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The iron-catalysed surface reactivity and health-pertinent physical characteristics of explosive volcanic ash from Mt. Etna, Italy

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Abstract

Mount Etna is Europe's largest and most active volcano. In recent years, it has displayed enhanced explosive activity, causing concern amongst local inhabitants who frequently have to live with, and clean up, substantial ashfall. Basaltic volcanic ash is generally considered unlikely to be a respiratory health hazard due to its often coarse nature (with few particles sub-10 μm diameter) and lack of crystalline silica. However, a previous study by the authors showed the capability of basaltic ash to generate the hydroxyl radical, a highly-reactive species which may cause cell damage. That study investigated a single sample of Etna ash, amongst others, with data giving an early indication that the Etnean ash may be uniquely reactive.

In this study, we analyse a suite of Etnean samples from recent and historical eruptions. Deposits indicate that Etna's past history was much more explosive than current activity, with frequent sub-plinian to plinian events. Given the recent increase in explosivity of Etna, the potential hazard of similarly, or more-explosive, eruptions should be assessed.

A suite of physicochemical analyses were conducted which showed recent ash, from 2001 and 2002 explosive phases, to be of similar composition to the historical deposits (trachy-basaltic) but rather coarser (< 2.4 c.v.% sub-10 μm material and <11.5 c.v.% sub-10 μm material, respectively), but the potential for post-depositional fragmentation by wind and vehicles should not be ignored. One recent sample contained a moderate number of fibre-like particles, but all other samples were typical of fine-grained ash (blocky, angular with electrostatic or chemical aggregation of finer particles on larger ones). The surface reactivity analyses (Fenton chemistry, on samples from recent eruptions only) showed that Etnean ash is more reactive in hydroxyl radical generation than other basaltic ash, and samples of intermediate composition. This high reactivity suggests that Etnean ash could promote oxidative stress in exposed cells. Therefore, further investigation of the potential toxicity, through cellular tests, is now warranted in order to provide a comprehensive health hazard assessment.

Keywords: Etna, Volcanic ash, Respiratory health, Surface reactivity, Fenton chemistry, Volcanic hazard
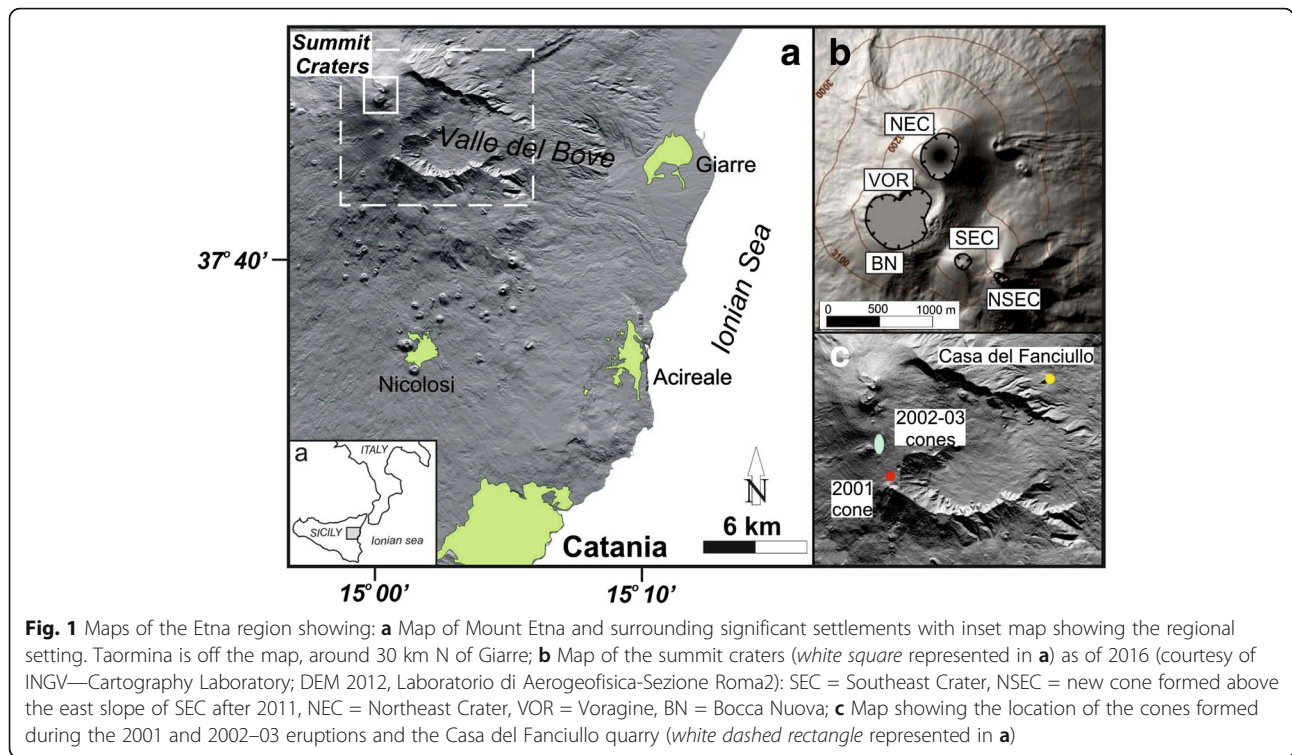
Introduction

Mt. Etna, Sicily is Europe's largest volcano and is one of the world's most active strato-volcanoes. Etna is located 25–30 km northwest of Catania, Sicily's second largest city (population of 315,000; Fig. 1) and frequent eruptions shower local populations with basaltic ash. Since 1998, the normally-effusive volcano has produced a series of more violent, explosive events characterised by tall eruption columns (up to 6–7 km above the summit), substantial tephra generation and magnitudes/eruption styles ranging from lava fountaining to violent strombolian to sub-plinian (Del Carlo et al. 2004; Andronico et al. 2015) (see Fig. 2). Investigation of Etna's past activity has revealed that explosive eruptions (including plinian eruptions) were more common in previous millennia (Branca and Del Carlo 2004, 2005) and the potential for a return to highly-explosive activity (based on the increase in magnitude and frequency of paroxysmal

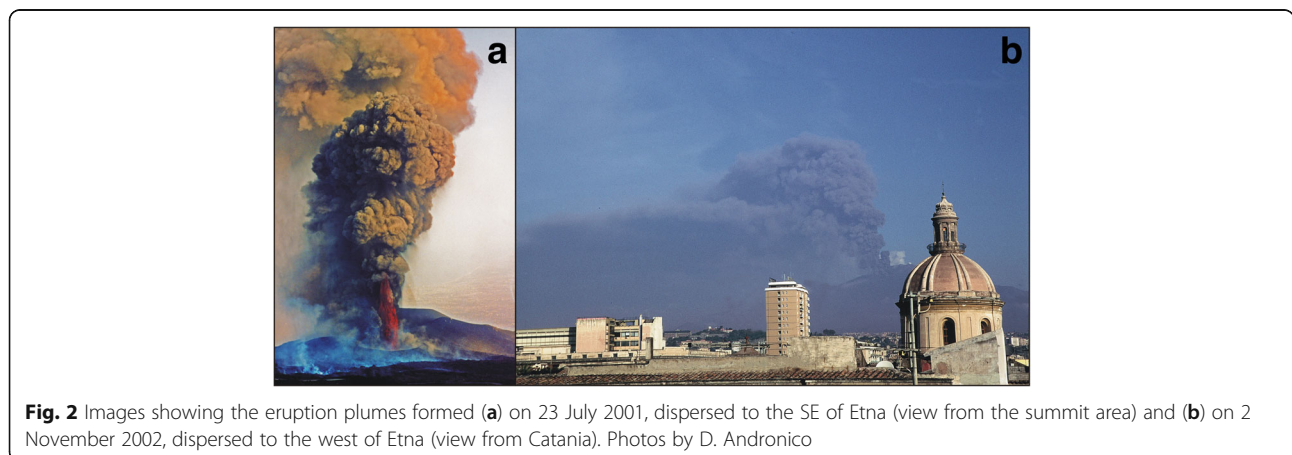* Correspondence: Claire.horwell@durham.ac.uk
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Fig. 1 Maps of the Etna region showing: **a** Map of Mount Etna and surrounding significant settlements with inset map showing the regional setting. Taormina is off the map, around 30 km N of Giarre; **b** Map of the summit craters (*white square* represented in **a**) as of 2016 (courtesy of INGV—Cartography Laboratory; DEM 2012, Laboratorio di Aerogeofisica-Sezione Roma2): SEC = Southeast Crater, NSEC = new cone formed above the east slope of SEC after 2011, NEC = Northeast Crater, VOR = Voragine, BN = Bocca Nuova; **c** Map showing the location of the cones formed during the 2001 and 2002–03 eruptions and the Casa del Fanciullo quarry (*white dashed rectangle* represented in **a**)

eruptions recorded in the last 20 years) has led to new considerations of the hazard presented by fine-grained Etnean ash.

