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# Ash leachates from some recent eruptions of Mount Etna (Italy) and Popocatépetl (Mexico) volcanoes and their impact on amphibian living freshwater organisms

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# Abstract

Leaching experiments were carried out on fresh ash samples from Popocatépetl 2012, Etna 2011 and 2012 eruptions, in order to investigate the release of compounds in both double-deionised and lake (Ohrid lake, FYR of Macedonia) waters. The experi-

- <sup>5</sup> ments were carried out using different grain sizes and variable time of stirring (from 30 min to 7 days). Results were discussed in the light of changing pH and release of compounds for the different leachates. In particular, Etna samples induced alkalinisation and PopocatépetI samples induced acidification of the corresponding leachates. The release of different elements does not show correlation with time of stirring, with
- the measured maximum concentrations reached in the first hours of washing. General inverse correlation with grain size was observed only for Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and Mn<sup>2+</sup>, while the other analysed elements show complex, scattering relationship with grain size.

Geochemical modelling highlights leachates saturation only for F and Si, with <sup>15</sup> PopocatépetI samples sometimes showing saturation in Fe.

The analysed leachates are classified as undrinkable for humans on the basis of Italian laws, due to excess in  $F^-$ ,  $Mn^{2+}$ , Fe, and  $SO_4^{2-}$  (the latter only for Popocatépetl samples).

Finally, the Etna 2012 and Popocatépetl leachates were used for toxicity experiments on living biota (*Xenopus laevis*). They are mild toxic, and no significant differences exist between the toxic profiles of the two leachates. In particular, no significant embryo mortality was observed, while even at high dilutions the leachates produced more than 20% of malformed larvae.

**BGD** 12, 13241-13282, 2015 Ash leachates from some recent eruptions of Mount Etna M. D'Addabbo et al. **Title Page** Introduction Abstract Conclusions References **Figures** Close Back Full Screen / Esc **Printer-friendly Version** Interactive Discussion

Discussion

Paper

**Discussion** Paper

Discussion Paper

**Discussion** Paper

# 1 Introduction

Volcanic ash is the most widely distributed product of explosive volcanic eruptions, and areas hundreds of kilometres from an erupting volcano could receive ash falls (Ruggieri et al., 2010; Sulpizio et al., 2014). Even minor quantities of deposited ash
<sup>5</sup> represent a major hazard for the modern technical society and the environment (Blong, 1984; Johnston and Houghton, 2000). Deposition of fresh volcanic ash can disrupt power lines (Wardman et al., 2012), transport networks and water supplies (Martin et al., 2009; Wilson et al., 2012), or induce pH variations and pollution in soils and surface water, which have a serious impact on vegetation, animals and people (Ayris and Delmelle, 2012).

In particular, deposition of volcanic ash into aqueous environments leads to dissolution of adsorbed salts and aerosols, increasing the bioavailability of both key nutrients and pollutants. This is because acids, metal salts and adsorbed gases on tephra (airborne volcanic particulate matter) surfaces are highly soluble, dissolving rapidly on

- <sup>15</sup> contact with water (Frogner et al., 2001). These soluble surface accumulations have been termed "ash-leachates" by previous investigators (e.g. Witham et al., 2005) and we use this term hereafter. Ash-leachate chemistry and volume can vary considerably, depending on different gas solubility and degree of magma degassing prior or during the eruption (Oppenheimer, 2003). These processes are largely governed by the com-
- <sup>20</sup> position of the source magma (Armienta et al., 2002), but additional factors are also important, like the tephra particle size, the gas/ash ratio, and the time the ash remains in the volcanic cloud (Óskarsson, 1980; Witham et al., 2005).

Over 55 soluble components have been reported in volcanic ash leachates, with the anions  $CI^-$ ,  $SO_4^{2-}$  and  $F^-$  and the cations  $Ca^{2+}$ ,  $Na^+$  and  $Mg^{2+}$  generally occurring at the highest concentrations (Witham et al., 2005).

The rapid release of nutrients and metals following the mixing of unhydrated ash or aerosols with surface waters has been the focus of field studies (Gíslason et al., 2002; Uematsu, 2004; Flaathen and Gislason, 2007), and experimental studies (Frogner



et al., 2001; Duggen et al., 2007). The effects of ash fall on natural waters and water supplies have focused mainly on the consequences of increased levels of turbidity (ash suspended in water), acidity and fluoride content (Collins, 1978; Óskarsson, 1980; Weniger and Blaser, 1983; Cronin and Sharp, 2002; Stewart et al., 2006; Smithsonian

- Institution, 1997). On the other hand, contamination of drinkable water is a major concern for public health, due to the potential for outbreaks of waterborne infectious diseases due to the inhibition of disinfection at high levels of turbidity. Moreover, elevated concentrations of fluoride increase the risks of dental and skeletal fluorosis (Stewart et al., 2006).
- Impacts of ash on environment have been reported subsequently to a number of historic eruptions. During the 1783–84 eruption of Laki (Iceland) 50% of the livestock in Iceland perished, many probably as a result of fluorine poisoning (Thorarinsson, 1969; Grattan and Charman, 1994; Steingrímsson and Kunz, 1998). After the 1947–1948 eruption of Hekla in Iceland, some rivers and streams showed temporarily elevated flucture in the stream showed temporarily elevated flucture.
- <sup>15</sup> oride concentrations (up to 9.5 mg L<sup>-1</sup>; Stefánsson and Sigurjónsson, 1957). The ash from 1969 Ruapehu eruptions contaminated water supplies, with pH values ranging from 4.4 to 6.0 (Collins, 1978; Stewart et al., 2006). Similar pH values in receiving waters following volcanic ash deposition have been reported in many other studies (Wilcox and Coats, 1959; Cronin and Sharp, 2002; Smithsonian Institution, 1997). Several re-
- <sup>20</sup> cent eruptions have had high quantities of fluorine adsorbed on the tephra, including: Hekla, Iceland in 1970, 1991, and 2000 (Frogner et al., 2001; Gudmundsson and Oskarsson, 1992; Thorarinsson and Sigvaldason, 1972), Lonquimay, Chile in 1989–1900 (Araya et al., 1990, 1993) and Ruapehu, New Zealand in 1995–1996 (Shanks, 1997; Cronin et al., 2003).
- Other than fluoride release and acidity, little attention has been paid to contamination of water supplies by other soluble components of ash. There are some reports of elevated levels of iron, sulphate and chloride (Smithsonian Institution, 1997, 2000; Cronin and Sharp, 2002; Baxter and Ancia, 2002) but little or no discussion of their environmental impact. Evidence for phytoplankton blooms as a result of volcanogenic sedi-



mentation have been observed in lakes (Smith and White, 1985) and in oceans, based on preliminary satellite data (Duggen et al., 2007). Bio-incubation experiments have shown diatoms utilizing nutrients from volcanic ash (Duggen et al., 2007). Mesoscale iron enrichment experiments have shown that Fe addition to low chlorophyll ocean waters can instigate elevated marine primary productivity (Boyd et al., 2000).

In order to supply new data useful for understanding the behaviour of release of water contaminants from fresh volcanic ash and their impact on water supplies and living organisms, we collected ash deposits from two recent eruptions of Mount Etna (Italy, August 2011 and April 2012) and from the eruption of May 2012 of Popocatépetl volcano (Mexico). The collected volcanic ash was washed using two different types of wa-

ter (double de-ionised and natural lake water), and the released compounds analysed for major and trace elements. The results were discussed in the light of international and Italian drinkable limits for public waters.

Since the decline of amphibian populations has been retained a major consequence of the anthropic and naturally occurring environmental changes (Hayes et al., 2010), the ash leachates were also tested for toxicity using the amphibian *Xenopus laevis* as biological model. The bioassays were performed using the standardized Frog Embryo Teratogenesis assay – *Xenopus* (FETAX) (ASTM, 1998), already successfully applied to eco-toxicological investigations for testing single compounds and mixtures (Dawson,

<sup>20</sup> 1991; Bacchetta et al., 2008), municipal sludge (Chenon et al., 2003), material and sediment extracts (Mantecca et al., 2007; Fort et al., 2001).

# 2 Materials and methods

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# 2.1 Bulk rock, glass composition and sublimates

The samples used in the experiments are fresh volcanic ash from the eruptions of

<sup>25</sup> 12 August 2011 and 24 April 2012 eruptions of Mount Etna (southern Italy), and the eruption of May 2012 of PopocatépetI (Mexico). The samples were placed in polyethy-



lene bags and carried to the laboratory for dry sieving between 63  $\mu$ m and 1 mm at 1 $\phi$  interval ( $\phi = \log_2 d$ , where *d* is the particle diameter).

The composition of bulk ash samples was obtained by XRF using a Philips PW1480/10 automatic spectrometer (Cr anticathode for major and minor elements,

- <sup>5</sup> Rh anticathode for Rb, Sr, Y, Zr, Nb and W anticathode for Ce, La, Ba, Ni, Cr, V) at Dipartimento di Scienze della Terra e Geoambientali (University of Bari) following the analytical techniques outlined by Franzini et al. (1975) and Leoni and Saitta (1976). EDS analyses were performed on glass and mineral phases of the different tephra samples embedded in epoxy resin, polished and coated with carbon at the Diparti <sup>10</sup> mento di Scienze della Terra (University of Pisa), using an EDAX-DX micro-analyzer
- mounted on a Philips SEM 515 (operating conditions: 20 kV acceleration voltage, 100 s live time counting, 10<sup>-9</sup> Å beam current, ZAF correction). Instrument calibration and performance are described in Marianelli and Sbrana (1998). Back-scattered electrons (BSE) SEM images of sublimate compounds on ash surfaces were obtained with a 50XVP LEO Scanning Electron Microscope at the Dipartimento di Scienze della Terra
- a 50XVP LEO Scanning Electron Microscope at the Dipartimento di Scienze della Terra e Geoambientali (University of Bari).

