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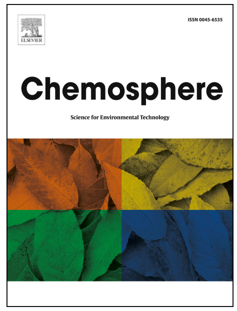

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Title

Development of a simulated lung fluid leaching method to assess the release of potentially toxic elements from volcanic ash

Authors

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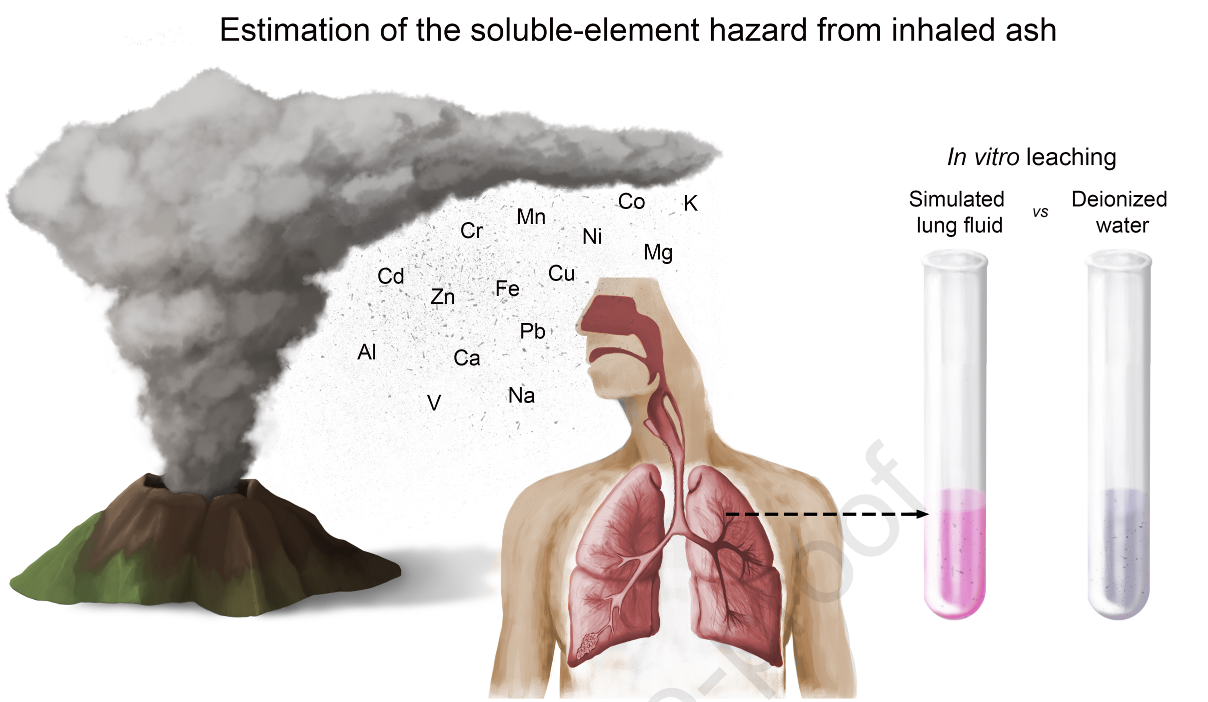
Estimation of the soluble-element hazard from inhaled ash
Cr
Mn
Co
K
Ni
Mg
Cd
Zn
Fe
Cu
Pb
Al
Ca
V
Na
In vitro leaching
Simulated lung fluid
vs
Deionized water

Abstract

Freshly erupted volcanic ash contains a range of soluble elements, some of which can generate harmful effects in living cells and are considered potentially toxic elements (PTEs). This work investigates the leaching dynamics of ash-associated PTEs in order to optimize a method for volcanic ash respiratory hazard assessment. Using three pristine (unaffected by precipitation) ash samples, we quantify the release of PTEs (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) and major cations typical of ash leachates (Mg, Na, Ca, K) in multiple simulated lung fluid (SLF) preparations and under varying experimental parameters (contact time and solid to liquid ratio). Data are compared to a standard water leach (WL) to ascertain whether the WL can be used as a simple proxy for SLF leaching. The main findings are: PTE concentrations reach steady-state dissolution by 24 h, and a relatively short contact time (10 min) approximates maximum dissolution; PTE dissolution is comparatively stable at low solid to liquid ratios (1:100 to 1:1000); inclusion of commonly used macromolecules has element-specific effects, and addition of a lung surfactant has little impact on extraction efficiency. These observations indicate that a WL can be used to approximate lung bioaccessible PTEs in an eruption response situation. This is a useful step towards standardizing *in vitro* methods to determine the soluble-element hazard from inhaled ash.

Keywords: volcanic ash, simulated lung fluid, leaching, potentially toxic elements, *in vitro* method, hazard assessment

1 Introduction

Some elements present in particulate matter, such as Al, Cd, Fe, Ni, Pb and V, can generate harmful effects in living cells (*e.g.*, oxidative stress) and, therefore, are considered potentially toxic elements (PTEs) (Chen and Lippmann, 2009; Wallenborn et al., 2009). Release of PTEs in the lung environment has been strongly linked with the toxicity of particles and associated adverse health effects (Utembe et al., 2015; Misra et al., 2012). Characterising the presence of these soluble species is thus a primary concern when assessing respiratory health hazards.

Freshly erupted volcanic ash contains a range of soluble compounds that are leached upon contact with water or body fluids. They predominantly consist of mixed sulphate and halide salts, which are emplaced by gas-ash interactions in the volcanic plume and various processes throughout ash transportation and deposition, leading to a variable element abundances on an ash surface (Stewart et al., 2020; Ayris et al., 2015; Witham et al., 2005). The principal method used to quantify species adsorbed onto ash particles is leaching (Stewart et al., 2020). Leachate analyses show that, although an array of cations and anions are readily mobilised, the most abundant soluble elements are usually Ca, Na and K, followed by Al, Mg, Fe and Cu, and the most common minor elements (defined as < 5 mg/kg ash) are Ni and Zn (Ayris and Delmelle, 2012). The release of these elements may result in the contamination of water bodies and soils with potential impactsto human and animal health in ash-affected areas (Stewart et al., 2020; Witham et al., 2005).

As a common hazard assessment strategy, leaching with simulated lung fluid (SLF) is used to investigate the lung bioaccessibility of PTEs for a wide range of inhalable materials (*e.g.*, Martin et al., 2018; Dean et al., 2017; Wiseman and Zereini, 2014; Wolf et al., 2011; Plumlee and Morman, 2011; Gray et al., 2010; Colombo et al., 2008; Twining et al., 2005). SLFs are solutions that comprise of a mixture of physiologically relevant constituents (electrolytes and organic molecules) representing the conditions in different compartments of the human respiratory system. Acellular *in vitro* studies are easily implemented and can provide a quick and cost-effective alternative to cellular *in vitro* and *in vivo* studies. Although leaching experiments do not reproduce the complex processes that occur in the human body and, thus, the health relevance cannot be directly extrapolated from the results (Boisa et al., 2014; Kastury et al., 2017), they provide a first-order understanding of the release of PTEs in the lung environment.

The most commonly used SLF is known as Gamble's solution. It is a near-neutral (pH 7.4) solution consisting of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (HCO_3^-, Cl^-, HPO_4^{2-}, SO_4^{2-}) at concentrations representative of those measured in lung lining fluid (Gamble, 1967), with acetate ($H_3C_2O_2^-$) and citrate ($H_5C_6O_7^{3-}$) substituting for macromolecules such as proteins and lipids, despite having different biochemical functionalities. There are now varying formulations of the original Gamble's solution, though modifications are often presented without a clear explanation(Kastury et al., 2017). These modified solutions include organic compounds that are representative of anions and functional groups in the lung lining fluid (*e.g.*, albumin, mucin, citrate, glycine, cysteine, glutathione, lactate, pyruvate, etc.), which can act as chelating agents towards specific metals or metalloids of interest and may promote dissolution of otherwise insoluble compounds (Caboche et al., 2011; Pelfrêne et al., 2017), as well as lung surfactants (*e.g.*, dipalmitoylphosphatidylcholine; DPPC), which can increase wettability of particles, improve contact between leachant and metals, and prevent aggregation (Caboche et al., 2011; Pelfrêne et al., 2017). Such modifications add to the complexity of the solution and hinder comparison among studies, particularly because the impacts of these modifications on overall leaching dynamics are not understood.

The viability of an SLF method to assess volcanic ash has not yet been specifically tested. In contrast to the highly polluted geological materials that are usually of interest for lung bioaccessibility studies (*e.g.*, mine waste, soils, urban dust; Kastury et al., 2017; Plumlee and Morman, 2011), volcanic ash contains very low concentrations of PTEs (Stewart et al., 2020), particularly where speciation is a primary concern for toxicity (As, Cd, Cr, Hg, Pb, Se). However, ash has an abundance of generally non-toxic elements like Ca, Na, S and Cl (Ayris and Delmelle, 2012). Since some of these ions are already present in SLF in substantial quantities, as either components of the SLF recipe or as impurities in the reagents, this can cause signal reduction or poor precision during measurements (*i.e.*, high background values). This can then cause difficulties in determining concentrations leached from the ash, especially for minor elements, including PTEs, because of the necessity of making large dilutions of the sample matrix. Thus, there is a clear need to test different parameters of a SLF method for volcanic ash to establish their influence on apparent PTE bioaccessibility.

There is no consensus on leaching parameters (such as extraction time and solid to liquid ratio (S:L)) appropriate for the inhalation pathway on which to base a method for ash (Kastury et al., 2017). Recommendations for a SLF leachate method applied to volcanic ash were an outcome of expert discussions hosted by the International Volcanic Health Hazard Network (IVHHN) (Stewart et al., 2013), but the method was not fully tested. Therefore, these recommendations were not included in the IVHHN protocol for the rapid assessment of hazards from leachable elements in ashfall (Stewart et al., 2020). This was mainly because testing of the 2013 protocol faced the aforementioned difficulties associated with measurement of low PTE concentrations from ash in typical SLF solutions. Additionally, there was the concern that an SLF method may not be readily spun up for eruption response work because of the number and expense of analytical-grade reagents required for SLF preparation. Rapid analysis and dissemination of results is the key intention of this method, which sits within a broader IVHHN protocol to rapidly assess health-relevant physicochemical and toxicological characteristics of volcanic ash (available at www.ivhhn.org). This leachate protocol currently includes a general-purpose deionised (DI) water leach (WL) that is appropriate for assessing the impacts of ashfall on water resources, such as drinking water supplies, and a ‘simple gastric’ leach that is intended to estimate the bioaccessible fraction of PTEs in the event of ash ingestion by humans or livestock (Stewart et al., 2020). An SLF method was not yet developed to a point where inclusion would provide timely data during an eruption response.

To date, only three studies have addressed leaching of volcanic ash in SLF. In the first, Damby (2012) investigated which minerals dissolve and the types of secondary minerals that might precipitate in the lung following inhalation of volcanic ash using samples from five different volcanoes (Colima, Merapi, Mt. St. Helens, Santiaguito and Unzen). After a four-week incubation of samples in SLF at 37 °C, a loss in mass, attributed to glass dissolution, was noted among all samples, but no new mineral precipitation was observed using X-ray diffraction. In the second study, Tomašek et al. (2019) leached synthetic ash laden with sulphate salts in water and determined that the majority of salts dissolved within 10 minutes. Using the resulting water-leach concentrations, saturation in SLF was simulated by reaction-path modelling. The SLF was under-saturated in sulphate salts ($CaSO_4$, Na_2SO_4 and $MgSO_4$), suggesting that no new phases were being formed and the predominant salt deposits found on ash surfaces would dissolve in lung fluid, likely prior to cellular uptake. In a recent study, Barone et al. (2020) quantified the soluble element burden of volcanic ash samples from Etna volcano in water and SLF according to the initial recommendations by Stewart et al. (2013). They found that the concentrations of elements released in SLF are lower than those measured in water.

The primary objective of this study is to develop a robust *in vitro* method to assess the release of PTEs from ash in the lung environment to evaluate the hazard of volcanic eruptions to public health. Given the scarcity of past ash leaching studies on which to base such a method, and the general lack of studies reporting comparative efficiencies of existing SLF approaches, this work establishes the effect of different SLF compositions and extraction parameters (ash to leachant ratio and extraction time) on the leaching efficiency of PTEs. This is a critical first step in the development of a standardised method for health hazard assessment and inclusion with other, existing IVHHN ash analysis protocols as the lung lining fluid is the first interface that inhaled materials come into contact with in the airways. A second objective of this work was to compare element leaching efficiency in SLF and DI water (*i.e.*, IVHHN's general-purpose WL). Toxicology studies of particulate matter indicate that water-soluble elements may be associated with toxic effects in the lungs (Oller et al., 2009; Costa and Dreher, 1997), and that their release into water may differ from their release into an SLF (Caboche et al., 2011; Pelfrêne et al., 2017). Hence, the present experiments were designed to ascertain whether WL could be used as a proxy for SLF leaching of volcanic ash. DI water is the most common leachant for ash studies (Stewart et al., 2020) due to its wide availability. Its use for rapid respiratory hazard assessment would bolster data comparability with previous assessments, and eliminate the need to perform multiple leachate analyses on a sample, which are often difficult to obtain in sufficient amounts.

2 Materials and Methods

2.1 Volcanic ash samples

For this study, three ash samples from recent volcanic eruptions were selected (**Table 1**). The samples were collected fresh (unaffected by precipitation or surface weathering) from ashfall deposits according to IVHHN ash collection recommendations (Stewart et al., 2020) and stored into self-sealing plastic bags. The SLF leaching experiments (***Section 2.3***) were carried out in batch conditions on bulk volcanic ash, which had not been oven dried. Each sample was homogenized by gently rotating in a sealed container before taking a sub-sample for leaching experiments.

Table 1 Sample and collection information for the volcanic ash samples used in this study.