The respiratory health hazards of volcanic ash have been extensively studied over the past 30 years, since the eruption of Mt. St. Helens, USA in 1980. However, few studies have addressed the hazard of inhaling basaltic ash, given that the prime concern is usually crystalline silica, which rarely occurs in mafic eruptions in health-relevant quantities. In addition, mafic eruptions tend to be effusive, generating rather coarse ash deposits (with little to no ash finer than 10 μm diameter) which pose

little respiratory concern (Horwell 2007) as these particles cannot easily penetrate into the lung. However, some mafic eruptions can generate fine-grained ash through explosive fragmentation, and may be particularly efficient at doing so when there is some interaction with water (Horwell 2007). At Etna, past sub-plinian to plinian eruptions have produced fine-grained deposits. Even during strombolian eruptions and lava fountains, the sand-sized ash may be fragmented and abraded, post-deposition, by vehicles and, potentially, aeolian processes. Little is done to remove the ash, thereby generating a prolonged exposure hazard. Here, we consider

Fig. 2 Images showing the eruption plumes formed (**a**) on 23 July 2001, dispersed to the SE of Etna (view from the summit area) and (**b**) on 2 November 2002, dispersed to the west of Etna (view from Catania). Photos by D. Andronico

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this exposure hazard through assessment of the physico-chemical characteristics of explosive Etnean ash of relevance to respiratory health.

Horwell et al. (2007) determined that a single ash sample, ejected during the 2002 eruption of Etna (Andronico et al. 2008b), generated substantial quantities of iron-catalysed hydroxyl radicals, exceeding those typically measured for more felsic ash types and other basaltic samples tested, such as from Pacaya, Guatemala and Cerro Negro, Nicaragua. This was the first indication that basaltic ash may pose a respiratory hazard, through a well-recognised mechanism involving the interaction of reduced iron on the particle surfaces with hydrogen peroxide, which is available in the lungs or can be generated through the Haber Weiss cycle (Fubini and Otero Arean 1999). This 'Fenton reaction' may lead to cellular changes (e.g., DNA damage (a pro-carcinogenic effect)) and lung inflammation (Hardy and Aust 1995; Kane 1996). Therefore, our ability to test for the potential for such damage through laboratory-based, cell-free tests allows insight into a potential mechanism of iron-catalysed toxicity which can then be further tested for in cellular assays.

Horwell et al. (2003a) first demonstrated that this mechanism of potential toxicity applied to ash, on samples from the Soufrière Hills volcano, Montserrat. Further to this, Horwell et al. (2007) confirmed that all ash, across the magmatic compositional spectrum, generated hydroxyl radicals, with basaltic samples (particularly Etna) appearing to be more reactive than other ash types. The ability of ash to generate the hydroxyl radical has now been confirmed at several other volcanoes (Damby et al. 2013; Hillman et al. 2012; Horwell et al. 2013; Horwell et al. 2010; Le Blond et al. 2010).

The work on volcanic ash surface reactivity builds on previous work which has shown that, when in contact with biological fluids, many mineral dusts generate free radicals and other reactive oxygen species (ROS) via various mechanisms (Fubini et al. 1995; Schoonen et al. 2006) and to varying degrees, including lunar dust (Turci et al. 2015), quartz (Fubini 1998) and asbestos (Fubini et al. 1995).

This study investigates the health-pertinent physical and chemical characteristics of a suite of fine-grained Etna ash samples, to determine likely bio-reactivity, to aid in the assessment of respiratory ash hazard. Few fine-grained samples exist due to the prevalence of Strombolian and lava-fountaining activity in recent years, which tend to produce coarser ash (including the large, December 2015 paroxysmal eruption; Corsaro et al. 2017). Therefore, in addition to the only available samples, from the 2001 and 2002–03 eruptions, stored in the archives of INGV, a suite of ancient, fine-grained

samples from sub-plinian activity was collected to widen our understanding of the potential characteristics of Etnean explosive ash generation.

The methods follow those used in recent years for analyses of ash for respiratory health hazard assessment, according to the protocol developed by the International Volcanic Health Hazard Network (e.g., Damby et al. 2013; Horwell et al. 2013; Le Blond et al. 2010 and downloadable from www.ivhhn.org). A full review of the respiratory health hazards of volcanic ash can be found in Horwell and Baxter (2006).

Review of Etna's explosive eruptive activity

The following review summarises the styles of explosive activity at Etna which likely generate fine-grained ash of respiratory health concern and gives oversight of the potential range of explosive activity which could occur in future eruptions, in the context of ash hazard. The review also puts into context the samples analysed in this study. Etna's magmatic composition has varied over its history among tholeiitic basalts, alkali olivine basalts and alkali basalts (Corsaro and Pompilio 2004). Its eruptive styles vary through lava fountaining and strombolian activity (the norm in the twentieth century and in the first years of the twenty-first century) to sub-plinian and plinian phenomena, with some phreatomagmatic activity (explosive interaction of magma with water).

Prehistoric and historic explosive eruptions

In the last century, Etna has been considered a volcano dominated by persistent activity from the summit craters (i.e., degassing phases and moderate strombolian activity), alternating with effusive eruptions producing large volumes of lava. However, the tephrostratigraphic record of Etna shows that, historically, Etna was not the effusive volcano that it is regarded as today or, at least, until 2001 (see below). It had periods of intense explosivity which, for the past 100 k.a., have been grouped by Del Carlo et al. (2004) into stratigraphic units corresponding to these periods. Plinian eruptions occurred between 80 and 100 k.a. B.P., sub-plinian eruptions characterised activity between 16 and 80 k.a. B.P. and plinian eruptions again dominated between 15 and 15.5 k.a. B.P. Recently, Albert et al. (2013) have recognised distal plinian and ignimbrite deposits and aged them between ca. 17–19 k.a. B.P.. The last 12 k.a. have been characterised by basaltic sub-plinian eruptions, with one plinian eruption in historical times, i.e. in 122 B.C., which severely damaged ancient Catania and the cultivated surroundings. Del Carlo et al. (2004) attributed the explosivity to high magmatic volatile contents during those times, although Coltelli et al. (1998) proposed a sudden decompression of the magma chamber, leading to bubble nucleation

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along with rapid increases in viscosity and density reductions as the trigger.

Since 1700, the location and timing of eruptive activity at Etna has been carefully recorded. During the past 400 years, some flank eruptions, characterised by intense, long-lasting, strombolian and lava fountaining activity, produced copious tephra fallouts similar to those that occurred during the 2001 and 2002–03 eruptions (Branca and Del Carlo 2005) (see below). Among these highly-explosive events, the eruption of 1763 lasted 84 days (Recupero 1815) and is thought to have been similar in nature to the 2002–03 eruption (Andronico et al. 2005). It displayed intense, continuous explosive activity, with some lava output, and formed La Montagnola scoria cone. Fire fountaining produced eruptive columns of lapilli and ash, which extended from the SE flank down to Catania. Several explosive eruptions occurred in the nineteenth Century (1811, 1852–53, 1886 and 1892), again producing continuous tephra-fall over prolonged periods. No twentieth Century eruptions exhibited such similar intensity (Branca and Del Carlo 2005).

2001 eruption

The eruption began on 17 July and lasted until 9 August with intense explosive and effusive activity originating from seven vents along the S and NE flanks of the volcano (Behncke and Neri 2003) (Fig. 2a). Two main systems of eruptive fissures opened, whereby one of the eccentric vents, at 2570 m elevation, exhibited vigorous phreatomagmatic activity (Taddeucci et al. 2002), which was caused by the feeder dike cutting through a shallow aquifer. The violent explosive activity led to the formation of a new cinder cone near La Montagnola cone (Calvari and Pinkerton 2004) (Fig. 1c), producing 5–10×10^6 m^3 of pyroclastic emissions (Behncke and Neri 2003). A dense ash plume occurred with a sustained column up to 5 km a.s.l. (Scollo et al. 2007), which caused heavy ashfall for around ten days, especially along the eastern flank between Taormina and Catania. Significant damage was caused, mostly to skiing areas (1900–2600 m) on Etna's southern flank. The ash comprised tachylite clasts, sideromelane glass fragments, felsic plagioclase feldspar crystals, mafic pyroxene and olivine crystals and altered volcanic and (rare) sedimentary lithic clasts (Taddeucci et al. 2002).