#### 2.2 Leachates analyses

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Two types of water were used for washing the ash samples: double de-ionised (mQ) water, and Lake Ohrid (Macedonia) water. Lake water was filtered immediately after sampling through 0.2 µm Millipore membranes (cellulose acetate).

Leaching experiments were performed on 2g of sieved ash, which was added in previously washed plastic cuvettes containing 20 mL of mQ water (18.2 M $\Omega$  cm<sup>-1</sup>) or lake water. The washing was performed at ambient temperature (25–28 °C) on a table shaker (stirring at 150 rpm), in order to ensure efficient mixing of the leaching suspension.

The stirring duration varied from 30 min to 7 days (intermediate steps at some hours, 1 day and 5 days) depending on the amount of available ash. The grain-size that were used varied from 1 to 0.063 mm.



The samples were centrifuged for 10 min at 3500 rpm and filtrated immediately. The pH of the leachates was measured using a glass electrode (ORION), sensitive of the activity of  $H^+$  ions, coupled with an Ion Analyzer EA920 (instrumental error less than 0.5 pH units, reproducibility of the data better than 5%).

- <sup>5</sup> The ammonia concentration was measured using a specific electrode (ORION) coupled with an Ion Analyzer EA920. The additions method (Harvey, 2000) was used for this analysis.  $NH_4CI$  standards were prepared starting from  $1000 \gamma mL^{-1}$  obtaining the standard  $NH_4CI$   $100 \gamma mL^{-1}$  and the standard  $NH_4CI$   $10 \gamma mL^{-1}$  (reproducibility of the data better than 10%).
- <sup>10</sup> Composition of major elements (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>) of ash leachates was determined by ion chromatography (IC). Trace elements were measured using an inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optimal 2000 DV instrument. Operating conditions were: power 1400 W, plasma argon flow rate 15 L min<sup>-1</sup>, nebulizer argon flow rate 0.55 l/min, and sample flow rate 2 mL min<sup>-1</sup>.

A Dionex-model 100 with AS4A ION CAP anion exchange column and chemical suppression of eluent conductivity technique were used to analyse anions ( $F^-$ ,  $CI^-$ ,  $SO_4^{2-}$ ), while the analysis of cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), was performed using a Model 600 Dionex with ION PAC CS12A and chemical suppression of eluent conductivity technique. The reproducibility of the data is better than 4 % for both anions and cations. The calibration curves for each element were prepared using calibration standards,

and repeated for the analysed elements every 10 samples. The samples were diluted by a factor of 1 : 10.

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The calibration curve for trace elements was carried out using calibration standards prepared diluting a stock solution (1000 ppm) with deionised water. Recovery experiments were carried out by adding measured volumes of aqueous standard solutions of each metal to measured volumes of an acidified deionised water samples. Calibration curves were repeated for the analysed elements every 14 samples. Reproducibility of the data is better than 3 %.



# 2.3 FETAX test

Ash leachates from Etna 2012 and Popocatépetl in mQ water were used for laboratory analysis on living biota. The methodology of the FETAX assay and the experimental design imply that adult *Xenopus laevis* were maintained in aquaria with de-chlorinated tap water at a  $22 \pm 2^{\circ}C$ , alternating 12 h light/dark cycles and fed a semi synthetic diet (Mucedola S.r.I., Settimo Milanese, Italy) three times a week.

- For a single bioassay, three males and three females received a 300 IU human chorionic gonadotrophin (HCG) via injection in the dorsal lymph sac to induce mating. Breeding tanks were filled with FETAX solution (composition in mgL<sup>-1</sup> was 625
  NaCl, 96 NaHCO<sub>3</sub>, 30 KCl, 15 CaCl<sub>2</sub>, 60 CaSO<sub>4</sub>-2H<sub>2</sub>O, and 70 MgSO<sub>4</sub>, pH 7.5–8.5) and aerated before introducing a couple. Amplexus normally ensued within 2 to 6 h and the deposition of fertilized eggs took place from 9 to 12 h later. After breeding, the adults were removed and the embryos were collected in 60 mm Petri dishes. Abnormally cleaved embryos and necrotic eggs were removed.
- <sup>15</sup> Normally cleaved embryos at midblastula stage (stage 8), 5 h post-fertilization (hpf) (Niewkoop and Faber, 1956) were selected for testing and then placed in 6 cm glass Petri dishes, each Petri containing 10 mL of control or test solutions. Test solutions were generated by diluting the Etna and Popo mQ leachates in FETAX solution, to obtain the final dilutions of 1 : 5, 1 : 10, 1 : 50, 1 : 100.
- For each female the plates were duplicated or triplicated when well-cleaved embryos were available. All the Petri were incubated in a thermostatic chamber at  $23 \pm 0.5$  °C until the end of the test, 96 hpf. At this moment mortality and malformation data were generated as endpoints of the assay.

The number of dead embryos vs. their total number at the beginning of the test led to the mortality percentages and the number of malformed larvae vs. the total number of surviving ones gave the malformed larva percentages.



#### 3 Ash composition and surface analysis

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The bulk rock composition, the glass/mineral phases and the sublimated composition of the collected samples were analysed by XRF and SEM-EDS techniques. The bulk composition (Table S1) of Etna samples plot in the hawaiite field, while the Popocatépetl sample can be classified as andesite (Fig. 1).

The EDS analyses on glass of Etna samples (Table S2) show an almost homogeneous, more evolved composition (mugearites) with respect to the parental bulk analyses (Fig. 1). The PopocatépetI glass analyses gather on a trend from andesite to rhyolite (Fig. 1).

- As from SEM-BSE images of polished samples, both Etna and PopocatépetI samples are porphyritic, with phenocrystals and groundmass microcrystals (Fig. 2). The mineralogical assemblage of Etna samples comprises Mg-rich olivine clinopyroxene, plagioclase, and oxides (Table 3). In particular, the clinopyroxene is diopside in both 2011 and 2012 samples (Fig. 3a). Plagioclase in the sample from the 2011 eruption
- <sup>15</sup> has an almost homogeneous bytownite composition (Fig. 3b), while in the sample from the 2012 eruption shows a compositional range between bytownite and labradorite (Fig. 3b).

The mineralogical assemblage of Popocatépetl comprises ortho- and clinopyroxenes, plagioclase and oxides (Tables 3). Orthopyroxenes are enstatite (Fig. 3a), while clinopyroxenes are augites (Fig. 3a). Plagioclase shows a small compositional range within the labradorite field (Fig. 3b).

SEM-BSE images are shown in Fig. 4. The sublimates recognized on ash surfaces of Etna 2011 (Fig. 4a and b) and Etna 2012 samples are mainly sodium chloride (NaCl, halite) and calcium di-fluoride (CaF<sub>2</sub>, fluorite) (Fig. 4c and d). PopocatépetI samples show abundant sublimate compounds, including sodium chloride, calcium sulphate (gypsum, CaSO<sub>4</sub> • 2H<sub>2</sub>O or anhydrite CaSO<sub>4</sub>), iron sulphide (pyrite FeS<sub>2</sub> or grigite Fe<sup>II</sup>Fe<sup>III</sup><sub>2</sub>S<sub>4</sub>) and native S (Fig. 4e and f).



### 4 Ash leachates

Leaching experiments (Tables 4 and 5) were performed using 2 g of sieved ash, which was added with 20 mL of mQ or lake water.

#### 4.1 pH variation

- 5 The pH of ash leachates ranges from ca. 4 (PopocatépetI 63 μm) to ca. 6.50 (Etna 2011 0.5 mm; Fig. 5). The pH variation is very limited when plotted vs. different times of stirring within each sample, for both mQ and lake waters (Fig. 5). This indicates that most of the pH variations are acquired within the first 30 min of stirring.
- As a general behaviour, the Popocatépetl leachates induce acidification in the solution, diminishing the pH values of 0.5 (lake water) to 1 (mQ water) pH units (Fig. 5). The Etna samples show opposite behaviour, i.e. induce slight (within 0.5 pH units for lake water) to moderate (1–1.5 pH units for mQ water) alkalization (Fig. 5). The pH variations show a slight dependence to decreasing grain size of leached ash (Fig. 5).

# 4.2 NH<sub>3</sub> concentration

<sup>15</sup> Ammonia (NH<sub>3</sub>) concentration in leachates is different when using mQ or lake water (Fig. 6). In particular, the ammonia concentration in mQ water is negligible for Etna samples, while it increases for PopocatépetI samples. In lake water, the PopocatépetI samples release NH<sub>3</sub> almost constantly (variation within 1 mgL<sup>-1</sup>), while the Etna samples either do not release NH<sub>3</sub> (samples Etna 2011) or have scattered release of NH<sub>3</sub> with time (samples Etna 2012; Fig. 6). When effective, also the release of NH<sub>3</sub> shows correlation with decreasing grain size (Fig. 6).

