptions, which would force evacuation of local towns.

If basaltic eruptions resume, hydroxyl radical generation would be expected to increase, as with the basaltic Manam sample observed here. However, the volume of ash generated would be much lower, and the grain size most probably coarser, compared with the current production (due to effusive emission of lava flows), hence, local population exposure would be reduced in comparison to current eruptions. It should be noted, however, that basaltic eruptions can be explosive as well as effusive, producing significant quantities of respirable material (e.g. Fuego, Guatemala, 1974 in Horwell 2007). The crystalline silica content would be expected to decrease slightly, but not significantly, given the lack of a mechanism for large-scale cristobalite production.

## Conclusions

This study is one of the first to apply a selective suite of mineralogical analyses and toxicological screening tests in a single formal evaluation of the health hazards of ash early on in an eruption crisis. The results from our investigation at Rabaul are reassuring in that they suggest that the volcanic ash has limited potential to cause acute inflammatory responses leading to attacks of asthma in asthma sufferers and exacerbation of respiratory symptoms in those people with pre-existing respiratory illnesses, such as chronic bronchitis and emphysema. The ash, with its modest RCS content, also appears to have low potential to cause chronic inflammation leading to silicosis. Of concern, however, is the high prevalence of tuberculosis in the local population living in the ash fall area and lack of availability of, or non-compliance with, anti-tuberculosis medication. Elevated levels of respirable ash in the ambient air for prolonged periods might exacerbate or contribute to respiratory conditions such as tuberculosis, chronic bronchitis and childhood pneumonia. The presence of asbestiform minerals was excluded.

This study has shown the feasibility of conducting a routine suite of analyses and assays for the preliminary assessment to determine the health hazard of volcanic ash in a timely manner during an ash emission crisis. These methodologies can be standardised for use in a wide range of future volcanic eruptions and provide rapid feed-back for allaying public concerns and for advising health professionals. Clinical and epidemiological studies, and routine air monitoring of ash concentration levels in the ambient air are, nevertheless, needed to clarify the impact and risk to

the population of the health hazards raised in this laboratory investigation.

**Acknowledgements** JSL's work is funded by a NERC studentship (NER/S/A/2006/14107). CJH acknowledges a NERC Postdoctoral Research Fellowship (NE/C518081/2). PJB was funded by the World Health Organization (WHO). Thanks to: William Rose (Michigan Technological University, US) for kindly providing Lang (L5); Nick Marsh at Leicester University for XRF analyses; Gordon Cressey and Hazel Hunter, NHM, London for XRD advice and support; Neil Cameron et al. Durham University, for BET advice; Raffaello Cioni (Università degli studi di Cagliari, Italy) and Mauro Rosi (Università di Pisa, Italy) for advice and insights into their own work on ejecta samples collected at Rabaul; Jon Pallister (Chief, Volcano Disaster Assistance Program, USGS) for volcanological advice and Catherine Skinner (Department of Geology and Geophysics, Yale University, CT, US) for guidance on fibre characterisation; Ken Donaldson and Fiona Murphy at the MRC Centre for Inflammation Research at the University of Edinburgh, for carrying out the Erythrocyte Lysis (Haemolysis) analysis; Frank Kelly at the Lung Biology Group at King's College, London for advice regarding the oxidative capacity results; Ben Williamson, Camborne School of Mines, for comments and advice and Anna Hansell and Ana Lillian Martin Del Pozzo for helpful reviews of the manuscript The authors would finally like to thank Alan Brooker of Renishaw plc. for the use of their SEM-Raman.