2002–2003 eruption

The eruption began on 26 October 2002 and ended on 28 January 2003 and featured continuous explosive activity (Andronico et al. 2005) (Fig. 2b). Following lava flow effusion and fire fountaining from fissures along Etna's NE and S flanks, after 5 November the eruption continued exclusively on the S flanks with continuous explosive activity and lava flows of relatively un-degassed, volatile-rich magma (Andronico et al. 2005). The explosions were characterised by lava fountains, which formed columns of ash and lapilli up to 7 km a.s.l. (Andronico et al. 2008b) and new cones (Fig. 1c). This activity generated heavy tephra falls in Etna's southern/south-eastern sectors, due to the prevailing wind direction. This caused severe disruption around Catania and east of the volcano, with ash travelling up to 500 km from the source. However, re-suspension was limited by rainfall (Fano et al. 2010). It is estimated that 43×10^6 m^3 of pyroclastics were erupted during the 2002–03 eruption (Andronico et al. 2008b) with a total of 4 kg/m^2 of ash deposited on Catania (Andronico et al. 2005). Overall, the tephra fallout affected ~900,000 people around the inhabited slopes of Etna. The ash comprised tachylite, sideromelane, crystals and lithic clasts, the proportions of which varied substantially over the eruption's duration (Andronico et al. 2009) but, in general, the ash had a lower lithic and crystal content than the 2001 ash (Taddeucci et al. 2002).

Sequences of paroxysmal episodes

In the past 20 years, Etna produced several 'episodic eruptions' from the summit craters (Andronico and Corsaro 2011; Andronico et al. 2014a; Andronico et al. 2014b), i.e. sequences of paroxysmal episodes which lasted from weeks to months. Each episode was characterized by powerful, strombolian to lava-fountaining activity lasting a few hours to 1–3 days, accompanied by tephra fallout over the inhabited volcanic slopes. Most of these episodes occurred from the South-East Crater (Fig. 1b). Since 2011, 46 episodes occurred, through three different sequences, from a lateral vent of this crater, building a new cone named New South-East Crater (Andronico et al. 2014a) (Fig. 1b). The first sequence was in 2011–12 while the latter two were in 2013 (Behncke et al. 2014; De Beni et al. 2015). In 2014, the New South-East Crater displayed two further strombolian episodes, each lasting 3 days.

In general, we have observed that the tephra erupted during these paroxysmal episodes is very coarse, usually coarser than that erupted during the 2001 and 2002–03 eruptions (see Results section). As examples, the 24 November 2006 paroxysm (Andronico et al. 2014b), 4–5 September 2007 (Andronico et al. 2008a) and 12–13 January 2011 (Andronico et al. 2014a) lava fountains produced low-to-negligible quantities of ash below 0.063 mm; more recently, the large-scale lava fountain episode which took place on 23 November 2013 emitted lapilli and coarse ash up to 25 km from the vent (Andronico et al., 2015). Between 3 and 5 December 2015, four high-energy, lava-fountaining episodes took placed at the Voragine crater, producing eruption plumes up to 15 km a.s.l. (Vulpiani et al. 2016) and dispersing fine tephra up to hundreds of km away from the vent (Corsaro et al. 2017).

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The 2001 and 2002–03 eruptions shared many features but, particular to this study, the strongly-explosive style of both eruptions caused prolonged ash emissions, which posed a hazard to local populations. Nonetheless, long-lived eruptive activity similar to the episodic eruptions may also have the same impact on urbanised areas surrounding Etna and thus people's health.

Summary of studies on the respiratory hazard of Etnean ash

As there have been no previous reviews of health-related literature related to Etnean ash, the following paragraphs summarise the existing studies related to environmental exposure to ash (as opposed to occupational exposure related to mining volcanic deposits). Several studies over the past decade have examined the respiratory hazard of Etnean ash, from exposure, epidemiology and toxicology standpoints.

Fano et al. (2005) conducted an epidemiological study on the acute health effects from ash inhalation during the 2002–03 eruption (106-day study including 59 eruption days and 47 non-eruption days during which unusually-high PM_{10} levels >200 μg/m^3 were recorded in the city of Catania). Mortality and hospital admissions datasets were collected for all residents of Catania and Acireale districts compared with the same period in 2001. No changes in all-cause and cardiovascular mortality were observed, although a significant decrease in mortality due to respiratory diseases was detected during the eruption period, potentially due to the implementation of preventative measures including staying indoors. However, a significant, albeit delayed, increase in hospital admissions for cardiovascular diseases was detected, especially among older people (>65 years) and was attributed to acute stress. There was also an increase in admissions for eye disorders.

Lombardo et al. (2013) also conducted a retrospective epidemiological study following the 2002–03 eruption to assess acute health effects in exposed communities. The number and nature of visits to the emergency departments (ED) of public hospitals in the Province of Catania were assessed between 20 October and 7 November and were compared with data for the same period in 2001. A significant increase in ED visits for acute respiratory and cardiovascular diseases and ocular issues was observed during the time period.

Diana et al. (2006) correlated the number of Etnean ash events between April 2003–January 2005, with the amount of total immunoglobulin E (IgE) antibody produced by a study population (925 patients) exposed to the ash. IgE is produced through a response to allergens. The study was devised following a noticeable increase in allergies during a period of low airborne allergens (e.g. pollen) following the 2001 and 2002–03 eruptions. IgE was observed to increase in the population concurrently with volcanic ash episodes, indicating that ash contributes to transitory respiratory pathologies such as allergopathies in the Etna area.

Barsotti et al. (2010) performed a quantitative assessment to determine the potential impacts of fine ash fallout from Etna on human exposure and infrastructure. Using the numerical model VOL-CALPUFF and Monte Carlo simulations, towns on the east of the volcano were confirmed to be significantly more exposed to ash hazards than elsewhere (due to prevailing wind conditions) and that the amount of 10 μm volcanic particles deposited was proportional to the eruption intensity. However, in the inhabited volcanic areas, concentrations of 10 μm volcanic particulate diameter, i.e. the upper limit of particles able to penetrate the upper airways, are likely to be highest during small events due to reduced dispersal of low altitude plumes. They also showed that particle re-suspension is an issue post-deposition.

Censi et al. (2011a) proposed that yttrium-lanthanide phosphate precipitation can occur in human lungs following inhalation and dissolution of volcanic ash. Individuals exposed to the 2001 Etna ash had phosphatic microcrysts within their lungs, which can lead to pulmonary fibrosis, diagnosed by enrichments of yttrium and lanthanides (trace elements which have an affinity for phosphate) in broncho-alveolar lavage fluid. Censi et al. (2011b) also showed that those exposed to the 2001 Etna ash had a strong enrichment of several other potentially-toxic heavy metals (V, Cr, Mn, Fe, Co and U) in their lung fluid compared with a control group from SE Sicily.

Also concerning trace elements, Varrica et al. (2014) used scalp hair as a bio-monitor to evaluate the exposure of school children to metals and metalloids. Twenty trace elements were determined in 376 samples of children's hair from ten towns around Etna. As, U and V were raised and Sr depleted in Etnean children in comparison to a control site, this was attributed to ingestion via drinking water and food derived from the Etnean slopes rather than to ash inhalation.

Sample collection and selection

For the physical characterisation of the ash, eight archived samples (from INGV Catania) collected from Etna's 2001 and 2002–03 eruptions at the time of deposition (which had been stored within sealed jars) were studied (see Table 1 for sample information).

Eight further ash samples were collected in September 2008 representing deposits of potentially fine-grained ash from historical explosive eruptions. Holocene deposits dating back to 12 k.a. (unit E of Del Carlo et al. 2004) mantle Etna's edifice and were accessed at the Casa del Fanciullo quarry on the north-eastern slope of

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Table 1 Sample information for archived INGV samples

Sample name	Year of eruption	Date erupted	Date collected	Sample location	Weather conditions during deposition	Notes
INGV_1	2001	20/7/01–21/7/01	22/7/01	Acireale	No rain	Phreatomagmatic activity
INGV_2	2002	28/10/02 (22.00) – 29/10/02 (08.20)	29/10/02	S. Agata li Battiati	No rain	
INGV_3	2002	3/11/02 (00.00–03.00)	3/11/02	Catania	No rain	
INGV_4	2002	13/11/02–14/11/02	14/11/02	Piedimonte Etneo	No rain	
INGV_5	2002	27/10/02	27/10/02	S. Agata li Battiati	No rain	Ash fallout occurred throughout day
INGV_6	2002	28/10/02 (07.00) – 29/10/02 (10.00)	29/10/02	Catania	No rain	
INGV_7	2002	31/10/02–1/11/02	2/11/02	Piedimonte Etneo	No rain	
INGV_8	2002	8/12/02	8/12/02	INGV Catania	Probably no rain	Ash fallout occurred throughout day

the Valle Del Bove (N 37°45.438, E 015°04.550; Fig. 1c). Samples were obtained from eight different pyroclastic fall events within a stratigraphic sequence (section 156/ 195; Del Carlo et al. 2004) younging, chronologically, from the basaltic plinian event in 122 B.C. (marker bed FG; Del Carlo et al. 2004). The sequence comprised a mixture of tephra and epiclastic deposits with some reworking by weathering and erosion. According to the Del Carlo et al. (2004) classification, the samples collected were basaltic to basic mugearite and correspond to stratigraphic layers between FG and N15/N16, roughly correlating to ages 2136–500 years B.P.. No samples were taken from the FG layer due to outcrop inaccessibility.

