Grain-size analysis of volcanic ash for the rapid assessment of respiratory health hazard

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Volcanic ash has the potential to cause acute and chronic respiratory diseases if the particles are sufficiently fine to enter the respiratory system. Characterization of the grain-size distribution (GSD) of volcanic ash is, therefore, a critical first step in assessing its health hazard. Quantification of health-relevant size fractions is challenging without state-of-the-art technology, such as the laser diffractometer. Here, several methods for GSD characterization for health assessment are considered, the potential for low-cost measurements is investigated and the first database of health-pertinent GSD data is presented for a suite of ash samples from around the world. Methodologies for accurate measurement of the GSD of volcanic ash by laser diffraction are presented by experimental analysis of optimal refractive indices for different magmatic compositions. Techniques for representative sampling of small quantities of ash are also experimentally investigated. GSD results for health-pertinent fractions for a suite of 63 ash samples show that the fraction of respirable (<4 μm) material ranges from 0–17 vol%, with the variation reflecting factors such as the style of the eruption and the distance from the source. A strong correlation between the amount of <4 and <10 μm material is observed for all ash types. This relationship is stable at all distances from the volcano and with all eruption styles and can be applied to volcanic plume and ash fallout models. A weaker relationship between the <4 and <63 μm fractions provides a novel means of estimating the quantity of respirable material from data obtained by sieving.

1. Introduction

At the onset of a volcanic eruption, volcanologists and hazard managers must make rapid decisions not only regarding the risks of volcanic hazards such as pyroclastic flows, but also of secondary hazards, such as the short-term and long-term effects of ash fall. Volcanic ash may stay in the environment for months or years following an eruption and can affect communities hundreds of kilometres from the volcano.

Volcanic ash may cause acute respiratory diseases (*e.g.* asthma and bronchitis[1,2]) and has the potential to instigate chronic diseases such as silicosis and lung cancer. Volcanic ash is considered a respiratory health hazard because of several potentially toxic components: (1) respirable crystalline silica, classed as a Group 1 human carcinogen.[3] In industry, crystalline silica is known to cause silicosis, a fibrotic lung disease, and lung cancer.[4] (2) Surface transition metals. Fe^{2+} in volcanic ash is capable of generating highly-deleterious hydroxyl radicals when in contact with H_2O_2 (found naturally in the lungs).[5,6] Hydroxyl radicals can damage DNA and other cellular components, potentially leading to cell mutation and cancer.[7,8] (3) Bio-toxic elements, trace elements and compounds. Volcanic ash can carry a variety of potentially-toxic adsorbed elements such as Cl, S, Na, Ca, K, Mg and F as well as metals such as Pb, Hg, Cu, Zn, Cd and As and other potentially-pathogenic trace elements. These elements may be carried hundreds of kilometres in a volcanic plume and will be inhaled with the ash particles unless leaching occurs first.[9–11] For an overview of the potential acute and chronic diseases relating to volcanic ash and of studies carried out to date, see Horwell & Baxter.[12]

Assessing the risk to human respiratory health by clinical or epidemiological studies can take decades, since the diseases may not manifest themselves for years following exposure. Toxicological assessment of the risk of chronic disease from volcanic ash has been inconclusive due to variations in study designs and the problems of relating *in vivo* or *in vitro* studies to human disease development. The decision to implement mitigation measures (*e.g.* dust masks, evacuation *etc.*) must be taken early in a volcanic crisis. There is an urgent need for a more rapid form of health hazard assessment which, ideally, should be available within hours of the onset of ash fallout.

Both acute and chronic respiratory diseases can only occur if particles are sufficiently small to enter the respiratory system. Therefore, the first step in assessing the potential toxicity of volcanic ash should be to rapidly determine whether the particles are sufficiently small to enter the lungs. In this context, the size of a particle is conventionally described by its diameter, however, diameter definitions vary according to the style of particle measurement. Air quality standards and health definitions are based on sedimentation techniques and

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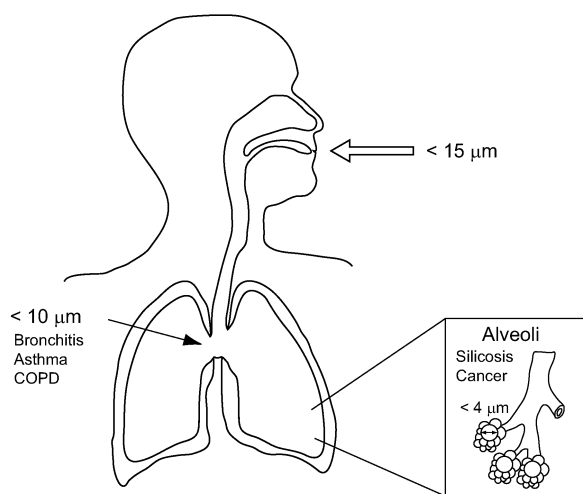
Fig. 1 Diagram of the lung showing the anatomy of the lung and the penetration of ash particles of different sizes associated with their potential health effects.

use aerodynamic diameter. In general, particles >15 μm aerodynamic diameter (AD) will not penetrate the respiratory tract beyond the nose (Fig. 1). Those between 10–15 μm AD will settle in the upper respiratory tract and may cause irritation of the throat and nasal passage. Particles less than 10 μm AD, the 'thoracic' fraction,[13] may enter the bronchioles and it is thought that it is this fraction that causes lung irritation, inflammation, asthma and bronchitis.[14] Fine particles less than 4 μm AD are termed 'respirable'.[13] Respirable particles can penetrate the alveolar region of the lung where chronic, particle-related respiratory diseases, such as silicosis, are activated.[4] Ultra-fine particles (sub-2.5 μm AD, and particularly those in the nanoparticle range, sub-0.5 μm) may have even greater disease-causing potential.[14]

Grain-size analysis (GSA) of volcanic ash can reveal whether the ash is a *potential* health hazard and provides decision makers with a rapid hazard assessment tool. GSA can be used to determine not only the quantity of ash in a sample capable of penetrating the lungs, but the percentage of ash in each of the health-pertinent fractions discussed above, facilitating a rapid analysis of the potential for acute and chronic disease development. This information will help emergency managers to decide whether a community should be prepared for fine ash fall, and whether further, more time-consuming studies should be initiated to determine specific health hazards.