## References

Africano F, Bernard A (2000) Acid alteration in the fumarolic environment of Usu volcano, Japan. J Volcanol Geotherm Res 97:475–495

Armienta MA, Martin-Del Pozzo AL, Espinasa R, Cruz O, Ceniceros N, Aguayo A, Butron MA (1998) Geochemistry of ash leachates during the 1994–1996 activity of Popocatepetl. Appl Geochem 13:841–850

Ayres JG, Brom P, Cassee FR, Castranova V, Donaldson K, Ghio A, Harrison RM, Hider R, Kelly F, Kooter IM, Marano F, Maynard RL, Mudway I, Nel A, Sioutas C, Smith S, Baeza-Squiban A, Cho A, Duggan S, Froines J (2008) Evaluating the toxicity of airborne particulate matter and nanoparticles by measuring oxidative stress potential—a workshop report and consensus agreement. Inhal Toxicol 20:75–99

Bargar KE, Keith TEC, Trusdell FA (1995) Fluid-inclusion evidence for past temperature fluctuations in the Kilauea East Rift Zone geothermal area, Hawaii. Geothermics 24:639–659

Bernstein S, Baxter PJ, Falk H, Ing R, Foster L, Frost F (1986) Immediate public health concerns and actions in volcanic eruptions: lessons from the Mount St. Helens eruptions, May 18–October 18, 1980. Am J Public Health 76(Suppl):25–38

Blong R (2003) Building damage in Rabaul, Papua New Guinea, 1994. Bull Volcanol 65:43–54

Blong R, McKee C (1995) The Rabaul eruption 1994—destruction of a town. Natural Hazard Research Centre, Macquarie University, Sydney, 52 pp

Burilkov T, Michailova-Dotschewa L (1990) Dangers of exposure to dust extraction and production of natural gypsum. Wiss Umwelt 0(2):89–91, Abstract from EMBASE 91094689

Castranova V, Pailes WH, Dalal NA, Miles PR, Bowman L, Vallyathan V, Pack D, Weber KC, Hubbs A, Schwegler-Beryy D, Xiang J, Dey R, Blackford J, Ma JYC, Barger M, Shoemaker DA, Pretty JR, Ramsey DM, McLaurin JL, Khan A, Baron PA, Childressa CP, Stettler LE, Teass AW (1996) Enhanced pulmonary response to the inhalation of freshly fractured silica as compared with aged dust exposure. Appl Occup Environ Hyg 11:937–941

Choudhury AH, Gordian ME, Morris SS (1997) Associations between respiratory illness and PM10 air pollution. Arch Environ Health 52:113–117

Clouter A, Brown D, Höhr D, Borm P, Donaldson K (2001) Inflammatory effects of respirable quartz collected in workplaces versus standard DQ12 quartz: particle surface correlates. Toxicol Sci 63:90–98

Cronin SJ, Sharp DS (2002) Environmental impacts on health from continuous volcanic activity at Yasur (Tanna) and Ambrym, Vanuatu. Int J Environ Health Res 12:109–123

Cronin SJ, Hedley MJ, Smith RG, Neall VE (1997) Impact of Ruapehu ash fall on soil and pasture nutrient status 1. October 1995 eruptions. NZJ Agric Res 40:383–395

Cullen RT, Jones AD, Miller BG, Donaldson K, Davis JMG, Wilson M, Tran CL (2002) Toxicity of volcanic ash from Montserrat. Report No. TM/02/01. Institute of Occupational Medicine, Edinburgh, 55 pp

Cunningham HS, Turner SP, Dosseto A, Patia H, Eggins SM, Arculus RJ (2009a) Temporal variations in U-series disequilibria in an active caldera, Rabaul, Papua New Guinea. J Petrol 50:507–529

Cunningham HS, Turner SP, Patia H, Wysoczanski R, Nichols ARL, Eggins S, Dosseto A (2009b) (210Pb/226Ra) variations during the 1994–2001 intracaldera volcanism at Rabaul caldera. J Volcanol Geotherm Res 184:416–426

Dollberg DD, Bolyard ML, Smith DL (1986) Evaluation of physical health effects due to volcanic hazards: crystalline silica in Mount St. Helens volcanic ash. Am J Public Health 76(Suppl): 53–58

Einbrodt HJ (1988) The health risks by dusts of calcium sulfate (Ger.). Wiss Umwelt 0(4):179–181, Abstract from EMBASE 89261036