#### 4.3 Anions

Figure 7 shows the variations of  $F^-$ ,  $CI^-$ , and  $SO_4^{2-}$  concentrations for different grain sizes vs. time of leaching. The general patterns show small variation of concentration



vs. time for all anions, indicating their release occurring in the first 30 min. It makes exception the  $SO_4^{2-}$  in mQ water, which reaches a constant release after 60 min.

The concentration of Cl<sup>-</sup> is below  $10 \text{ mg L}^{-1}$  for most of the samples in both mQ and lake water, with the exception of PopocatépetI ash with grain size of 63 µm and some scattered anomalous values (Fig. 7).

Irrespective of water used, the release of  $SO_4^{2-}$  is negligible in Etna samples, while it is the most significant in PopocatépetI samples. For the latter, the concentration of  $SO_4^{2-}$  significantly increases with diminishing grain size and moderately increases with leaching time (Fig. 7).

The concentration pattern of F<sup>-</sup> is more complex than those of the other anions, with different release in the two types of leaching water. In particular, the 2011 Etna samples produce the greatest concentrations in both water types, although higher in mQ water (Fig. 7). The 2012 Etna samples show lower concentrations, and in lake water they are below 10 mgL<sup>-1</sup>. The PopocatépetI samples have concentration of few mgL<sup>-1</sup> (below 10 mgL<sup>-1</sup>), and a slight correlation with decreasing grain size in mQ water (Fig. 7). In

both types of waters, all the samples show a general slight correlation with increasing leaching time.

#### 4.4 Major cations

Figure 8 shows the variations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> concentration for different
grain sizes vs. time of leaching. The general patterns show small variation of concentration vs. time for all cations indicating their release occurring generally in the first 30–60 min, while the PopocatépetI samples reach the highest concentration after 3–5 days in lake waters. The concentration of Na<sup>+</sup> is below 20 mg L<sup>-1</sup> in Etna samples in both mQ and lake water, and it is between 30 and 60 mg L<sup>-1</sup> in PopocatépetI samples.
The concentration of K<sup>+</sup> is below 7 mg L<sup>-1</sup> for most of the samples in both mQ and lake

water, with the exception of Etna 2012-1mm sample in mQ water (Fig. 8). It is worth noting that the concentration of Na<sup>+</sup> and K<sup>+</sup> for the Etna 2012 samples in lake wa-



ter leachate is close or below the concentration these cations have in pure lake water (Fig. 8).

Irrespective of the water type used, the release of  $Ca^{2+}$  and  $Mg^{2+}$  is negligible for Etna samples, while it is the most relevant in PopocatépetI samples (Fig. 8). Their concentration increases at diminishing grain size except for lake water after 24 h (Fig. 8).

#### 4.5 Trace elements

Figure 9 shows the variations of B, Si, Fe<sub>Tot</sub>, Mn<sup>2+</sup> and As<sup>3+</sup> concentration for different grain sizes vs. time of leaching. The general patterns show irregular variation of concentration vs. time for all the trace elements. B concentration shows a scattered distribution vs. time of leaching in mQ water, although a fair anti-correlation is visible for 3 out of 4 Etna samples (Fig. 9). It is below the lake water concentration for almost all the analysed samples (Fig. 9). The concentration of Si is scattered in both mQ and lake water leachates, although a fair increase in concentration is visible with time of leaching for both Etna and Popocatépetl samples (Fig. 9).

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Irrespective of water typology used, the release of  $Fe_{tot}$  and  $Mn^{2+}$  is lower in Etna samples than in PopocatépetI ones, showing a scattered distribution with some very high peaks (Fig. 9).

#### 5 Biological impact of leachates

The results from the FETAX test clearly show that the leachates from Etna and PopocatépetI ash are very poorly embryotoxic. At the dilutions used, no significant increase in embryo mortality was indeed observed (Fig. 10a and b). The percentages of malformed larvae at the end of the test progressively increased with decreasing dilutions in the groups exposed to Etna leachates (Fig. 10a), while a non-linear increase was observed in those exposed to PopocatépetI leachates (Fig. 10b). The maximum



values of about 40 % malformed larvae were registered at the highest concentrations of leachates.

These results do not evidence significant differences in the effects induced by Etna and Popocatépetl leachates, although it is worth noting the higher scores obtained <sup>5</sup> in larvae exposed to Etna leachates at low concentrations (1 : 100 and 1 : 50), with respect to the Popocatépetl ones.

# 6 Discussion

The data presented in the preceding sections illustrate the complexity that accompanies the leaching of compounds from fresh volcanic ash. Analysing the figures and the

tables presented, it emerges clearly how the physical and chemical processes occurring during the simple washing of fresh volcanic ash interact with the surrounding aqueous environment. It follows that to extract simple laws of compound release at different boundary conditions is not straightforward, having to face with dynamic processes that changes in function of the progressive variation of the experimental geochemical envi ronment.

In the following, we analyse the data taking into account the major variables potentially influencing the experimental results. Finally, the potential toxicity of ash leachates will be discussed in the light of potable water pollution and alteration of life cycle of living biota (tadpoles embryos, *Xenopus laevi*).

# 20 6.1 Origin of leached elements

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The mQ water is almost pure water, thus it does not contains any other element or compound that could react with the leaching material. Therefore, it is better suitable for the analysis of leached compounds from volcanic ash than lake water, whose dissolved elements and molecules can react with leached elements and alter their original assemblage.



The sublimates on ash surfaces of Etna 2011 (Fig. 4a and b) include mainly (Na,K)Cl (sodium/potassium chloride), (Ca,Mg)F<sub>2</sub> (calcium/magnesium fluoride), and (Ca,Mg)SO<sub>4</sub> (calcium/magnesium sulphate). The formation of leachates from solubilization of these superficial salts is also confirmed by the stoichiometry of mQ water analysis, where the relative abundance of these elements is almost completely balanced. Only few residual fractions of  $Ca^{2+}$ ,  $Mq^{2+}$  and  $F^{-}$  scattered in the different grain-size fractions remain unbalanced (Table S4). The concentration of all the elements is below their respective solubility limit, except than Si<sup>2+</sup> and F<sup>-</sup> (Table S5). It means that all the salts from the ash surface passed into the leachates, with the exception of Si and F ones, which may have been remained partially not dissolved. The 10 slight excess of Mg<sup>2+</sup> and Ca<sup>2+</sup> in most of the Etna 2011 samples (Table S4) might indicate the presence of carbonates in the leachates, since  $CO_2^{2-}$  was not analysed. When considering the stoichiometry of the leachates, it emerges that  $F^-$  compounds are the most dissolved in Etna 2011 samples, along with variable amount of  $SO_{\lambda}^{2-}$  and minor Cl<sup>-</sup> compounds (Table S4). 15

The Etna 2012 sample shows very similar stoichiometry of leachates to Etna 2011, with fractional remnants of unbalanced elements that comprise  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  (Table S4). Mg concentration is close to the maximum solubility limit, and dissolved F compounds dominate the leachates (Table S4).

The sublimates on ash surfaces of PopocatépetI samples (Fig. 4e and f) include mainly (Ca,Mg)SO<sub>4</sub> (calcium/magnesium sulphate), and minor (Na,K)CI (sodium/potassium chloride). Also in these cases the leachates reflect the dissolution of the salts observed on ash surfaces, as confirmed by stoichiometric calculations (Table S4). It is observable a slight excess of Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> not balanced by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>, which might indicate the occurrence of carbonates (not analysed) in the leachates. The concentration of elements in the two samples (0.125 and 0.063 mm) slightly differs (Table S5), with the coarser one that shows saturation with respect to Ca, Si and Fe compounds, and the finer one that shows saturation in fluorite, gypsum guartz and chalcedony (Table S5). The Mg<sup>2+</sup> content in mQ leachates



from PopocatépetI samples is higher than in Etna samples (Table S4). Taking into account the surface analysis on sublimates, it seems that most of the Mg<sup>2+</sup> comes from dissolution of Mg-sulphates. This inference is also supported by the strong correlation among Ca<sup>2+</sup>, Mg<sup>2+</sup> and NH<sub>3</sub> (Fig. 11), which indicate the presence of the ammonium <sup>5</sup> as catalyst for (Ca, Mg) salt dissolution.

The composition of leachates in lake water can be quite different from those in mQ water, due to the presence of chemical compounds already present (Table 2), which can react with elements released from ash surface. Lake Ohrid water is slightly alkaline (pH 8.02; Table 2) and contain carbonates (Ca =  $28 \text{ mg L}^{-1}$ ; Mg =  $9.92 \text{ mg L}^{-1}$ ). In order to evaluate the buffering effect of lake water, its chemical composition was subtracted

- to evaluate the buffering effect of lake water, its chemical composition was subtracted from that of the leachates (Table 3). This allows compare the net release of the different elements using the two water typologies. It is evident comparing data from Tables 4 and 6 how the release of elements from Etna samples is variably lower in lake water than in the mQ one, with loss of some 10 % in abundance of F<sup>-</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup> and especially
- B, which has a negative net release in lake water (Table 3). This general behaviour is also confirmed by PopocatépetI samples, with the exceptions of a greater release of Mg<sup>2+</sup> and Ca<sup>2+</sup> in lake water for the 0.125 μm fraction (Table 3). Because borates are usually highly soluble, it may suggest the occurrence of adsorption/reaction processes of B with compounds present in lake water.