Around 20–25 cm above FG is bed FF, a reverse-graded scoria lapilli fall deposit (Del Carlo et al. 2004), which is thought to have been formed by a sub-plinian eruption ~44 B.C. and was sampled for this study (Sample CdF_1), forming the lowest layer of our sequence. The younger deposits sampled are

interpreted as small sub-plinian eruptions (see Table 2 for full description).

For the chemical studies (hydroxyl radical generation and iron release), a subset of four of the fresh, archived INGV Etna samples were chosen. They were deemed the most 'hazardous', due to their particle size distribution (they all contain particles sub-10 μm diameter, see Table 4) and lack of weathering/alteration. The sample of ash studied by Horwell et al. (2007), erupted on 4 November 2002 and collected that day, was also reanalysed (here known as ETNA4/11/02).

Alongside these samples, three samples of ash from other volcanoes were analysed. These samples, from Soufrière Hills volcano, Montserrat (which produces andesitic to dacitic ash), Pinatubo volcano, Philippines (also dacitic) and Cerro Negro, Nicaragua (basaltic) have previously been analysed extensively in these assays and, as in this study, have previously been used as 'standard' samples to represent a range of iron release and hydroxyl radical generation potential (e.g., Damby et al.

Table 2 Description of stratigraphic units sampled at Casa del Fanciullo quarry

Sample #	Stratigraphic layer in Del Carlo et al. (2004)	Depth from bottom of sequence (from FG marker bed)	Age (years B.P. ± 80)[a]	Description
CdF_1	FF	25–38 cm	1970	From 44 B.C. sub-plinian eruption. Coarse ash layer
CdF_2	-	38–48 cm		Grey/violet-coloured fine-grained tuff
CdF_3	-	89–109 cm		Yellow/brown reworked epiclastic fine-grained deposit
CdF_4	N11	109–129 cm	1860	Dark grey scoriaceous lapilli layer
CdF_5	N14	141–146 cm	560	Whitish-coloured fine-grained tuff
CdF_6	N15	218–226 cm		Whitish-coloured fine-grained tuff
CdF_7	-	237–256 cm		Yellow/brown reworked epiclastic fine-grained deposit
CdF_8	-	266–272 cm		Violet-coloured fine-grained tuff

[a]Ages from Del Carlo et al. (2004)

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2013; Horwell et al. 2007; Horwell et al. 2013; Le Blond et al. 2010 and unpublished analyses; Hillman et al. 2012). Due to logistical and timing constrictions of the assays, no more than a total of 8 samples were analysed.

Methods

Sample preparation
Sample masses were recorded prior to, and after, oven drying within pyrex dishes at 80 °C for 24 h. Samples were then passed through 2 mm and 1 mm sieves, with the mass of each fraction recorded. Some of the quarry samples contained organic matter (i.e. visible roots), which was removed from the <1 mm and 1–2 mm fractions using tweezers under a light microscope. Samples were then re-weighed.

Physical analyses
A range of physical analyses were performed on the <1 mm ash, according to the IVHHN ash analysis protocol (www.ivhhn.org) and the methods therein. These methods are detailed elsewhere using the same techniques in the same laboratories (Damby et al. 2013; Horwell 2007; Horwell et al. 2013; Le Blond et al. 2009) so are only briefly mentioned here. For rapid analyses (for which the IVHHN protocol was designed), the sub-1 mm fraction is used as separation of the respirable fraction is extremely time consuming. Here, this fraction was used because of the relatively-coarse nature of most of the samples (and, hence, the mass of ash required to separate sufficient respirable material was beyond the mass available for the INGV samples). In addition, use of the sub-1 mm fraction allows direct comparison with all previous health-relevant characterisation work conducted using the IVHHN protocol in recent years, including the study which originally analysed the hydroxyl radical generation potential of Etna ash (Horwell et al., 2007).

For all samples, the magmatic composition was confirmed through X-ray fluorescence (XRF), performed at the University of Leicester, UK on a PANalytical Axios Advanced XRF spectrometer. Particle size analysis was conducted in the Department of Geography, University of Cambridge, UK, on a Malvern Mastersizer 2000 with Hydro MU platform, to determine the amount of health-pertinent material in the samples. Scanning electron microscopy (SEM) was performed at the School of Earth Sciences, University of Bristol (ETNA4/11/02 only, Hitachi S3500 N, 20 KeV) and GJ Russell Microscopy Facility, Durham University (INGV_1, 5, 8 and CdF_5, 6, Hitachi SU-70, 8 KeV), to examine particle morphology and to search for fibre-like particles in secondary electron mode. Energy dispersive spectrometry (SEM-EDS at Durham; Oxford Inca x-act LN2-free analytical Silicon Drift Detector) gave an indication of the elemental composition of any fibre-like particles.

The Brunauer-Emmett-Teller method of nitrogen adsorption allowed the determination of the surface area of the particles (Durham University, UK; Micromeritics TriStar 3000 Surface Area and Porosimetry Analyser).

Chemical analyses
Electron paramagnetic spectroscopy with spin-trap was conducted at the Dipartimento di Chimica, Università degli Studi di Torino, Italy (Miniscope 100 ESR spectrometer, Magnettech) to evaluate the ability of ash samples to catalyse hydroxyl radical generation in solution. In this experiment, the Fenton reaction is replicated, where Fe^{2+} reacts with hydrogen peroxide to produce the deleterious hydroxyl radical ($HO^{\bullet}$):

$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH- + HO^{\bullet}$.
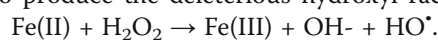
The short-lived radicals are stabilised through the use of a 'spin-trap' (DMPO) to allow measurement. One hour experiments were conducted and aliquots measured after 10, 30 and 60 min. The amount of removable Fe^{2+} and Fe^{3+} available for participation in the Fenton reaction was quantified using a Fe^{2+} specific chelator (ferrozine) in the presence or absence of ascorbic acid, which reduces the Fe^{3+} to Fe^{2+}. Suspensions were centrifuged and measured daily by spectrophotometry (at 562 nm; Uvikon spectrophotometer) for 7 days. Results are expressed per unit surface area. The above techniques are defined in detail in the original papers describing the use of these assays for volcanic ash (Horwell et al. 2007; Horwell et al. 2003a).

Results
Whole rock elemental data (in oxide wt.%) obtained by XRF (Table 3), are plotted on a total alkali versus silica plot (Fig. 3). The data confirm the magmatic composition of Etna ash to be trachy-basaltic for the 2001, 2002 and historical samples, with the exception of CdF_4 (a scoriaceous lapilli layer) which was more mafic and less alkaline, plotting on the basalt/tephrite boundary.

Raw particle size data were re-scaled, where necessary, to account for any particles within the 1–2 mm fraction (as these were not analysed), so that data reflect the cumulative volume (c.v.) % of particles in the whole 'ash-fraction' (sub-2 mm). The data (Table 4) revealed samples from the 2001 and 2002 eruptions to be rather coarse, with four of the 2002 samples having no material sub-10 µm diameter. The 2001 sample (related to phreatomagmatic activity; Scollo et al. 2007; Taddeucci et al. 2002) was the finest, with 2.4 c.v.% sub-10 µm material. The historical CdF samples were much finer, containing between 0.5–5.2 c.v.% sub-4 µm material and 1.4–11.5 c.v.% sub-10 µm material. Horwell (2007) demonstrated a strong correlation for a range of ash samples ($R^2 = 0.995$) when the sub-4 and sub-10 µm fractions are plotted against each other, with a ratio of roughly

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Table 3 Whole-rock XRF data for Etna ash samples (oxide weight %)