Fruchter JS, Robertson DE, Evans JC, Olsen KB, Lepel EA, Laul JC, Abel KH, Sanders RW, Jackson PO, Wogman NS, Perkins RW, Van Tuyl HH, Beauchamp RH, Shade JW, Daniel JL, Erikson RL, Sehmel GA, Lee RN, Robinson AV, Moss OR, Briant JK, Cannon WC (1980) Mount St. Helens ash from the 18 May 1980 eruption: chemical, physical, mineralogical, and biological properties. Science 209:1116–1125

Fubini B (1998) Surface chemistry and quartz hazard. Ann Occup Hyg 42:521–530

Fubini B, Hubbard A (2003) Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) generation by silica inflammation and fibrosis. Free Radic Biol Med 34:1507–1516

Fubini B, Otero Arean C (1999) Chemical aspects of the toxicity of inhaled mineral dusts. Chem Soc Rev 28:373–381

Fubini B, Giamello E, Volcante M, Bolis V (1990) Chemcial functionalities at the silica surface determining its reactivity when inhaled. Formation and reactivity of surface radicals. Toxicol Ind Health 6:571–598

Fubini B, Mollo L, Giamello E (1995) Free radical generation at the solid/liquid interface in iron containing minerals. Free Radic Res 23:593–614

Fubini B, Fenoglio I, Elias Z, Poirot O (2001) Variability of biological responses to silicas: effect of origin, crystallinity, and state of surface on generation of reactive oxygen species and morphological transformation of mammalian cells. J Environ Pathol Toxicol 20(Suppl 1):95–108

Ghio AJ, Kennedy TP, Whorton AR, Crumbliss AL, Hatch GE, Hoidal JR (1992) Role of surface complexed iron in oxidant generation and lung inflammation induced by silicates. Am J Physiol 263:511–517

Greene HG, Tiffin DL, McKee CO (1986) Structural deformation and sedimentation in an active caldera, Rabaul, Papua New Guinea. J Volcanol Geotherm Res 30:327–356

Gregg SJ, Sing KSW (1982) Adsorption, surface area and porosity, 2nd edn. Academic, London

Handbook of Minerals Raman Spectra (2008) Laboratoire de Sciences de la Terre ENS-Lyon France. http://www.ens-lyon.fr/LST/Raman/index.php. Last viewed 24 July 2009

Hardy JA, Aust AE (1995) Iron in asbestos chemistry and carcinogenicity. Chem Rev 95:97–118

Heal MR, Ellton RA, Hibbs LR, Agius RM, Beverland IJ (2009) A time-series study of the health effects of water-soluble and total-extractable metal content of airborne particulate matter. Occup Environ Med 66:636–638

Heming RF (1974) Geology and petrology of Rabaul caldera, Papua New Guinea. Geol Soc Am Bull 85:1253–1264

Hinkley T, Smith KS (1982) Leachate chemistry of the tephra from the May 18, 1980 eruption of Mount St. Helens. EOS, Transactions, American Geophysical Union 63(45):1143

Hnizdo E, Murray J (1998) Risk of pulmonary tuberculosis relative to silicosis and exposure to silica dust in South African gold miners. Occup Environ Med 55:496–502

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, Fenoglio I, Ragnarsdottir KV, Sparks RSJ, Fubini B (2003a) Surface reactivity of volcanic ash from the eruption of Soufrière Hills volcano, Montserrat, with implications for health hazards. Environ Res 93:202–215

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

Horwell CJ, Fenoglio I, Fubini B (2007) Iron-induced hydroxyl radical generation from basaltic volcanic ash. Earth Planet Sci Lett 261:662–669

Horwell CJ, Michnowicz SAK, Le Blond JS (2008) Report on the mineralogical and geochemical characterisation of Hawai'i ash for the assessment of respiratory health hazard. Report issued to the Hawai'i Volcano Observatory

Horwell CJ, Le Blond JS, Michnowicz SAK, Cressey G (2010a) Cristobalite in a rhyolitic lava dome: evolution of ash hazard. Bull Volcanol 72:249–253