This paper has three goals, all of which are essential to forwarding our understanding of rapid health hazard assessment through grain-size analysis: (1) to review the GSA techniques most commonly used in the health assessment of volcanic ash. For laser diffraction technology, experimental data are presented for identification of optimal refractive indices for different ash types and techniques for representative sampling are also experimentally assessed. (2) To present a laser diffraction analysis of all health-relevant size fractions for a suite of 63 volcanic ash samples collected from around the world. Where rapid GSAs are impracticable, this database

may be used to roughly estimate amounts of respirable material from future eruptions or from similar volcanoes. (3) To introduce a simple method for estimating the amount of respirable material in a sample, following sieving of volcanic ash at the lowest practicable mesh size (63 μm). This novel method will allow rapid analysis of the potential respiratory health hazard of volcanic ash where state-of-the-art techniques are unavailable.

2. Methodological review

There are many GSA techniques available, ranging from state-of-the-art laser diffractometry to basic sieving. They vary greatly in their applicability, technology and cost. More sophisticated techniques, such as laser diffractometers, are seldom found outside well-resourced laboratories. Measurement of health-relevant size fractions is far less precise with the more basic techniques, making rapid, accurate hazard assessment a challenge.

2.1 Laser-diffraction analysis (Low Angle Laser Light Scattering)

The most time-efficient and robust way to obtain a GSA is by laser diffractometry. There are many laser diffractometers on the market, such as the Malvern Mastersizer, the Coulter LS Particle Size Analyzer, or the Microtrac S3500 Analyzer. The latest laser diffractometers can detect particle sizes in the range of ∼0.1 to 2000 μm equivalent spherical diameter (ESD) using either Mie or Fraunhofer light scattering theory. The technique assumes a spherical particle shape, as no theory exists that enables laser light scattering instruments to determine the shape of the particles under analysis. Powders can be measured by laser diffraction either in water or air. If water is used, aggregation of volcanic particles can be reduced by treating with ultrasound.

2.2 Sieving

Sieving is a simple, portable, inexpensive and widely-used method of classifying powders according to their physical size alone, independent of other physical or chemical properties. Ash samples are dried in an oven (at <90 °C), then passed through a series of woven wire or punch plate sieves arranged in decreasing order of aperture size. Ash is typically sieved down to 63 μm (4 Phi) if sieving alone is used, or to 2 mm if sieving is used in conjunction with laser diffraction, for the finer fractions. Sieving can be performed manually or by machine agitation.

Key variables that influence sieving results include particle shape, presence of very fine particles, initial sieve loading, duration and method of agitation, and aggregation of the powder. Furthermore, it is easy to lose much of the fine fraction through lofting during the sieving. Reproducibility is often poor due to these variables. An alternative to dry sieving is wet sieving, which alleviates some of the size difficulties but also has poor reproducibility. Where sieving is the only technique to be used, care must be taken to clean sieves thoroughly and to regularly check for breaks.

Despite its limitations, sieving is valuable for estimating the amount of fine material, particularly where an inexpensive

technique is a priority. It is not regarded as suitable for the direct assessment of the quantity of respirable material (< 4 μm) in a sample, however, a technique is presented for estimating the respirable fraction from the amount of < 63 μm material in a sample in Section 5.2.

2.3   Microscopy

Scanning electron microscopy (SEM) can be used to count the number of particles in different size fractions. This technique is especially valuable for assessing the GSD of samples containing few particles, such as filter-collected airborne samples, but is time consuming and potentially expensive. Image analysis software can be used to automate the acquisition of GSDs, but is susceptible to errors arising from aggregation of particles.

2.4   Other techniques

Other techniques useful for assessing GSDs of fine volcanic ash samples include sedimentation methods, based on the application of Stokes' Law, image analysis techniques (used by, for example, the Malvern Pharmavision 830) and the electrical zone sensing (EZS) technique, based on the Coulter principle.

In general these different methods use different physical properties of the particles to measure the grain-size distribution and, consequently, are not necessarily comparable. If two different techniques are being used on the same sample for different grain-size ranges there should be sufficient overlap to allow calibration and integration of the methods with one another. These techniques are not considered further in this paper but further details are available in the document 'Guidelines for grain-size distribution analysis' produced by the International Volcanic Health Hazard Network (www.ivhhn.org).

3.   Refractive index determination for LALLS

The GSAs for this paper were carried out on all samples using a Malvern Mastersizer 2000 HydroMU laser diffractometer. The Mastersizer calculates results using Mie light scattering theory, which requires the complex refractive index of the particles under analysis as an input parameter. It is important, therefore, to have accurate data for the real and imaginary parts of the complex refractive index of the powder being tested. The complex refractive index is given by:

$$m = n - ik$$

where $i = \sqrt{-1}$, n is the real part of the refractive index (from here on n is referred to as RI) and k, the imaginary component of the refractive index, is the absorption coefficient (AC) of the material. For non-absorbing (i.e., transparent) particles, $k = 0$. Both RI and k are wavelength-dependent. Lists of the RI of minerals are available e.g. ref. 15, however, the RI of a mineral may vary with its precise composition, and volcanic ash may be composed of tens of different minerals, where the proportions of the minerals in the sample are unknown. Allocating generally-applicable RIs appropriate for the main magmatic types (e.g. basaltic, andesitic, phonolitic etc.) is crucial for laser diffraction analysis of volcanic ash and experiments to determine these are described below.