Sample #	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	SO$_3$	LOI	Total
INGV_1	48.82	1.61	17.72	10.30	0.171	4.66	9.43	4.16	2.049	0.599	0.045	−0.09	99.48
INGV_2	46.74	1.79	16.96	11.59	0.177	5.16	10.50	3.45	2.039	0.558	0.047	0.03	99.05
INGV_3	47.73	1.78	17.20	11.51	0.169	5.67	10.38	3.28	1.866	0.536	0.080	−0.19	100.00
INGV_4	47.37	1.72	16.84	11.44	0.177	5.68	10.16	3.41	1.928	0.560	0.020	0.09	99.40
INGV_5	46.76	1.81	16.63	11.79	0.181	5.64	10.50	3.52	1.925	0.557	0.123	−0.10	99.34
INGV_6	46.69	1.82	16.72	11.87	0.177	5.41	10.64	3.41	1.931	0.542	0.061	−0.23	99.04
INGV_7	46.59	1.78	16.93	11.86	0.177	5.77	10.48	3.39	1.915	0.527	0.067	−0.24	99.26
INGV_8	47.91	1.69	17.61	10.86	0.172	4.80	10.10	3.71	2.142	0.577	0.060	0.00	99.62
CdF_1	49.28	1.44	19.84	9.10	0.151	3.12	8.98	4.14	1.593	0.620	0.017	0.95	99.22
CdF_2	49.01	1.41	19.52	9.19	0.150	3.43	9.09	4.09	1.540	0.602	0.023	0.70	98.74
CdF_3	48.41	1.46	19.96	9.41	0.154	3.33	8.84	3.83	1.465	0.624	0.038	1.71	99.23
CdF_4	45.21	1.69	19.48	10.56	0.199	3.35	7.66	3.09	1.246	0.711	0.026	5.92	99.15
CdF_5	47.81	1.51	19.80	9.61	0.161	3.39	8.35	3.74	1.441	0.621	0.035	3.13	99.60
CdF_6	48.09	1.59	18.77	8.95	0.122	2.64	6.96	3.74	1.796	0.746	0.240	5.71	99.36
CdF_7	48.57	1.58	18.77	8.64	0.134	2.74	7.37	3.79	1.720	0.715	0.220	4.94	99.19
CdF_8	49.04	1.48	19.67	9.34	0.155	3.41	9.79	4.09	1.545	0.553	0.036	0.24	99.36
ETNA4/11/02	47.46	1.73	16.72	11.56	0.17	5.72	10.10	3.84	2.10	0.61	-	−0.18	99.84

1:2. Here, the data demonstrate a similarly-strong trend, for both the recent and historical samples (Additional file 1: Fig. S1). This indicates that neither set of samples had lost any fine material (or any other fractions) since deposition, and that the historical samples had not been substantially weathered (producing finer particles than the original particle distribution) nor had additional, substantial fine-grained organic matter.

Figure 4 is a compilation of SEM images of respirable particles from both recent and historical samples; as
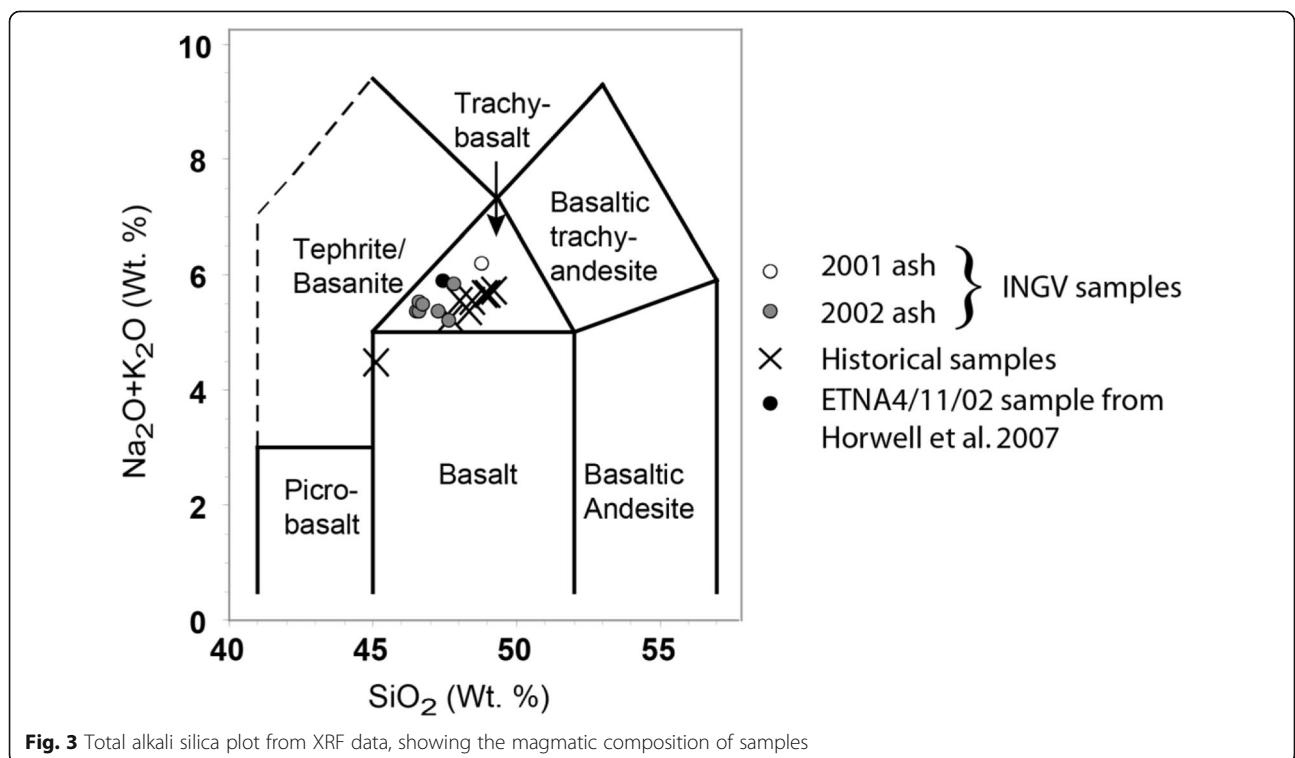

Fig. 3 Total alkali silica plot from XRF data, showing the magmatic composition of samples

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Table 4 Health-pertinent particle size data (cumulative volume %)

Sample #	< 1 μm	< 2.5 μm	< 4 μm	< 10 μm
INGV_1	0.00	0.33	0.83	2.40
INGV_2	0.00	0.00	0.00	0.00
INGV_3	0.00	0.00	0.00	0.00
INGV_4	0.00	0.01	0.20	0.87
INGV_5	0.00	0.17	0.57	1.66
INGV_6	0.00	0.00	0.00	0.00
INGV_7	0.00	0.00	0.00	0.00
INGV_8	0.00	0.04	0.30	1.42
CdF_1	0.00	0.16	0.46	1.51
CdF_2	0.61	1.71	2.76	6.58
CdF_3	0.50	1.37	2.13	5.10
CdF_4	0.25	0.80	1.33	3.40
CdF_5	1.38	2.90	4.24	10.79
CdF_6	1.51	3.51	5.20	11.47
CdF_7	0.51	1.12	1.75	4.44
CdF_8	0.61	1.85	2.95	6.86
ETNA4/11/02[a]	0.27	1.09	1.83	4.59
MON5/6/99[a]	1.94	6.74	10.7	23.1
CER30/11/95[a]	0	0.22	0.64	2.55
PIN4/7/91[a]	1.33	6.18	9.82	18.93

[a]Data from Horwell (2007) where sample information can also be found

with other published images of the inhalable fractions of ash (e.g., Damby et al. 2013; Horwell et al. 2013; Le Blond et al. 2010; Hillman et al. 2012), it is not easy to distinguish mineralogical phases based on particle morphology at this scale, although crystalline morphologies were apparent for some particles (Fig. 4b). The recent samples generally looked 'fresh' with some smaller particles either electrostatically or chemically aggregated on larger particles and there was also evidence of surface crystallisation of salts (Fig. 4d). The historical samples were markedly different, with most particles either being aggregated or being covered in a 'crust' of smaller particles and salts, perhaps chemically cemented together (Fig. 4c). Samples contained negligible fibre-like particles, with the exception of sample INGV_8 which contained many particles, with fibre-like habits, adhered to their surfaces. Figure 5 shows a compilation of images of these morphologies. The fibres were spindle-like and conformed to the WHO definition in dimension (3:1 ratio) if not length (> 5 μm) (World Health Organization 1986). Compositional analysis (by SEM-EDS) of the fibres was challenging due to their ubiquity on the surface of other particles, and narrow width, but they clearly contained Mg, distinct from Si, Al, Na and Ca which were also present in the underlying particles.

Surface area analyses confirmed the Etna ash to have extremely low surface areas, as was also found by Horwell et al. (2007) on the single sample analysed in that study (ETNA4/11/02) (Table 5).

Hydroxyl radical and iron release data are presented in Table 5. As with previous papers which have analysed the surface reactivity of volcanic ash (Damby et al. 2013; Hillman et al. 2012; Horwell et al. 2007; Horwell et al. 2003a; Le Blond et al. 2010), the data are best represented in a plot of hydroxyl radical generation versus total iron release at 7 days (Fig. 6). In previous work, we have presented the hydroxyl radical data for 30 min after the start of the experiment; here we present the final reading, at 60 min as the kinetics of the experiments showed that the reactions were still sustained at that time point. These data better represent the full potential of the samples for radical generation.