Volcano	**Country**	**Eruption date**	**Magma type**	**Collection date**	**Collection location**
Ambae	Vanuatu	17/03/2018	Basalt to trachybasalt[1]	17/03/2018	Vinangangwe, West Ambae
Kīlauea	USA	10-28/05/2018	Basalt[2]	28/05/2018	Kaʻū Desert, Hawai'i
Whakaari/White Island	New Zealand	27/04/2016	Andesite[3]	28/04/2016	North rim of the crater

[1]*Moussallam et al. (2019),* [2]*Neal et al. (2019),* [3]*Mayer et al. (2015).*

The sample selection was based on available mass to test a number of different leaching parameters, and because samples were previously characterised for their water-leachable element content. All three ash samples have relatively high leachable concentrations. Element concentrations (in mg/kg dry weight ash) were determined by WL for 1 h at a solid to liquid ratio of 1:100 (Damby et al., 2018; Stewart C., unpublished) using a standardised protocol by Stewart et al. (2020). These concentrations were normalized to mean concentrations reported in a global dataset on water-extractable elements from volcanic ash (Ayris and Delmelle, 2012) (**Fig. 1**, Appendix A). All three samples have abundant soluble major elements (> 5 mg/L global mean concentration), particularly the ash from Whaakari/White Island volcano. Water-soluble minor elements (< 5 mg/L global mean concentration), except for Cu, are present in lower concentrations than global means and some were below detection limits (BDL) in Ambae and Kīlauea ash (namely Co in Ambae, Zn in Kīlauea, Cd, Cr, Pb and V in both). These 1 h WL data are compared with the concentrations determined in the present study using the same ash to leachant ratio (1:100) for 24 h WL and SLF at different time points in ***Section 3.4.***

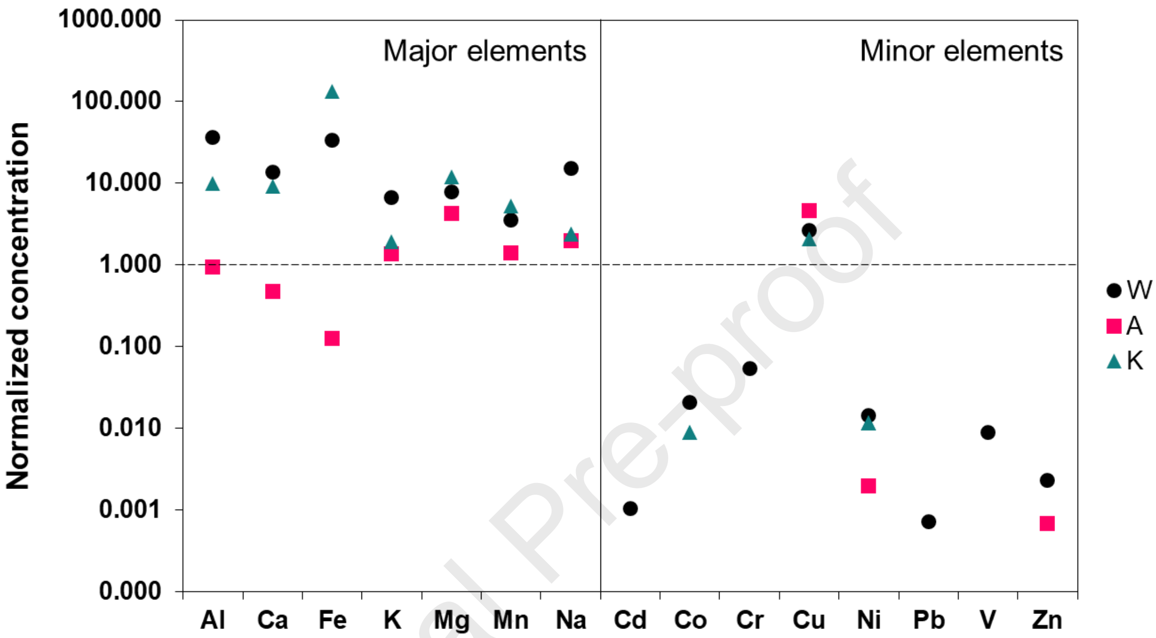

Figure 1 Water-extractable major (> 5 mg/L) and minor (< 5 mg/L) element abundances in analysed ash samples (black circles – **W**haakari/White Island, red squares – **A**mbae, green triangles – **K**īlauea) normalized to global mean values (Ayris and Delmelle, 2012). Elements not shown were below detection limit (Appendix A).

2.2 Selection of leaching parameters

The recommendations for ash leaching in SLF provided by the expert working group convened by IVHHN to standardize the leachate protocols are taken as a starting point for our SLF testing (Stewart et al., 2013). These include an SLF based on Gamble's solution (Table 2), a contact time of 24 h and a 1:100 ash (mass) to leachant (volume) ratio. In the following sections, we summarise the parameter modifications tested in this study.

2.2.1 Leachant

In general, the dissolution rate of elements is dictated by their solubility in different media (*e.g.*, water or SLF) which is predominantly controlled by the pH and composition of the solution (Kastury et al., 2017; Misra et al., 2012). Earlier studies argued that simple leachants, such as water, are not 'physiologically based' and, thus, are not representative of pulmonary exposure (reviewed in Kastury et al. (2017)). It is thought that a WL may underestimate the lung bioaccessibility of metal components due to the absence of organic compounds.

In addition to deionized water, we used four different SLF solutions of a near-neutral pH, all with the same base composition (see **Table 2**). This range of solution compositions allows determination of the effects of inclusion, or exclusion, of commonly used molecules (glycine, citrate) and a surfactant (DPPC) to deduce whether they are essential components for assessing the ash hazard. For these experiments, the 24 h time-point and 1:100 solid to liquid (S:L) ratio were set as constant.

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2.2.2 Extraction time

To be relevant for inhalation exposures, the sample extraction time *in vitro* should be representative of the residence time of particles in the lung. This is difficult to constrain as particle removal depends on the deposition site within the lungs and clearance mechanisms involved (mucociliary transport, uptake by phagocytic cells, *in situ* dissolution, etc.). These processes operate on the order of hours to days and months (Bailey et al., 2007; Morgan et al., 2004; Gehr et al., 1990). It has also been argued that the short-term toxic effect of particles that release ions at a fast rate could be identical to those of the dissolved ions (Studer et al., 2010), whereas, for particles that release ions at a slow rate, there is a greater likelihood that the particles will be the cause of the observed adverse effects (Oberdörster, 2000).

The contact times used in previous lung bioaccessibility studies on non-volcanic material vary greatly, ranging from 5 min to 1 year (Kastury et al., 2017), with most studies using ≤ 24 h. Reported timeframes in ash-water leachate studies range from 5 min to 2 years (Stewart et al., 2020). A shorter duration timepoint is supported by previous work on volcanic ash leachate studies. Ash leachate studies using water demonstrated that the majority of surfaces phases were dissolved within the first 10-15 minutes (Olsson et al., 2013; Duggen et al., 2007), and most sulphate salts were dissolved within 10 minutes (Tomašek et al., 2019).

To determine how extraction varies over a relevant timeframe for volcanic ash in SLF, we tested contact times of 10 min, 1 h, 4 h, 24 h and 48 h, each as a separate experiment. The 24 h time-point was kept as a constant parameter for the S:L ratio and leachant composition tests. This is the time-point at which the measured concentrations of all elements became approximately stable and provides a direct comparison with cellular toxicity tests which commonly use 24 h exposures.

2.2.3 Solid to liquid ratios

The mass of particles that deposits in the lung (*i.e.*, particle loading) following inhalation is variable and largely dependent on ambient particle concentrations, size distribution and personal exposure. To determine *in vitro* S:L ratios relevant for real human exposure, we calculated the potential particle loading following a single ash exposure. We assume 100% particle deposition and a daily inhaled air volume of 25 m^3, corresponding to a healthy, moderately-active adult (ICRP, 1994), for airborne ash concentrations of 0.02 and 1 mg/m^3, reported as minimum and maximum daily averages in the literature (Searl et al., 2002). Using 20 mL as the total volume of lung lining fluid (Macklin, 1955), when ambient concentrations of ash are low (0.02 mg/m^3) the S:L ratio would correspond to 1:4000, whereas when ambient concentrations are high (1 mg/m^3) it would be 1:800. In case of an exposure to higher ambient concentrations, which could be experienced during ash clean-up activities (*e.g.*, 10 mg/m^3) (Searl et al., 2002), the ratio could be even larger and equate to 1:80.

The S:L ratios used in lung bioaccessibility studies to date range from 1:20 to 1:50000, with the majority of studies using ratios < 1:100 (Kastury et al., 2017), whereas ash-water leachate studies use ratios from 1:5 to 1:1000 (Stewart et al., 2020). The ratios tested in this study (1:10, 1:20, 1:100, 1:500, 1:1000) reflect this wide range, accounting for experimental/analytical constraints, and include the existing IVHHN recommended ratios of 1:20 and 1:100 (Stewart et al., 2020). The 1:100 ratio was selected as a constant in the time-series and varying leachant composition tests.

2.2.4 Other method parameters

Other parameters that may affect extraction and have direct relevance to the respiratory system but were not specifically tested in the framework of this study are temperature and particle size. Whereas most SLF studies incubate particles at 37 °C to replicate body temperature (Kastury et al., 2017), we performed the extractions at room temperature (25 °C) as a system to maintain the elevated temperature and agitate the samples simultaneously was not available. This was justified through preliminary experiments that compared extraction at 25 °C and 37 °C (without agitation) and resulted in little difference in leaching efficiency (*unpublished data*). Therefore, we leached all samples at room temperature to reduce experimental complexity.

Considering that the focus of the current exercise was on the methodological parameters affecting bioaccessibility rather than sample properties, we choose to perform the extractions on bulk (un-sieved) ash samples. Isolation of respirable (sub-4 µm) material from bulk ash, in amounts sufficient for leachate analysis, is time-consuming and often impractical. The percentage of sub-4 µm particles also varies greatly among samples, depending on the sample collection distance from the vent and the magnitude and explosivity of the eruption, but is typically < 17 % (Horwell, 2007; Horwell and Baxter, 2006). This is the case for sub-10 µm particles as well, which are generally used in lung bioaccessibility assessment studies (Kastury et al., 2017). While it is assumed that analysis of the respirable fraction may be more predictive of real bioaccessibility, and is likely to give higher concentration values than those of bulk extractions due to higher particle surface area, it is not always possible to demonstrate the size effect in isolation from other properties (Misra et al., 2012).

2.3 Leaching experiments

Assay parameters evaluated (see **Table 3**) included composition of the leachant, contact time and ash to leachant (S:L) ratio to determine their influence on the leaching efficiency (**Table 3**). Each test was performed in triplicate. Depending on the experiment, different amounts of ash were weighed into 50-

mL polypropylene centrifuge tubes and corresponding volumes of leachant were added. Samples were then agitated on a platform (horizontal) shaker at 60 rpm at room temperature throughout the extraction duration. Subsequently, samples were centrifuged for 5 min at 3392 × *g* and filtered through 0.45 µm cellulose acetate membrane filters (VWR Chemicals, Belgium) into 15 mL polypropylene tubes using syringe filtration. Leachates were acidified with concentrated nitric acid (HNO_3) and stored at 4 °C until analysis.

In order to keep the background concentrations low, all reagents used to prepare the SLF (**Table 2**) were of analytical grade (*AnalaR® NORMAPUR®*), purchased from VWR Chemicals (Belgium). The solutions were prepared in deionized water (Milli-Q®, resistivity of 18.2 MΩ). The pH of the solution was adjusted to 7.40 ± 0.05 using concentrated hydrochloric acid (HCl).

Table 2 Composition of the simulated lung fluid (SLF) solutions used in this study (see ***Section 2.2.1***). Base composition (SLF1) is after Stewart et al. (2013), and modifications are to include lung surfactant (DPPC; SLF2) and to remove citrate (SLF3) or glycine (SLF4). All concentrations are as mg/L.

	SLF1	**SLF2**	**SLF3**	**SLF4**
NaCl	6400	6400	6400	6400
$CaCl_2.2H_2O$	255	255	255	255
Na_2HPO_4	150	150	150	150
$NaHCO_3$	2700	2700	2700	2700
NH_4Cl	118	118	118	118
$MgCl_2.6H_2O$	212	212	212	212
$Na_2SO_4.10H_2O$	179	179	179	179
Na_3 citrate.$2H_2O$	160	160	-	160
Glycine	190	190	190	-
DPPC* (0.01%)	-	100	-	-

**DPPC = 1,2-Dipalmitoyl-sn-glycero-3-phosphocholine*

Table 3 Experimental parameters: leachant, extraction time and S:L ratio. Each test was performed in triplicate.

	SLF1	**SLF2**	**SLF3**	**SLF4**	**WL***

10 min	1:100				
1 h	1:100				
4 h	1:100				
24 h	1:10 1:20 1:100 1:500 1:1000	1:100	1:100	1:100	1:100
48 h	1:100				

**WL = water leach, using deionized water (Milli-Q®, resistivity of 18.2 MΩ, pH 7.95 ±0.05)*

2.4 Trace elements analysis

We analysed a large suite of PTEs (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) and cations that are the main constituents of ash surface coatings (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}). All element concentrations were measured using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Thermo Finnigan Element II) at the facilities of the Analytical, Environmental and Geochemistry group of the Vrije Universiteit Brussels. Calibration curves of the selected elements were made from dilutions of an acidified multi-element stock solution (ICP-MS Calibration standard 2, VWR Chemicals, Belgium) and single element standards (Certipur® 1000 ppm, Merck, Belgium), with Rh103 as internal standard. The procedural blanks and experimental samples were diluted 10-fold in 2 % HNO_3 solution prior to the analysis. Operational parameters are listed in the Appendix B (**Tables B.1** and **B.2**). The limits of quantification (LOQs) were calculated as 3-fold standard deviation of the mean elemental concentration measured in the leachates of procedural blanks which underwent the whole extraction procedure (**Table 4**).

Table 4 Limits of quantification (LOQ) for selected elements in µg/L obtained by HR-ICP-MS in deionized water (DI) and SLF solutions, calculated as three times the SD for the mean of n=8 procedural blanks for SLF1 and n=3 for DI, SLF2, SLF3 and SLF4.

	DI	SLF1	SLF2	SLF3	SLF4
Na	100	94831	506282	412779	425928
Ca	5	1340	7445	6320	6451
Mg	0.7	634	3471	2824	2752
K	1.3	5.4	35	5.1	204
Al	2.5	31.3	3.4	3.7	14.1
Fe	1.2	3.3	10.9	2.6	1.2
Mn	0.06	1.10	0.27	0.12	0.11
Cu	0.11	0.21	0.11	0.13	0.08
Cd	0.003	0.008	0.004	0.007	0.009
Co	0.006	0.005	0.010	0.005	0.002
Cr	0.23	0.30	0.26	0.27	0.25
Ni	0.24	0.33	0.28	0.26	0.26
V	0.006	0.027	0.009	0.004	0.008
Pb	0.008	0.116	0.027	0.019	0.030
Zn	0.84	10.77	1.59	1.00	1.32

2.5 Data processing and statistical analysis

Graphical representation and statistical analysis of the data were performed using GraphPad Prism (version 8.3.0; *GraphPad Software*, San Diego, CA). Statistical significance between different experimental parameters was determined using a one-way analysis of variance (ANOVA) with subsequent Tukey's tests. The alpha value was set at 0.05. In the figures, significant differences are denoted by lowercase letters; for all parameters with the same letter, the difference between the means is not statistically significant ($p > 0.05$), whereas, for parameters with a different letter, the difference is statistically significant ($p < 0.05$).

3 Results

3.1 Influence of leachant composition on PTE release

The results of ash extraction in four preparations of SLF (SLF1-SLF4) are shown in **Fig. 2** (major elements) and **Fig. 3** (minor elements). All extractions were for 24 h at 1:100. Across the four SLFs tested, there were notable differences in measured concentrations that were consistent for all ash samples: Al, Fe (**Fig. 2**) and Cr (**Fig. 3**) were all found BDL in SLF3; Cu was significantly ($p < 0.05$) lower in SLF4 (**Fig. 3**); Mg was significantly ($p < 0.05$) lower in SLF2, but was otherwise equivalent ($p > 0.05$) across all leachants (**Fig. 2**); Ca and K were higher in SLF3 (**Fig. 2**). The concentration of leached Cd was the same ($p > 0.05$) in all SLFs (**Fig. 3**). There were no differences in concentrations of K (**Fig. 2**) and minor elements determined in SLF1 and SLF2 (**Fig. 3**). While low levels of Pb and Zn were leached in water (Appendix C), their concentrations were BDL in all SLFs. The substantial component of Na in SLF solutions (**Table 4**) prevents the accurate quantification of Na (Appendix C).