The dominant phase in volcanic ash is often silicate glass. A summary of the variation of the real part of the refractive index for yellow light for volcanic silicate glass was published by Williams et al.[16] These data show that volcanic glass containing 75% SiO_2 has an RI value of ~ 1.48 while 45% SiO_2 glass has an RI between 1.60–1.62. Thus, the RI for an andesitic glass with SiO_2 of 55% can be expected to fall in the range of 1.54–1.56. To apply this RI to laser diffractometer data, a correction to the RI is needed, which depends on the colour of the laser light (< -0.01 for red laser and $< +0.01$ for blue laser). Volcanic ash commonly contains 20–80% glass, with the remainder comprising between two and six important mineral phases. Most of these minerals have much higher RI values than glass, for example: olivine: 1.65–1.72; clinopyroxene: 1.68–1.73; othopyroxene: 1.65–1.71; labradorite: 1.56–1.57.[15]

Where glass is not the dominant phase, more accurate results may be obtained by using the optical properties of the most abundant mineral present. Alternatively, the average RI for a sample can be estimated by summing the RIs for the component minerals, adjusted to the proportion of the minerals in the ash sample being analysed. Although this is an excellent method for determining RI of a heterogeneous powder, it relies upon an accurate mineralogical determination of the sample, which is not always practical. For this paper, the averaging technique was used for a Soufrière Hills ash sample (MBA5/6/99[17]) yielding an average RI of 1.56, which is the same as for its dominant mineral, plagioclase (labradorite).

To test the effect of varying RI on GSDs, GSAs were conducted with the Malvern Mastersizer 2000 on three ash samples representative of different magma types (Soufrière Hills, Montserrat, andesitic–dacitic; Cerro Negro, Nicaragua, basaltic; Vesuvius, Italy, tephritic–phonolitic). For each sample, an average GSD for three runs was obtained using an RI of 1.48. The Mastersizer software was then used to re-calculate the average GSD for each sample as RI was varied by 0.2 RI intervals between 1.48 and 1.66 RI (representing the likely extremes in RI for a bulk ash sample). Fig. 2a–c shows cumulative GSDs and it can be seen that RI varies most in the 0.1–10 μm range—the grain-sizes most pertinent for health hazard research. In general, the Mastersizer software appears to calculate more fine material when lower RI values are used, with RI variation being most significant for basaltic samples.

It is helpful to determine specific RIs for use with different magma types. From Fig. 2a we can infer that, for the Soufrière Hills ash, the RIs of 1.56 (calculated above) and 1.63 (previously used by Bonadonna et al.[18]) produce similar GSDs and both are likely to be close to the optimal RI. The data in Fig. 2a suggest that results obtained are insensitive to choice of RI within this range. For this paper, an RI of 1.63 was used for andesitic and dacitic samples.

For basaltic samples (48–52% SiO_2), which are predominantly composed of volcanic glass with olivine, pyroxene and plagioclase phenocrysts, an RI of ~ 1.6 is probably appropriate, based on the data in Williams et al.[16] but determination of an exact RI is difficult due to the large compositional differences among samples. One can use the Becke Line method (see Appendix) to assign an RI for
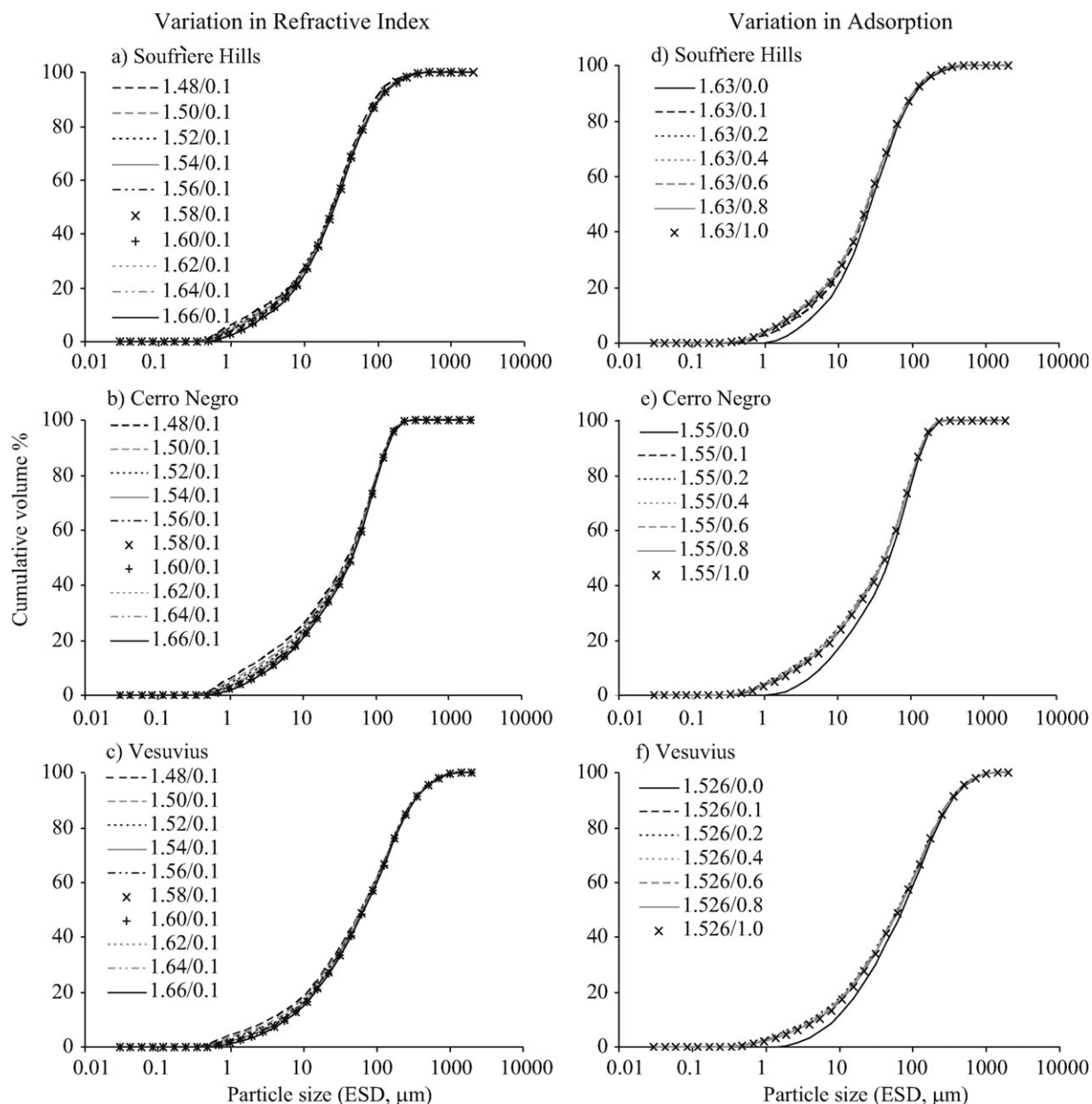
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Fig. 2 Laser diffractometer RI and absorption tests. (a)–(c) RI variation experiments: (a) 5 June 1999 Soufrière Hills ash with absorption = 0.1. (b) 30 November 1995 Cerro Negro ash with absorption = 0.1. (c) 15 April 1906 Vesuvius ash with absorption = 0.1. (d)–(f) Absorption variation experiments: (d) Soufrière Hills ash with RI = 1.63. (e) Cerro Negro ash with RI = 1.55. (f) Vesuvius ash with RI = 1.526. ESD = equivalent spherical diameter.