#### 20 6.2 Influence of ash grain size on leachates

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It has been suggested that concentration of deposited species on surface particles depends upon the size-fraction of the tephra, and it is higher for smaller particles (Fruchter et al., 1980; Rose et al., 1973; Óskarsson, 1980; Rubin et al., 1994). Particles with smaller diameters have a higher surface area to mass ratio than larger particles so are more efficient scavengers of volatiles for the same tephra volume. This means that as the particle size decreases, the proportion of available volatiles scavenged increases (Witham et al., 2005).

# **Discussion** Paper BGD 12, 13241-13282, 2015 Ash leachates from some recent eruptions of Mount **Discussion** Paper Etna M. D'Addabbo et al. **Title Page** Introduction Abstract **Discussion** Paper References Conclusions Figures Close Back **Discussion** Paper Full Screen / Esc **Printer-friendly Version** Interactive Discussion

In order to investigate the influence of grain size of ash on release of elements, the Etna 2011 samples in mQ water are the most suitable, being available leachates from three different grain sizes (Table 1). Analysing the release of elements with different times of stirring, it is evident the inverse correlation with grain size for  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ ,

- and Ca<sup>2+</sup>. The trends for these elements are quite similar for the different times of stirring, indicating a time-independent release for these elements (Fig. 12). A general decrease of release with increasing grain size is visible for Cl<sup>-</sup>, although the trends for different times of stirring are not identical (Fig. 12). Release of Mg<sup>2+</sup> is almost constant for the different grain sizes and for different times of stirring. The release of Mn<sup>2+</sup> is
- <sup>10</sup> contrasting. It is inversely related to grain size for time of stirring up to 21 600 s (6 h), while it increases with grain size for times of stirring of 43 200 s (12 h) and 86 400 s (24 h; Fig. 11). B also shows similar pattern, with opposite trends below and above 21 600 s (6 h; Fig. 11). These behaviours suggest different kinetics for dissolution of sublimates containing Mn<sup>2+</sup> and B and precipitation of their salts.
- The release of F<sup>-</sup> shows a unique pattern, with similar values for 0.25 and 1 mm grain sizes and lower values for the 0.5 mm grain size (Fig. 12). This behaviour is quite well defined by all the times of stirring, which indicates this is not an aleatory behaviour. Finally, the patterns of Si and Fe are randomly arranged, without any clear correlation of release with grain size and/or timing of stirring (Fig. 12). The different patterns for the
- various elements of Etna 2011 samples demonstrate how the dependence of element release with grain size is not a general rule. Indeed, a greater release at decreasing grain size holds for alkali and alkaline earth elements together with the sulphate radical SO<sub>4</sub><sup>2-</sup>, which is a component of most of their original sublimated salts. This is in agreement with already suggested greater capacity of particles with larger surface vs.
- volume ratio to scavenge elements from the eruptive cloud.

The release of B seems to reflect a complex kinetic of adsorption/reaction of B, which can account for the difference in release at different times of stirring (Fig. 12).



The scatter release of Fe and Si reflects the random formation of soluble salts of these elements, which are not related to the grain size but more probably to the redox conditions at time of sublimation.

Among the most abundant elements, F<sup>-</sup> shows a unique pattern, whose explanation is puzzling. It is not related to the active surface of the particles, nor to the composition of the eruptive plume, having all the particles underwent the same eruptive conditions. It may be speculated that some gaseous F might be entrapped in the vesicles that are more abundant in the 1 mm particles than in the 0.25 and 0.5 mm, and then may be related to the presence of gaseous F in the vesicles of the coarse ash particles of 1 mm grain size, which can compensate the lower active surface of this grain size.

To explore the dependence of element release with grain size for PopocatépetI samples is less significant, being available only two grain-size fractions. However, as a general behaviour, the release of elements is significantly greater for the finer grain size (0.063 mm) than for the 0.125 mm fraction (Figs. 7 and 8).

# 15 6.3 Origin of pH changes

The changes in pH values of leachates with respect to those of mQ and lake water relates to the release of  $OH^-$  and  $H^+$  ions due to hydrolysis reactions of the salts dissolved from the ash surfaces (Sect. 6.1).

For Etna samples, the main hydrolysis reactions can be summarized as:

<sup>20</sup> NaCl + 
$$H_2O = Na(OH) + HCl = Na^+OH^- + H^+Cl^-$$
 (R1)

 $(Na, K)F + H_2O = (Na, K)(OH) + HF = (Na, K)^+OH^- + [H^+F^-]_K$ 

$$(Ca, Mg)SO_4 + H_2O = (Ca, Mg)(OH)_2 + H_2SO_4 = [(Ca, Mg)^{2+}2OH^{-}]_{\mathcal{K}} + 2H^+SO_4^{2-}$$
 (R3)

 $(Mg, Ca)F_2 + H_2O = (Mg, Ca)(OH) + 2HF = [(Mg, Ca)^{2+}2OH^{-}]_{\mathcal{K}} + 2[H^+F^-]_{\mathcal{K}}$ (R4)

Reaction (R1) is neutral for pH, producing a strong base and a strong acid that are totally dissociated in water. Reaction (R2) produces a strong base and a weak acid, which is only partially dissociated to supply H<sup>+</sup> ions. It induces alkalinization of the



(R2)

leachates. Reaction (R3) produces a strong acid and a weak base, which induce acidification of the leachates. Reaction (R4) produces a weak acid and a weak base. Being the equilibrium constants  $K_{\rm HF} = 6.6 \times 10^{-4}$  and  $K_{\rm Ca(OH)_2} = 5.5 \times 10^{-6}$ , the reaction induce slight alkalinization of the leachates. Being the sublimates on Etna ash dominated

- <sup>5</sup> by F salts (Tables 4 and 5), the hydrolysis reactions are dominated by Reactions (R2) and (R4). This explains why the pH of Etna leachates is more alkaline with respect to the mQ water. The alkalinisation is less effective when considering leachates in lake water, due to the presence of dissolved carbonates (Table 2) that buffers the hydrolysis reactions.
- The same hydrolysis equations hold for the PopocatépetI samples, although they are dominated by dissociation of (Ca,Mg)SO<sub>4</sub> salts (Tables 4 and 5). This explains why the PopocatépetI leachates are more acid with respect to the mQ water (Fig. 5). The correlation of pH value with SO<sub>4</sub><sup>2-</sup> is also testified by the higher acidification of 0.063 mm leachates with respect to the 0.125 mm ones (Fig. 5; Tables 4 and 5). The pH varies very little when considering lake water also for PopocatépetI samples, due to
- the buffering effect of already dissolved carbonates (Fig. 5; Tables 4 and 5).

# 6.4 Drinkability of water leachates

Drinking water quality is commonly regulated using a two-tier system. Primary standards are legally enforceable limits set for contaminants posing a health risk (Table S7).

- Secondary standards are non-enforceable guideline values for contaminants which are not known to be a health risk but which make drinking water unacceptable to consumers because of aesthetic factors such as taste, colour or odour (Table S7), or effects on the supply system such as staining or scale deposition (Stewart et al., 2006). Inspection of Etna and PopocatépetI mQ leachates shows that F<sup>-</sup> and Mn<sup>2+</sup> ele-
- <sup>25</sup> ments are always well above the legal limits for drinkable water (Table 1). Also Fe exceeds the limits in most of the Etna samples and in all the PopocatépetI ones (Table 1). This makes it the water dark in colour, bitter, with metallic taste and can induce dental fluorosis and gastrointestinal disease on consumers. The SO<sub>4</sub><sup>2-</sup> also exceeds



the limits in the Popocatépetl samples, adding salty taste to the water and possible diarrhoea disease to consumers.

The inspection of leachates with lake water shows a similar behaviour of mQ water for F<sup>-</sup>, which exceeds the legal limits in all the samples. Mn<sup>2+</sup> is in excess for all the <sup>5</sup> Etna 2011 and PopocatépetI samples, but only in two samples of Etna 2012 (Table 2). Fe exceeds the limits for most of the analysed samples, while SO<sub>4</sub><sup>2-</sup> is in excess in all the PopocatépetI samples (Table 2). Overall, the effects on water and consumers are the same than in mQ water.

The inspection of Tables 4, 6 and 9 highlights how the F<sup>-</sup> content is the most sensitive element for drinkability of leachates of Etna samples, being its abundance 6 to 14 (mQ water) or 1.5 to 10 (lake water) times the acceptable limit for potability (Tables 4, 6 and 9). The Mn<sup>2+</sup> and Fe are the most sensitive elements for PopocatépetI samples in mQ water (Tables 4, 6 and 9), with abundances between 10 and 50 times (Mn<sup>2+</sup>) and 7 to 58 times (Fe) the legal limits. Considering lake water, the most sensitive element for <sup>15</sup> PopocatépetI is Mn<sup>2+</sup> (Tables 4, 6 and 9), being its abundance 3 to 50 times the legal limits for potability.