In Fig. 6, the four INGV samples (collected fresh, soon after ashfall) are plotted along with ETNA4/11/02 and three other 'standard' ash samples used by the above authors, previously. The data presented are averages of these multiple analyses (see figure caption for detail). ETNA4/11/02 is highly reactive, yet variably so, with the data presented in Horwell et al. (2007), at 9.7 μmol/m^2, for hydroxyl radical generation at 30 min, far exceeding the average value of 4.72 μmol/m^2 presented here (5.03 μmol/m^2 at 60 min; Table 5). The data collected from the four INGV samples are mostly within the range of the average value for ETNA4/11/02.

When compared with samples from other volcanoes, the Etna samples are more reactive and certainly are capable of releasing iron (mainly Fe^{3+}, Table 5) far in excess of the other samples. CER30/11/95, erupted from Cerro Negro volcano, Nicaragua is another fine-grained basaltic ash sample analysed by Horwell et al. (2007). It consistently shows lower reactivity than the Etna samples. MON5/6/99 is from the andesitic-dacitic Soufrière Hills, Montserrat eruption and PIN4/7/91 was erupted in a dacitic sub-plinian eruption soon after the cataclysmic Pinatubo, Philippines eruption of 30 June 1991 (see Horwell et al., 2007 or Horwell, 2007 for detailed sample information). Soufrière Hills ash has consistently demonstrated low hydroxyl radical generation capacity and low iron release whereas Pinatubo, whilst also having little available iron, consistently generates more radicals. This observation (low iron release but variable hydroxyl radical generation potential) has been previously noted for many intermediate to felsic samples (see references above). A general trend of increasing radical generation with iron release is apparent (R^2 = 0.68; Fig. 6) with the Etna samples having considerably more potential to generate these deleterious radicals than the other samples.
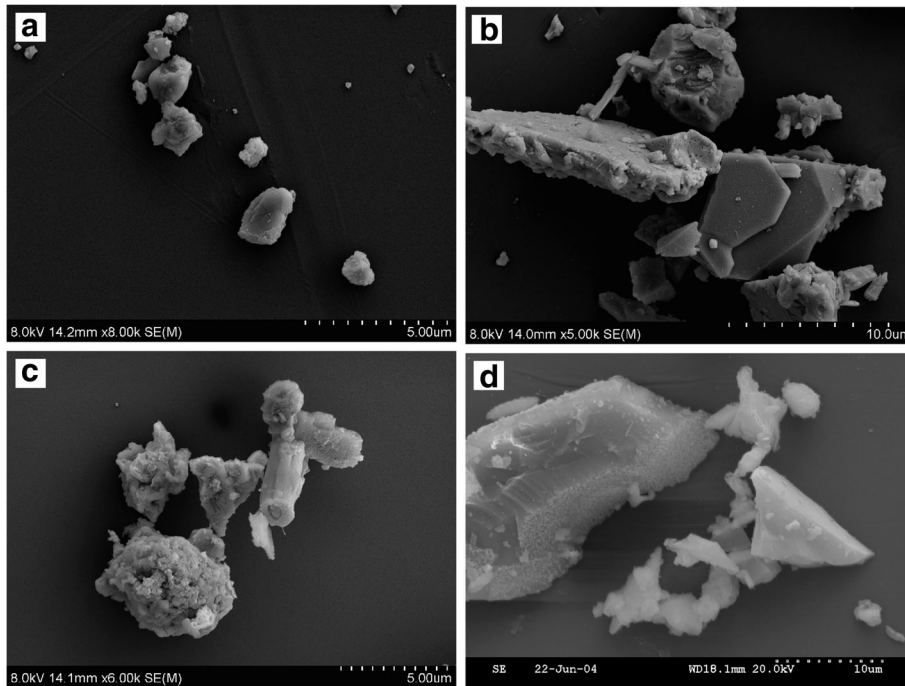
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Fig. 4 Images of respirable ash from Etna. **a** INGV_5; **b** INGV_1; **c** CdF_5; **d** ETNA4/11/02 showing particles of ash of varying sizes down to <1 μm diameter. The larger particles have smaller particles adhered to them and some particles have adsorbed salts crystallised on the surface (**d**, *top left*) or appear as clusters or potentially cemented aggregates of particles (**c**)
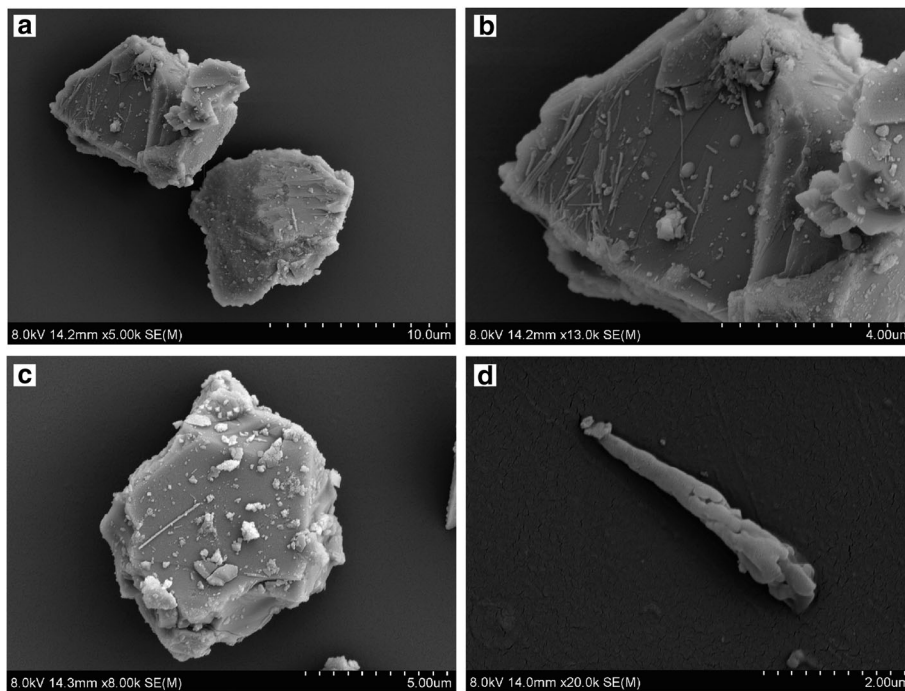

Fig. 5 Images of fibre-like particles. **a**, **b** and **c** from INGV_8 (**b** is a close up of **a**). **d** is from INGV_1

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Table 5 Data on surface area, generation of hydroxyl radicals and iron release

Sample #	Surface area (m^2/g)[c]	Hydroxyl radical generation at 30 min ($\mu mol/m^2$)[c]			Iron release at 7d ($\mu mol/m^2$)		
		10 min	30 min	60 min	Fe^{2+}	Fe^{3+}	Total Fe
INGV_1	0.27	1.39	2.87	3.71	83.9	680.8	745.2
INGV_4	0.10	1.12	2.98	5.06	326.8	701.2	1028.0
INGV_5	0.13	1.35	3.08	7.02	77.8	583.3	661.1
INGV_8	0.08	1.68	3.52	6.75	226.9	1120.3	1347.2
ETNA4/11/02[a]	0.19[b]		4.72[a]	5.03[a]			502.5[a]
MON5/6/99[a]	1.28[b]		0.58[a]	0.58[a]			25.5[a]
CER30/11/95[a]	0.47[b]		2.03[a]	2.22[a]			238.3[a]
PIN4/7/91[a]	0.89[b]		1.88[a]	2.06[a]			29.9[a]

[a]These samples were used by Horwell et al. (2007) and have since been reanalysed on up to seven separate occasions, including for this study. The hydroxyl radical and iron release data presented here are the averages of these analyses. The original data in Horwell et al. (2007) for the Etna sample were 9.7 $\mu mol/m^2$ for hydroxyl radical generation at 30 min and 655.1 $\mu mol/m^2$ for total iron release at 7 days, and all data collected following that publication were less than these values
[b]Surface area data from Horwell et al. (2007)
[c]Data are the average of three runs for the samples in this study

Discussion

Exposure to particulate matter (PM) causes adverse health effects including pulmonary and cardiovascular disease. The 2013 World Health Organization REVIHAAP review (World Health Organization 2013) confirmed that acute and chronic exposures to PM less than 2.5 μm diameter ($PM_{2.5}$) increase both mortality and morbidity and that acute exposure to $PM_{2.5-10}$ is also associated with premature mortality. The 2010 Global Burden of Disease Study ranks exposure to ambient PM as the 9th highest cause of disease globally, with more than 3 million attributable deaths in 2010 (Lim et al. 2012) and, in October 2013, IARC classified PM as a lung carcinogen (Loomis et al. 2013). According to these studies, this evidence applies to all PM, including all crustal particles. The importance of protecting populations from acute and chronic exposures to fine-grained volcanic ash during eruptions is, therefore, clear.