volcanic glass. Here, RIs of 1.67 for olivine,[15] 1.48 (lowest volcanic glass value)[15] and 1.55 (Becke Line value for Cerro Negro volcanic glass) were assessed. Pyroxene and plagioclase values also fall between 1.48 and 1.67. An intermediate value of 1.55 (Cerro Negro glass) was used for basaltic samples in this paper.

For alkali-rich phonolitic, tephritic and trachytic samples, such as from Vesuvius and the Campanian region, tens to hundreds of mineral species may be present in ash samples. An RI of 1.509[15] was tested for the often-dominant mineral leucite and an RI of 1.526 quoted for the Gray Campanian Tuff, which is leucite free.[19] These RIs also cover the range for another common mineral, sanidine, found in Vesuvius ash.

These similar RIs gave almost identical GSDs and 1.526 was used for Vesuvius samples in this paper.

The influence of the absorption coefficient (AC, the imaginary part of refractive index, k) also becomes important as particle size decreases. Fig. 2d–f shows results of calculations on laser diffractometer data for each ash type where absorption values were varied and RI kept constant. In each case, absorption values were varied between 0.0 and 1.0 at 0.2 AC intervals. Results show that the AC can be set anywhere between 0.1 and 1.0 without significantly affecting the GSD but that an RI of 0.0 gives significantly less fine material and a lack of sub-1 µm material. (It is known from SEM work that all samples contain particles <1 µm diameter.) The AC for a

Table 1 Eruption and collection information for samples with data presented in Table 2. Numbers in brackets indicate the number of samples from the eruption used in Fig. 4

Volcano	Eruption date	Collection date	Eruption style[d]	Magma type[d]	Distance from vent/km	Location of collection
Cerro Negro, Nicaragua (2)	30 Nov 1995	1 Dec 1995	Strombolian-vulcanian	Basaltic	20.1	Leon city
El Reventador, Ecuador (1)	3 Nov 2002	3 Nov 2002	Vulcanian	Andesitic	90	Tombaco Valley, Quito
Etna, Italy (1)	4 Nov 2002	4 Nov 2002	Strombolian	Basaltic	11–12	S. Venerina
Fuego, Guatemala (1)	14 Oct 1974	29 Oct 1974	Sub-plinian	Basaltic	78	3 km W of Cuyotenango
Fuego, Guatemala (1)	22 May 1999	22 May 1999	Vulcanian	Basaltic	28	Amatitlan
Langila, Papua New Guinea (1)	1 Apr 1963	1 Apr 1963	Vulcanian	Basaltic-andesitic	9.5	Not documented
Merapi, Indonesia (1)	11–19 Jul 1998	9 Aug 1998	Dome collapse	Basaltic-andesitic	0.2	Volcano flanks
Mt St Helens, USA (6[a])	18 May 1980	18 May 1980	Plinian	Dacitic	378	Spokane
Pacaya, Guatemala (1)	14 Jun 1992	14 Jun 1992	Strombolian-vulcanian	Basaltic	1	Volcano Observers' Hut
Pacaya, Guatemala (1)	27 May 1994	27 May 1994	Strombolian-vulcanian	Basaltic	1	Volcano Observers' Hut
Pinatubo, Philippines (1)	30 Jun 1991	30 Jun 1991	Plinian	Dacitic	31.5	San Filipe
Pinatubo, Philippines (1)	4 Jul 1991	4 Jul 1991	Sub-plinian	Dacitic	20	Road between Balin Baquera and Bucau rivers
Ruapehu, New Zealand (20[b])	17 Jun 1996	18 Jun 1996	Sub-plinian	Andesitic	~140	Rotorua
Sakurajima, Japan (1)	1 Jan 1994	5 Jan 1994	Vulcanian	Andesitic	2.7	Arimura
Soufrière Hills, Montserrat (1)	5 Jun 1999	5 Jun 1999	Dome collapse	Andesitic	4	Salem
Soufrière Hills, Montserrat (1)	12 Jul 2003	12 Jul 2003	Dome collapse	Andesitic	4	Olveston
Soufrière Hills, Montserrat (1)	25 Sep 1997–6 Oct 1997	25 Sep 1997–6 Oct 1997	Vulcanian explosion	Andesitic	4–5	NW of volcano
Tungurahua, Ecuador (1)	2–3 Nov 1999	3 Nov 1999	Strombolian-vulcanian	Andesitic	10	Barrio Bilbao
Ulawun, Papua New Guinea (1)	15–16 Oct 1973	15–16 Oct 1973	Strombolian	Basaltic	10.2	Ulamona Catholic Mission
Vesuvius, Italy (2[c])	24–26 Aug 79 AD	21 Jan 2005	Plinian	Tephritic-phonolitic	6.3	Ranieri Quarry
Vesuvius, Italy (3[c])	AD79–472	21 Jan 2005	Strombolian-vulcanian	Tephritic-phonolitic	4	Villa Telesi