Taking into account the concentration of these elements in Etna and Popocatépetl leachates, it is possible to calculate the minimum weight of ash needed to exceed the legal limits of potability. As an example, for Etna 2011 samples in lake water, only 12 kg of ash per m<sup>3</sup> of water are sufficient for making it undrinkable (using F<sup>-</sup> as benchmark). It means that, depending on the bulk density of the ash deposit, a thickness of 8 mm m<sup>-2</sup> (bulk density of 1500 kg m<sup>-3</sup>) or 6 mm m<sup>-2</sup> (bulk density of 2000 kg m<sup>-3</sup>) is sufficient for contaminating the water beyond the potability limits. The same exercise for Popocatépetl samples yields a mean weight of only 8 kg of ash per m<sup>3</sup> (using Mn<sup>2+</sup> as benchmark), which corresponds to 5 mm m<sup>-2</sup> (bulk density of 1500 kg m<sup>-3</sup>) or 4 mm m<sup>-2</sup> (bulk density of 2000 kg m<sup>-3</sup>). It is evident how such small amounts of ash can impinge significantly the availability of a primary resource like drinkable water. This is an underestimated volcanic hazard, which can impact large areas and severely affect population if no preventive civil protection actions are taken in advance. Authorities



were generally unable to allay public fears because of a lack of supporting information on specific effects of volcanic ash on water supplies, including considerations such as the quantity of ash necessary to produce adverse effects, and the specific nature of contaminants that may pose a health risk to consumers or otherwise compromise the integrity of water supplies. A good example of this hazard is the potential contamination

of water reservoirs of southern Italy, which are exposed to ash deposition in case of renewal of explosive activity of Italian volcanoes (Sulpizio et al., 2014).

# 6.5 Effects on living biota

The ash leachates obtained in mQ water were diluted in FETAX solution to obtain sequential dilutions from 1 : 5 to 1 : 100 vol/vol. This was planned to mime natural conditions in which ash leachates are likely progressively diluted in the water basins. Under these experimental conditions both Etna and PopocatépetI leachates results mild toxic to developing *Xenopus laevis* and no significant differences exist between the toxic profiles of the two materials. Anyway, we outline that the higher content in F exhibited

- <sup>15</sup> by the leachates from Etna may ring a bell in term of potential teratogenic risk. Indeed, F<sup>-</sup> is known to be a powerful teratogen, as also demonstrated in *Xenopus laevis* (Goh and Neff, 2003). In this optic, it may be useful to focus on the induced malformations more than on the deaths of embryos. It is evident that for both leachates the number of malformations is greater for low dilutions (Fig. 13), with a good logarithmic fit of the
- data. This means that even few % of leachates (high dilutions) suddenly increases the malformations above 20 %, which only augment of about 10 % at higher concentrations (Fig. 13).

Also the changing pH did not induce any big differences in teratogenesis. This allows us to consider the experimental results as non-dependent from pH variations.

<sup>25</sup> Although promising, these preliminary data on ecotoxicity of Etna and Popocatépetl ash leachates claim for more experimental evidences to fully understand the specific and comparative reactivity of the different leachates in term of teratogenicity.



# 7 Conclusions

Leaching experiments on fresh ash samples from Etna 2011, Etna 2012 and Popocatépetl 2012 eruptions highlights some interesting clues about behaviour of compound release in mQ and lake water. Surface analysis on unwashed ash demonstrates

<sup>5</sup> the presence of sublimated salts, and their leaching accounts for the observed composition of leachates in mQ water. The balance of leachates in lake water is more complex, due to the reaction of leached compounds with chemical elements dissolved in the lake water.

The hydrolysis reactions of the leached compounds accounts also for the observed pH variations in mQ and lake water, with Etna 2011–2012 samples that induce alkalinisation and PopocatépetI samples that induce acidification of the original water samples.

Leaching experiments using different times of stirring (from 30 min to 7 days) demonstrate the general poor dependence of compound release vs. time, with most of the release concentrated in the first hour of washing.

Grain size of ash particles has different and sometimes contrasting effects on release of compounds, with general inverse correlation only for Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>,  $SO_4^{2-}$ , and  $Mn^{2+}$ .

Saturation calculations highlights how Etna samples are always saturated for F and Si in mQ water, while leachates in lake water are saturated in F, Si, and carbonates, reflecting the contribution of elements already present in the used solvent. Popocatépetl samples show general saturation in some Ca, Si, F, and Fe compounds in mQ water, similar to those calculated for lake water.

When compared with limits for potability imposed by Italian laws, it emerges of <sup>25</sup> both mQ and lake leachates from Etna and PopocatépetI samples are classified as not allowed for human drinking due to the excess of F<sup>-</sup>, Mn<sup>2+</sup>, Fe, and SO<sub>4</sub><sup>2-</sup> (only PopocatépetI samples).



Etna 2012 and PopocatépetI leachates were used also for investigating the potential toxicity on living biota (*Xenopus laevis*). Experiments demonstrated they are mild toxic, and no significant differences exist between the toxic profiles of the two leachates. In particular, no significant increase of embryos deaths was observed, while even at high dilutions the leachates produced more than 20% of malformed larvae.

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**Table 1.** Ash leachates in mQ water for the Etna 2011, Etna 2012 and PopocatépetI samples with different grain sizes and various time of stirring. In bold are reported the element concentrations that exceed the potability limits. b.d.l. = below detection limit; n.a. = not assessed.