Regarding the extraction behaviour among the three samples, some exceptions could be observed across the different leachants. The concentration of Mn was largely comparable in different SLFs for Whaakari/White Island and Ambae ash but showed significant ($p < 0.05$) differences in Kīlauea ash (**Fig. 2**). Although following the same qualitative pattern for all samples, the concentration of Fe was not statistically different ($p > 0.05$) across all SLFs for Whaakari/White Island, whereas it was significantly different ($p < 0.05$) across all SLFs for Ambae and Kīlauea ash (**Fig. 2**). While concentrations of Cu and Ni were statistically equivalent in SLF1-SLF3 in Ambae and Kīlauea ash, this was not the case in leachates of Whaakari/White Island ash (**Fig. 3**). Leaching of V was similar for Whaakari/White Island and Kīlauea ash, with lower concentrations in SLF3, in contrast to Ambae ash where the concentrations were equivalent across all SLFs (**Fig. 3**). Concentrations of Co indicated different magnitudes of leaching across all samples (**Fig. 3**).

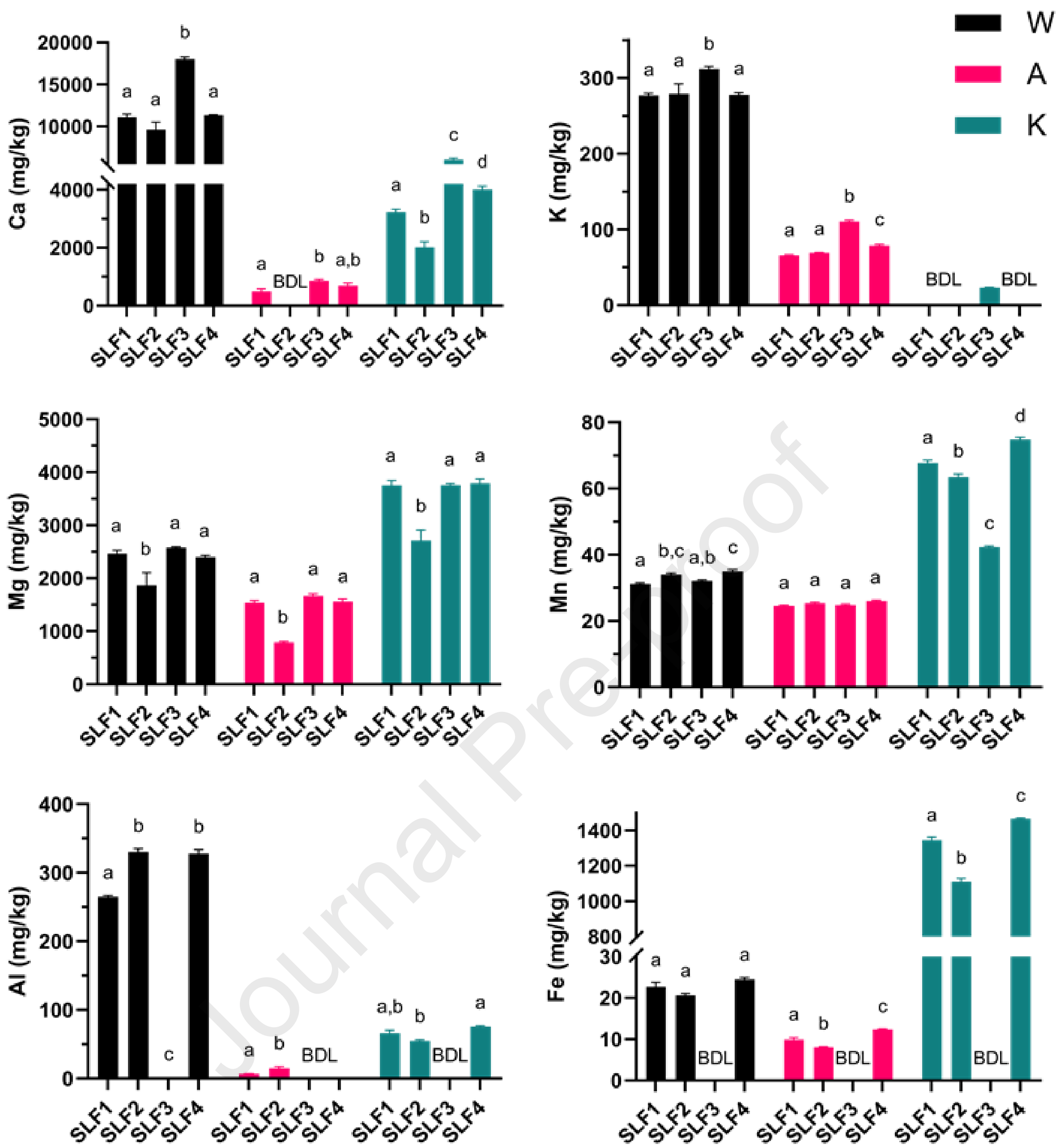

Figure 2 Major element concentrations (> 5 mg/kg, global mean concentration) in three ash samples (black – **W**haakari/White Island, red – **A**mbae, green – **K**īlauea) obtained through the extractions in four different simulated lung fluids (24 h, 1:100 S:L). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference ($p < 0.05$) between the mean concentrations of leachants for each ash sample.

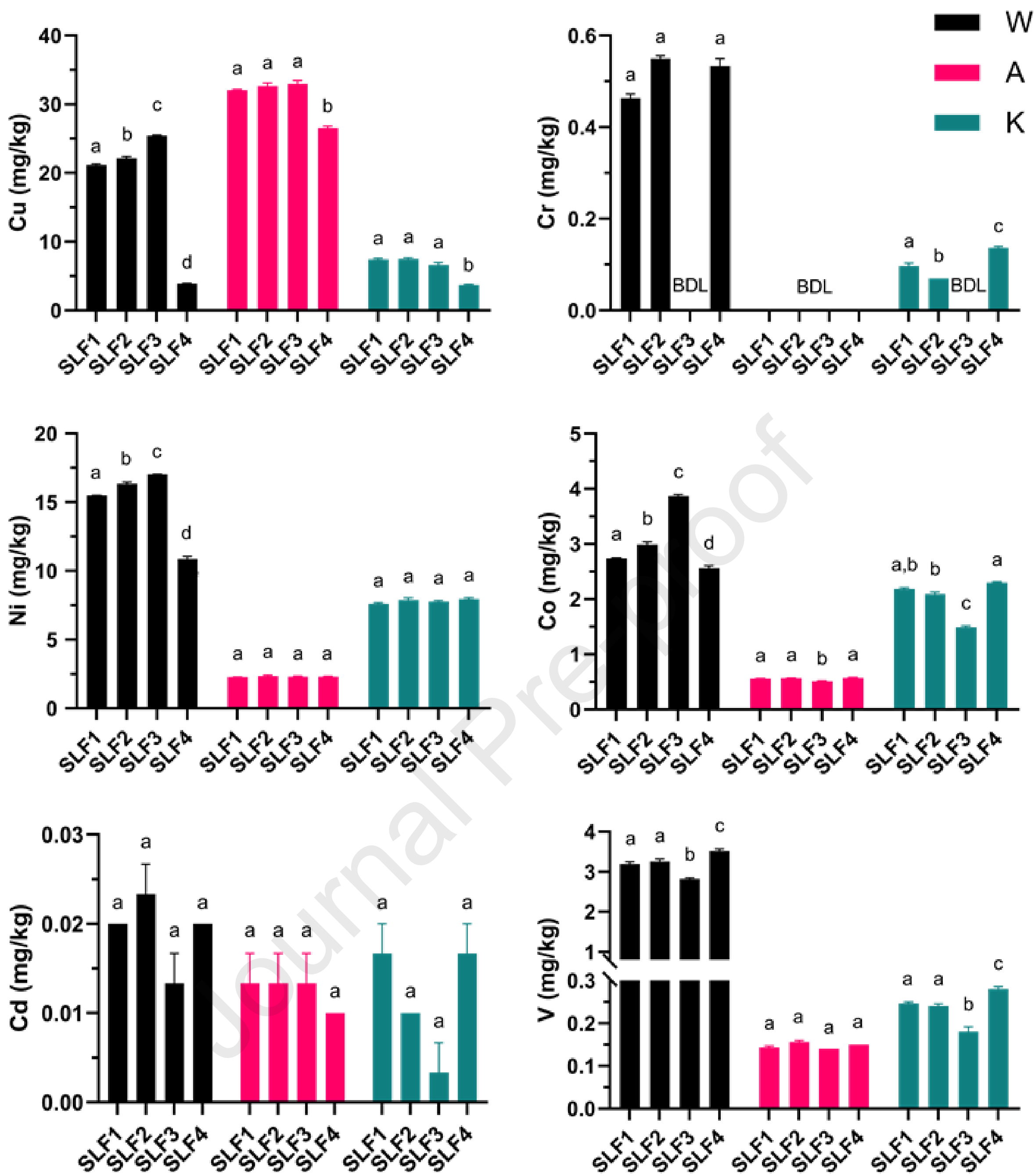

Figure 3 Minor element concentrations (< 5 mg/kg, global mean concentration) in three ash samples (black – **W**haakari/White Island, red – **A**mbae, green – **K**īlauea) obtained through the extractions in four different simulated lung fluids (24 h, 1:100 S:L). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachants for each ash sample.

3.2 Influence of extraction time on PTE release

Release of PTEs in SLF was tracked over five time intervals, from 10 min to 48 h. Overall, the concentration of individual elements over different time intervals varied among the different samples. Only Mg concentrations remaining constant ($p > 0.05$) across all measured time-points in all samples (**Fig. 4**). Except for Fe in Ambae ash, the time-series for Al, Fe and Mn were largely consistent with their highest concentrations recorded after the initial 10 min leaching period, after which concentrations decreased by the 4 h time-point and then remained stable, as seen from the little difference ($p > 0.05$) between concentrations at 4 h, 24 h and 48 h time-points (**Fig. 4**). This trend was the most prominent for Whaakari/White Island ash leachates and could also be observed for leached Cd, Co, Cr and Ni, whereas their concentrations were constant over time in Ambae and Kīlauea ash (**Fig. 5**). Similar behaviour in Whaakari/White Island was exhibited for Cu and V, whereas their concentrations slightly increased by the 48 h time-point in Ambae and Kīlauea ash (**Fig. 5**). Leached Ca and K showed a similar qualitative pattern, with a decrease at 1 h compared to the initial concentration at 10 min then followed by an increase over time (**Fig. 4**).

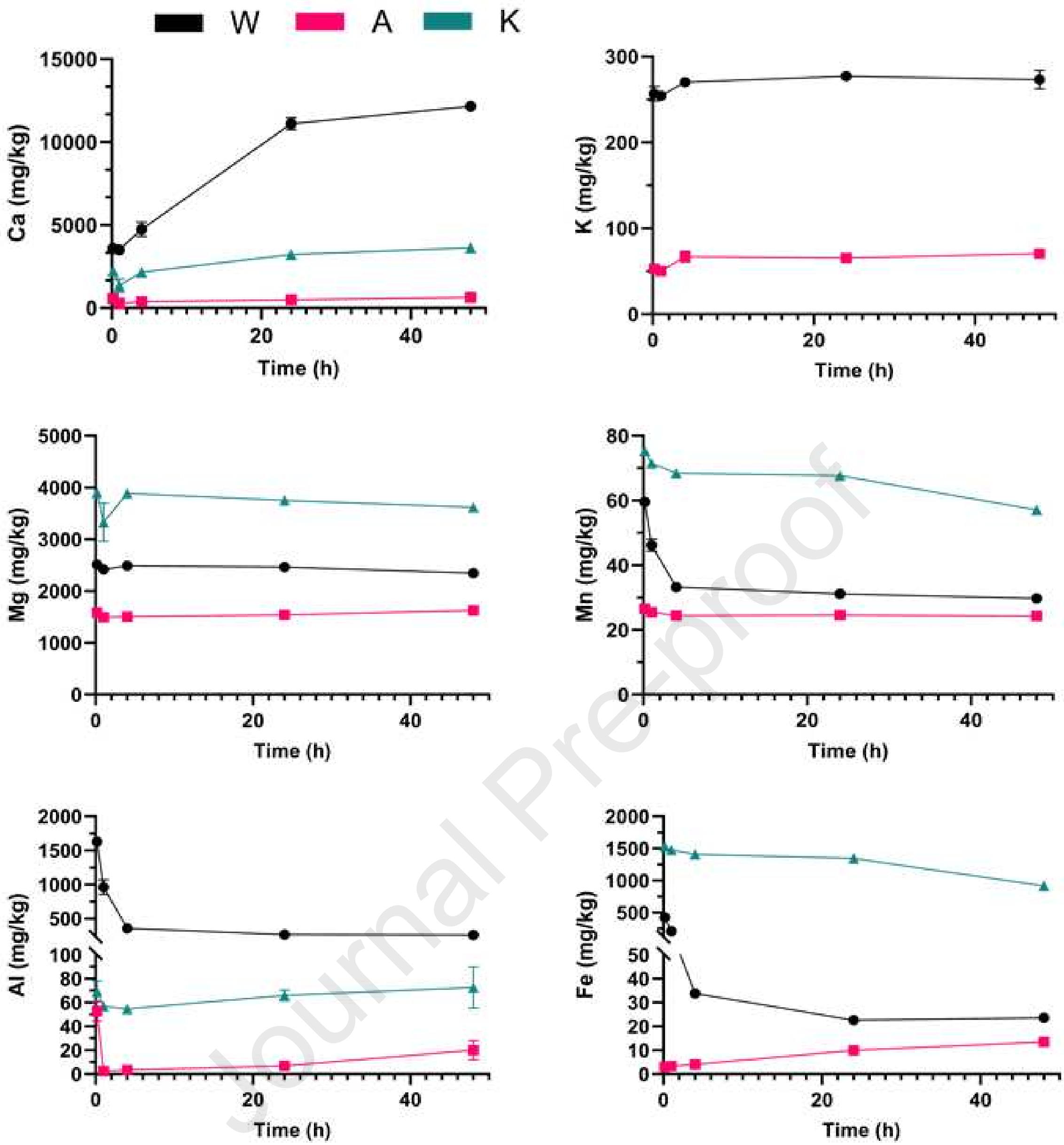

Figure 4 Major element concentrations (> 5 mg/kg, global mean concentration) in three ash samples (Whaakari – black, Ambae – red, Kīlauea – green) obtained through the extractions over varying time-points (for 1:100 S:L in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol.