[a] Mt St Helens samples collected between 150–600 km from source from 18 May 1980 eruption. [b] Ruapehu samples collected between 50–180 km from source from 17 June 1996 eruption. [c] All Vesuvius samples for AD79 and AD79–472 were collected from same locations as in table (different strata from same sections). In Fig. 4, 14 further samples were analysed from Vesuvius, spanning a range of eruption styles, dates and locations. [d] Eruption style and magmatic composition information are based, where possible, on data for the individual eruptions. Where data were not available, the information is based on the general composition of volcanic products and style of eruption for the volcano.

rhyolitic ash sample from the eruption of Toba (~74 kyr BP) was also tested, with the same results. The AC used for all volcanic ash samples in this paper is 0.1 (close to transparent).

4. Sample collection, preparation and analysis

4.1 Volcanic ash collection

A suite of volcanic ash samples was collected from around the world, from volcanoes with different magmatic compositions (Table 1). Samples were collected at varying distances from the volcano, ranging from a few hundred metres to hundreds of kilometres. Some samples were collected soon after eruption, whilst others were collected centuries following an eruption from deposits that had *not* been reworked since deposition. In general, only one sample was obtained per volcano or eruption but for the eruptions of Mt St Helens, USA and Mt Ruapehu, New Zealand, analyses were carried out on many samples from the same eruption.

4.2 Pre-analysis sample preparation

Achieving a representative sample prior to size analysis is vital for powders that are of heterogeneous composition and grain-size, especially when a sub-sample may consist of only a few mg of material. Inverting or shaking a sealed container of volcanic ash several times is sufficient to mix the sample, which should then be left for several minutes to allow the fines to settle before removing the sub-sample. Fig. 3 compares the grain-size distribution (by laser diffraction analysis) of a sample of ash from the Soufrière Hills Volcano, Montserrat (MBA5/6/99),[17] where the sample has been prepared by 'container shaking' and by several other standard techniques, which include: (i) the 'cone and quartering' technique where a sample is formed into a cone, then cut into four piles using a knife. Two opposing piles are removed and re-bagged and the other two again formed into a cone, and the procedure repeated until a sample of the correct size is obtained. This method can leave fines on the cutting surface from the discarded piles and risks high levels of fine ash exposure for the worker. (ii) The 'spinning riffler' technique where the ash is slowly vibrated down a shaft at the end of which are twenty
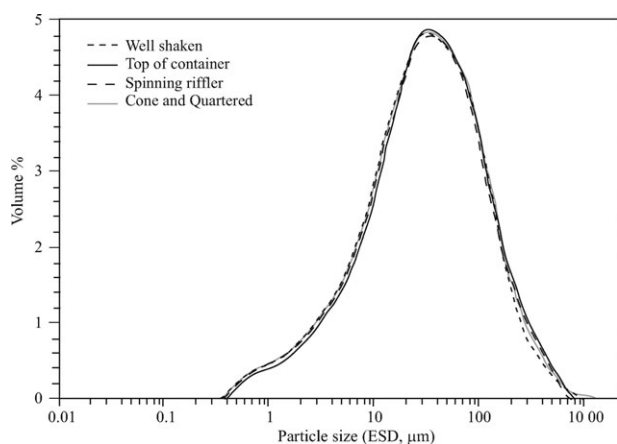
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Fig. 3 Averaged results (3 runs) of grain-size distributions using different representative sampling techniques for the 5 June 1999 Soufrière Hills, Montserrat ash. For all data, RI = 1.63 and absorption = 0.1. ESD = equivalent spherical diameter.

trays which rotate at a slow speed. The ash drops into the trays and each tray passes under the shaft at least twenty times (depending on the amount of sample being separated). One tray is then removed from the rotator, the contents emptied onto paper and mixed and then samples removed for grain-size analysis. The 'riffle box' technique, where a dry powder is poured into a box containing dividers, can also be used but both the spinning riffler and riffle box equipment may be difficult to obtain. (iii) Ash is simply removed from the top of a bag or container without prior agitation. Fig. 3 shows that inverting or shaking a container is as accurate, particularly for the health-pertinent fractions, as other more time-consuming, expensive techniques, and more accurate than simply removing the sub-sample from the top of the container. Therefore, in the work presented here, sub-samples were obtained using the 'container shaking' method.