Implications of chemical characteristics

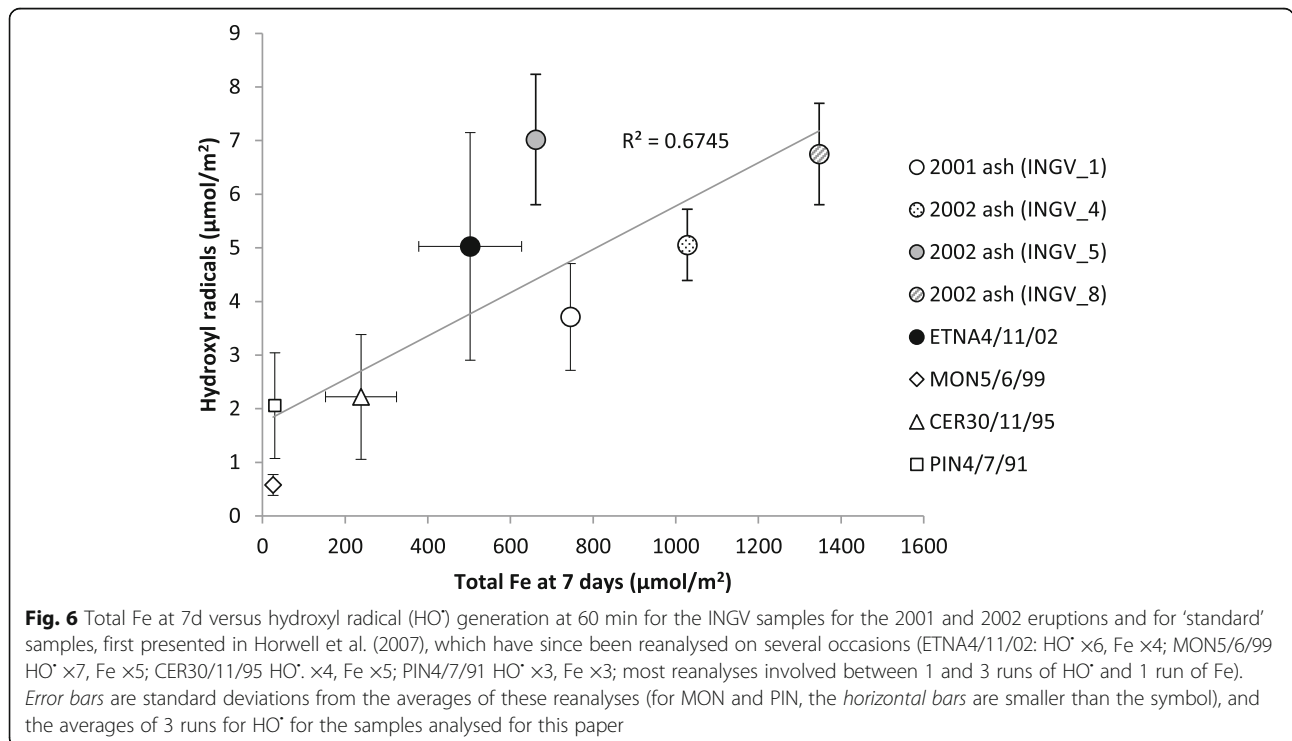A key aim of this study was to determine whether the Etna ash is unusual in its capability to generate

Fig. 6 Total Fe at 7d versus hydroxyl radical (HO˙) generation at 60 min for the INGV samples for the 2001 and 2002 eruptions and for 'standard' samples, first presented in Horwell et al. (2007), which have since been reanalysed on several occasions (ETNA4/11/02: HO˙ ×6, Fe ×4; MON5/6/99 HO˙ ×7, Fe ×5; CER30/11/95 HO˙. ×4, Fe ×5; PIN4/7/91 HO˙ ×3, Fe ×3; most reanalyses involved between 1 and 3 runs of HO˙ and 1 run of Fe). *Error bars* are standard deviations from the averages of these reanalyses (for MON and PIN, the *horizontal bars* are smaller than the symbol), and the averages of 3 runs for HO˙ for the samples analysed for this paper

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the hydroxyl radical through Fenton chemistry. Hydroxyl radicals are the most reactive among the oxygen-centred radicals, leading to widespread, unspecific reactions with biological molecules (Valko et al. 2004). Hydroxyl radical generation mainly takes place within the phagolysosomes (cytoplasmic bodies within cells) upon particle uptake by alveolar macrophages, the cells which clear inhaled particles from the lung. A sustained release of hydroxyl radicals and other reactive oxidant species, either mediated by the particle itself or by cells, may cause oxidant injury to the lung parenchyma, stimulating the production of growth factors and of pro-inflammatory cytokines, resulting in inflammatory responses (Barnes 2014).

The analysis of an ash sample from the 2002 eruption in a previous study (Horwell et al. 2007) evidenced the high reactivity of Etnean ash in the release of hydroxyl radicals. The data in this study, from four ash samples collected fresh, upon deposition (i.e. no weathering), confirm that Etnean ash is more reactive than other ash samples (including other mafic ones), with the sample analysed by Horwell et al. (2007), and in subsequent studies (Hillman et al. 2012; Horwell et al. 2013 and other unpublished work), encompassing the range observed for the INGV samples in this study.

In fact, the average number of hydroxyl radicals generated for the INGV samples at 60 min was 5.63 μmol/m^2, compared with 5.03 μmol/m^2 for ETNA4/11/02 (with a combined average of 5.51 μmol/m^2 for all Etna samples) and values of <2.2 μmol/m^2 for Cerro Negro, Pinatubo and Soufrière Hills volcanoes (Table 5 and Fig. 6) averaging at 1.62 μmol/m^2. There was no difference between the 2001 sample and 2002–03 sample data.

All of the Etna samples also released substantial quantities of iron - considerably more than has been seen for any other ash samples (e.g., Horwell et al. 2007) - although most of this was Fe^{3+} (Table 5). Iron ions, both leached in solution or bound at the particle surface, are responsible for hydroxyl radical generation in presence of H$_2$O$_2$, as shown above. Additionally, in experiments in vivo, the transition metals have been found to mediate inflammation caused by PM$_{10}$ (e.g., Costa and Dreher 1997). In vitro studies with various epithelial cell types have shown that transition metals can activate signalling pathways and stimulate release of pro-inflammatory molecules. For example, presence of easily removable iron ions has been associated with the release of the chemokine Interleukin-8 (Il-8) in coal fly ash (Smith et al. 2000).

A positive correlation between the amount of removable iron and the oxidative potential was observed in Etna samples, as has previously been reported for basaltic rocks (Horwell et al. 2007). Such correlation is not necessarily expected, since not all iron is active in free radical release, as documented for silica and asbestos

(Fubini and Hubbard 2003; Turci et al. 2011). No correlation is found with the amount of iron in the reduced form, only. This is not surprising considering that both Fe^{2+} and Fe^{3+} are able to generate hydroxyl radicals as long as they have at least one free coordinative site to bind H$_2$O$_2$ (Graf et al. 1984), although Fe^{2+} is expected to react immediately through the Fenton reaction, while Fe^{3+} must first be reduced. The slow kinetics of hydroxyl radical release (the small amount of radicals generated in the first minutes of incubation with H$_2$O$_2$ followed by a progressive increase; Table 5) observed for all INGV samples could suggest a major involvement of iron in the oxidized state.

From the work of Taddeucci et al. (2004) and Andronico et al. (2009), the 2002–03 ash had a lower lithic content than the 2001 ash and a different crystal distribution, although the componentry will vary slightly amongst samples collected in different locations. Regardless, these compositional differences do not seem to be clearly reflected in the data presented, and total iron content by XRF (Table 5) also did not reflect iron release. To better understand the possible importance of the ash componentry, similar physicochemical analyses deserve to be repeated in the future, together with ash samples from lava fountain deposits which are typically characterised by componentry almost, or totally, composed of fresh glass (sideromelane) particles (Andronico et al. 2008a).

The ash samples chosen for the hydroxyl radical generation and iron release experiments were purposefully pristine, in order to understand the potential surface reactivity of fresh Etnean ash. However, after deposition, ash will be exposed to rainfall and other environmental processes which may modify surface reactivity. The historical samples from the Casa del Fanciullo quarry were too old to be representative of freshly-weathered ash. However, Horwell et al. (2003a) studied hydroxyl radical formation in ash from the Soufrière Hills volcano, Montserrat using the same techniques as those in the current study. They tested a range of ash samples including 'aged' ash (MRAmix) which was extracted from a deposit spanning the entire eruption sequence, from 1995 to 2000 and had, therefore, been subjected to erosion, winnowing and leaching from rainwater percolation. In addition, in order to simulate weathering, each of the ash samples was systematically leached in solutions of varying acidity to determine how surface reactivity was impacted. The authors found that MRAmix was consistently less reactive than the fresh samples (see their Fig. 3) and that even leaching in weak acid substantially decreased hydroxyl radical generation (see their Fig. 8). These findings would likely also apply to ash from Etna.