Horwell CJ, Stannett GW, Andronico D, Bertagnini A, Fenoglio I, Fubini B, Le Blond JS, Williamson BW (2010b) A mineralogical health hazard assessment of Mt. Vesuvius volcanic ash. J Volcanol Geotherm Res 191:222–232

Hoskins JA (2001) Mineral fibres and health. Indoor Built Environ 10:244–251

IARC (1980) Some metals and metallic compounds. IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, vol 23. Lyon, France, pp 39

IARC (1993) Cadmium and cadmium compounds, IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, vol 58. Lyon, France, p 119

IARC (International Agency for Research on Cancer) (1997) Silica and some silicates. IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, vol 42. Lyon, France, p 289

Johnson RW, McKee C, Eggins SM, Woodhead JD, Arculus J, Chappell BW (1995) Taking petrologic pathways toward understanding Rabaul's restless caldera. EOS Trans Am Geophys Union 76(17):171

Kane AB (1996) Mechanisms of mineral fibre carcinogenesis. In: Kane AB, Boffetta P, Saracci R, Wilburn JD (eds) Mechanisms of fibre carcinogenesis. International Agency for Research on Cancer, Lyon, pp 11–34

Kelly FJ (2003) Oxidative stress: its role in air pollution and adverse health effects. Occup Environ Med 60:612–616

Kelly FJ, Mudway I, Blomberg A, Frew AJ, Sanström T (1999) Altered lung antioxidant status in patients with mild asthma. Lancet 354:482–483

Kullman GJ, Jones WG, Cornwell RJ, Parker JE (1994) Characterisation of air contaminants formed by the interaction of lava and sea water. Environ Health Perspect 102:478–482

Le Bas MJ, Streckeisen AL (1991) The IUGS systematics of igneous rocks. J Geol Soc Lond 148:825–833

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. Powder Diffrac 24:17–23

Li N, Hao M, Phalen RF, Hinds W, Nel E (2003) Particulate air pollutants and asthma: a paradigm for the role of oxidative stress in PM-induced adverse health effects. Clin Immunol 3:250–265

McKee CO, Johnson RW, Lowenstein PL, Riley SJ, Blong RJ, Desaintours P, Talai B (1985) Rabaul caldera, Papua New Guinea—volcanic hazards, surveillance, and eruption contingency planning. J Volcanol Geotherm Res 23:195–237

MDHS (Method for the Determination of Hazardous Substances) (1998) Health and safety laboratory. Health and safety executive, C10. No. 87: fibres in air. http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs87.pdf

Mudway IS, Stenfors N, Duggan ST, Roxborough H, Zeilinski H, MArklund SL, Blomberg A, Frew AJ, Sanström T, Kelly FJ (2004) An in vitro and in vivo investigation of the effects of diesel exhaust on human airway lining fluid antioxidants. Arch Biochem Biophys 423:200–212

Nairn IA, Talai B, Wood CP, McKee CO (1989) Rabaul Caldera, Papua New Guinea—1:25,000 reconnaissance geological map and eruption history. Report prepared for the Ministry of External Relations and Trade, New Zealand, pp 1–75

Nairn IA, McKee CO, Talai B, Wood CP (1995) Geology and eruptive history of the Rabaul caldera area, Papua New Guinea. J Volcanol Geotherm Res 69:255–284

Oakes D, Douglas R, Knight K, Wusteman M, McDonald JC (1982) Respiratory effects of prolonged exposure to gypsum dust. Ann Occup Hyg 26:833–840

Ohba T, Nakagawa M (2003) Minerals in volcanic ash. 2: non-magmatic minerals. Glob Environ Res 6:53–59

Patia H (2004) Petrology and geochemistry of the recent eruption history at Rabaul caldera, Papua New Guinea: implications for magmatic processes and recurring volcanic activity. M.Phil thesis, Australian National University, Canberra

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

Rice TM, Clarke RW, Godleski JJ, Al Mutairi E, Jiang NF, Hauser R, Paulauskis JD (2001) Differential ability of transition metals to induce pulmonary inflammation. Toxicol Appl Pharmacol 177:46–53