4.3 Sample analysis

Prior to analysis, all samples were dried in an oven at $\sim 90\ ^{\circ}C$ for 24 h. Samples were sieved to <1 mm diameter (0 Phi) to ensure that grains greater than 2000 μm AD were not analysed (both because this is greater than the classification for particles of ash—sub-2 mm—and because laser diffractometers can only analyse particles smaller than this) and any organic material was removed. None of the samples analysed had significant material greater than 1 mm diameter, so no adjustment of results was required to take into account coarser fractions not included in the laser diffraction analysis.

All ash samples were analysed by laser diffraction using the Malvern Mastersizer 2000 Hydro MU with ultrasonics, a standard operating procedure of 20 s measurement time, obscuration of 5–20% and pump speed 2500 rpm. Three measurement cycles were recorded for each sample and an average taken. Results are obtained as volume percentages assuming that the particles are spherical. Data were then converted into cumulative vol% to assess the quantity of material in health-pertinent fractions. Data were collected in size bins determined by the laser diffractometer's setup. To

obtain precise data on the health fractions, the data points were then interpolated.

5. Results and discussion of grain-size analyses

Following quantification of the health-relevant size fractions, it is instructive to compare the results among volcanic eruptions, especially those where health hazard assessment has been carried out. Although there is much literature on GSA of volcanic ash e.g. ref. 20 and 21, it is only in health-related papers that data are presented on the health-relevant fractions.[17,22–24] Furthermore, the health relevant 'respirable' fraction was reclassified from sub-10 μm to sub-4 μm in the 1990s;[13] to date, Horwell et al.[17] present the only published data for the sub-4 μm and sub-10 μm fractions.

Table 2 shows the amount of material in the health-pertinent fractions for volcanic ash samples from around the world, measured by laser diffraction. The amount of respirable material (<4 μm) in bulk ash samples (<1 mm diameter) varies from 0–17 vol%. In general, basaltic volcanoes displaying vulcanian or strombolian activity, such as Pacaya and Ulawun, produce relatively small amounts of respirable material (<1%) when compared with andesitic, dacitic or phonolitc eruptions displaying sub-plinian or plinian activity (>9%). Table 2 is ordered by increasing VEI (volcanic explosivity index[25]) and it is clear that there is a positive correlation between the explosivity of the eruption and the amount of fine ash produced. Exceptions to this rule occur during dome-collapse eruptions. These eruptions are not highly explosive, therefore rating relatively low on the VEI scale (e.g. Merapi, VEI 2 or Soufrière Hills, VEI 3) yet these eruptions generate large amounts of respirable material (10.7–12.7%). This highlights a fundamental difference in fragmentation efficiency between ash generated from pulverisation of dome rock in a pyroclastic flow and ash generated from explosive fragmentation of fresh magma and also shows the effect of preferential elutriation of fine material into a lofting co-ignimbrite plume (see Soufrière Hills samples in Table 2 and ref. 17 and 26).

Only three volcanoes have had significant medical or toxicological studies carried out. The eruption of Mt St Helens in May 1980 prompted many investigations, as has the on-going eruption of the Soufrière Hills volcano, Montserrat (see Horwell & Baxter[12] and references therein for an overview of all studies). Table 2 shows that both volcanoes produce significant quantities of fine ash ($\sim$11% for both volcanoes). The population near Sakurajima volcano, Japan, have also been subjected to at least twelve epidemiological or clinical studies.[12] However, results here show that <1% of the ash from Sakurajima volcano is respirable. This result is based on just one sample, however, and may not be representative of normal tephra deposition.

The amount of fine-grained material in each sample reflects several factors including: (i) the style and dynamics of the eruption. Volcanic ash is produced by fragmentation of magma, either explosively or through collapse of an existing lava dome. The resultant ash is composed of particles derived from whole and fragmented phenocrysts, microlites and groundmass. (ii) Processes within the eruption plume (including

Table 2 Amount of material for health-pertinent fractions found in selected samples of volcanic ash. The table is ordered by increasing VEI (volcanic explosivity index). See Table 1 for further information on samples. Grain-size distributions measured on Malvern Mastersizer 2000 with Hydro MU