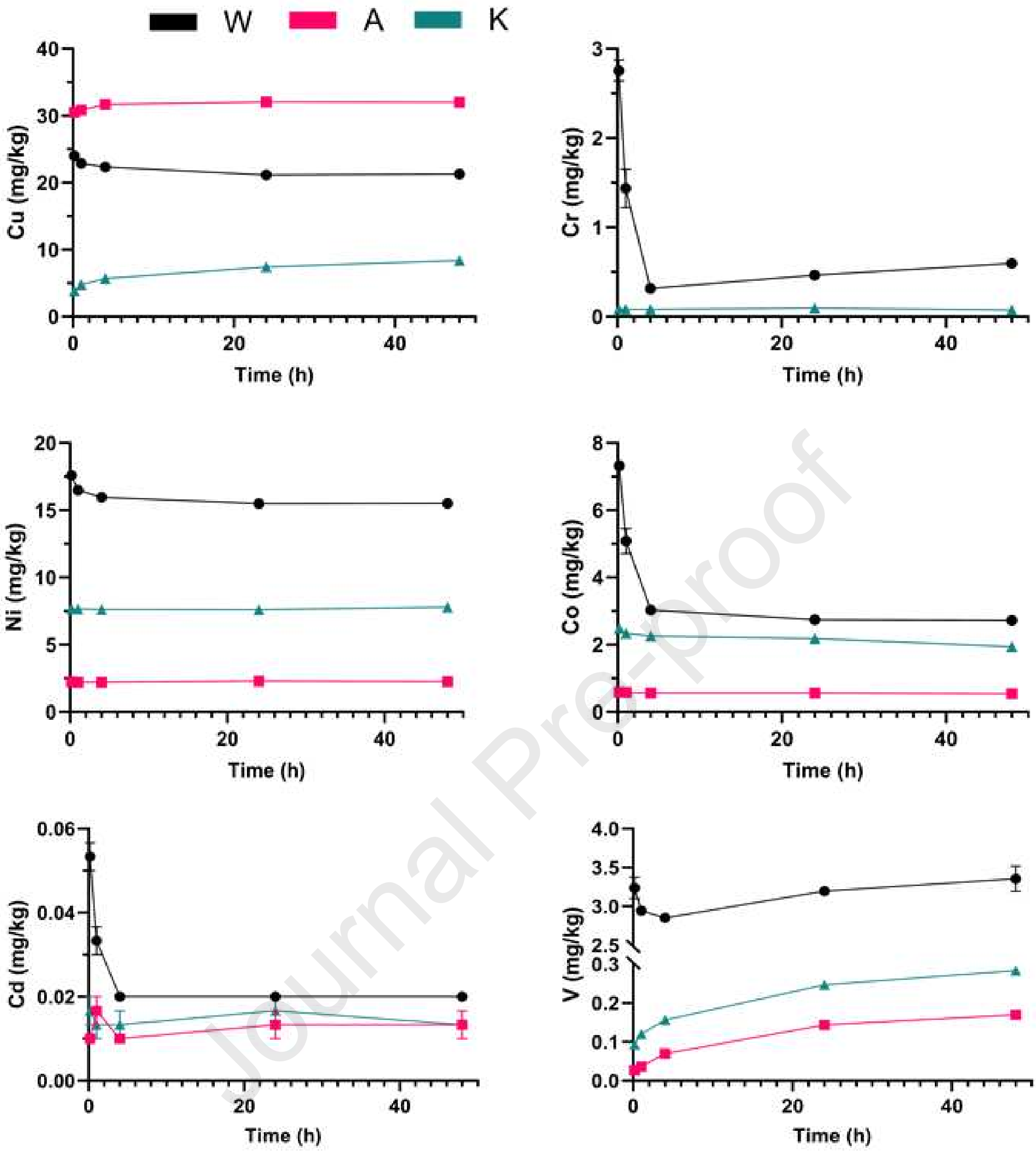

Figure 5 Minor element concentrations (< 5 mg/kg, global mean concentration) in three ash samples (Whaakari – black, Ambae – red, Kīlauea – green) obtained through the extractions over varying time-points (for 1:100 S:L in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol.

3.3 Influence of the ash to leachant ratio on PTE release

Five S:L ratios, ranging from 1:10 to 1:1000, were used to assess the influence of ash to leachant ratio on the PTE dissolution from ash in SLF. Among the different tested ratios, concentrations of Mg were found to be stable in all samples (**Fig. 6**). Concentrations at the two lowest S:L ratios, 1:500 and 1:1000, showed no significant differences (p > 0.05) for Cd, Cr, Cu, Mg, Mn and Ni across all samples, whereas K was lower or BDL in these ratios. As an overall trend, recorded element concentrations increased with decreasing sample loading for Al, Co, Cr, Cu, Fe, Mn and V, and were largely independent of S:L ratios in a range 1:100 to 1:1000 for Ambae and Kīlauea ash, with the exceptions observed in Whakaari/White Island leachates which generally had higher concentrations for these elements. For Whakaari/White Island ash, there was a drop in concentration at 1:20 and/or 1:100 for Al, Co, Fe and Mn. This was the case for Cd as well, which was found to be constant in all S:L ratios for Ambae and Kīlauea samples (**Fig. 7**). Ni concentrations varied across different samples (**Fig. 7**).

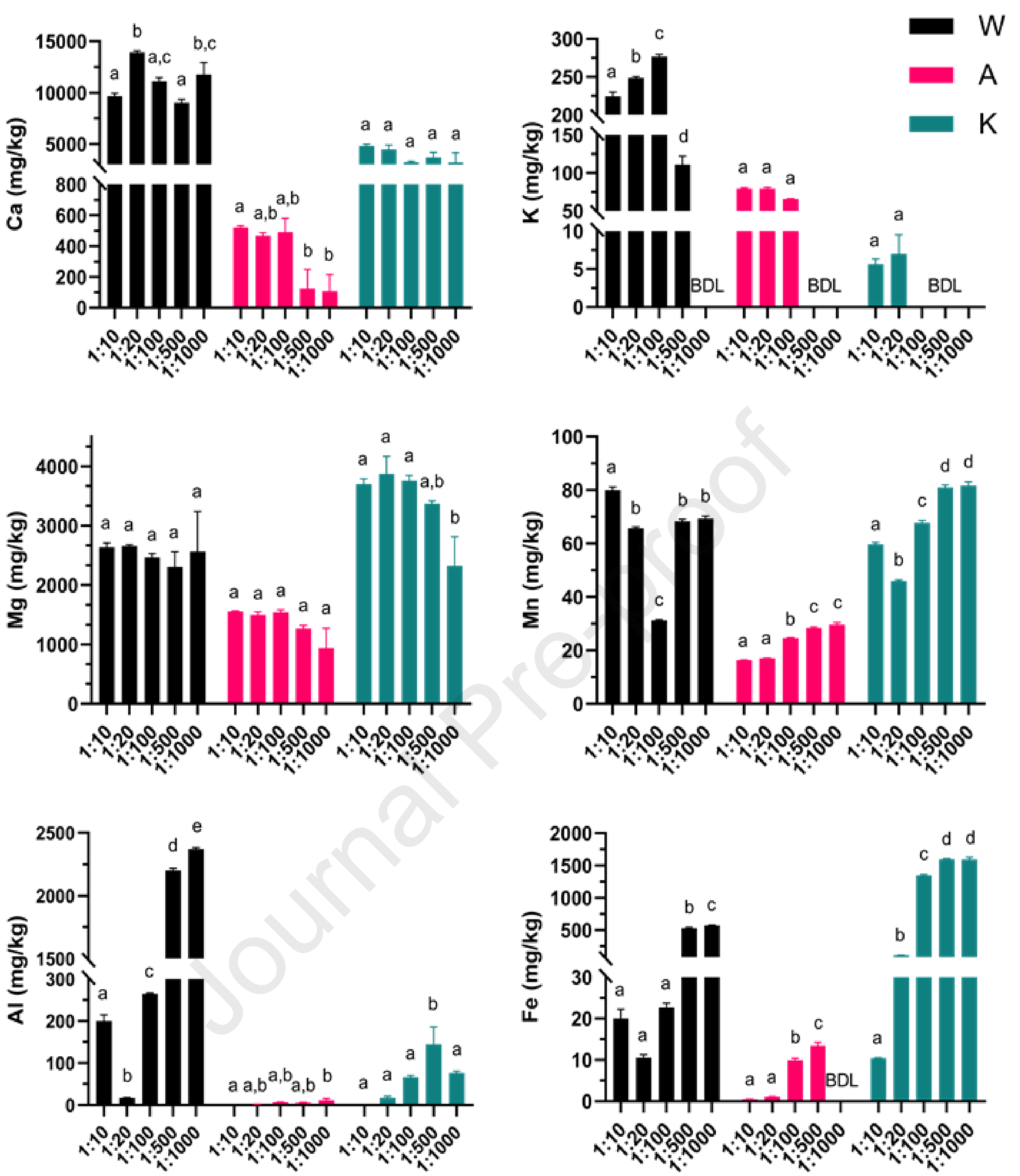

Figure 6 Major element concentrations (> 5 mg/kg, global mean concentration) in three ash samples (**W**haakari/White Island – black, **A**mbae – red, **K**īlauea – green) obtained through the extractions in varying ash to leachant (S:L) ratios (24 h in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference ($p < 0.05$) between the mean concentrations of leachants for each ash sample.

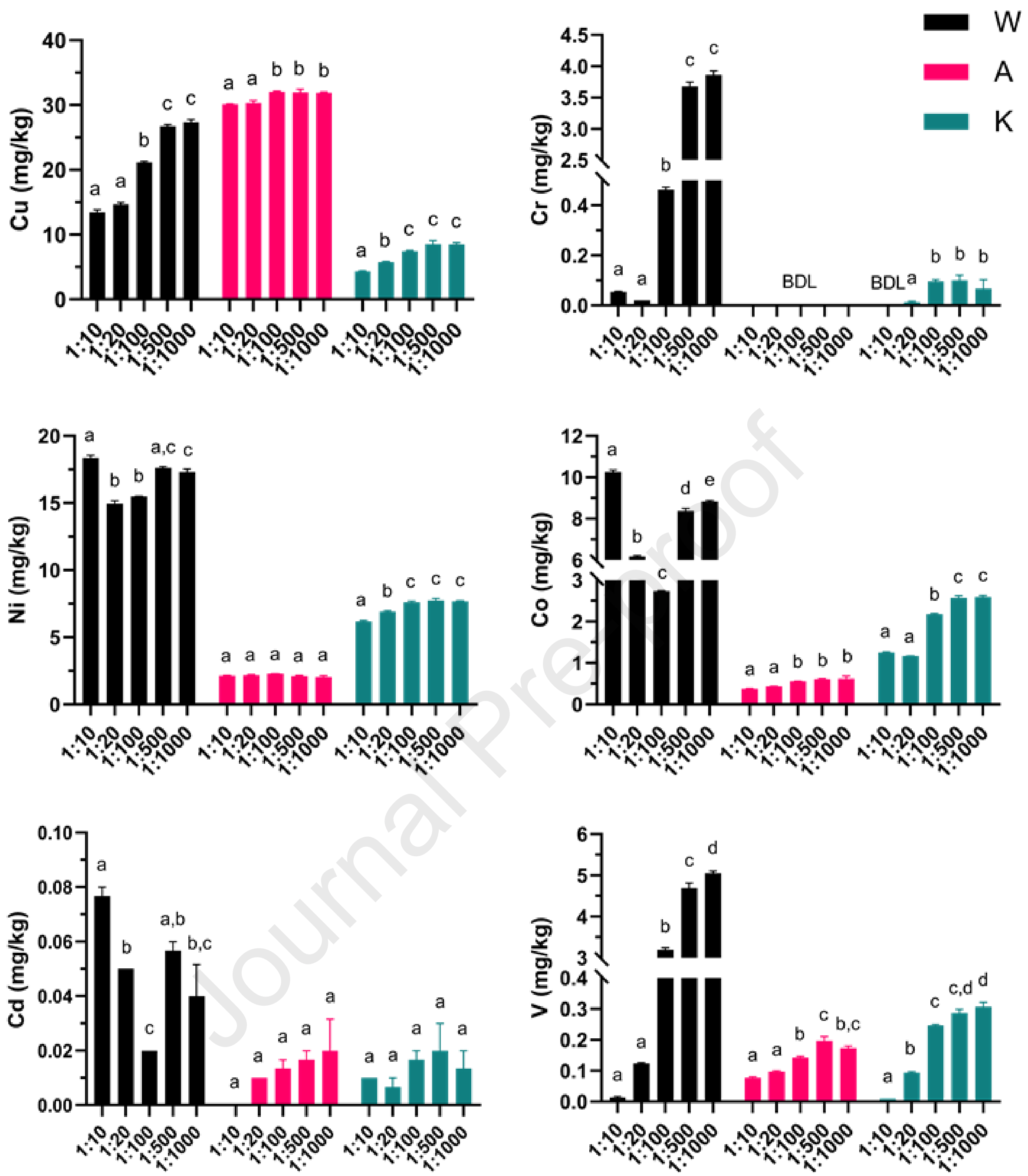

Figure 7 Minor element concentrations (< 5 mg/kg, global mean concentration) in three ash samples (**W**haakari/White Island – black, **A**mbae – red, **K**īlauea – green) obtained through the extractions in varying ash to leachant (S:L) ratios (24 h in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachants for each ash sample.

3.4 Comparison of DI water and SLF leach

A comparison of the concentrations determined in standard WL after 1 h (from Damby et al. (2018) and Stewart C. (unpublished)) and 24 h, and SLF1 leach for 10 min, 1 h and 24 h (at 1:100 and 1:1000 S/L) is shown in **Fig. 8** (major elements) and **Fig. 9** (minor elements).

The results demonstrate that most of the water-soluble elements in the analysed ash samples were found in similar or higher concentrations at 24 h than those measured in 1 h WL, with the exception of K and Cr from Whaakari/White Island ash, and Al, Ca, Mn and Fe from Kīlauea ash, which were higher in the 1 h WL (**Fig. 8**).

The overall trends indicated that the SLF1 leached concentrations of major elements were either comparable to, or significantly ($p < 0.05$) lower than, those in the 1 h and 24 h WL, with only Mg concentrations being the same across the compared parameters (**Fig. 8**). The concentrations of minor elements in SLF1 leachates were either comparable to the WL or were higher than the 1 h WL, but lower than the 24 h WL (**Fig. 9**), except for V, which was significantly ($p < 0.05$) lower or BDL in the WL.