					Anions	(mg L <sup>-1</sup>	)		Cations	(mgL <sup>-1</sup>	)		Trace	e elements	(µg L <sup>-1</sup> )		
Sample	t (10 <sup>3</sup> s)	pН	$\rm NH_3$	F	CI	NO <sub>3</sub>	SO4	Na	К	Ňg	Ca	в	Si	Mn	Fe	Hg	As
mQ water		4.96	b.d.l	0	1.09	b.d.l	0.57	0.02	b.d.l	b.d.l	b.d.l	0.28	0.26	2	3.5	b.d.l	b.d.l
E2011-0.25mm	1.8	6.32	0.03	21.29	4.66	b.d.l.	41.93	16.05	4.85	3.33	12.89	143.31	3594.99	272.50	880.40	n.a.	n.a.
E2011-0.25mm	3.6	6.15	0.02	20.86	4.03	b.d.l.	33.86	14.72	4.33	3.13	11.90	89.25	916.47	194.63	158.00	n.a.	2.68
E2011-0.25mm	10.8	6.32	0.10	20.60	4.25	b.d.l.	37.98	13.38	4.49	3.23	13.31	67.32	1420.86	233.88	418.00	n.a.	1.8
E2011-0.25mm	21.6	5.93	0.03	19.94	4.00	b.d.l.	35.06	14.87	4.29	3.28	12.41	58.14	1403.52	216.00	78.13	n.a.	n.a.
E2011-0.25mm	43.2	6.29	0.14	21.02	4.01	b.d.l.	45.52	14.80	5.04	3.96	15.33	53.04	2123.64	280.13	79.00	n.a.	241
E2011-0.25mm	86.4	6.45	n.a.	21.38	6.49	1.75	41.14	16.10	5.05	3.94	16.69	48.45	3174.75	n.a.	234.00	n.a.	n.a.
E2011-0.50mm	1.8	6.03	0.03	15.67	3.32	b.d.l.	8.87	6.72	2.55	3.11	9.61	105.06	673.71	133.25	317.75	n.a.	0.92
E2011-0.50mm	3.6	6.01	0.03	16.64	3.74	b.d.l.	9.26	6.32	2.34	3.20	10.00	82.11	668.61	134.88	154.50	n.a.	n.a.
E2011-0.50mm	10.8	6.05	0.01	16.55	3.95	b.d.l.	11.62	7.84	2.68	3.40	9.81	58.14	1151.58	149.75	98.50	n.a.	0.92
E2011-0.50mm	21.6	6.14	0.03	17.59	3.04	b.d.l.	10.20	7.15	2.55	3.57	10.00	430.44	2361.81	164.63	449.50	n.a.	0.51
E2011-0.50mm	43.2	6.05	0.02	17.19	2.90	b.d.l.	9.41	7.20	2.62	3.65	10.32	240.72	1378.02	147.25	16.75	n.a.	n.a.
E2011-0.50mm	86.4	6.11	0.04	17.36	3.34	b.d.l.	9.35	7.52	2.72	3.74	10.41	178.50	2659.14	157.25	307.13	n.a.	n.a.
E2011-0.50mm	259.2	6.40	0.07	18.03	3.79	b.d.l.	10.33	7.91	2.94	4.04	11.81	n.a.	46/1.83	n.a.	n.a.	n.a.	n.a.
E2011-0.50mm	432	6.48	0.06	17.99	3.30	0.52	9.84	8.04	3.02	4.12	11.84	n.a.	5645.58	n.a.	n.a.	n.a.	n.a.
E2011-0.50mm	604.8	6.56	0.04	17.96	2.80	0.52	9.35	8.18	3.10	4.19	11.88	2/1.83	6619.33	210.75	166.00	n.a.	n.a.
E2011-1mm	1.8	5.76	n.a.	19.67	2.99	b.d.l.	7.17	6.73	1.71	2.16	7.66	435.03	462.57	123.25	22.50	n.a.	0.46
E2011-1mm	3.6	5.82	0.02	20.29	3.03	b.d.l.	7.79	7.94	1.88	2.35	8.43	236.64	3746.97	134.56	736.00	n.a.	n.a.
E2011-1mm	10.8	5.95	0.02	20.81	2.95	b.d.l.	7.09	6.83	1.77	2.42	7.94	176.46	532.44	145.88	121.50	n.a.	0.77
E2011-1mm	21.6	5.64	0.06	20.84	2.85	b.d.l.	7.24	7.39	2.04	2.58	8.47	145.35	1325.49	158.50	468.63	n.a.	0.77
E2011-1mm	43.2	5.91	0.19	21.19	2.99	b.d.l.	7.31	7.55	2.09	2.66	8.79	132.86	2002.26	167.94	313.31	n.a.	0.44
E2011-1mm	86.4	6.18	0.31	21.54	3.13	b.d.l.	7.39	7.72	2.13	2.75	9.11	120.36	2679.03	177.38	158.00	n.a.	0.1
E2011-1mm	259.2	6.70	0.02	21.32	2.98	D.d.I.	6.93	7.62	2.28	3.06	9.40	216.83	12088.33	212.63	1470.38	n.a.	n.a.
E2011-1mm	432	6.70	0.03	21.33	3.02	D.d.I.	7.44	8.10	2.49	3.23	9.99	n.a.	n.a.	208.38	798.31	n.a.	n.a
E2011-1mm	604.8	6.69	0.04	21.35	3.06	D.d.I.	7.96	8.58	2.70	3.39	10.57	n.a.	n.a.	204.13	126.25	n.a.	n.a.
E2012-1mm	1.8	6.70	0.06	9.50	7.14	b.d.l.	3.54	6.00	9.00	2.50	8.50	228.48	1048.05	101.25	170.00	n.a.	0.82
E2012-1mm	3.6	6.65	0.74	9.05	7.56	b.d.l.	4.38	6.00	9.50	2.50	9.00	126.99	201.45	n.a.	80.00	n.a.	n.a.
E2012-1mm	10.8	6.59	0.40	9.50	7.24	b.d.l.	n.a	6.25	9.50	2.75	9.75	115.26	361.34	n.a.	42.75	n.a.	n.a
E2012-1mm	21.6	6.54	0.05	9.94	6.91	b.d.l.	n.a.	6.50	9.50	3.00	10.50	103.53	521.22	92.50	5.50	n.a.	n.d.
E2012-1mm	43.2	6.40	0.11	10.93	6.66	b.d.l.	3.65	5.50	9.00	3.00	10.50	84.66	1646.79	108.75	91.00	n.a.	n.a.
E2012-1mm	86.4	6.37	0.05	10.56	6.86	D.d.I.	3.48	6.00	9.50	3.00	10.00	/1.91	1958.91	105.75	44.00	n.a.	0.41
E2012-1mm	259.2	6.58	0.02	11.45	7.66	D.d.I.	3.98	7.50	10.00	3.50	18.50	209.00	3378.33	67.50	286.75	n.a.	n.a
E2012-1mm	432	6.71	0.04	11.19	n.a.	D.d.I.	n.a.	7.50	10.00	3.75	n.a.	189.50	3816.73	105.13	348.88	n.a.	n.a
E2012-Imm	604.8	0.83	0.06	10.93	28.25	D.d.I.	44.19	7.50	10.00	4.00	12.00	170.00	4255.13	142.75	411.00	n.a.	n.a.
Po2012-0.125mm	1.8	4.52	0.93	3.39	8.45	b.d.l.	441.14	28.19	2.34	30.09	85.04	228.67	218.17	774.50	4194.00	n.a.	0.2
Po2012-0.125mm	3.6	4.57	0.68	3.42	10.22	b.d.l.	466.39	28.31	2.33	28.04	92.23	206.33	297.33	784.00	3873.25	n.a.	0.21
Po2012-0.125mm	10.8	4.55	0.63	4.27	6.01	b.d.l.	495.46	29.80	3.01	29.97	104.55	214.25	368.75	776.00	3732.25	n.a.	0.56
Po2012-0.125mm	21.6	4.54	0.76	4.67	7.12	b.d.l.	519.61	30.61	2.91	31.85	109.93	281.54	3/8.1/	926.88	4883.13	n.a.	n.a.
P02012-0.125mm	43.2	4.62	0.62	4.94	6.16	D.d.I.	496.57	30.74	3.10	30.44	111.30	348.83	747.83	524.67	23/1.6/	n.a.	0.62
P02012-0.125mm	86.4	4.7	0.7	3.70	5.27	D.d.I.	505.98	29.57	2.83	32.21	111.53	241.83	580.00	794.70	5027.60	n.a.	0.71
P02012-0.125mm	259.2	4.59	0.78	4.35	6.52	D.d.I.	528.55	32.60	3.51	32.98	121.35	236.00	1695.00	836.00	3422.83	n.a.	0.1
Po2012-0.125mm Po2012-0.125mm	432 604.8	4.86	0.66	4.25	9.91	b.d.i.	511.45 531 74	36.65	6.54 3.39	31.58	117.61	337.00	2326 75	861.25 795.75	9336.38	n.a. n.a	0.56
D-0010 0.000	1.0	4.00	1.01	4.00	10.1	1.00	400.00	00.01	1.00	40.01	114.01	04.00	440.00	0510.01			5.07
P02012-0.063mm	1.8	4.01	1.91	3.35	10.1	1.33	492.00	39.64	1.92	43.64	114.31	94.26	446.20	2510.84	7202.00	n.a.	n.a.
P02012-0.063mm	3.6	4.04	3.29	5.29	13.6	2.1	770.00	49.67	2.79	00.53	213.86	84.38	468.46	2916.22	7302.96	n.a.	n.a.
Po2012-0.063mm	10.8	4.07	3.32	0.52	14.1	1.03	000.00	00.00	4.47	03.33	234.98	237.00	238.82	1007.35	1450 54	n.a.	n.a.
Po2012-0.063mm	∠1.0 49.0	4.05	3.10	1.49	14.1	1.90	795.00	34.06	3.90	00.31	231.09	200.41	1150 70	1007.90	1458.51	n.a.	n.a.
F02012-0.063mm	43.Z	4.24	3.03	0.00	14.2	1.4/	100.00	48.45	7.20 2.49	00./1	219.33	102.47	1153.76	2100.08	2403.93	n.a.	n.a.
Po2012-0.003000	250.2	4.13 / 1F	3.49	10.2	14.3	2.4 h.d.l	926.00	53.50 53.5	J.40	62.04	209.30	102.45	2009.21	2035.04	n.a.	n.a.	11.d.
Po2012-0.003000	209.2	4.10	3.31 3.4F	10.3	12.1	b.u.i.	945.00	56 1	4.3	66.1	200	n.a.	11.d.	n.a.	n.a.	n.a.	11.d.
1 02012-0.003000	432	4.10	0.40	10.0	12.0	D.U.I.	045.00	30.1	3.5	00.1	215	n.a.	n.a.	n.a.	n.a.	n.d.	n.a.

BGD 12, 13241-13282, 2015 Ash leachates from some recent eruptions of Mount Etna M. D'Addabbo et al. Title Page Abstract Introduction Conclusions References Tables Figures **I**◄ ► Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion

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**Table 2.** Ash leachates concentrations in lake water and pH values for the Etna 2011, Etna 2012 and PopocatépetI samples with different grain sizes and various time of stirring. In bold are reported the element concentrations that exceed the potability limits. b.d.l. = below detection limit; n.a. = not assessed.