Risacher F, Alonso H (2001) geochemistry of ash leachates from the 1993 Lascar eruption, northern Chile. Implication for recycling of ancient evaporates. J Volcanol Geotherm Res 109:319–337

Roggensack K, Williams SN, Schaefer SJ, Parnell RA Jr (1996) Volatiles from the 1994 eruptions of Rabaul: understanding large caldera systems. Science 273:490–493

Rojas-Ramos M, Catalan-Vazquez M, Martin-Del Pozzo AL, Garcia-Ojeda E, Villalba-Caloca J, Perez-Neria J (2001) A seven months perspective study of the respiratory effects of exposure to ash from Popocatepetl voclano, Mexico. Environ Geochem Health 23:379–392

Shi X, Mao Y, Daniel LN, Saffiotti U, Dalal NS, Vallyathan V (1995) Generation of reactive oxygen species by quartz particles and its

implication for cellular damage. J Occup Environ Hyg 10:1138–1144

Skinner HCW, Ross M, Frondel C (1988) Asbestos and other fibrous materials: mineralogy, crystal chemistry, and health effects. Oxford University Press, US

Skoza L, Snyder A, Kikkawa Y (1983) Ascorbic acid in bronchoalveolar wash. Lung 161:99–109

Smith K (2001) Environmental hazards: assessing risk and reducing disaster, 3rd edn. Routledge, London, pp 171–173

Smith DB, Zielinski RA, Rose WI Jr (1982) Leachability of uranium and other elements from freshly erupted volcanic ash. J Volcanol Geotherm Res 13:1–30

teWaterNaude JM, Ehrlich RI, Churchyard GJ, Pemba L, Dekker K, Vermeis M, White NW, Thompson ML, Myers JE (2006) Tuberculosis and silica exposure in South African gold miners. Occup Environ Med 63:187–192

US Department of Heath and Human Service (2006) EPA/IRIS United States Environmental Protection Agency/Integrated Risk Information System data base. http://cfpub.epa.gov/ncea/iris/index.cfm. Cited 25 Mar 2009

Vallyathan V, Robinson V, Reasor M, Stettler L, Bernstein R (1984) Comparative in vitro cytotoxicity of volcanic ashes from Mount St. Helens, El Chichon, and Galunggung. J Toxicol Environ Health 14:641–654

Vallyathan V, Castranova V, Pack D, Leonard S, Shumaker J, Hubbs AF, Shoemaker DA, Ramsay DM, Pretty JR, McLaurin JL, Khan A, Teass A (1995) Freshly fractured quartz inhalation leads to enhanced lung injury and inflammation in rats. Am J Respir Crit Care Med 152:1003–1009

van der Vleit A, O'Neill CA, Cross CE, Koostra JM, Volz WG, Halliwell B, Louie S (1999) Determination of low-molecular-mass antioxidant concentrations in human respiratory tract lining fluids. Am J Physiol 276:L289–L296

Varekamp JC, Luhr JF, Prestegaard KL (1984) The 1982 eruptions of El Chichon Volcano (Chiapas, Mexico): character of the eruptions, ash-fall deposits, and gas phase. J Volcanol Geotherm Res 23:39–68

WHO (1986) Asbestos and other natural mineral fibres. Environmental health criteria 53. WHO, Geneva

WHO (World Health Organisation) (2006) Air quality guidelines global update 2005. WHO, Geneva

Willis RJ, Kratzing CC (1974) Ascorbate acid in rat lung. Biochem Biophys Res Commun 59:1250–1253

Witham CS, Oppenheimer C, Horwell CJ (2005) Volcanic ash-leachates: a review and recommendations for sampling methods. J Volcanol Geotherm Res 114:299–326

Wood CP, Nairn IA, McKee CO, Talai B (1995) Petrology of the Rabaul caldera area, Papua New Guinea. J Volcanol Geotherm Res 69:285–302

Yano E, Yokoyama Y, Nishii S (1986) Chronic pulmonary effects of volcanic ash: an epidemiologic study. Arch Environ Health 41:94–99