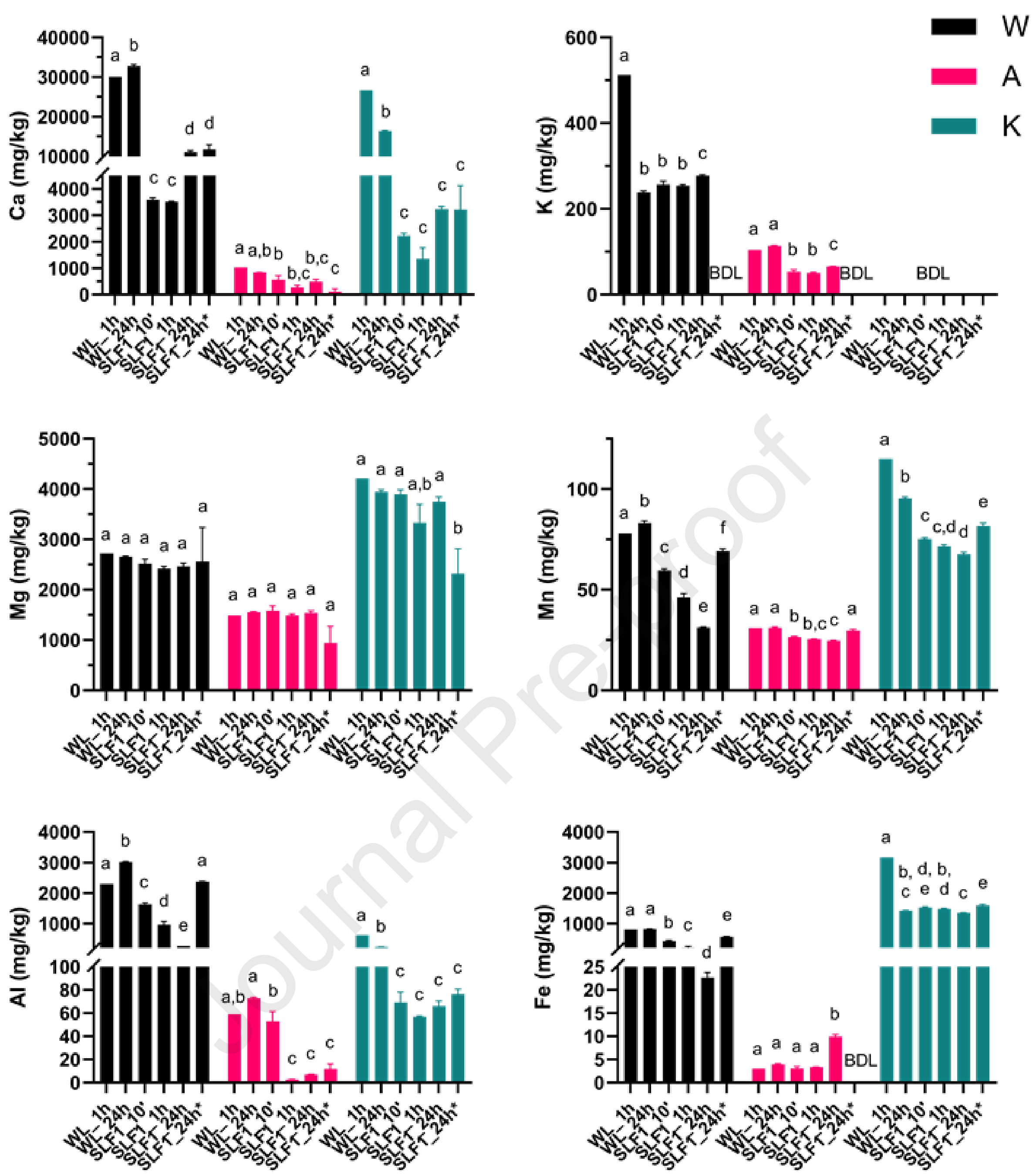

Figure 8 Major element concentrations (> 5 mg/kg, global mean concentration) in three ash samples obtained through the extractions in water (WL) and SLF1 over varying time-points. All data are for S:L 1:100, except SLF1 at 24 h denoted with a star (*), which was extracted at S:L 1:1000. Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample, except for WL at 1 h (n=1). Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachates for each ash sample.

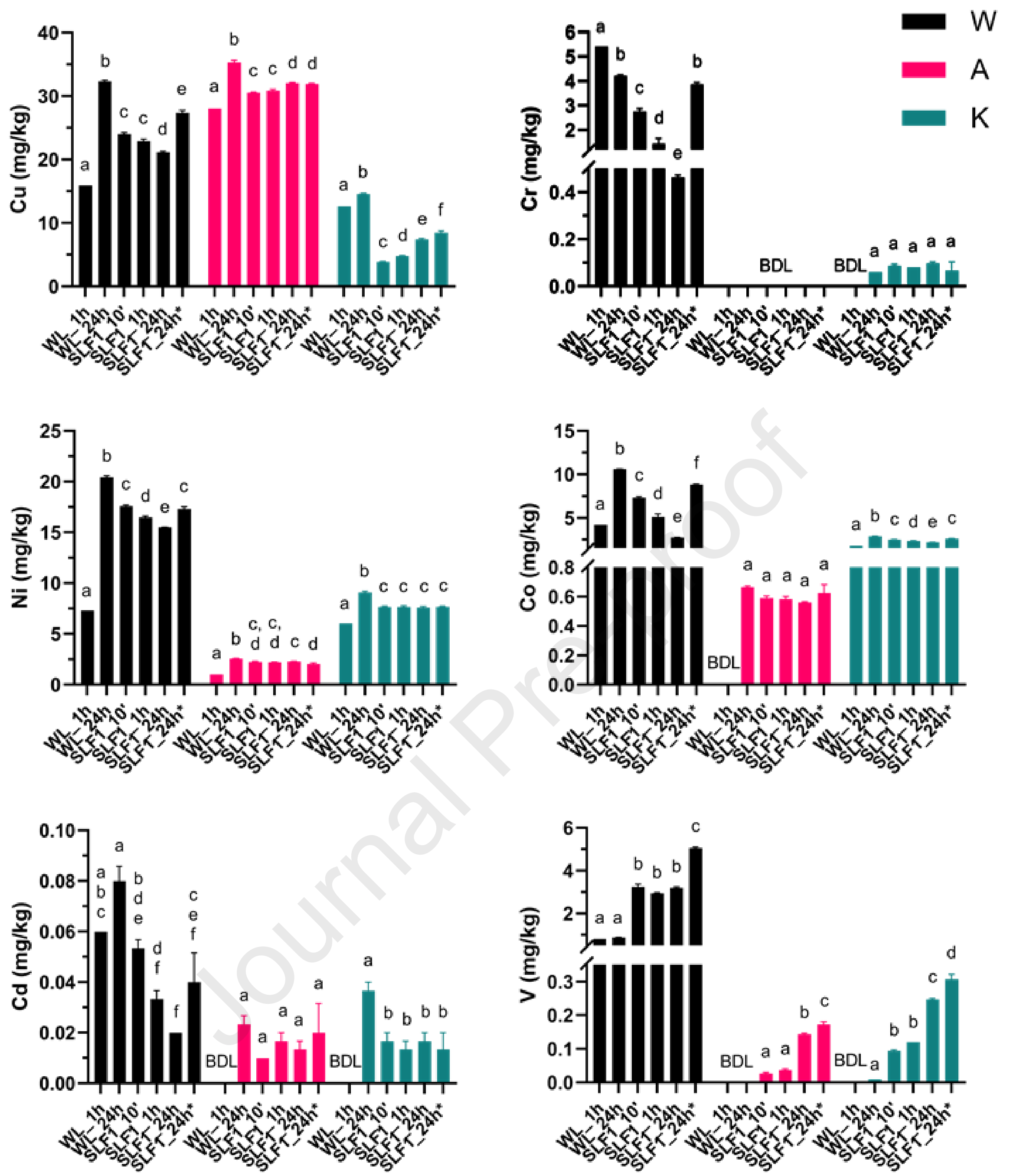

Figure 9 Minor element concentrations (< 5 mg/kg, global mean concentration) in three ash samples obtained through the extractions in water (WL) and SLF1 over varying time-points. All data are for S:L 1:100, except SLF1 at 24 h denoted with a star (*), which was extracted at S:L 1:1000. Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample, except for WL at 1 h (n=1). Error bars are the standard error of the mean. Lowercase letters indicate a significant difference ($p < 0.05$) between the mean concentrations of leachates for each ash sample.

4 Discussion

4.1 Influence of leaching parameters on release of elements from volcanic ash

The results demonstrate the influence of operational conditions on the measured PTE concentrations in SLF. In most cases, changing the parameters had an equivalent effect across all samples, which allowed for an overview of the direct impact of each method parameter.

The affect of specific compounds in the solubilisation of certain elements in SLF was clearly demonstrated. The observed differences in the release of PTEs among the four SLF compositions used (**Fig. 2** and **Fig. 3**) can likely be attributed to differences in their mobilities and tendencies to form soluble complexes with organic components present in the tested SLF solutions (**Table 2**). This was shown for glycine, a component of SLF1-SLF3, which likely formed soluble complexes with Cu (**Fig. 3**). Similarly, Al, Cr and Fe have high affinities for the citrate ion and were not as efficiently released in SLF3 in the absence of citrate (**Fig. 2** and **Fig. 3**). Furthermore, =there was little difference in leachate concentrations between SLF1 and SLF2, suggesting that inclusion of lung surfactant (DPPC) in SLF imparts limited impact on extraction of PTEs associated with volcanic ash (**Fig. 3**). The relevance of including DPPC in an SLF has been repeatedly highlighted in the literature (see review by Kastury et al., 2017), mostly due to it being the dominant component of the lung surfactant by mass and its ability to promote dissolution efficiency. While it was shown that DPPC increases the bioaccessibility of certain elements, *e.g.*, Pb, Zn and Sr (Boisa et al., 2014; Caboche et al., 2011; Pelfrêne et al., 2017), it has also been reported that the addition of DPPC results in no significant changes to bioaccessibility (Pelfrêne et al., 2017).

The concentrations of PTEs in the leachates in the time-series experiments (**Fig. 4** and **Fig. 5**) follow three general trajectories up to 24 h, when most PTE concentrations reach a plateau: increasing, flat, or decreasing. Whereas increasing concentrations can be explained by prolonged release, and a stable concentration explained by rapid dissolution, a decrease in concentration requires sequestering of previously leached elements, which decreases the fraction that remains in the solution over time. This decrease for some elements is possibly a consequence of formation of new, insoluble phases and/or adsorption onto the particles. Such formation of new, insoluble complexes or, alternatively, lack of dissociation of soluble complexes, can be facilitated by the neutral pH of the SLF solution (Pelfrêne et al., 2017; Schaider et al., 2007; Marschner et al., 2006). These processes may be also associated with the differences in PTE extraction in varying S:L ratios. The results indicated that PTE concentrations in SLF1 were largely independent of ratio in the range 1:100 to 1:1000 at 24 h (**Fig. 6** and **Fig. 7**), except for Whakaari/White Island ash, where the concentrations were higher in 1:1000 (and 1:500) than 1:100 for some elements (Al, Fe, Cr, Cu, V). It is possible that, in this case, the saturation effect was reduced due to lower particle mass loading in the solution during the extraction.

Overall, it could be seen that some element releases in SLF changed with the different substrate (sample), but the observed leaching behaviours could be summarised as follows:

1) The concentrations of Mg measured in the SLF leachates were the most stable across the different experiments in all samples;
2) The dissolution of Ni in SLF was the least affected by variation in test parameters among analysed PTEs and samples;
3) The other elements showed different sensitivities to changes in test parameters and exhibited variability among the three ash samples, with the strongest effects observed for Al, Fe and Mn.

Any sample-specific deviations from these broad effects are likely due to the differences in ash leachable burden (**Fig. 1**, **Table 1**), including the state in which PTEs are bound to the ash particles (Wolf et al., 2011).

4.2 Comparison of SLF and water leach

Our results showed that leachants of similar near-neutral pH with different complexity in their chemical composition affect the release patterns of elements from volcanic ash (**Fig. 8** and **Fig. 9**). The solubilisation potential of SLF solutions was particularly noticeable for V, which increased over time in SLF1 and was measured in all SLF leachates (**Fig. 3)** yet found in significantly (p < 0.05) lower concentrations (or was BDL) in the WL at 1 h and 24 h (**Fig. 9**).

Comparison of WL and SLF data demonstrates that the initial release of major elements in SLF1 at 10 min is, to some extent, comparable to that in WL at 1 h (**Fig. 8**), while minor PTE concentrations are higher in 10 min SLF1 than in 1 h WL, and more similar to those measured in 24 h WL (**Fig. 9**). In some cases, for the 24 h time-point, it seems that the WL overestimates the amounts extractable in SLF, but this apparent lower leaching efficiency of SLF relative to earlier time-points in SLF1 and WL, in general, is likely a consequence of solution reaching saturation state. This may be explained by progressive dissolution of less soluble surface phases and/or dissolution of the ash grains, which, in the case of the WL, does not result in solution saturation, as seen from the differences in PTE concentrations between the 1 h and 24 h WL.

In summary, the results showed that:

1) The concentrations of Mg measured in the leachates (WL and SLF) were the most stable in all samples;
2) The dissolution of V in SLF was found to be more efficient than in WL regardless of the sample;
3) The WL reflects the SLF-soluble PTEs for shorter contact times, except for Cu, Co and Ni in some samples.

4.3 SLF analytical challenges

Although we successfully characterised the leaching behaviour of most of the analysed elements in SLF, determining the concentration of Na yielded poor results (Appendix C). These results are probably due to the initial levels of Na in the SLF solutions (**Table 2**), so the measured concentrations are likely to be less reliable since they are generally similar to those in the blanks: WL concentrations for Na from the 3 samples are 8.1-67.3 mg/L (Appendix C), whereas the limits of quantification for Na are approximately 100-500 mg/L (**Table 4**). Pb and Zn were BDL in the SLF leachates, even though they were measured in the WL (**Fig. 1**). The finding of minor elements BDL of the method but present in WL likely results from the solution being too dilute for quantification, or because the concentrations measured in samples are, again, too similar to, or lower than, the blank concentration.

We note, though, that WL concentrations of Pb and Zn were comparatively low in our samples relative to other ash samples (**Fig. 1**). Therefore, we cannot comment in detail on whether solubilization of these elements would increase if present in higher concentrations, or whether previously observed increases from other materials were specific to the sample matrix. The mean and median concentrations of soluble elements in ash are generally found at the lower end of their reported ranges (Ayris and Delmelle, 2012), but it is possible that other ash types might exhibit higher PTE concentrations than those analysed here. The range of PTEs investigated in this study are generally the most abundant in ash (Ayris and Delmelle, 2012), and are also commonly analysed in lung bioaccessibility studies (Kastury et al., 2017; Plumlee et al., 2003). Other elements usually present in ash leachates, such as As, Ba, Li, Mo, Se, Si, Sr, were not considered here and their leaching behaviour in SLF is yet to be investigated.

4.4 Implications for the ash hazard assessment

Based on our experiments, an overview of possible steps towards operationalizing an SLF method for ash leaching is given below:

1) **Leachant composition.** While previous SLF studies have excluded use of phospholipids such as DPPC without justification or explanation, here we clearly show that non-inclusion in a modified Gamble's solution (SLF1, **Table 2**) is a reasonable SLF modification when determining bioaccessible concentrations of elements from volcanic ash. More profound effects on extraction efficiency were noted for some of the analysed elements in the absence of citrate (SLF3) or glycine (SLF4), confirming the postulation by Stewart et al. (2020) that omission of these key organic compounds could lead to potential underestimation of the real bioaccessibility of PTEs.
2) **Extraction time.** While the release of elements is time-dependent, we show that ash-associated PTEs may approximate maximum dissolution in an environment resembling lung lining fluid (**Fig. 5**) in the first 10 minutes of leaching. Therefore, even though ash particles may reside in the

lung for extended periods of time, our data suggest that a short contact time (up to 4 h) will adequately estimate the upper limit of PTE release, but a longer extraction period (*e.g.*, 24 h) would be necessary for research considering the steady state of bioaccessible PTEs. While still not too time-consuming for an *in vitro* extraction procedure, 24 h extraction would reflect the availability of more slowly soluble compounds. This would also allow comparison with published SLF dissolution data and acute toxicity data (*e.g.*, Tomašek et al., 2019).