Volcano	Magma type/eruption style	VEI[a]	Grain-size distribution, cumulative volume%					
			<1 μm	<2.5 μm	<4 μm	<10 μm	<15 μm	<63 μm
Pacaya, Guatemala 1994	Basaltic, stromb.-vulc.	1	0.00	0.00	0.04	0.41	0.7	2.23
Pacaya, Guatemala 1992	Basaltic, stromb.-vulc.	1	0.00	0.26	0.76	2.43	3.76	16.6
Fuego, Guatemala 1999	Basaltic, vulcanian	2	0.00	0.00	0.00	0.00	0.00	1.56
Ulawun, Papua New Guinea	Basaltic, strombolian	2	0.00	0.02	0.27	0.88	1.63	4.14
Cerro Negro, Nicaragua	Basaltic, stromb.-vulc.	2	0.00	0.22	0.64	2.55	4.17	14.64
Tungurahua, Ecuador	Andesitic, stromb.-vulc.	2	0.65	2.49	4.11	10.49	15.46	41.8
Langila, Papua New Guinea	Bas.-and., vulcanian	2	0.87	3.29	5.63	13.95	19.83	52.71
Merapi, Indonesia	Bas.-and., dome collapse	2	1.95	8.02	12.66	27.24	38.11	83.06
Vesuvius, Italy AD79–472	Tephr.-phon., stromb.-vulc.	2–3	0.72	2.09	3.24	7.13	10.14	33.99
Sakurajima, Japan	Andesitic, vulcanian	3	0.00	0.5	0.86	1.95	2.87	14.74
Etna, Italy	Basaltic, strombolian	3	0.27	1.09	1.83	4.59	6.75	22.17
Ruapehu, New Zealand	Andesitic, sub-plinian	3	0.51	2.44	4.14	9.43	13.37	32.19
Soufrière Hills, Montserrat 1997	Andesitic, vulc. explosion	3	1.00	3.6	5.9	13.4	18.5	44.08
Soufrière Hills, Montserrat 1999	Andesitic, dome collapse	3	1.94	6.74	10.7	23.1	31.9	76.88
Soufrière Hills, Montserrat 2003	Andesitic, dome collapse	3	2.7	7.87	11.47	22.49	30.75	74.63
Fuego, Guatemala 1974	Basaltic, sub-plinian	4	0.88	2.43	3.66	7.99	12.04	46.64
El Reventador, Ecuador	Andesitic, vulcanian	4	0.9	3.21	4.88	10.16	15.12	72.93
Mt St Helens, USA	Dacitic, plinian	5	1.69	7.39	11.74	24.5	33.15	78.76
Vesuvius, Italy AD79	Tephr.-phon., plinian	5	4.81	11.62	16.93	32.83	43.39	83.7
Pinatubo, Philippines 3/6/91	Dacitic, plinian	6	1.07	5.49	8.97	17.88	23.12	54.05
Pinatubo, Philippines 4/7/91	Dacitic, sub-plinian	6	1.33	6.18	9.82	18.93	24.34	60.69

[a] VEI values taken from the Smithsonian Institute catalogue of volcanic eruptions.[31]

magma fragmentation, column dynamics, wind dispersal and interaction with ice, water and electrostatic forces). (iii) The distance from the volcano to the site of sample deposition. Table 1 shows that some samples were collected very close to the vent, whilst others were collected at great distances. It may be expected that ash which was erupted during a plinian eruption (*e.g.* Vesuvius AD 79) would contain a higher proportion of fine material at distances of tens to hundreds of km from the volcano. The AD 79 sample in this study was collected only 6.3 km from the vent, yet is the most fine-grained sample analysed to date (16.93% <4 μm).

The data presented in Table 2 give an indication of the variation in the quantity of health-pertinent material produced by different volcanoes and may be used to predict the GSD from those volcanoes, and volcanoes of similar eruption style, during future eruptions.

5.1 Comparison of eruption styles

Two samples of ash were analysed from Fuego, Guatemala, which generates high-Al basaltic magma.[27,28] In general, basaltic volcanoes erupt lava effusively but, occasionally, explosive basaltic volcanism can result in the generation of fine-grained material, which may constitute a health hazard.[12] Historically, Fuego (Guatemala) alternates between effusive eruptions and explosive vulcanian to sub-plinian eruptions.[29] The 1974 sub-plinian eruption analysed here was the largest eruption recorded in a series of events which started in 1944 [30] and is classified as VEI 4, which is high for a basaltic eruption. The 1999 eruption was a small, explosive eruption with accompanying lava flow and is classified as VEI 2. Although samples were collected at different distances from the vent (78 km and 28 km, respectively), it is clear that the sub-plinian eruption generated significant quantities of <4 μm material

for a basaltic eruption (3.66%) and the 1999 sample contains almost no fine-grained material with only 1.56% material in the <63 μm fraction. This highlights the importance of analysing material from different eruptions where a volcano is known to switch between different eruptive styles.

Similarly, the GSD of samples from Vesuvius varies greatly depending on the explosivity of the eruption. Throughout its history, Vesuvius has shown many different styles of volcanic activity, ranging from large-scale plinian eruptions to small-scale effusive events, which characterise the latter stages of the most recent (1631–1944) eruptive cycle. Table 2 shows grain-size data for contrasting eruptions of Vesuvius: the AD 79 plinian eruption, and the period between AD 79 and AD 472 (Pollena) eruptions, characterised by periods of continuous low-level ash emission which deposited the Santa Maria sequence (D. Andronico and R. Ciono, pers. comm.). The proportion of <4 μm material in the AD 79 sample is five times greater than that in the Pollena sample (16.93% and 3.24%, respectively).

Where samples have been analysed from different eruptions from the same volcano where eruption style was similar, there is little difference in grain-size distribution. For this study, three samples of ash were analysed from the Soufrière Hills volcano. Table 2 shows that the dome collapse samples are very similar in GSD, despite having been erupted two years apart, whereas the explosive sample is much coarser grained.

5.2 Correlation of health-pertinent fractions

The relative abundances of the different health-pertinent fractions correlate strongly across the ash samples investigated in this study. Fig. 4 shows three correlation plots. Fig. 4(a) demonstrates a very strong relationship between the