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Implications of physical characteristics

Particle size and surface area

Particle size (PM_{10} and finer health-pertinent fractions such as PM_4 and $PM_{2.5}$) is the primary health risk factor to be taken into account when planning preventive measures to protect the respiratory health of populations from particulate air pollution, including from volcanic ash; if particles are too large to enter the lung then they will not present a respiratory hazard. The results from this study have shown that Etna ash deposited from early twenty-first Century explosive activity (in 2001 and 2002–03; INGV samples) is uniformly coarse grained with <2.5 vol.% sub-10 μm material (roughly equivalent to PM_{10}) and also has an extremely low surface area.

Half of the recent samples examined contained no health-pertinent particles; none of the samples contained material that was sub-1 μm diameter, nor did any of the samples have more than 1 vol.% sub-4 μm material. This suggests that the volume of directly-inhalable dust able to penetrate the deep lungs, where chronic respiratory disorders could potentially be triggered, is likely to be limited in such eruptions, unless the ash is further fragmented and re-suspended by wind and vehicles, and this should be investigated in future research. To our knowledge, no study has been conducted which looks at changes in re-suspended particle-size distributions over time, but Horwell et al. (2003b) found that the concentration of ash particles re-suspended by road vehicles from the Soufrière Hills volcano, Montserrat decreased exponentially with height above the ground, indicating higher exposure for children than adults. They also found that the re-suspended roadside dust contained fewer respirable (sub-4 μm) particles (by mass) than deposited ash, possibly because the finest particles are winnowed over time through multiple suspension episodes. The 'lost' particles may still be available for human exposure in the nearby vicinity, however.

An investigation of the timescale of particle abrasion by wind and vehicles is warranted, to confirm the production of additional respirable particulate and the likelihood of exposure whilst ash is still readily available in the environment. Barsotti et al.'s (2010) modelling highlighted the importance of remobilization and re-suspension of 10 μm volcanic particles following ash deposition, so lofting of the finest material, such as it is, following ash deposition may yet be important for respiratory hazard. Unfortunately, the medical evidence is currently insufficient to support this; Lombardo et al. (2013) did find a significant increase in ED visits for acute respiratory conditions during the 2002–03 eruption but this was in contrast to Fano et al. (2005) who did not find an increase in hospital admissions for respiratory ailments and, in fact, found a significant decrease in mortality for respiratory diseases during the eruption period.

During future eruptions, particle concentrations should be rapidly determined by ambient monitoring of airborne particles (see pilot study by Andronico and Del Carlo 2016) and particle-size analysis conducted on deposited particles, as a relatively-minor increase in explosivity could result in more fine-grained material being generated than has been observed in recent years. If particle-size distributions are found to be similar to the samples in this study, disaster managers may be able to advise on potential hazard through reference to this study, without conducting a full physicochemical investigation.

Of note, the sample analysed here from the 2001 eruption (classified as violent Strombolian by Scollo et al. (2007), based on the features of the tephra fallout deposit) was erupted during the preliminary, short phase of phreatomagmatic activity and this appears to be reflected in the slightly finer particle-size distribution than the 2002–03 samples. Phreatomagmatic activity has been previously correlated to increased quantities of respirable ash in comparison to drier explosive events (Horwell 2007; Horwell et al. 2013; Horwell et al. 2010).

The historical samples (from 44 B.C. to ~560 ± 80 years B.P.) all contained sub-10 μm material with samples CdF_5 and CdF_6 containing >10 vol.%, and >1 vol.% sub-1 μm material, respectively. These samples were whitish, fine-grained tuffs, most likely erupted during sub-plinian eruptions. It is clear that these must have been of an order of explosivity not observed in recent times. An eruption of this explosivity today, depositing 5–10 cm of fine-grained ash (as was seen in these deposits; Table 2), would be unprecedented and present a substantial challenge to surrounding local and regional agencies, in terms of public health protection, clean-up (Hayes et al. 2015) and impact on infrastructure and utilities (Wilson et al. 2012).

This study has focussed on particles generated during explosive, ash-rich eruptions. It is worth noting that Martin et al. (2008) investigated the composition and particle-size distribution of aerosol in the Mt. Etna plume (during periods of quiescent, persistent degassing in 2004–05) and found ultra-fine particles composed of silicates and sulphates, down to nanoparticle sizes (0.01 μm diameter). They estimated an emission flux of fine silicates (< 10 μm) of 7000 kg/day, and ~10^{18} nanoparticles per second, generated by the bursting of bubbles at the surface of the lava (in the crater) as well as through sulphate aerosol formation. This indicates that, even during periods of quiescent degassing, the Etna plume presents a persistent, potential particulate health hazard downwind.

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Morphology

The differences in morphology between the historical and recent samples ('crusted' and aggregated in the former) probably reflect the differences in particle size, with the historical samples being substantially finer, hence promoting electrostatic aggregation of very fine particles onto larger ones (see Brown et al. 2012, and references therein). However, the impact of time is also likely to have aided aggregation through formation of salt crusts and chemical cementation within the tuff deposit.

The fibre-like particles within INGV_8, in particular, are noteworthy. It was not possible to determine whether these fibres were strongly adhered to the particle surfaces (in which case they are unlikely to present a respiratory hazard) or would detach upon contact with lung fluid. It was also impossible to determine the exact mineralogical composition because they sat on/were adhered to larger particles; if they are composed of soluble salts, again they would unlikely be a hazard, but a more bio-durable crystalline phase cannot be ruled out. Although Mg rich, the likelihood of the particles being asbestos-related is remote. The Fe/Mg silicate fibre-like particles identified within ash from Eyjafjallajökull, Iceland, were found to be unrelated to asbestos through transmission electron microscopy diffraction pattern indexing (Horwell et al. 2013).

The slopes of Etna are actually infamous in terms of mineral-fibre hazard, due to the discovery of fluoro-edenite (a rare fibrous amphibole) in the Monte Calvario dome rocks at Biancavilla, on Etna's SW slopes. The rocks were frequently used as building materials, and inhalation of the fibres caused malignant pleural mesothelioma in residents of the village and surrounding areas (Gianfagna and Oberti 2001; Comba et al. 2003). Recently, fibrous orthopyroxene has also been identified in volcanic rocks for the first time, in a neighbouring dome (Santa Maria di Licodia) (Gianfagna et al. 2012). As the 2002 ash was collected fresh, the fibre-like morphologies observed in this study will not be related to the altered rock from which the fluoro-edenite and fibrous orthopyroxene originate.

It is not clear why INGV_8 appears to have more fibre-like particles than the other 2002 samples. There is the potential for contamination from the surface where the ash was collected, but all samples were collected from visually-clean surfaces. The presence of Mg-silicates suggests that the fibres are an original component of the ash as opposed to other anthropogenic or crustal contaminants.

Conclusions

The modern Etnean ash, even that emitted from paroxysmal explosive activity during the 2001 and 2002–03 eruptions, is rather coarse-grained but is capable of unusual surface reactivity in the laboratory setting, through substantial hydroxyl radical generation by Fenton reaction. Hence, there is the potential for iron-catalysed cellular toxicity within the lungs if particles are able to be inhaled in sufficient quantities.

Due to the very high frequency of both paroxysmal, episodic and long-lasting explosive eruptions, and the proved increased hazard from tephra remobilization and possible suspension in the air (Barsotti et al. 2010), further toxicological research is recommended, to investigate the propensity of the Etnean ash to have a pro-inflammatory effect and to cause damage to, and oxidative stress within, lung cells. This could potentially be conducted using recent, explosive ash which has been milled (in the laboratory) to simulate abrasion in the natural environment. The prevalence of fibre-like particles in Etnean ash should also be further investigated.

Given that the results of this study show that the bulk composition of modern Etnean ash is not substantially different from that erupted in historical times, it might be expected that fine-grained ash erupted over the centuries, in plinian phases which are not experienced currently, would also be capable of substantial hydroxyl radical generation. Given their fine-grained nature and, hence, potential to be inhaled into the deep lungs, the prospect of future, highly-explosive eruptive activity at Etna should not be ignored and plans should be put in place for public health protection and rapid, effective clean-up operations.

Additional file

Additional file 1: Figure S1. Correlation plot of health-pertinent size fractions (sub-4 and sub-10 μm) for historical and INGV samples. (DOCX 12 kb)

Authors' contributions
CJH conceived the research, designed the project, supervised PS with analyses and fieldwork and wrote the manuscript. PS conducted the fieldwork and analyses and wrote the MSci thesis on which the manuscript was based. DA and MDLC led the fieldwork, provided INGV ash samples and advised on Etna's eruptive history. MT and BF led the laboratory analyses at the University of Turin. SEH and SAKM assisted with analyses, and SAKM

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accompanied the fieldwork team. All authors read and approved the final manuscript.

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