3) **S:L ratio.** We show that PTE dissolution in SLF is relatively stable at our lower S:L ratios (1:100 through 1:1000), but at ratios 1:500 and 1:1000 the repeatability is lower (Appendix C) and there is increased risk of introducing potential errors due to small abundances of some elements (*e.g.*, Cd, Cr, Pb, Zn), as a consequence of large sample dilution. Therefore, 1:100 could be adopted as an optimal ratio. This ensures sufficient volume of leachant for the subsequent analysis, while using a minimal amount of ash to produce reliable data. In this way, impracticable scaling up with lower ratios, which require large volumes of SLF, is avoided as well.

Considering the challenges with the method application outlined in this paper, and for the mentioned practical reasons, the SLF leach may be difficult to implement and include on a routine basis within the standardised IVHHN leachates protocol for rapid hazard assessment (Stewart et al., 2020). Our results showed that the WL largely reflects the SLF soluble element concentrations for shorter contact times. This suggests that the general-purpose WL could be considered a suitable analogue for SLF and used as a conservative estimate of soluble elements, for the purposes of rapid respiratory hazard assessment from leachable elements, while acknowledging that some elements may be underreported (*e.g.*, Cu, Ni, V). The WL is much easier to implement in laboratories, thus offering a practical approach to assessing the potential lung bioaccessible PTEs from ash, especially in time-sensitive situations during volcanic crises. Further, previous rapid ash hazard assessments have used a WL (*e.g.*, Damby et al., 2017, 2013; Horwell et al., 2013), so continued use of a WL allows data to be comparable with past case studies. However, given the observed differences between WL and SLF, SLF leach should still be a preferred method for detailed investigations of PTEs of specific concern to respiratory health outside of a response situation.

5 Conclusions

This study aimed to understand the leaching dynamics of PTEs from volcanic ash to inform a choice of parameters for an *in vitro* protocol to estimate the soluble-element hazard from inhaled ash. The release of PTEs was evaluated in varying formulations of SLF and under varying experimental conditions, and compared to a standardized water leach (Stewart et al., 2020). Our findings show that:

- Release of elements in SLF is affected by changes in assay parameters, including S:L ratio, extraction time and solution composition;
- The differences among ash samples are element specific, indicating the role of ash composition in PTE bioaccessibility;
- The addition of lung surfactant (DPPC) is not necessary when assessing bioaccessible concentrations of elements in volcanic ash;
- Some major elements (Ca, Na) are less reliably quantified than minor elements, likely due to their initial, high concentrations in SLF;
- The elements found as the most sensitive to changes in test parameters are Al, Fe and Mn, whereas the least affected were Ni and Mg;
- SLF is more efficient than WL in extracting V, but also Cu and Ni over shorter time periods ($\leq$ 1 h);
- A WL may be used as a conservative estimate of lung bioaccessibility in a response situation.

This study provides a useful step in the development of a leachate protocol which could form a standard method for volcanic ash respiratory hazard analysis. Future application would allow acquisition of leachate composition data that can be more easily compared to that of other ash characterisation studies, and it will foster the development of a global database of information relevant for informing volcanic health hazard from leachable elements (Stewart et al., 2020).

6 Abbreviations

BDL	below detection limit
DI	deionized water
DPPC	dipalmitoylphosphatidylcholine
HR-ICP-MS	high resolution inductively coupled plasma mass spectrometry
IVHHN	International Volcanic Health Hazard Network
LOQ	limit of quantification
PTE	potentially toxic element
SLF	simulated lung fluid
S:L	solid (mass) to liquid (volume) ratio
WL	water leach

7 Supplementary Material

Appendix A: Water-leachable element content of ash samples

Appendix B: Instrumental parameters

Appendix C: Experimental data

Journal Pre-proof

8 Author contributions

***Ines Tomašek**: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. **David E. Damby**: Conceptualization, Methodology, Resources, Writing – review & editing. **Carol Stewart:** Conceptualization, Resources, Writing – review & editing. **Claire J. Horwell:** Conceptualization, Writing – review & editing. **Geoff Plumlee:** Conceptualization, Writing – review & editing. **Pierre Delmelle:** Conceptualization, Writing – review & editing. **Christopher J. Ottley:** Conceptualization, Writing – review & editing. **Suzette Morman:** Conceptualization, Writing – review & editing. **Sofian El Yazidi**: Investigation. **Philippe Claeys**: Funding acquisition, Resources, Supervision, Writing – review & editing. **Matthieu Kervyn**: Resources, Supervision, Writing – review & editing. **Marc Elskens**: Resources, Supervision, Writing – review & editing. **Martine Leermakers**: Methodology, Investigation, Writing – review & editing.*

9 Declaration of competing interest

The authors declare no conflict of interest.

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use of trade, firm or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Table A.1 Water-extractable element concentrations (in µg/kg or mg/kg dry weight ash) from samples used in the study, determined by water leach for 1 h at 1:100 solid to liquid ratio (Damby et al., 2018; Stewart C., unpublished) and the mean concentrations reported in the global dataset on water-extractable elements from volcanic ash (Ayris and Delmelle, 2012).

	Whaakari/ White Island[1]	**Ambae[1]**	**Kīlauea[2]**	**Global mean[3]**
µg/kg				
Cd	0.06	BDL	BDL	57
Co	4.2	BDL	1.81	204
Cr	5.4	BDL	BDL	100
Ni	7.3	1	6.06	516
Pb	0.1	BDL	BDL	139
V	0.8	BDL	BDL	91
Zn	9.3	2.7	BDL	4013
mg/kg				
Al	2297	59	620	63
Ca	30062	1022	19900	2172
Cu	16	28	13	6
Fe	809	3	3170	24
K	512	104	148	76
Mg	2721	1493	4210	349
Mn	78	31	115	22
Na	6254	808	972	407

[1]Stewart C. (unpublished data); [2]Damby et al. (2018); [3]Ayris and Delmelle (2012).
BDL = below detection limit.

Table B.1 Instrumental parameters of the ICP-MS used for trace element analysis.

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min^{-1} (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min^{-1}
Cool argon flow rate	16 L min^{-1}
Auxiliary argon flow rate	1.0 L min^{-1}
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10^6 cps per 1 ng mL^{-1} ^{115}In (in Low Resolution)
Autosampler	ESI SC 3 Fast
Take-up time	15 s
Wash time	10 s
Number of acquisition	6 (3 runs and 2 pass)
Isotopes in LR	Cd111, Cd114, Pb208 Rh103(IS)
Mass window LR	150% for each isotope
Search window LR	150% for each isotope
Samples per peak LR	20
Integration window LR	80% for each isotope
Isotopes in MR	Al27, V51, Cr52, Mn55, Fe56, Co59, Ni60, Cu63, Zn66 Rh103(IS)
Mass window MR	125%
Search window MR	80%
Samples per peak MR	20
Integration window MR	80%
Scan type	E scan for each isotope
Integration type	Average for each isotope

Table B.2 Instrumental parameters of the ICP-MS used for major cations analysis.

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min^{-1} (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min^{-1}
Cool argon flow rate	16 L min^{-1}
Auxiliary argon flow rate	1.0 L min^{-1}
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10^6 cps per 1 ng mL^{-1} ^{115}In (in Low Resolution)
Autosampler	ESI SC 3 Fast
Take-up time	15 s
Wash time	10 s
Number of acquisition	6 (3 runs and 2 pass)
Isotopes in HR	Na23, Mg26, K39, Ca44 Rh103(IS)
Mass window HR	125%
Search window HR	60%
Samples per peak HR	20
Integration window HR	60%
Scan type	E scan for each isotope
Integration type	Average for each isotope

Mg	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	2531	2614	2773	2639	123	**4.66**	1575	1531	1556	1554	22	**1.42**	3868	3673	3560	3700	156	**4.21**
1:20	2083	2073	2008	2055	41	**1.98**	1595	1427	1469	1497	87	**5.84**	4455	3678	3478	3870	516	**13.34**
1:500	1891	2709	2250	2283	441	**19.16**	1271	1303	1100	1225	102	**8.04**	3441	3394	3275	3370	86	**2.54**
1:1000	1971	3908	1811	2563	1167	**45.54**	1402	313	1039	938	581	**61.93**	2354	3032	1579	2322	851	**36.64**
WL (24h)	2029	2070	2071	2057	24	**0.96**	1548	1582	1544	1558	21	**1.34**	3971	3995	3879	3948	61	**1.55**
SLF1 1:100 24h	2531	2403	2278	2404	113	**4.57**	1622	1484	1512	1539	73	**4.74**	3654	3937	3671	3754	159	**4.23**
SLF2	2386	1388	1638	1804	419	**22.47**	756	790	824	790	34	**4.30**	2567	3098	2485	2717	333	**12.25**
SLF3	2553	2613	2561	2576	33	**1.28**	1617	1733	1658	1670	60	**3.59**	3743	3810	3710	3754	51	**1.36**
SLF4	2455	2341	2402	2399	57	**2.38**	1559	1637	1491	1562	85	**5.47**	3900	3625	3839	3788	144	**3.81**
10 min	2546	2033	2349	2310	150	**6.21**	1408	1640	1708	1585	157	**9.92**	4024	3940	3724	3896	155	**3.97**
1 h	2507	2390	2358	2418	78	**3.24**	1515	1450	1519	1495	39	**2.59**	3608	2604	3780	3331	635	**19.07**
4 h	2419	2643	2401	2488	136	**5.46**	1579	1473	1471	1508	62	**4.10**	3902	3829	3944	3892	58	**1.50**
48 h	2396	2460	2185	2347	144	**6.13**	1706	1507	1673	1629	107	**6.55**	3766	3503	3593	3619	136	**3.66**

Ca	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	9234	9537	10217	9663	503	**5.21**	541	501	520	521	20	**3.84**	5096	4519	4806	4807	289	**6.00**
1:20	14033	13636	14144	13938	267	**1.92**	503	447	455	468	30	**6.47**	5303	4087	4044	4478	715	**15.96**
1:500	8917	9629	8513	9020	565	**6.26**	BDL	373	BDL	373	--	**--**	4144	4226	2736	3702	838	**22.63**
1:1000	9908	13917	11472	11766	2021	**17.17**	323	BDL	BDL	323	--	**--**	2626	5004	2021	3218	1578	**49.09**
WL (24h)	32302	32355	33673	32777	777	**2.37**	844	837	831	837	7	**0.78**	10182	10474	10501	10406	199	**1.91**
SLF1 1:100 24h	10643	10862	11811	11105	621	**5.59**	633	515	323	490	156	**31.91**	3052	3364	3282	3233	162	**5.00**
SLF2	11381	8870	8882	9644	1507	**15.63**	BDL	BDL	BDL	--	--	**--**	1893	2396	1752	2014	339	**16.81**
SLF3	17534	18169	18404	18036	450	**2.50**	775	913	889	859	74	**8.58**	5743	6007	6346	6032	302	**5.01**
SLF4	11306	11443	11311	11352	81	**0.71**	566	853	654	691	147	**21.28**	3908	3832	4218	3986	196	**4.89**
10 min	3464	3580	3723	3589	130	**3.61**	257	713	720	563	265	**47.10**	2466	2206	2008	2227	176	**7.83**
1 h	3524	3532	3482	3513	27	**0.76**	427	212	202	280	127	**45.34**	1725	536	1817	1359	715	**52.56**
4 h	4557	5666	4259	4741	751	**15.84**	483	331	349	388	83	**21.42**	2144	2139	2162	2155	10	**0.45**
48 h	12491	11981	11990	12154	292	**2.40**	667	524	734	642	107	**16.72**	3736	3578	3582	3632	108	**2.96**

K	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	214	227	233	225	10	**4.32**	82	79	78	80	2	**2.61**	7	5	5	6	1	**20.38**
1:20	256	251	243	249	3	**1.29**	83	78	78	80	3	**3.62**	12	5	4	7	4	**62.27**
1:500	98	133	102	111	19	**17.26**	BDL	BDL	BDL	--	--	**--**	BDL	BDL	BDL	--	--	**--**
1:1000	BDL	BDL	BDL	--	--	**--**	BDL	BDL	BDL	--	--	**--**	BDL	BDL	BDL	--	--	**--**
WL (24h)	233	236	246	238	7	**2.86**	116	112	113	114	2	**1.83**	BDL	BDL	BDL	--	--	**--**
SLF1 1:100 24h	272	277	282	277	5	**1.81**	67	65	65	66	1	**1.76**	BDL	BDL	BDL	--	--	**--**
SLF2	305	263	269	279	23	**8.14**	69	70	68	69	1	**1.45**	BDL	BDL	BDL	--	--	**--**
SLF3	306	317	313	312	6	**1.78**	107	111	113	110	3	**2.77**	22	24	23	23	1	**4.35**
SLF4	279	272	282	278	5	**1.85**	76	82	78	79	3	**3.88**	BDL	BDL	BDL	--	--	**--**
10 min	241	269	260	257	14	**5.57**	44	61	54	53	9	**16.12**	BDL	BDL	BDL	--	--	**--**
1 h	250	257	256	254	4	**1.49**	54	49	47	50	4	**7.21**	BDL	BDL	BDL	--	--	**--**
4 h	273	1221	267	270	4	**1.57**	59	80	62	67	11	**16.95**	BDL	BDL	BDL	--	--	**--**
48 h	267	294	258	273	19	**6.86**	72	67	73	71	3	**4.35**	BDL	BDL	BDL	--	--	**--**

Na	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	6261	6360	10181	7601	2235	**29.41**	2157	1083	1940	1727	567	**32.81**	1787	419	BDL	1103	967	**87.70**
1:20	9473	7875	8950	8766	815	**9.29**	2122	563	3544	2076	1491	**71.81**	14028	64	BDL	7046	9874	**140.14**
1:500	BDL	118737	65	59401	83914	**141.27**	BDL	40398	BDL	40398	--	**--**	BDL	17077	BDL	17077	--	**--**
1:1000	BDL	210282	BDL	210282	--	**--**	135689	BDL	41196	88443	66958	**75.62**	BDL	60403	BDL	60403	--	**--**
WL (24h)	6533	6662	7001	6732	242	**3.59**	1015	1007	826	949	107	**11.26**	787	823	812	807	18	**2.29**
SLF1 1:100 24h	1252	18519	19970	13247	10413	**78.61**	11635	1917	3462	5671	5222	**92.08**	BDL	11360	8208	9784	2229	**22.78**
SLF2	BDL	BDL	BDL	--	--	**--**	BDL	BDL	BDL	--	--	**--**	BDL	BDL	BDL	--	--	**--**
SLF3	11339	14135	18542	14672	3631	**24.75**	9334	15474	9565	11458	3480	**30.37**	8697	11339	8078	9371	1732	**18.48**
SLF4	10404	1265	9199	6956	4965	**71.38**	BDL	3038	BDL	3038	--	**--**	BDL	BDL	269	269	--	**--**
10 min	BDL	2941	8979	5960	4270	**71.64**	BDL	18810	8175	13493	7520	**55.74**	11132	BDL	BDL	11132	--	**--**
1 h	11327	6907	4005	7413	3687	**49.74**	1790	7314	BDL	4552	3906	**85.81**	BDL	BDL	BDL	--	--	**--**
4 h	6342	14786	14721	11950	4856	**40.64**	5612	BDL	1586	3599	2847	**79.10**	15296	7638	8864	10599	4113	**38.81**
48 h	12239	22207	BDL	17223	7048	**40.92**	21081	13353	26644	20359	6675	**32.79**	3707	BDL	BDL	3707	--	**--**