					Anions	(mgL <sup>-1</sup>	)	Cations (mgL <sup>-1</sup> )			Trace elements (μgL <sup>-1</sup> )						
Sample	t (10 <sup>3</sup> s)	pН	$\rm NH_3$	F	CI	NO <sub>3</sub>	SO4	Na	к	Mg	Ca	В	Si	Mn	Fe	Hg	As
Lake Ohrid		8.02	0.08	0.20	3.60	b.d.l.	7.55	4.68	2.29	9.92	28.00	430.00	350.00	1.25	1.62	b.d.l.	0.84
E12/08/2011-1mm	1.8	8.13	b.d.l.	12.08	6.11	b.d.l.	13.95	10.44	3.19	11.10	37.79	190.00	240.00	105.62	894.25	b.d.l.	0.62
E12/08/2011-1mm	3.6	8.31	b.d.l.	12.16	4.60	b.d.l.	14.03	12.66	3.58	11.66	41.52	190.00	360.00	75.10	68.10	b.d.l.	0.56
E12/08/2011-1mm	10.8	8.32	b.d.l.	13.10	6.19	b.d.l.	13.81	10.30	3.41	11.75	38.79	190.00	2010.00	95.87	331.50	b.d.l.	6.31
E12/08/2011-1mm	21.6	8.37	b.d.l.	14.27	6.22	b.d.l.	14.10	9.06	2.93	9.75	33.05	195.00	1655.00	n.a.	64.50	b.d.l.	0.00
E12/08/2011-1mm	43.2	8.35	b.d.l.	13.68	7.67	b.d.l.	14.36	9.35	2.78	11.20	33.23	200.00	1300.00	91.87	122.00	b.d.l.	0.80
E12/08/2011-1mm	86.4	8.14	b.d.l.	14.27	6.97	b.d.l.	14.00	10.16	2.71	10.47	35.68	310.00	1820.00	98.00	367.00	b.d.l.	1.13
E12/08/2011-1mm	259.2	8.28	b.d.l.	14.99	5.84	b.d.l.	14.08	11.07	3.69	11.90	39.29	310.00	n.a.	87.25	105.00	b.d.l.	1.29
E12/08/2011-1mm	432	8.41	b.d.l.	15.44	6.50	b.d.l.	13.50	11.64	3.26	11.31	36.93	310.00	12 450.00	126.00	1559.40	b.d.l.	0.51
E12/08/2011-0.5mm	1.8	8.19	b.d.l.	11.95	6.10	b.d.l.	15.06	10.14	3.24	10.20	35.32	210.00	3770.00	112.60	438.50	b.d.l.	1.06
E12/08/2011-0.5mm	3.6	8.35	0.08	11.75	5.93	b.d.l.	15.57	10.44	3.30	11.28	36.74	310.00	7480.00	162.40	3534.40	b.d.l.	1.03
E12/08/2011-0.5mm	10.8	8.35	b.d.l.	12.98	5.66	b.d.l.	15.92	11.10	3.31	11.46	38.71	220.00	1440.00	97.00	246.37	b.d.l.	0.92
E12/08/2011-0.5mm	21.6	8.38	b.d.l.	14.95	7.20	b.d.l.	18.06	12.40	3.44	12.54	43.39	300.00	1090.00	102.20	56.00	b.d.l.	0.51
E12/08/2011-0.5mm	43.2	8.37	b.d.l.	13.00	6.04	b.d.l.	16.20	10.44	2.94	10.47	36.38	370.00	2360.00	93.50	248.12	b.d.l.	1.06
E12/08/2011-0.5mm	86.4	8.28	b.d.l.	13.77	5.89	b.d.l.	15.97	10.60	3.11	10.19	37.00	300.00	2070.00	119.60	392.80	b.d.l.	1.72
E12/08/2011-0.5mm	259.2	8.43	b.d.l.	13.96	5.84	b.d.l.	16.52	11.26	3.55	11.70	37.82	200.00	3110.00	100.75	231.12	b.d.l.	0.80
E12/08/2011-0.5mm	432	8.43	b.d.l.	16.07	6.53	b.d.l.	17.70	13.92	3.75	12.25	41.77	310.00	12700.00	n.a.	n.a.	b.d.l.	1.47
E24/04/2012-1mm	1.8	8.46	0.67	2.47	6.72	b.d.l.	9.04	5.20	2.04	9.93	34.66	300.00	380.00	3.87	24.25	b.d.l.	0.95
E24/04/2012-1mm	3.6	8.46	0.04	1.51	3.86	b.d.l.	7.27	5.57	1.37	10.27	35.55	250.00	430.00	5.00	40.50	b.d.l.	0.72
E24/04/2012-1mm	10.8	8.46	0.13	4.32	6.45	b.d.l.	8.38	6.29	2.69	10.47	36.64	550.00	1260.00	36.87	262.25	b.d.l.	1.03
E24/04/2012-1mm	21.6	8.43	1.40	2.74	6.41	b.d.l.	9.77	6.88	1.91	9.76	35.82	210.00	2100.00	10.40	99.10	b.d.l.	1.16
E24/04/2012-1mm	43.2	8.46	0.04	4.50	6.04	b.d.l.	7.88	5.25	1.94	10.28	34.73	220.00	1610.00	38.25	231.50	b.d.l.	1.11
E24/04/2012-1mm	86.4	8.46	b.d.l.	4.55	6.58	b.d.l.	8.36	5.59	1.96	10.65	36.68	300.00	1500.00	40.12	444.75	b.d.l.	0.72
E24/04/2012-1mm	259.2	8.47	b.d.l.	4.92	6.64	b.d.l.	8.59	7.39	1.78	11.26	37.44	330.00	n.a.	49.12	665.50	b.d.l.	0.72
E24/04/2012-1mm	432	8.47	D.d.I.	9.41	10.26	D.d.I.	10.65	8.65	2.09	9.91	34.66	360.00	11760.00	284.90	11478.00	D.d.I.	1.16
E24/04/2012-0.5mm	1.8	8.18	2.52	2.62	6.74	b.d.l.	10.21	5.59	2.88	9.62	34.86	320.00	860.00	6.90	190.70	b.d.l.	1.03
E24/04/2012-0.5mm	3.6	8.34	0.84	1.86	4.72	b.d.l.	8.20	5.26	1.39	10.17	35.01	270.00	390.00	9.00	39.75	b.d.l.	1.35
E24/04/2012-0.5mm	10.8	8.47	2.70	1.17	12.27	b.d.l.	7.82	2.90	0.61	9.13	31.91	150.00	780.00	16.62	340.25	b.d.l.	1.03
E24/04/2012-0.5mm	21.6	8.43	1.90	4.21	11.98	D.a.i.	10.79	5.70	2.47	10.36	36.27	290.00	1500.00	54.25	252.25	D.a.I.	10.71
E24/04/2012-0.5mm	43.2	8.47	0.04	1.54	3.53	D.a.i.	7.42	3.09	1.10	9.83	34.97	220.00	800.00	15.13	143.50	D.a.I.	23.26
E24/04/2012-0.5mm	86.4	8.18	0.08	0.85	3.06	D.d.I.	6.76	4.23	2.30	9.89	34.18	210.00	880.00	6.75	69.12	D.d.I.	1.03
Popo2012-0.125mm	1.8	8.09	1.43	2.07	8.00	b.d.l.	499.00	33.49	3.70	44.21	130.90	48.78	683.45	1348.92	955.04	b.d.l.	n.a.
Popo2012-0.125mm	3.6	8.02	1.30	2.55	9.27	D.a.i.	485.00	35.07	2.21	46.77	142.52	102.22	7264.43	1495.83	3.68	D.a.I.	n.a.
Popo2012-0.125mm	10.8	7.95	1.41	2.21	7.59	D.a.i.	565.00	36.92	2.99	47.50	157.73	38.25	2068.75	139.08	n.a.	D.a.I.	n.a.
Popo2012-0.125mm	21.6	7.97	1.84	2.39	7.44	D.d.I.	494.00	34.60	5.15	43.94	156.70	22.59	703.98	1093.73	n.a.	D.Q.I.	n.a.
Popo2012-0.125mm	43.2	7.85	1./1	2.47	8.48	D.G.I.	5/3.00	40.18	2.97	50.26	174.00	28.45	1403.03	1347.89	n.a.	D.Q.I.	n.a.
Popo2012-0.125mm	86.4	7.81	1.03	2.55	7.88	D.G.I.	526.00	30.00	6.01	46.47	159.58	22.22	457.16	410.25	12.27	D.Q.I.	n.a.
Popo2012-0.125mm	209.2	7.03	1.00	2.10	7.34 E 00	b.d.l.	545.00	40.00	6.01	01.90	217.00	41.40	11 101 60	1529.50	40.40	b.d.l.	n.a.
Popo2012-0.12511111	432	7.65	1.50	3.15	5.90	D.U.I.	576.00	49.00	0.91	90.00	317.00	156.10	11 101.00	2430.90	1905.90	D.u.i.	II.d.
Popo2012-0.063mm	1.8	7.73	3.06	2.82	16.30	1.79	763.00	54.54	5.68	/2.03	231.52	60.98	394.35	629.13	40.65	b.d.l.	n.a.
Popo2012-0.063mm	3.0	7.00	2.20	3.14	17.20	1.50	043.00	51.16	3.24	70.00	1/0.04	07.24 70.05	392.84	203.25	207.13	b.d.	n.a.
Popo2012-0.063mm	21.6	7.5/	∠.0ð 2.90	3.24 5.44	21.20	1.79	800.00	04.01 40.06	4.03	70.82	234.11	12.20	019.10	2100.27	04.11	b.d.l.	n.a.
Popo2012-0.003mm	49.2	7.44	2.09	2.44	15.00	4.77	882.00	49.00	4.91	69.70	244.48	00.02	1207.21	2330.00	11.d.	b.u.i.	n.a.
Popo2012-0.063mm	43.2 86.4	7.69	3.02	3.03	16.80	2 11	859.00	49.06	4.01	64 55	243.00	143.60	1970 70	2684 62	3310 99	b.d.i.	n a
Popo2012-0.003mm	259.2	7.03	2 90	3 79	15.60	2.11 n.a	842 00	48 70	4.51	63.00	200.00	n a	na	n a	5510.30 n a	b.d.l.	n a
Popo2012-0.003mm	432	7.58	2.50	3 70	7 32	n a	862.00	45.00	4.74	59.00	188.00	na.	na.	n a	n.a.	b.d.l.	n a
· 5002012 0.0000000		7.55	2.70	0.70	1.02	ma.	302.00	+0.00	4.01	55.00	.00.00	n.a.	n.a.	m.a.		0.0.1.	n.a.



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13268

**Table 3.** Net release of leachates in lake water for the Etna 2011, Etna 2012 and Popocatépetl samples with different grain sizes and various time of stirring. In Italic are reported the negative release of elements in lake water. b.d.l. = below detection limit; n.a. = not assessed.