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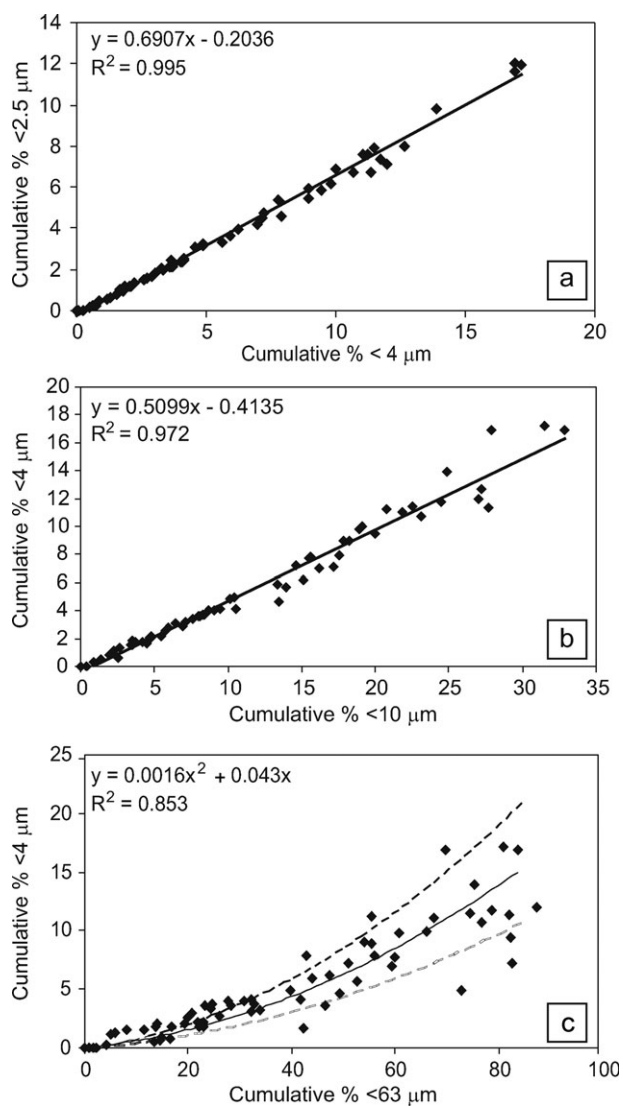*J. Environ. Monit.*, 2007, **9**, 1107–1115 | 1113

Fig. 4 Correlation plots of health-pertinent size fractions. All samples were measured by laser diffraction using a Malvern Mastersizer 2000 Hydro MU. Total number of samples analysed for plots = 63.

sub-4 μm fraction and the sub-2.5 μm fraction. The data suggest that the finest volcanic particles fall out together, possibly joined by electrostatic forces. This relationship is independent of other factors, such as distance from vent or the style of eruption, allowing a single relationship to be proposed for all volcanic eruptions. Furthermore, these data may have relevance to models of fallout of volcanic particles from plumes and give insight into processes of particle interactions within ash clouds. From a health perspective, we can use the results to estimate the abundance of hazardous ultra-fine particles where only data on respirable particles are available. Likewise, Fig. 4(b) shows a strong, linear relationship between the sub-10 μm and sub-4 μm fractions. The linear regression equation presented in this figure can be used to predict the amount of respirable material in a sample where only data on the thoracic (sub-10 μm) fraction are available. This is particularly useful for extrapolating from existing data, where only the quantity of sub-10 μm material was measured.

Fig. 4(c) shows the relationship between the sub-63 μm fraction and the sub-4 μm fraction. Although the relationship is not as strong as for the finer size fractions, the regression equation is useful for estimating the quantity of respirable material where only data for the sub-63 μm fraction are available. This should be of particular use for rapid assessment of the health hazard of volcanic ash in areas where measurements must be made by basic sieving techniques. Below 63 μm, sieving becomes unreliable as fine particles aggregate and adhere to coarser particles and are also lost through lofting during agitation. When plotting the relationship between coarser grain sizes, a polynomial relationship gives a better fit to the trend of the data than a linear fit (see Fig. 4(c)). For estimation of the quantity of sub-10 μm material in a sub-63 μm sieve fraction, a correlation of data from this paper produces the best-fit polynomial equation:

$$y = 0.0009x^2 + 0.236x \ (R^2 = 0.88).$$

Fig. 4(a–c) shows that the scatter of the data about the best-fit line increases as the difference between the sizes of the fractions increases. For Fig. 4(c), the error due to this scatter is quantified by adding "error fits" to the data. The error fits are constructed by scaling the best-fit line by an error factor, which is adjusted until the error fits encompass approximately two thirds of the data points. In Fig. 4(c), the error fits shown give an error factor of 1.4. This means that values of y calculated according to the best-fit equation are subject to an error; the maximum value is $1.4y$ and the minimum is $y/1.4$.

6. Conclusions

The grain-size distribution of volcanic ash fall varies according to the style and explosivity of an eruption, and the distance from the volcano and plume axis. Until now, quantitative data for the variation of the health-relevant grain-size fractions amongst different eruptions were scarce, making rapid hazard assessment of health risk impossible. It is unusual, following an ash fall, for multiple samples to be collected within hours of eruption at different distances from the volcano. Indeed, most of the ash samples presented here are single samples collected following an eruption and give no indication of the GSD at other locations. Such samples are important for the assessment of the health hazard at a particular location, for example in a particular town, but it is unusual to have enough data to extrapolate the findings to other areas downwind of the eruption. It is recommended, therefore, that a network of ash collection sites is setup prior to an eruption so that a rapid assessment of health hazards may be made across a region.

The data presented in this paper cover a range of ash types and allow generalisations to be made about the likely quantities of health-pertinent material erupted at different volcanoes. The relationship between different grain-size fractions also allows estimation of amounts of respirable material when state-of-the-art techniques are unavailable, thereby reducing a barrier which has hitherto prevented rapid initial assessment of health hazards in developing areas.

Appendix

The Becke Line method: the particles are set on a glass slide and immersed in a few drops of liquid with a known refractive index. A bright line, the 'Becke Line', is observed with a petrological microscope on the edge of the grain if the refractive index of the mineral and liquid are different. The apparent movement of this line into the mineral or into the liquid during lowering or lifting of the objective determines whether the mineral or liquid has the higher refractive index. Grains are immersed in several liquids until one is found where the Becke Line cannot be seen because the grain and liquid have almost identical refractive indices. The Becke Line moves into the medium with the higher refractive index when the objective is lifted or the stage is lowered.

Acknowledgements

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