Cd	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	0.08	0.08	0.07	0.08	0.01	**7.53**	BDL	BDL	BDL	--	--	**--**	0.01	0.01	0.01	0.01	0.00	**0.00**
1:20	0.05	0.05	0.05	0.05	0.00	**0.00**	0.01	0.01	0.01	0.01	0.00	**0.00**	0.01	0.01	BDL	0.01	0.00	**0.00**
1:500	0.06	0.06	0.05	0.06	0.01	**10.19**	0.01	0.02	0.02	0.02	0.01	**34.64**	0.03	0.03	BDL	0.03	0.00	**0.00**
1:1000	0.06	0.04	0.02	0.04	0.02	**50.00**	BDL	0.04	0.02	0.03	0.01	**47.14**	0.02	BDL	0.02	0.02	0.00	**0.00**
WL (24h)	0.07	0.09	0.08	0.08	0.01	**12.50**	0.03	0.02	0.02	0.02	0.01	**24.74**	0.04	0.04	0.03	0.04	0.01	**15.75**
SLF1 1:100 24h	0.02	0.02	0.02	0.02	0.00	**0.00**	0.01	0.02	0.01	0.01	0.01	**43.30**	0.02	BDL	0.02	0.02	0.01	**34.64**
SLF2	0.02	0.02	0.03	0.02	0.01	**24.74**	0.02	0.01	0.01	0.01	0.01	**43.30**	0.01	0.01	0.01	0.01	0.00	**0.00**
SLF3	0.01	0.01	0.02	0.01	0.01	**43.30**	0.01	0.02	0.01	0.01	0.01	**43.30**	BDL	BDL	0.01	0.01	--	**--**
SLF4	0.02	0.02	0.02	0.02	0.00	**0.00**	0.01	0.01	0.01	0.01	0.00	**0.00**	0.02	0.02	0.01	0.02	0.01	**34.64**
10 min	0.06	0.05	0.05	0.05	0.01	**10.83**	0.01	0.01	0.01	0.01	0.00	**0.00**	0.01	0.02	0.02	0.02	0.01	**34.64**
1 h	0.04	0.03	0.03	0.03	0.01	**17.32**	0.02	0.02	0.01	0.02	0.01	**34.64**	0.01	0.01	0.02	0.01	0.01	**43.30**
4 h	0.02	0.02	0.02	0.02	0.00	**0.00**	0.01	0.01	0.01	0.01	0.00	**0.00**	0.02	0.01	0.01	0.01	0.01	**43.30**
48 h	0.02	0.02	0.02	0.02	0.00	**0.00**	0.02	0.01	0.01	0.01	0.01	**43.30**	0.01	0.02	0.01	0.01	0.01	**43.30**

Between parameter means, SD, RSD

Element	Parameter	Whaakari Mean	Whaakari SD	Whaakari RSD %	Ambae Mean	Ambae SD	Ambae RSD %	Kilauea Mean	Kilauea SD	Kilauea RSD %
Mg	S:L	2525	145	**5.75**	1359	263	**19.32**	3403	633	**18.59**
	Leachant	2392	311	**13.02**	1424	371	**26.06**	3592	496	**13.81**
	Time	2447	66	**2.71**	1551	56	**3.59**	3698	235	**6.36**
Ca	S:L	11098	1929	**17.38**	433	84	**19.20**	3887	726	**18.68**
	Leachant	16583	9616	**57.99**	719	127	**17.71**	6338	3814	**61.74**
	Time	7020	4232	**60.37**	473	143	**30.16**	2321	910	**38.09**
K	S:L	215	73	**33.79**	75	8	**10.70**	6	1	**14.89**
	Leachant	277	26	**9.43**	87	23	**26.11**	23	--	**--**
	Time	266	16	**5.80**	61	9	**14.90**	--	--	**--**
Na	S:L	59059	86866	**145.02**	28863	38278	**132.55**	19083	23802	**124.73**
	Leachant	10402	4150	**39.90**	5279	5587	**105.83**	5058	5226	**103.33**
	Time	11159	4550	**40.78**	9535	7208	**75.60**	8806	3444	**39.11**
Cd	S:L	0.05	0.02	**42.94**	0.02	0.01	**50.09**	0.02	0.01	**47.88**
	Leachant	0.03	0.03	**87.60**	0.01	0.01	**60.98**	0.02	0.01	**60.86**
	Time	0.03	0.01	**49.79**	0.01	0.00	**22.02**	0.01	0.00	**12.45**

Al	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	191.4	229.1	180.0	200.2	25.7	**12.85**	1.3	1.2	1.2	1.2	0.1	**4.56**	1.8	1.6	1.7	1.7	0.1	**5.92**
1:20	14.7	16.9	18.8	16.8	2.0	**12.17**	2.3	2.0	2.2	2.2	0.2	**7.12**	9.7	21.1	20.2	17.0	6.4	**37.35**
1:500	2232.8	2182.4	2191.6	2202.3	26.8	**1.22**	312.12*	7.0	4.3	5.7	1.9	**33.52**	148.7	214.3	70.3	144.4	72.1	**49.90**
1:1000	2387.3	2351.2	2377.3	2372.0	18.6	**0.79**	17.5	14.8	3.1	11.8	7.7	**65.12**	80.3	80.9	67.9	76.4	7.3	**9.60**
WL (24h)	2976.1	3034.3	3043.4	3017.9	36.5	**1.21**	73.2	74.1	71.1	72.8	1.5	**2.10**	222.3	235.1	230.4	229.2	6.5	**2.82**
SLF1 1:100 24h	263.4	263.0	268.6	265.0	3.1	**1.17**	6.3	7.1	7.2	6.9	0.5	**7.53**	75.1	61.4	61.8	66.1	7.8	**11.83**
SLF2	324.7	325.8	340.6	330.4	8.9	**2.69**	20.5	11.5	12.1	14.7	5.0	**34.04**	52.1	57.0	55.7	54.9	2.5	**4.55**
SLF3	0.9	0.6	1.2	0.9	0.3	**29.41**	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	--
SLF4	332.5	316.3	335.3	328.1	10.2	**3.12**	BDL	BDL	BDL	--	--	--	74.1	73.9	78.2	75.4	2.4	**3.19**
10 min	1546.6	1721.1	1622.6	1630.1	87.5	**5.37**	69.1	41.1	48.6	52.9	14.5	**27.36**	60.8	86.9	60.2	69.3	15.3	**22.05**
1 h	1159.6	793.2	933.0	961.9	184.9	**19.22**	2.8	2.3	2.6	2.6	0.3	**10.10**	58.3	56.6	55.9	56.9	1.2	**2.16**
4 h	332.6	362.2	367.4	354.1	18.7	**5.29**	2.8	5.3	2.3	3.4	1.6	**46.86**	54.9	55.4	54.0	54.7	0.7	**1.29**
48 h	254.4	263.2	256.2	257.9	4.6	**1.80**	9.9	14.4	35.7	20.0	13.8	**68.75**	50.9	60.2	107.0	72.7	30.1	**41.36**

Al	Whaakari			Ambae			Kilauea		
S:L	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	1011.2	1169.8	**115.68**	5.5	4.2	**75.94**	61.1	56.3	**92.09**
Leachant	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	788.5	1253.7	**159.00**	31.4	35.2	**112.10**	106.4	82.3	**77.34**
Time	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	693.8	599.6	**86.42**	17.2	21.2	**123.45**	64.0	7.8	**12.21**

Cr	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	0.05	0.06	0.05	0.05	0.01	**10.83**	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	--
1:20	0.02	0.02	0.02	0.02	0.00	**0.00**	BDL	BDL	BDL	--	--	--	0.01	0.01	0.02	0.01	0.01	**43.30**
1:500	3.69	3.55	3.79	3.68	0.12	**3.28**	BDL	BDL	BDL	--	--	--	0.09	0.14	0.07	0.10	0.04	**36.06**
1:1000	3.99	3.79	3.80	3.86	0.11	**2.92**	BDL	BDL	BDL	--	--	--	0.03	0.14	0.03	0.07	0.06	**95.26**
WL (24h)	4.17	4.15	4.29	4.20	0.08	**1.80**	BDL	BDL	BDL	--	--	--	0.06	0.06	0.06	0.06	0.00	**0.00**
SLF1 1:100 24h	0.45	0.46	0.48	0.46	0.02	**3.30**	BDL	BDL	BDL	--	--	--	0.09	0.11	0.09	0.10	0.01	**11.95**
SLF2	0.55	0.56	0.54	0.55	0.01	**1.82**	BDL	BDL	BDL	--	--	--	0.07	0.07	0.07	0.07	0.00	**0.00**
SLF3	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	--
SLF4	0.55	0.50	0.55	0.53	0.03	**5.41**	BDL	BDL	BDL	--	--	--	0.13	0.14	0.14	0.14	0.01	**4.22**
10 min	2.58	2.98	2.71	2.76	0.20	**7.40**	BDL	BDL	BDL	--	--	--	0.08	0.10	0.08	0.09	0.01	**13.32**
1 h	1.84	1.10	1.37	1.44	0.37	**26.07**	BDL	BDL	BDL	--	--	--	0.08	0.08	0.08	0.08	0.00	**0.00**
4 h	0.29	0.33	0.33	0.32	0.02	**7.29**	BDL	BDL	BDL	--	--	--	0.09	0.07	0.08	0.08	0.01	**12.50**
48 h	0.58	0.59	0.62	0.60	0.02	**3.49**	BDL	BDL	BDL	--	--	--	0.06	0.07	0.09	0.07	0.02	**20.83**

Cr	Whaakari			Ambae			Kilauea		
S:L	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	1.61	1.97	**122.31**	--	--	**--**	0.07	0.04	**58.02**
Leachant	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	1.44	1.84	**128.30**	--	--	**--**	0.09	0.03	**37.71**
Time	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	1.11	1.02	**91.20**	--	--	**--**	0.08	0.01	**10.58**

Fe	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	18.3	24.4	17.5	20.0	3.8	**18.78**	0.5	0.6	0.5	0.5	0.0	**7.98**	10.7	10.3	10.3	10.4	0.2	**2.17**
1:20	9.0	11.1	11.5	10.5	1.3	**12.52**	1.1	1.1	1.2	1.1	0.0	**1.77**	104.3	106.5	109.7	106.8	2.7	**2.56**
1:500	530.0	500.6	552.8	527.8	26.2	**4.95**	14.8	13.4	12.0	13.4	1.4	**10.44**	1600.0	1610.4	1585.2	1598.5	12.6	**0.79**
1:1000	566.9	552.2	584.9	568.0	16.4	**2.88**	BDL	BDL	BDL	--	--	--	1559.1	1658.9	1559.3	1592.4	57.6	**3.62**
WL (24h)	807.5	817.5	830.8	818.6	11.7	**1.43**	4.3	3.9	3.7	4.0	0.3	**7.86**	1414.5	1438.5	1406.2	1419.7	16.8	**1.18**
SLF1 1:100 24h	22.6	20.8	24.6	22.7	1.9	**8.53**	9.0	10.5	10.2	9.9	0.8	**7.95**	1364.7	1359.1	1307.1	1343.6	31.8	**2.36**
SLF2	20.2	20.1	21.6	20.6	0.8	**3.89**	7.9	8.4	7.9	8.0	0.3	**3.27**	1086.7	1142.8	1104.6	1111.4	28.7	**2.58**
SLF3	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	--
SLF4	24.7	23.7	25.2	24.5	0.7	**3.05**	12.3	12.1	12.7	12.4	0.3	**2.51**	1459.0	1464.8	1473.2	1465.7	7.2	**0.49**
10 min	379.2	467.5	419.9	422.2	44.2	**10.47**	3.8	2.8	2.5	3.0	0.7	**23.23**	1485.4	1565.4	1532.8	1527.9	40.2	**2.63**
1 h	282.6	147.6	197.9	209.3	68.2	**32.59**	3.5	3.3	3.4	3.4	0.1	**2.99**	1505.4	1437.5	1488.2	1477.0	35.3	**2.39**
4 h	31.3	35.8	34.4	33.8	2.3	**6.76**	4.3	4.1	4.0	4.1	0.1	**3.49**	1425.9	1399.7	1399.8	1408.5	15.1	**1.07**
48 h	23.3	24.3	23.2	23.6	0.6	**2.58**	13.9	13.5	13.1	13.5	0.4	**2.82**	987.8	822.8	941.5	917.4	85.1	**9.28**

Fe	Whaakari			Ambae			Kilauea		
S:L	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	229.8	290.8	**126.52**	6.2	6.4	**102.97**	930.4	803.1	**86.32**
Leachant	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	221.6	398.0	**179.60**	8.6	3.3	**38.78**	1335.1	157.4	**11.79**
Time	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	142.3	175.4	**123.20**	6.8	4.7	**69.03**	1334.9	243.6	**18.25**

Ni	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	18.5	18.6	17.9	18.4	0.4	**2.04**	2.1	2.2	2.1	2.1	0.0	**0.71**	6.1	6.3	6.3	6.2	0.1	**1.93**
1:20	15.3	14.6	15.0	15.0	0.3	**2.24**	2.3	2.1	2.2	2.2	0.1	**3.96**	6.8	7.0	6.9	6.9	0.1	**1.61**
1:500	17.8	17.6	17.5	17.6	0.2	**0.89**	2.0	2.1	2.2	2.1	0.1	**4.83**	7.6	8.0	7.6	7.7	0.3	**3.40**
1:1000	17.8	17.2	16.9	17.3	0.4	**2.38**	2.1	1.9	2.2	2.0	0.2	**8.10**	7.8	7.6	7.6	7.7	0.1	**1.47**
WL (24h)	20.2	20.3	20.8	20.4	0.3	**1.56**	2.5	2.6	2.6	2.6	0.1	**3.14**	8.8	9.1	9.2	9.1	0.2	**2.29**
SLF1 1:100 24h	15.5	15.5	15.5	15.5	0.0	**0.16**	2.3	2.3	2.3	2.3	0.0	**0.67**	7.8	7.6	7.5	7.6	0.2	**2.14**
SLF2	16.6	16.3	16.2	16.4	0.2	**1.26**	2.3	2.3	2.5	2.4	0.1	**4.65**	7.6	8.0	8.1	7.9	0.3	**3.33**
SLF3	17.1	17.0	17.0	17.0	0.1	**0.32**	2.2	2.2	2.4	2.3	0.1	**4.90**	7.8	7.9	7.6	7.8	0.1	**1.83**
SLF4	11.2	10.6	10.9	10.9	0.3	**2.80**	2.3	2.4	2.3	2.3	0.1	**2.41**	7.8	8.1	8.0	8.0	0.2	**2.22**
10 min	17.8	17.4	17.5	17.6	0.2	**1.09**	2.2	2.2	2.3	2.2	0.1	**4.02**	7.5	7.8	7.7	7.7	0.2	**2.03**
1 h	16.7	16.3	16.5	16.5	0.2	**1.21**	2.2	2.2	2.3	2.2	0.1	**2.76**	7.7	7.5	7.8	7.7	0.2	**2.20**
4 h	15.7	16.1	16.1	16.0	0.2	**1.49**	2.2	2.2	2.2	2.2	0.0	**1.14**	7.6	7.5	7.7	7.6	0.1	**1.19**
48 h	15.6	15.3	15.7	15.5	0.2	**1.40**	2.5	2.2	2.1	2.3	0.2	**8.72**	7.8	7.7	8.0	7.8	0.2	**1.95**