		Anions (mgL <sup>-1</sup> )					ions (mg	L <sup>-1</sup> )		Trace elements (µg L <sup>-1</sup> )				
Sample	t (10 <sup>3</sup> s)	F	CI	SO4	Na	К	Mg	Ca	В	Si	Mn	Fe	As	
E12/08/2011-1mm	1.8	11.88	2.51	6.40	5.76	0.90	1.18	9.79	-240.00	- 110.00	104.37	892.63	-0.22	
E12/08/2011-1mm	3.6	11.96	1.00	6.48	7.98	1.29	1.74	13.52	-240.00	10.00	73.85	66.48	-0.28	
E12/08/2011-1mm	10.8	12.90	2.59	6.26	5.62	1.12	1.83	10.79	-240.00	1660.00	94.62	329.88	5.47	
E12/08/2011-1mm	21.6	14.07	2.62	6.55	4.38	0.64	-0.17	5.05	-235.00	1305.00	- 1.25	62.88	-0.84	
E12/08/2011-1mm	43.2	13.48	4.07	6.81	4.67	0.49	1.28	5.23	-230.00	950.00	90.62	120.38	-0.04	
E12/08/2011-1mm	86.4	14.07	3.37	6.45	5.48	0.42	0.55	7.68	- 120.00	1470.00	96.75	365.38	0.29	
E12/08/2011-1mm	259.2	14.79	2.24	6.53	6.39	1.40	1.98	11.29	- 120.00	n.a.	86.00	103.38	0.45	
E12/08/2011-1mm	432	15.24	2.90	5.95	6.96	0.97	1.39	8.93	- 120.00	12 100.00	124.75	1557.78	-0.33	
E12/08/2011-0.5mm	1.8	11.75	2.50	7.51	5.46	0.95	0.28	7.32	-220.00	3420.00	111.35	436.88	0.22	
E12/08/2011-0.5mm	3.6	11.55	2.33	8.02	5.76	1.01	1.36	8.74	- 120.00	7130.00	161.15	3532.78	0.19	
E12/08/2011-0.5mm	10.8	12.78	2.06	8.37	6.42	1.02	1.54	10.71	-210.00	1090.00	95.75	244.75	0.08	
E12/08/2011-0.5mm	21.6	14.75	3.60	10.51	7.72	1.15	2.62	15.39	- 130.00	740.00	100.95	54.38	-0.33	
E12/08/2011-0.5mm	43.2	12.80	2.44	8.65	5.76	0.65	0.55	8.38	-60.00	2010.00	92.25	246.50	0.22	
E12/08/2011-0.5mm	86.4	13.57	2.29	8.42	5.92	0.82	0.27	9.00	- 130.00	1720.00	118.35	391.18	0.88	
E12/08/2011-0.5mm	259.2	13.76	2.24	8.97	6.58	1.26	1.78	9.82	-230.00	2760.00	99.50	229.50	-0.04	
E12/08/2011-0.5mm	432	15.87	2.93	10.15	9.24	1.46	2.33	13.77	- 120.00	12 350.00	n.a.	n.a.	0.63	
E24/04/2012-1mm	1.8	2.27	3.12	1.49	0.52	-0.25	0.01	6.66	- 130.00	30.00	2.62	22.63	0.11	
E24/04/2012-1mm	3.6	1.31	0.26	-0.28	0.89	-0.92	0.35	7.55	- 180.00	80.00	3.75	38.88	-0.12	
E24/04/2012-1mm	10.8	4.12	2.85	0.83	1.61	0.40	0.55	8.64	120.00	910.00	35.62	260.63	0.19	
E24/04/2012-1mm	21.6	2.54	2.81	2.22	2.20	-0.38	-0.16	7.82	-220.00	1750.00	9.15	97.48	0.32	
E24/04/2012-1mm	43.2	4.30	2.44	0.33	0.57	-0.35	0.36	6.73	-210.00	1260.00	37.00	229.88	0.27	
E24/04/2012-1mm	86.4	4.35	2.98	0.81	0.91	-0.33	0.73	8.68	- 130.00	1150.00	38.87	443.13	-0.12	
E24/04/2012-1mm	259.2	4.72	3.04	1.04	2.71	-0.51	1.34	9.44	- 100.00	n.a.	47.87	663.88	-0.12	
E24/04/2012-1mm	432	9.21	6.66	3.10	3.97	-0.20	-0.01	6.66	- 70.00	11 410.00	283.65	11476.38	0.32	
E24/04/2012-0.5mm	1.8	2.42	3.14	2.66	0.91	0.59	-0.30	6.86	-110.00	510.00	5.65	189.08	0.19	
E24/04/2012-0.5mm	3.6	1.66	1.12	0.65	0.58	-0.90	0.25	7.01	- 160.00	40.00	7.75	38.13	0.51	
E24/04/2012-0.5mm	10.8	0.97	8.67	0.27	-1.78	- 1.68	-0.79	3.91	-280.00	430.00	15.37	338.63	0.19	
E24/04/2012-0.5mm	21.6	4.01	8.38	3.24	1.02	0.18	0.44	8.27	- 140.00	1150.00	53.00	250.63	9.87	
E24/04/2012-0.5mm	43.2	1.34	-0.07	-0.13	- 1.59	-1.19	-0.09	6.97	-210.00	450.00	13.88	141.88	22.42	
E24/04/2012-0.5mm	86.4	0.65	-0.54	-0.79	-0.45	0.01	-0.03	6.18	-220.00	530.00	5.50	67.50	0.19	
Popo2012-0.125mm	1.8	1.87	4.40	491.45	28.81	1.41	34.29	102.90	-381.22	333.45	1347.67	953.42	n.a.	
Popo2012-0.125mm	3.6	2.35	5.67	477.45	30.39	-0.08	36.85	114.52	-327.78	6914.43	1494.58	2.06	n.a.	
Popo2012-0.125mm	10.8	2.01	3.99	557.45	32.24	0.70	37.58	129.73	-391.75	1718.75	137.83	n.a.	n.a.	
Popo2012-0.125mm	21.6	2.19	3.84	486.45	29.92	2.86	34.02	128.70	-407.41	353.98	1092.48	n.a.	n.a.	
Popo2012-0.125mm	43.2	2.27	4.88	565.45	35.50	0.68	40.34	146.00	-401.55	1053.03	1346.64	n.a.	n.a.	
Popo2012-0.125mm	86.4	2.35	4.28	518.45	31.98	3.72	36.55	131.58	-407.78	107.16	415.00	10.65	n.a.	
Popo2012-0.125mm	259.2	2.90	3.74	535.45	58.32	4.51	71.98	242.00	-388.55	384.04	1528.33	43.84	n.a.	
Popo2012-0.125mm	432	2.95	2.30	568.45	44.32	4.62	86.08	289.00	-273.90	10831.68	2435.71	1904.28	n.a.	
Popo2012-0.063mm	1.8	2.62	12.70	755.45	49.86	3.39	62.11	203.52	-369.02	44.35	627.88	39.03	n.a.	
Popo2012-0.063mm	3.6	2.94	13.60	635.45	46.48	0.95	56.18	148.04	-362.76	42.84	262.00	205.51	n.a.	
Popo2012-0.063mm	10.8	3.04	13.60	807.45	49.93	1.74	60.90	206.11	-357.75	469.15	2099.02	62.49	n.a.	
Popo2012-0.063mm	21.6	5.24	27.70	801.45	44.38	2.62	54.63	216.48	-343.98	937.21	2349.63	n.a.	n.a.	
Popo2012-0.063mm	43.2	2.83	12.30	874.45	48.53	1.72	58.78	217.00	n.a.	n.a.	n.a.	n.a.	n.a.	
Popo2012-0.063mm	86.4	2.95	13.20	851.45	44.38	2.62	54.63	216.48	-286.40	1620.70	2683.38	3309.36	n.a.	
Popo2012-0.063mm	259.2	3.59	12.00	834.45	44.02	2.45	53.08	172.00	n.a.	n.a.	n.a.	n.a.	n.a.	
Popo2012-0.063mm	432	3.50	3.72	854.45	40.32	2.02	49.08	160.00	n.a.	n.a.	n.a.	n.a.	n.a.	



13269



**Figure 1.** Total alkali vs. silica (TAS) diagram for bulk rock and glass analyses of Etna 2011, Etna 2012 and PopocatépetI samples.







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Figure 3. Ternary diagrams for the classification of (a) pyroxenes and (b) feldspars.





**Figure 4.** SEM-BSE images of fresh ash particles from Etna 2011 (**a** and **b**), Etna 2012 (**c** and **d**), and PopocatépetI samples (**e** and **f**). The inserts in the lower left corner indicate the investigated area. In yellow are the detected sublimated salts.





**Figure 5. (a)** pH variation of ash leachates in mQ; and, **(b)** pH variation of ash leachates in lake water. The samples were washed using variable time of stirring and different grain-size. The pH of mQ and lake water is reported for comparison.



13274





**BGD** 

Figure 6. NH<sub>3</sub> (ammonium) variation of ash leachates in: (a) mQ; and, (b) lake water for variable time of stirring and different grain-size. The NH<sub>3</sub> content of mQ and lake water is reported for comparison.



**Figure 7.** Anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and F<sup>-</sup>) variation of ash leachates in mQ (left column) and in lake water (right column) for variable time of stirring and different grain-size. The different anions contents of mQ and lake water are reported for comparison.







**Figure 8.** Cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) variation of ash leachates in mQ (left column) and in lake water (right column) for variable time of stirring and different grain-size. The different cations contents of mQ and lake water are reported for comparison.





**Figure 9.** Trace elements ( $B^-$ ,  $Si^{2+}$ ,  $Mn^{2+}$ , and Fe) variation of ash leachates in mQ (left column) and in lake water (right column) for variable time of stirring and different grain-size. The different trace elements contents of mQ and lake water are reported for comparison.















**Figure 12.** Dependence of element release to grain-size and times of stirring for Etna 2011 samples. The colours indicate different time of stirring, expressed as  $s \times 10^3$ .