Ni	Whaakari			Ambae			Kilauea		
S:L	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	16.8	1.4	**8.62**	2.1	0.1	**4.29**	7.2	0.7	**9.16**
Leachant	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	16.0	3.4	**21.41**	2.4	0.1	**3.94**	8.1	0.6	**7.22**
Time	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	16.2	0.9	**5.40**	2.2	0.0	**1.68**	7.7	0.1	**1.00**

Cu	White Island						Ambae						Kilauea					
	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %	Rep 1	Rep 2	Rep 3	Mean	SD	RSD %
1:10	13.2	14.2	12.9	13.4	0.7	**5.15**	30.2	30.0	30.1	30.1	0.1	**0.27**	4.4	4.1	4.5	4.3	0.2	**4.41**
1:20	15.2	14.1	14.7	14.7	0.6	**3.78**	30.9	29.6	30.5	30.3	0.7	**2.16**	5.6	5.7	6.0	5.8	0.2	**3.67**
1:500	27.2	26.2	26.8	26.7	0.5	**1.79**	31.5	32.9	31.6	32.0	0.8	**2.42**	8.9	9.2	7.5	8.6	0.9	**10.66**
1:1000	28.2	26.8	27.0	27.3	0.7	**2.61**	31.9	31.7	32.1	31.9	0.2	**0.64**	8.5	9.0	8.1	8.5	0.5	**5.36**
WL (24h)	32.1	32.2	32.7	32.3	0.4	**1.10**	34.8	36.0	35.1	35.3	0.6	**1.73**	14.4	14.7	14.7	14.6	0.2	**1.32**
SLF1 1:100 24h	21.1	20.9	21.5	21.1	0.3	**1.40**	32.2	31.8	32.1	32.0	0.2	**0.60**	7.7	7.4	7.2	7.4	0.3	**3.93**
SLF2	22.6	21.9	21.9	22.1	0.4	**1.93**	32.8	31.8	33.3	32.6	0.8	**2.41**	7.4	7.3	7.8	7.5	0.3	**3.80**
SLF3	25.6	25.2	25.4	25.4	0.2	**0.69**	31.9	33.5	33.4	33.0	0.9	**2.71**	6.5	6.1	7.3	6.6	0.6	**9.12**
SLF4	4.0	3.8	3.9	3.9	0.1	**1.94**	26.1	26.4	27.1	26.5	0.5	**1.93**	3.6	3.6	3.9	3.7	0.1	**3.35**
10 min	23.7	24.5	23.8	24.0	0.4	**1.79**	30.6	30.3	30.6	30.5	0.2	**0.58**	3.6	4.0	3.9	3.8	0.2	**4.67**
1 h	23.4	22.3	23.0	22.9	0.6	**2.51**	30.6	30.8	31.2	30.8	0.3	**1.06**	4.9	4.6	4.9	4.8	0.2	**3.21**
4 h	22.0	22.5	22.6	22.4	0.3	**1.40**	31.4	31.6	32.0	31.7	0.3	**0.96**	5.7	5.6	5.8	5.7	0.1	**1.60**

Cu	Whaakari			Ambae			Kilauea		
S:L	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	20.7	6.5	**31.52**	31.3	1.0	**3.11**	6.9	1.8	**26.55**
Leachant	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	21.0	10.5	**50.08**	31.9	3.2	**10.18**	8.0	4.0	**50.33**
Time	Mean	SD	RSD %	Mean	SD	RSD %	Mean	SD	RSD %
	22.3	1.2	**5.32**	31.4	0.7	**2.25**	6.0	1.9	**31.00**

48 h	21.4	20.8	21.7	21.3	0.5	**2.24**	33.1	31.7	31.3	32.0	0.9	**2.94**	8.2	8.3	8.6	8.4	0.2	**2.50**

Mn	**White Island**						**Ambae**						**Kilauea**					
	Rep 1	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**
1:10	81.0	81.3	77.8	80.0	2.0	**2.45**	16.3	16.3	16.6	16.4	0.2	**1.11**	58.5	60.5	60.2	59.7	1.1	**1.78**
1:20	66.6	64.8	65.8	65.7	0.9	**1.40**	17.1	17.0	17.1	17.0	0.1	**0.38**	45.6	45.4	46.8	45.9	0.7	**1.63**
1:500	69.3	66.9	68.7	68.3	1.3	**1.84**	28.1	29.2	27.8	28.4	0.8	**2.68**	80.3	82.8	79.7	80.9	1.7	**2.07**
1:1000	71.2	69.0	67.6	69.3	1.8	**2.63**	29.0	28.9	31.0	29.7	1.2	**4.02**	81.4	84.2	79.2	81.6	2.5	**3.08**
WL (24h)	82.0	82.3	85.2	83.2	1.8	**2.12**	30.5	31.8	31.0	31.1	0.7	**2.14**	94.5	96.7	95.0	95.4	1.2	**1.21**
SLF1 1:100 24h	31.2	30.6	31.7	31.2	0.5	**1.73**	24.2	25.0	24.6	24.6	0.4	**1.53**	69.1	67.9	66.0	67.7	1.6	**2.33**
SLF2	34.6	33.2	34.3	34.0	0.7	**2.18**	25.5	24.7	25.9	25.3	0.6	**2.33**	61.7	65.0	63.5	63.4	1.7	**2.66**
SLF3	31.6	32.0	32.7	32.1	0.6	**1.79**	24.3	25.0	25.1	24.8	0.4	**1.78**	42.2	42.9	41.8	42.3	0.6	**1.36**
SLF4	35.8	34.0	35.2	35.0	0.9	**2.55**	25.6	25.9	26.6	26.0	0.5	**1.93**	73.3	75.5	75.5	74.8	1.3	**1.68**
10 min	58.5	61.1	59.1	59.6	1.3	**2.25**	26.9	26.0	26.7	26.5	0.5	**1.73**	74.1	75.7	76.1	75.3	1.1	**1.43**
1 h	49.8	43.4	45.2	46.1	3.3	**7.17**	25.2	25.6	25.6	25.5	0.2	**0.89**	73.2	70.0	71.4	71.5	1.6	**2.24**
4 h	32.7	33.8	33.2	33.2	0.6	**1.66**	24.4	24.4	24.4	24.4	0.0	**0.04**	68.9	68.3	68.2	68.5	0.4	**0.52**
48 h	29.8	29.5	30.1	29.8	0.3	**1.09**	25.1	24.1	23.7	24.3	0.7	**3.00**	58.2	54.2	59.0	57.1	2.6	**4.51**

Mn	**Whaakari**			**Ambae**			**Kilauea**		
S:L	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	62.9	18.5	**29.48**	23.2	6.2	**26.81**	67.2	15.0	**22.37**
Leachant	**Whaakari**			**Ambae**			**Kilauea**		
	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	43.1	22.5	**52.11**	26.4	2.6	**9.75**	68.7	19.2	**27.95**
Time	**Whaakari**			**Ambae**			**Kilauea**		
	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	40.0	12.7	**31.84**	25.1	1.0	**3.79**	68.0	6.8	**9.98**

V	**White Island**						**Ambae**						**Kilauea**					
	Rep 1	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**
1:10	0.01	0.02	0.01	0.01	0.01	**43.30**	0.08	0.08	0.07	0.08	0.01	**7.53**	0.01	0.01	0.01	0.01	0.00	**0.00**
1:20	0.12	0.12	0.13	0.12	0.01	**4.68**	0.10	0.09	0.10	0.10	0.01	**5.97**	0.09	0.09	0.10	0.09	0.01	**6.19**
1:500	4.72	4.46	4.89	4.69	0.22	**4.62**	0.21	0.21	0.17	0.20	0.02	**11.74**	0.27	0.31	0.28	0.29	0.02	**7.26**
1:1000	5.07	4.97	5.13	5.06	0.08	**1.60**	0.16	0.18	0.18	0.17	0.01	**6.66**	0.31	0.33	0.28	0.31	0.03	**8.21**
WL (24h)	0.86	0.90	0.89	0.88	0.02	**2.36**	BDL	BDL	BDL	--	--	--	0.01	0.01	0.01	0.01	0.00	**0.00**
SLF1 1:100 24h	3.29	3.13	3.17	3.20	0.08	**2.60**	0.15	0.14	0.14	0.14	0.01	**4.03**	0.25	0.25	0.24	0.25	0.01	**2.34**
SLF2	3.15	3.37	3.24	3.25	0.11	**3.40**	0.15	0.16	0.16	0.16	0.01	**3.69**	0.23	0.25	0.24	0.24	0.01	**4.17**
SLF3	2.80	2.78	2.88	2.82	0.05	**1.88**	0.14	0.14	0.14	0.14	0.00	**0.00**	0.16	0.20	0.18	0.18	0.02	**11.11**
SLF4	3.47	3.50	3.61	3.53	0.07	**2.09**	0.15	0.15	0.15	0.15	0.00	**0.00**	0.27	0.28	0.29	0.28	0.01	**3.57**
10 min	3.09	3.51	3.11	3.24	0.24	**7.32**	0.03	0.02	0.03	0.03	0.01	**21.65**	0.09	0.09	0.10	0.09	0.01	**6.19**
1 h	2.90	3.00	2.93	2.94	0.05	**1.74**	0.03	0.04	0.04	0.04	0.01	**15.75**	0.12	0.12	0.12	0.12	0.00	**0.00**
4 h	2.83	2.85	2.88	2.85	0.03	**0.88**	0.07	0.07	0.07	0.07	0.00	**0.00**	0.17	0.15	0.15	0.16	0.01	**7.37**
48 h	3.55	3.03	3.49	3.36	0.28	**8.48**	0.17	0.16	0.18	0.17	0.01	**5.88**	0.28	0.28	0.29	0.28	0.01	**2.04**

V	**Whaakari**			**Ambae**			**Kilauea**		
S:L	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	2.62	2.43	**92.82**	0.14	0.05	**36.75**	0.19	0.13	**69.06**
Leachant	**Whaakari**			**Ambae**			**Kilauea**		
	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	2.74	1.07	**38.96**	0.15	0.00	**3.39**	0.19	0.11	**56.23**
Time	**Whaakari**			**Ambae**			**Kilauea**		
	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	3.12	0.21	**6.76**	0.09	0.06	**71.89**	0.18	0.08	**45.46**

Co	**White Island**						**Ambae**						**Kilauea**					
	Rep 1	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**
1:10	10.27	10.41	10.08	10.25	0.17	**1.62**	0.39	0.38	0.38	0.38	0.01	**1.51**	1.21	1.28	1.27	1.25	0.04	**3.02**
1:20	6.28	6.10	6.13	6.17	0.10	**1.56**	0.45	0.42	0.43	0.43	0.02	**3.53**	1.18	1.16	1.17	1.17	0.01	**0.85**
1:500	8.37	8.15	8.60	8.37	0.23	**2.69**	0.60	0.61	0.63	0.61	0.02	**2.49**	2.49	2.67	2.56	2.57	0.09	**3.53**
1:1000	8.90	8.71	8.86	8.82	0.10	**1.14**	0.66	0.51	0.70	0.62	0.10	**16.07**	2.54	2.65	2.60	2.60	0.06	**2.12**
WL (24h)	10.61	10.57	10.62	10.60	0.03	**0.25**	0.65	0.68	0.66	0.66	0.02	**2.30**	2.85	2.91	2.87	2.88	0.03	**1.06**
SLF1 1:100 24h	2.75	2.72	2.75	2.74	0.02	**0.63**	0.55	0.56	0.57	0.56	0.01	**1.79**	2.21	2.20	2.14	2.18	0.04	**1.73**
SLF2	3.05	2.89	3.03	2.99	0.09	**2.92**	0.56	0.56	0.58	0.57	0.01	**2.04**	2.02	2.12	2.14	2.09	0.06	**3.07**
SLF3	3.91	3.81	3.88	3.87	0.05	**1.33**	0.50	0.51	0.53	0.51	0.02	**2.98**	1.49	1.53	1.45	1.49	0.04	**2.68**
SLF4	2.63	2.47	2.58	2.56	0.08	**3.20**	0.58	0.59	0.55	0.57	0.02	**3.63**	2.28	2.33	2.28	2.30	0.03	**1.26**
10 min	7.13	7.53	7.30	7.32	0.20	**2.74**	0.61	0.56	0.60	0.59	0.03	**4.48**	2.41	2.54	2.49	2.48	0.07	**2.64**
1 h	5.81	4.58	4.86	5.08	0.64	**12.68**	0.57	0.56	0.62	0.58	0.03	**5.51**	2.39	2.27	2.36	2.34	0.06	**2.67**
4 h	2.96	3.11	3.03	3.03	0.08	**2.47**	0.56	0.56	0.56	0.56	0.00	**0.00**	2.24	2.24	2.29	2.26	0.03	**1.28**
48 h	2.72	2.76	2.70	2.73	0.03	**1.12**	0.60	0.53	0.51	0.55	0.05	**8.64**	1.95	1.90	1.99	1.95	0.05	**2.32**

Co	**Whaakari**			**Ambae**			**Kilauea**		
S:L	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	7.27	2.93	**40.25**	0.52	0.11	**20.77**	1.96	0.70	**35.75**
Leachant	**Whaakari**			**Ambae**			**Kilauea**		
	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	4.55	3.42	**75.11**	0.58	0.05	**9.47**	2.19	0.50	**22.65**
Time	**Whaakari**			**Ambae**			**Kilauea**		
	Mean	SD	**RSD %**	Mean	SD	**RSD %**	Mean	SD	**RSD %**
	4.18	2.01	**48.10**	0.57	0.02	**3.18**	2.24	0.20	**8.84**

Pb	**White Island**						**Ambae**						**Kilauea**					
	Rep 1	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**
WL (24h)	0.03	0.02	0.02	0.03	0.00	**10.31**	BDL	BDL	BDL	--	--	--	BDL	BDL	BDL	--	--	**--**

Zn	**White Island**						**Ambae**						**Kilauea**					
	Rep 1	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**	**Rep 1**	**Rep 2**	**Rep 3**	**Mean**	**SD**	**RSD %**
WL (24h)	10.1	10.3	10.2	10.2	0.1	**1.37**	2.2	2.2	--	2.2	0.0	**2.21**	4.8	--	4.6	4.7	0.1	**2.67**

Highlights

- Investigation of a lung fluid leachate method to assess inhalation hazards of ash.
- Element release in leachates is both method-parameter and sample dependent.
- Inclusion of lung surfactant is not necessary when assessing ash leachates.
- Optimal method parameters are extraction up to 24 h at 1:100 ratio.
- Water leach can be used as a conservative estimate of lung bioaccessible elements.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: