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RESEARCH ARTICLE

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Key Points:

- Mechanical grinding of volcanic deposits may be an important source of trace elements in water
- Rapid release of Ca, Na, Al, Si, and K was observed during 1 h leaching experiments
- The pH of leached solutions also increases by several log units

Supporting Information:

- Table S1

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Posteruptive impacts of pyroclastic deposits from basaltic andesite stratovolcanoes on surface water composition

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Abstract Volcanic ash deposition following explosive eruptions can pose significant hazards for water quality, human health, agriculture, and infrastructure functionality. Many studies have examined how fresh ash deposition may lower the pH of, and introduce a range of potentially toxic elements into, exposed surface waters. However, no study has yet determined the effects on water composition as a result of mechanical pyroclast disaggregation and production of new fresh particle surfaces and increasingly fine grained particles. Such disaggregation could result from natural posteruptive processes such as debris avalanches, lahars, or fluvial/aeolian transport and human activities such as cleanup efforts or mining of pyroclastic deposits. The posteruption time scales of pyroclast disaggregation may vary from months in moist tropical or temperate environments to years or decades in arid settings. Here we show, for the first time in experimental studies, that mechanical milling of pyroclasts will introduce a range of elements into exposed waters, including Al, which can be toxic at elevated levels, and Na, which increases the electrical conductivity of solutions. The pH of leaching solutions also increases by several log units. Such dramatic changes on the experimental scale may have implications for surface water composition in posteruptive settings, necessitating longer-term risk assessments for ecosystem health and consideration of the role of pyroclastic deposits in element cycling in volcanically active regions.

1. Introduction

Eruptions of volcanic ash rapidly deliver many trace elements into agricultural, urban, and aquatic environments, with immediate impacts caused by a range of soluble compounds and complexes adhering to particles [Taylor and Stoiber, 1973; Rose, 1977; Óskarsson, 1980; Smith et al., 1982; Cronin et al., 1998; Delmelle et al., 2005; Witham et al., 2005; Stewart et al., 2006; Flaathen and Gislason, 2007; Jones and Gislason, 2008]. Volcanic ash is produced and transported high into the atmosphere by explosive fragmentation of erupting magma and is composed of rock fragments <2 mm in diameter. In large eruptions, the finest particles (commonly with modal grain size of ~125 μm) are transported tens to thousands of kilometers by upper atmosphere winds. Explosive eruptions create typically vesicular ash particles, with high surface area to volume ratio. The finer the ash size and the more complex the particle shape, the greater potential for surface adsorption of volcanic gases and aerosols during the eruption. Acidic plume gases such as HCl, HF, and H₂SO₄ (formed from SO₂) readily adsorb onto ash surfaces, followed by exchange of protons with cations within silicate matrices and subsequent formation of sulfate and halide salts such as NaCl and NaF [Ayrís et al., 2014]. These compounds are rapidly released upon contact between ashfall and water, and have the potential to cause impacts on water supplies, agriculture, and infrastructure [Stewart et al., 2006; Wilson et al., 2010, 2012], due to their acid-generating potential and, at times, highly fertilizing impacts (e.g., due to sulfur and selenium) [Cronin et al., 1998]. Some elements, such as fluorine, are also a significant risk factor for human drinking water and the water/food supplies of grazing livestock [Cronin et al., 2003; Stewart et al., 2006; Allibone et al., 2012; Wilson et al., 2010]. The input of minor ash components, such as iron (Fe), into the ocean stimulates marine primary productivity, initiating blooms of phytoplankton [Boyd et al., 2000; Frogner et al., 2001], as has been documented following the eruption of the Kasatochi stratovolcano in Alaska [Hamme et al., 2010].

In order to characterize the potential chemical changes to ecosystems, and hazards posed to local populations following explosive volcanic events, ash leachate studies are performed on pristine ash samples, with minimum interaction with surface substrates and water [Witham et al., 2005; Stewart et al., 2013]. Numerous studies have

found that soluble salts bound to ash grain surfaces may be quickly released into exposed waters [Óskarsson, 1980; Smith *et al.*, 1982; Jones and Gislason, 2008], often lowering pH and adding trace metals with both beneficial and deleterious effects on local flora and fauna [Ayrís and Delmelle, 2012]. Leaching from fresh volcanic ash also contributes micronutrients which are immediately available for uptake by plants (S and major element cations Na, K, and Ca) [Cronin *et al.*, 1998], although most of the cation content of the ash is only released more slowly into the environment through natural weathering and mineral alteration processes. However, intermediate pathways exist for contribution of elements from volcanic deposits into the environment before chemical weathering, through the physical breakup of tephra by landslide, fluvial, and aeolian processes, as well as anthropogenic activities (e.g., driving, cleanup, and cultivation). In this case, mechanical fracturing of volcanic pyroclasts will expose new, fresh glass and mineral-reactive particle surfaces [e.g., White and Claassen, 1980; White, 1983; Dahlgren *et al.*, 1999]. This environmental pathway was noted to potentially increase the toxicity of ash when combined with biologic fluids [Horwell *et al.*, 2003] but has never before been examined in relation to water composition.

1.1. Volcanic Hazards

Explosive eruptions regularly occur at active composite volcanoes (i.e., stratovolcanoes) in subduction zones around the globe. Many of these volcanoes are characterized by magmas of intermediate (or andesitic) bulk composition (55–70 wt % SiO₂) with H₂O contents ranging from 3 to 6 wt % and typically display both dome-building and explosive activity during the same eruption. Recent examples include the 2010 eruption of Gunung Merapi and the 2014 eruption of Gunung Kelud, both located in Java, Indonesia, and both having a bulk magma composition of basaltic andesite (55–60 wt % SiO₂) [Hammer *et al.*, 2000; Costa *et al.*, 2013; Jeffery *et al.*, 2013]. Both of these eruptions were characterized by the collapse of viscous lava domes, along with explosive events, all generating pyroclastic density currents (PDCs). PDCs involve a mixture of hot gases and fragmented ash-sized (<2 mm) up to large, meter-sized boulders of pyroclastic material that accelerates down the slopes of the volcanic edifice, filling valleys with loose, unstable debris. In addition to the primary hazards created by PDCs, secondary hazards may occur for years after the eruptive event due to remobilization of the pyroclastic deposits by landslides, wind, and water. Volcanic mudflows, or lahars, are common when pyroclastic fall and PDC deposits are affected by heavy precipitation (or snowmelt in temperate latitudes). One of the more spectacular series of long-lived lahars occurred after the Mount Pinatubo (Philippines) eruption of 1991 when PDC deposits buried the upper volcanic catchments [see Newhall and Punongbayan, 1996]. In the decades since this eruption, infrastructure and local communities in downstream areas have repeatedly been affected by lahar flow and sediment accumulation, building up ground levels by tens of meters in many locations.

The 18 May 1980 eruption of Mount St. Helens provided an excellent opportunity for researchers to examine the chemical effects of several types of volcanic deposits (ashfall and lahars) on local and regional water supplies (rivers, lakes, and groundwater). Many of these studies are summarized in Lee [1996] and reveal wide variations in water compositions and effects on biologic activity dependent upon location of the water source relative to the volcano. The most affected rivers in the area showed increased conductivity values (up to an order of magnitude) in addition to increased solid and suspended sediment concentrations compared to measurements made prior to 18 May [Lee, 1996, and references therein]. The studies presented in Lee [1996] did not examine the role of deposit disaggregation, but many of the surface processes that occurred during the eruption (e.g., debris avalanche and lahars) included those that would mechanically grind down volcanic clasts.

1.2. Ecological Effects of Elements in Silicate Rocks

Disturbances to species assemblages in response to tephra fall are well documented [e.g., Telford *et al.*, 2004]. Increased inputs of dissolved silica may act as a direct source of nutrients for phytoplankton. In lakes, increases in diatom abundance may occur due to changing Si/P ratios, which may in turn alter the ratio of siliceous to nonsiliceous primary productivity [Ayrís and Delmelle, 2012]. Dissolved silica plays an important role in biogeochemical cycles, with environmental input apparently controlled by weathering of silicate minerals [White and Blum, 1995; Struyf and Conley, 2012]. Few studies have measured the silica pool of various ecosystems, but of these, andisols derived from volcanic parent materials show the greatest amounts [Meunier *et al.*, 1999; Struyf and Conley, 2012]. However, there is a dearth of data concerning the role of silicate mineral weathering rates in varying the amorphous silica contents of different environments. Concentrations

of dissolved Si in most freshwaters are typically low [Andrews *et al.*, 2004]. Therefore, increased Si runoff from disaggregated PDC material may produce a marked change.

Marked changes in freshwater composition in response to tephra fall have been observed previously for metal ions such as Fe and Al, which typically have very low dissolved concentrations in freshwaters [Cronin *et al.*, 2014]. However, for minor quantities of ashfall, effects on water composition are typically transient. Many trace metals can be either beneficial or deleterious to local ecosystems, depending upon their relative concentrations to each other, because they are usually depleted in both marine and freshwater environments. In nutrient-limited environments, studies have shown that microorganisms will preferentially colonize minerals and glasses containing essential trace metals such as K [Valsami-Jones *et al.*, 1998] and Fe [Rogers *et al.*, 1998; Bennett *et al.*, 2001; Rogers and Bennett, 2004]. However, in elevated concentrations, K can have a destructive effect on the gill function of freshwater bivalves, leading to asphyxiation [Fisher *et al.*, 1991; Wildridge *et al.*, 1998]. Cu and Fe can act in either a synergistic or antagonistic fashion during uptake by various species of phytoplankton [Sunda *et al.*, 1981; Brand *et al.*, 1983; Murphy *et al.*, 1984; Sunda, 1989; Bruland *et al.*, 1991]. The presence of Ca, Mg, and Na ions in water will inhibit the toxicity of Cu by binding to fish gills in the place of this hazardous metal [e.g., de Schampheleere and Janssen, 2002]. Numerous biological processes utilize Ca and Na from the environment, such as growing vegetation [e.g., Grattan and Grieve, 1999; Parida and Das, 2005] and nearshore marine ecosystems where calcite and aragonite are precipitated by a wide variety of invertebrates. Although potential Ca and Na increases would increase water electrical conductivity (EC), these elements are likely not to harm local fauna in most cases.

Al can be toxic to a variety of organisms at various concentrations, and although there are a limited number of studies that have examined this [see Golding *et al.*, 2015], volcanic deposits may pose a level of both acute and chronic exposure, depending upon the degree of deposit disaggregation over time. A study by Hidayati *et al.* [2014] examined the biologic effects of discharge from the Lusi mud volcano, also on the island of Java, through the examination of metal concentrations and exposed fish species in the local river system. Water and sediments downstream from the mud volcano showed elevated concentrations of several metals, particularly Al and Fe, compared to upstream areas. These metals were also elevated in fish caged at sampling locations, which were found to have lesions on their gills, and showed a 0–10% survival rate compared to fish captured at unaffected control sites, which had a survival rate of 66–93% [Hidayati *et al.*, 2014]. Although the Lusi mud volcano does not produce pyroclasts resulting from a magmatic eruption, sediments effusing from it are derived from the physical and chemical weathering of volcanic deposits present on the island of Java. The study of Hidayati *et al.* [2014] clearly demonstrates the adverse effects of elevated Al concentrations to local biota on the same island occupied by the Merapi and Kelud stratovolcanoes.

Dramatic changes in water pH (i.e., over 1.4 log units) can have significant effects on biologic activity, as increasing pH inhibits the ionization of ammonia (NH₃), which can result in ammonia toxicity for existing biota in the local environment [e.g., Warren, 1962; Armstrong *et al.*, 1978; Randall and Tsui, 2002]. Additionally, ammonia intoxication will result in enhanced uptake of Ca and Na by biologic receptors, causing eventual cell death [Marcaida *et al.*, 1992; Randall and Tsui, 2002]. Aquatic ecosystem protection guidelines typically specify an acceptable pH range of 6.5 to 8.5 for freshwaters [Anzecc, 2000]. A water body is considered to have a high pH if the pH exceeds this upper limit for extended periods of time. Biological effects of high pH include damage to the skin, gills, and eyes of aquatic macrofauna. There are relatively few case studies available for comparison, as high pH is an uncommon stressor for freshwater systems. Combustion ash from wildfires is known to be strongly alkaline, with pH values as high as 13 in 1:20 water leaches [Hageman *et al.*, 2008]. Elevated pH levels of up to 9.5 have also been recorded in streams following wildfires, but these are reportedly transient [Neary *et al.*, 2008]. The change in pH induced by volcanic deposits may be particularly notable in small-volume or isolated freshwater systems where evaporation or limited input may allow elevated concentrations to persist.

1.3. Motivation of Study

Despite how strongly pyroclastic ashfall impacts water quality, agriculture, infrastructure, and human health, no study has yet examined longer-term chemical impacts of volcanic deposits on the environment. In the intermediate stage, before these materials become the basis of fertile volcanic soils (andisols), we know very little about the effect of *pyroclast disaggregation* on the composition of surface waters. Primary pyroclasts are rapidly abraded as the result of collisional and frictional forces during transport in violent PDCs [Freundt and Schmincke,

1992; Cagnoli and Manga, 2004; Dufek and Manga, 2008; Kueppers et al., 2012] but are also subject to considerable change in subsequent lahar, fluvial, glacial, and land-sliding processes that may occur after initial deposition. During the mechanical grinding and crushing of deposits resulting from surface processes, particle collisions, enduring frictional contact, or loading breaks grains into progressively smaller fragments, increasing the bulk surface area of the sample [e.g., Attal and Lavé, 2009]. Previous experiments on abrasion of river sediments have shown that the rate of abrasion is dominantly influenced by the lithology and porosity of the material [Kodama, 1994; Attal and Lavé, 2009; Domokos et al., 2014]. The same trends were observed in experiments conducted on pyroclastic deposits [Kueppers et al., 2012], where high-porosity samples experience more abrasion, but crystal content will also play a role due to the higher tensile strength of some minerals compared to glass. For all of these experiments, abrasion is most significant at the onset and gradually levels off or decreases with time due to the reduction of larger clast sizes and homogenization of variations in initial grain size distribution. Other studies have shown that a range of Earth surface processes can reduce sediment grain size. Wright et al. [1998] and Wright [2001] used experimental simulations of aeolian, fluvial, glacial, and mechanical weathering processes to show that silt-sized particles can be produced from sand-sized quartz in a variety of environments. The most efficient processes included fluvial tumbling, glacial grinding, and aeolian abrasion, which all reduced the sand to material $<63 \mu\text{m}$ [Wright, 2001], comparable to the size of fine volcanic ash.

Large explosive eruptions may cover areas of hundreds of square kilometers in new ash and pyroclastic deposits (e.g., pyroclastic flow and surge deposits on volcano flanks) that are later remobilized by lahars, landslides, debris avalanches, aeolian processes, and fluvial entrainment. The study presented here examines the potential effects that the rapid disaggregation of pyroclastic rocks by posteruptive processes will have on surface water composition following a volcanic eruption.

The laboratory-scale study presented here carries out a first attempt at evaluating the ongoing effects of volcanic deposits by experimental, mechanical milling of pyroclasts and the evaluation of released micronutrients into exposed waters using the PDC deposits of both the 2010 eruption of Merapi and the 2014 eruption of Kelud.

2. Materials and Methods

Samples of PDC deposits were collected following the 2010 eruption of Merapi and the 2014 eruption of Kelud, 80 days and 47 days after original deposition, respectively. These PDC samples consist of various lapillus-sized pyroclasts of both dense lava and vesicular pumice, in addition to accidental lithic fragments, within a matrix of ash (Figure 1). Experiments on the Merapi 2010 deposits were carried out using the bulk ash portion, in addition to broken, crushed, and milled lava lapilli. Experiments on the Kelud 2014 deposits were carried out using the bulk ash portion, in addition to whole, crushed, and milled lapilli. Milling of the samples resulted in all particles having the diameter of very fine ash ($<32 \mu\text{m}$). For comparison, leaching of fresh distal ash samples from the 2014 Kelud eruption was also conducted. Further details of the analyses can be found below, with the primary objective being to examine variations in the chemistry of exposed waters to pyroclasts at different stages of mechanical breakdown.

The lapilli and ash were separated and leachates were analyzed from the ash component. Because samples were collected following deposition, the analyses provided here do not represent the original soluble compounds resulting from particle interaction with the eruptive plume and the gases within it but were subsequently altered by surface processes, including precipitation and chemical weathering. Thus, the water compositions of ash samples reported for both eruptions are provided as a baseline value for comparison with the subsequent analyses of water samples derived from whole, crushed, and milled pyroclasts. Two different sets of experiments were then performed on the lapilli: one to determine the amount of elements released during recurrent stages of pyroclast disaggregation and the other to examine the “lifetime” of these element concentrations in exposed water samples (i.e., the time period before oxidation produced precipitates). The lapilli were sieved from the ash component and sonicated in deionized water to remove adhering ash particles that would contribute to the results of subsequent testing. All Merapi samples were lava lapilli, but for the Kelud samples, several different types of lapilli were utilized, including lava, pumice, and accidental lithics. A standard ash leachate protocol [Witham et al., 2005; Stewart et al., 2013] was then performed at different stages of pyroclast disaggregation using a sample to deionized water mass ratio of 1:20: (1) original lapilli of 1–2 cm with adhering ash removed, (2) crushed fragments broken with a stainless steel mortar and pestle into ash-sized fragments ($<2 \text{ mm}$), and (3) powdering of samples using a McCrone agate micronizing mill to achieve particle diameters $<32 \mu\text{m}$ (very fine ash). For the

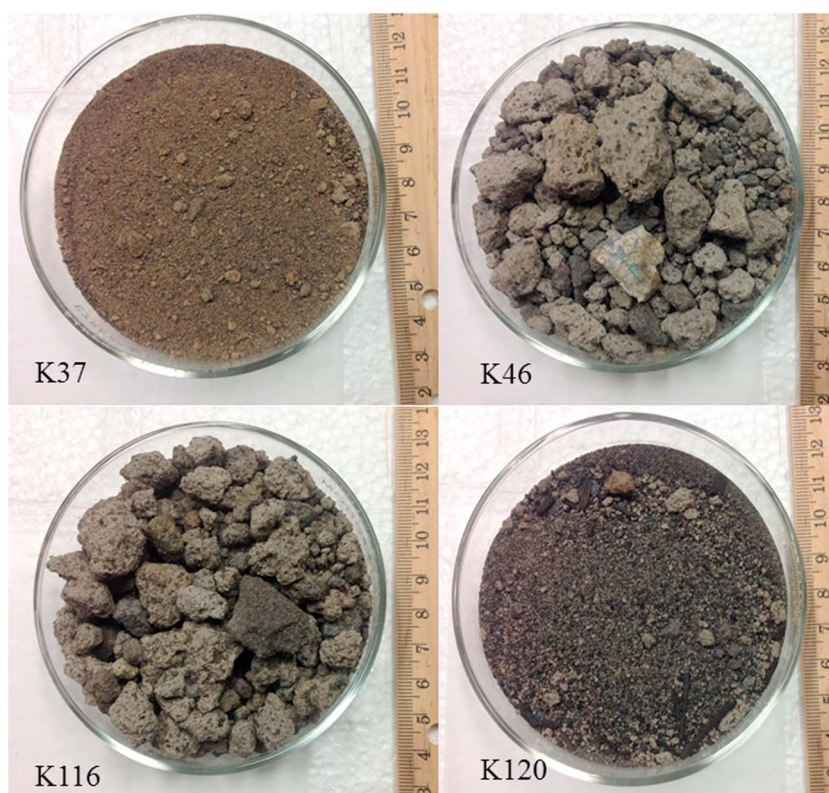


Figure 1. Samples of pyroclastic density current (PDC) deposits from the February 2014 eruption of Gunung Kelud, Java, Indonesia, used in this study. Ash and lapillus portions of the samples were separated for analysis. Scale in the right of each image is centimeter.

Merapi samples, sample quantity was limited, so whole lapilli were not utilized, but an additional disaggregation step was performed prior to the crushing stage (referred to as “broken” to obtain particles 5–10 mm in diameter). For the purposes of this study, we have not determined the surface area of the samples following the various stages of disaggregation, as previous dissolution experiments have revealed that the geometric surface area and the reactive surface area are not synonymous [e.g., *Garrels and Howard, 1959*] and may vary greatly depending on initial grain size of the samples [e.g., *Anbeek, 1992*]. Following sonication in deionized water for 60 min, each sample was centrifuged at 7000 rpm for 30 min, filtered (0.45 μm cellulose acetate membrane), and the water analyzed with the PerkinElmer Optima 3000 DV inductively coupled plasma–optical emission spectrometer (ICP-OES) to determine the concentration of elements. Three sets of lapilli were left within the deionized water, each for different time periods. The first was filtered after 1 h of direct water exposure, the second after 48 h, and the third after 1 week. Following water filtration, samples were dried and the process was repeated after further disaggregation of the sample. Filtered water samples were also measured at 25°C with the VWR Traceable Conductivity Meter and the Mettler Toledo pH meter following meter calibration to standards. All water samples were stored in screw-top polyethylene vials at 25°C prior to ICP-OES analyses in order to reduce evaporation.

For the analyses of the distal fresh ash samples, methods were also based on the standard protocol developed by *Stewart et al. [2013]*. Extractions were carried out using deionized water at ratios of both 1:20 and 1:100 g ash:mL extractant. Samples were extracted for 1 h on a rotary end-over-end shaker, centrifuged at 8000 rpm for 3 min, and filtered through 0.45 μm nitrocellulose filters. Subsamples were collected for cation analysis by ICP-OES and inductively coupled plasma–mass spectroscopy (ICP-MS). Conductivity and pH were measured in-house using a Hanna HI 2300 EC meter and a Meterlab PHM 210 pH meter. Quality assurance and control were assessed by running a blank of the extracting solution through the entire procedure, and by performing a duplicate extraction of one ash sample, and were satisfactory.

Table 1. Summary Data for Water-Extractable Elements, Electrical Conductivity (EC), and pH for Samples Derived From PDC Deposits of the Merapi 2010 Eruption and the Kelud 2014 Eruption^a

	n	Ca (mg/kg)			Na (mg/kg)			Al (mg/kg)			K (mg/kg)			Si (mg/kg)			EC (m S/cm)			pH	
		Range	Median	Range	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
2010 Merapi eruption Fresh distal ash ^b	3	1351–4590	1900	87–822	397	16.3–63.7	20	41–189	no data (nd)	<10–181	21	nd	nd	nd	nd	nd	nd	nd	nd	5–6	5–6
Ash	14	14–1995	44	28–153	64	0.12–90	7.5	12–169	34	7.5–182	43	15–605	72	4–7	4–7	4–7	4–7	4–7	4–7	4–7	4–7
Lava lapilli, broken	10	3–818	106	2.2–30	8	0.14–18	0.35	nd–48	3.7	0.74–4.2	2.3	2–316	44	4–6	4–6	4–6	4–6	4–6	4–6	4–6	4–6
Lava lapilli, crushed	10	5–208	22	6.1–17	8.4	0.2–3.8	0.47	1.9–37	3.6	3.6–15	6.6	4–87	12	5–6	5–6	5–6	5–6	5–6	5–6	5–6	5–6
Lava lapilli, milled	2	210–243	227	290–473	381	4.1–6.0	5	44–59	51.3	42–85	64	208–265	237	9–10	9–10	9–10	9–10	9–10	9–10	9–10	9–10
2014 Kelud eruption Fresh distal ash	2	338–628		58–118		1.4–27		4.2–36		nd		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ash	19	7.3–124	29	3.3–15	6.2	0.15–2.1	0.59	3.4–66	6.3	1.1–11	3.2	4–43	11.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5
Lava and pumice lapilli, whole	10	7.2–123	14	2.4–7.5	4.3	nd–0.13	0.05	1.7–68	5.8	nd–5.1	1.6	7–41	8	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5
Lava and pumice lapilli, crushed	10	2.7–45	9.7	3.5–7.7	5.9	0.13–0.32	0.19	5.3–14	9.4	1.1–8.1	3.1	3–28	6	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5	5–6.5
Lava and pumice lapilli, milled	9	52–121	76	237–521	394	3.5–41	8.2	22–127	29.4	82–203	135	89–157	131	9–10	9–10	9–10	9–10	9–10	9–10	9–10	9–10

^aErrors in all measurements are < 10%, and the number of samples (n) is given for the measured range and median value. nd = values not determined (because they were not measured or were below detection limits).

^bMerapi fresh distal ash data are reproduced from Damby et al. [2013].

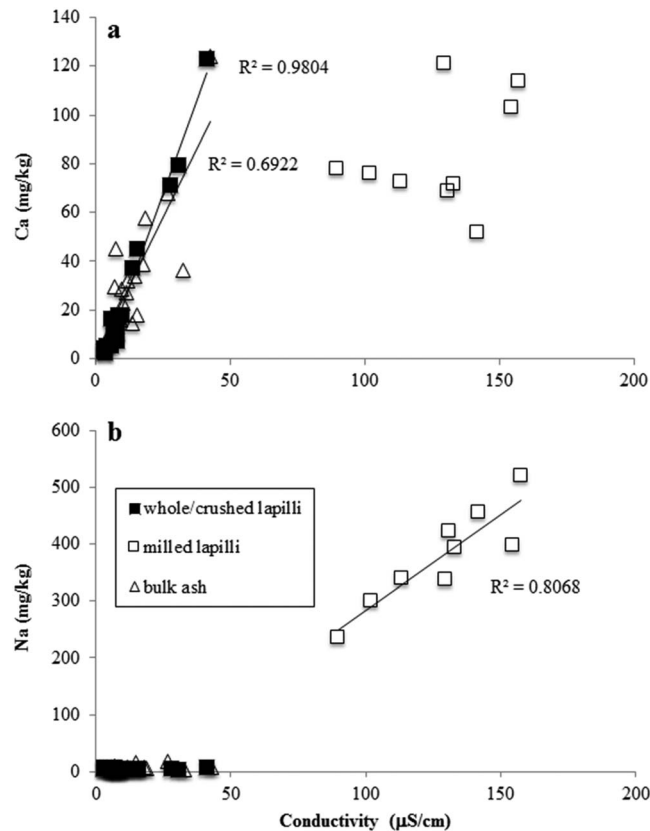


Figure 2. Relationship between the electrical conductivity (EC) of water samples and dissolved element concentrations. (a) Ca concentration and (b) Na concentration for the 2014 Kelud PDC deposits. For conductivities below $\sim 60 \mu\text{S}/\text{cm}$, there is a linear relationship with Ca concentration, but at higher conductivities ($>80 \mu\text{S}/\text{cm}$), values are linearly related to Na concentration. Solutions from milled samples showed the highest values of both Na concentration and electrical conductivity. Errors lie within the size of the symbols.

whole, broken, or crushed pyroclasts. EC of water samples positively correlates to the Ca concentration for bulk ash, in addition to the whole, broken, and crushed lapilli, for all Kelud and Merapi samples (Figure 2a). However, when samples are milled, EC positively correlates to the Na concentration instead (Figure 2b). All other element values for both sets of samples are widely scattered and show no correlation with the EC. The pH value of the solutions does not correlate with any element concentrations. The trends described above are consistent with both eruptions, despite the fact that only lava lapilli were utilized from the Merapi 2010 deposits, while pumice lapilli, in addition to some lava and accidental lithic clasts, were utilized from the Kelud 2014 deposits.

3.1. Merapi 2010 Deposits

Leachate solutions derived from the milled samples, relative to the other stages of pyroclast disaggregation, show an increase in Al, K, Ca, Na, and Si (Table 1). Ash components of the 2010 Merapi PDC deposits provide water samples with conductivities ranging from 15 to $605 \mu\text{S}/\text{cm}$. EC values of the broken and crushed lapilli show a similarly wide range, from 2 to $316 \mu\text{S}/\text{cm}$. Only two samples contained enough lapilli to perform the leachate protocol on milled pyroclasts, and for these the EC increase ranges from 7.5 to 9.5 times the bulk ash value. EC values, in addition to Ca concentrations, are generally higher in both ash and lapillus components of PDCs from the 26 October surges compared to the 5 November surges resulting from the 2010 eruption. All samples of both ash and lapilli provided water pH values ranging from 4 to 7, but milled samples produced pH values of 9–10 (Figure 3a).

3. Data

For the milled lapillus samples, relative to bulk ash or other stages of pyroclast disaggregation, the greatest increases in leached solution-dissolved concentrations were observed for Al, Ca, Na, K, and Si. For the other elements (As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, Sb, Ag, Sn, Sr, Ti, Zn, and V), their concentrations either showed only minor increases, no increases, or decreases, and they are not discussed further. Due to the inability to remove 100% of adhering ash particles from the lapilli, leachates from whole lapillus clasts are not zero but are measurably lower than the bulk ash value. Table 1 provides the range in concentrations for those elements that displayed the largest variations between samples, in addition to other measured water properties and sample characteristics. Values are reported for all of the ash samples subjected to a 1 h water/sample contact time, based on international leachate protocols [Witham *et al.*, 2005; Stewart *et al.*, 2013]. Sustained water contact times (48 h and 1 week) were also tested on some of the samples but generally showed no statistically relevant variation from the 1 h time period. Both electrical conductivity (EC) and pH of leaching solutions increase for all milled samples relative to bulk ash,

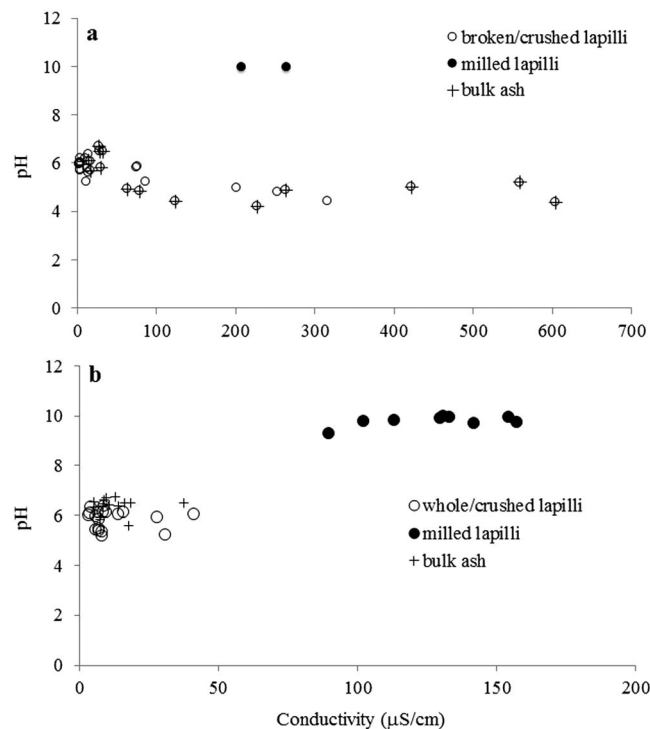


Figure 3. Relationship between the electrical conductivity (EC) of leachates and pH values. (a) Merapi 2010 PDC deposits, which show a wide range of electrical conductivities, while only the milled lapilli produced a higher pH. (b) Kelud 2014 PDC deposits, where milled samples produce both higher pH and higher electrical conductivities compared to other samples. Errors lie within the size of the symbols.

(12–18 times). In addition to the increased EC observed in water samples from the milled pyroclasts, the pH of the water also increased. All samples of both ash and lapilli, regardless of water contact time, produced pH values ranging from 5 to 7, but water from milled samples showed pH values of 9–10 (Figure 3b).

4. Discussion

Previous studies have shown that the overall “soluble cargo” of ash grains will vary according to the size distribution of the ash [e.g., *Witham et al.*, 2005; *Cronin et al.*, 1998]. Fine ash (<63 μm) has a higher surface area to volume ratio than coarser grains and thus greater reactive surface areas for gas and aerosol adsorption during transport within the eruption plume [*Bagnato et al.*, 2013]. During explosive volcanic eruptions, magma is fragmented into ash particles by the bursting of overpressured gas bubbles within a melt phase, which occupies the interstitial space between mineral crystals. The crystals typically range in size from several millimeters down to a few micrometers. Crystals may also fragment during particularly violent explosive eruptions, but generally, fractures occur at crystal margins and certain grain sizes of ash may reflect the original crystal modal size distribution (e.g., in phreatomagmatic or phreatic eruptions) [*Pardo et al.*, 2014]. In basaltic andesite/andesite magmas with moderate to high H₂O contents, the typical crystals include plagioclase feldspar, pyroxene, and titanomagnetite, along with less common hornblende and/or olivine. Plagioclase feldspar (Na/Ca aluminosilicate) is a dominant mineral phase, forming both phenocrysts and groundmass microlites. This is the case for both the Merapi and Kelud magmas, where plagioclase represents ~25% [*Hammer et al.*, 2000] and ~30–35% [*Jeffery et al.*, 2013] of the mineral phases, respectively. The melt portion of the magma, comprising up to 40 vol % of the clast (dependent upon style of eruption), is quenched to an amorphous glass at the point of fragmentation.

4.1. Source of Variations in Leachate Chemistry

The mechanical disaggregation induced by milling acts on both the solidified groundmass of magmas (microlites and glass) as well as the larger phenocrysts, effectively creating new fresh reactive surfaces

3.2. Kelud 2014 Deposits

As shown in Table 1, leachates derived from the milled samples show at least an order of magnitude increase in Na and Si relative to the other samples derived from whole and disaggregated pyroclasts. The K and Al also increase for the milled samples, with values comparable to those of the PDC ash component. Ash components of the 2014 Kelud PDC deposits produced water leachates with conductivities ranging from 4 to 43 μS/cm. Regardless of water contact time, EC values are similar between whole and crushed pyroclasts but increase significantly after samples are milled. The increase ranges from 3.4 to 19.9 times the whole clast value. Additionally, oxidized lapilli produce water samples with higher EC readings than unoxidized lapilli. This oxidation was evidenced by a red discoloration. Oxidized pumice and lava lapilli display the largest increase in EC (20 times), bulk lapilli (composed of a mixture of lava, pumice, and accidental pyroclasts) display the smallest increase (4 times), and unoxidized pumice and lava lapilli lie in between these end-members

[White and Claassen, 1980; White, 1983; Dahlgren et al., 1999; Horwell et al., 2003] that will release cations and anions upon contact with water. Because the glassy portion of the groundmass has a lower strength compared to the crystalline portion, it is easily broken into very fine grained particles during milling, and/or breaks occur along glass-grain boundaries. This glass contains a variety of oxides, compounds, and incompatible elements that were not incorporated into growing crystals, including any residual volatile components. There are two dominant processes interpreted to produce the analytical results presented here: (1) physical breaking of cation-hydroxyl compounds present in the residual groundmass glass and (2) exchange of H^+ for cations in the reactive surface sites of milled particles. Both processes would increase the major element concentrations and pH of leachates.

Numerous studies have attempted to determine the state of water in volcanic glasses because it is the dominant volatile that drives explosive eruptions. Several spectroscopic analyses [Bartholomew, 1982; Stolper, 1982; Newman et al., 1988; Eckert et al., 1988] indicate that glasses contain both molecular H_2O and hydroxyl (OH), but OH is the dominant species in glasses with low total water contents. The 2010 Merapi lapilli contained <0.5 wt % H_2O within the lava groundmass at the point of deposition [Genareau et al., 2014], low amounts (relative to initial contents in the magma at depth, ~ 5 wt %) resulting from volatile exsolution during magma ascent to the surface. At such low water contents, the OH^- dominantly exists in bonds with Si^+ [Eckert et al., 1988; Davis and Tomozawa, 1996], Al^+ , and other cations. The elevated pH level in leachates from milled samples suggests the release of OH^- into solution. Exposure to H_2O results in an exchange reaction with the fresh grain surfaces: reactive H^+ within the water binds with OH^- on glass and mineral surfaces, replacing cations (K^+ , Al^+ , Si^+ , etc.). These cations are released to solution, and the loss of H^+ to the grain surface creates a free OH^- in solution, resulting in both an increased dissolved element concentration and an increased pH.

The interpretation described above is supported by numerous experimental studies involving rates of various mineral reactions and glass dissolution in aqueous solutions. Tamm [1930] examined a suspension of fine-grained feldspar in water and observed the release of K and Na into solution, in addition to an increase of water pH to 10.7. Armstrong [1940] observed an increase in K and Na of solutions using ground feldspar in water. Garrels and Howard [1959] performed experiments using K-feldspar and mica samples, and observed a rapid reaction with water at room temperature, where both OH^- and K^+ releases were controlled by the available surface area of the minerals. These various experiments, and many other following studies [e.g., Anbeek, 1992; Wollast and Chou, 1992; Stillings and Brantley, 1995], were primarily concerned with the dissolution of feldspar minerals and the relative roles of water pH, temperature, initial solute composition, feldspar crystal structure, and grain size in order to constrain rates of chemical weathering. Other studies have examined weathering of amorphous glasses in aqueous or acidic solutions and found an initial rapid release of cations (e.g., Ca^{2+} and Na^+) due to H^+ exchange and/or silicate hydrolysis [White and Claassen, 1980; White, 1983; Dahlgren et al., 1999]. The data presented here show that the longer-duration experiments (48 h and 1 week sample-water exposure) did not produce elevated element concentrations compared to the 1 h experiments. This suggests that the rapid exchange mechanism occurred within the 1 h time frame, and further exchange was halted, either due to saturation of solution or formation of a protective leached layer on grain surfaces [e.g., Garrels and Howard, 1959; Muir et al., 1990].

The micronutrients examined in this study are typically released into the environment through natural chemical weathering processes. Chemical weathering will induce a range of changes: first, hydration, creating hydroxyl groups in altered glass surfaces [e.g., Hellmann et al., 2015]. These hydroxyl groups are removed as the glass breaks down, releasing cations into the environment [Dahlgren et al., 1999; Oelkers and Gislason, 2001; Gislason and Oelkers, 2003]. The chemical weathering occurs in addition to mechanical weathering. The latter will create higher surface areas, which will accelerate the former. Plagioclase, the dominant mineral in both the Merapi and Kelud magmas, is particularly susceptible to chemical weathering [Nesbitt et al., 1996; Nesbitt and Young, 1996], and milling of pyroclasts not only breaks down the larger phenocrysts but also exposes the surfaces of plagioclase microlites, which make up commonly $>50\%$ of the groundmass in these magmas. Weathering of amorphous volcanic glass occurs at an accelerated rate compared to mineral constituents [White, 1983]. Thus, disaggregation of pyroclasts during post-eruptive transport processes will accelerate the chemical weathering of volcanic deposits in their respective environments. This weathering may then be further enhanced through

acid-enriched precipitation, particularly in volcanically active regions where degassing contributes acidic compounds to the local atmosphere.

4.2. Water Conductivity

Electrical conductivity of water measures the ionic strength of solution. The EC of water leachates is directly proportional to the concentrations of Ca for bulk ash and lapilli. However, the mechanical milling of lapilli into very fine ash introduces a significant influx of Na, which raises the EC of the water by over an order of magnitude (Table 1). Ca and Na derive from the breakdown of (1) residual volcanic glass, (2) plagioclase feldspar crystals, and possibly (3) carbonate/calc-silicate xenoliths (known to be incorporated into the Merapi magma prior to eruption) [Chadwick *et al.*, 2007; Deegan *et al.*, 2010; Genareau *et al.*, 2014]. The Merapi samples show higher Ca values compared to the Kelud samples. Additionally, Merapi PDC deposits show higher Ca concentrations in the 26 October deposits when compared to the 5 November deposits. This variation is likely the result of assimilated carbonate xenoliths, which occupy a higher proportion of the 26 October (relative to the 5 November) deposits from the 2010 eruption [Genareau *et al.*, 2014]. However, the role of assimilated xenoliths is likely minor, as they comprise such a low volume of the bulk sample (~1%).

During mechanical milling, a higher proportion of the residual glass is exposed, and this is where Na is concentrated in pyroclasts of intermediate bulk composition. The increase in Na for all milled samples stems from the breakdown of residual groundmass glass in addition to ultrafine particles generated from the milling of minerals, including plagioclase feldspar. Water-extractable Si is also substantially higher in milled pyroclasts than in whole, broken, or crushed lapilli, or ash, particularly for the Kelud PDC deposits (Table 1), and this element is concentrated in the residual groundmass glass as well.

4.3. Other Considerations

The methods utilized to filter leachates prior to analyses removed all particles from solution $>0.45\ \mu\text{m}$. Smaller solid particles may have remained, contributing to “apparently dissolved” concentrations, but any environmental process that remobilizes preexisting volcanic deposits will generate a range of particle sizes, including nanometer-scale particles. It should be noted that the majority of elements analyzed using the ICP-OES did not show increased concentrations in leachates following sample milling, including many elements known to be present in these magmas (e.g., Fe, Ti, and Mg). The elements that do show increased concentrations (Al, Na, Ca, Si, and K) are those that have been shown to easily exchange in dissolution experiments on both feldspars [Armstrong, 1940; Garrels and Howard, 1959] and natural glasses [White and Claassen, 1980; White, 1983; Dahlgren *et al.*, 1999]. Based on these observations, it appears that we are measuring the dissolved element load in the leachates instead of nanoscale solid particles. The time scale of our experiments limits the role that dissolution is playing, as most dissolution experiments are conducted over days to months. It is unlikely that significant dissolution of the milled particles was able to occur over a period of just 1 h, suggesting that the mechanical breaking of hydroxyl compounds and the exposure of fresh reactive surface sites, the latter allowing the exchange of H^+ for available cations on these surfaces (as described in section 4.1), were the primary mechanisms.

In addition to the effects of pyroclast disaggregation on exposed waters, other potential subaerial hazards exist due to the creation of fresh reactive surfaces, as previously revealed by work on cristobalite-rich samples from the Soufrière Hills volcano [Horwell *et al.*, 2003]. The generation of very fine ash particles, some of which may be respirable, could result in the creation of free radicals in the human lung as cations bound to ash grain surfaces interact with biological fluids [Fubini and Hubbard, 2003; Horwell *et al.*, 2003; Schoonen *et al.*, 2006]. These free radicals, which include hydroxyl radicals, can damage cell structure and function upon their release from grain surfaces. Experiments conducted to determine variations in mineral dust toxicity to human health have verified that SiO_2 minerals, when freshly ground into finer particles, will develop highly reactive surface sites that increase toxicity [Castranova *et al.*, 1996; Fubini, 1998]. Milling of the samples used in this study also created these fresh reactive surfaces within various silicate minerals and glass, permitting dissolution of micronutrients into exposed waters as shown and potentially generating free radicals hazardous to human health if grinding occurs subaerially. This may occur during cleanup efforts following an eruption, during construction in areas with pyroclastic deposits, or in mining efforts to extract volcanic products for infrastructure.

This study reveals that previously deposited pyroclastic material, even after the immediate syneruptive and posteruptive stripping of soluble compounds, may continue to introduce elements into surface waters. While ashfall effects on water bodies are typically quite transient, the reworking of volcanic debris has the potential to be a sustained source of element input. The mechanical milling of pyroclasts also raises the water pH by up to three log units. However, differences between pH levels in leachate solutions and those in a natural receiving environment are likely due to dilution and buffering effects. The laboratory-scale experiments presented here do not replicate natural environments where initial element concentrations, pH, and biologic effects may differ substantially and may exert a fundamental control on the resulting chemical impacts to the affected area. Because only the milled samples show a significant effect on leachate compositions (where all particles were $<32\ \mu\text{m}$), and water properties were not altered to reflect potential variations in initial solutes, the potential dose of elements to environments is a topic for future studies.

5. Conclusions

This laboratory-scale study shows, for the first time, that mechanical grinding of volcanic deposits may be an important source of trace elements and nutrients to surface waters well after the initial volcanic activity that produced the deposits has ceased. Compared to other samples examined, milled lapillus-sized fragments produce a significant increase in Ca, Na, Al, K, and Si. The EC of water samples positively correlates with Ca concentrations in the case of bulk ash, whole, and crushed lapilli but correlates with Na for the milled samples. These elements are supplied from residual glass and possibly minerals including plagioclase feldspar (a dominant mineral phase in the basaltic andesite samples). Milling of pyroclasts mechanically grinds down minerals and glass, in addition to any products of secondary glass alteration, resulting in an increased EC, pH, and dissolved micronutrient concentration of exposed waters. Leachate analyses performed on mechanically milled volcanic deposits of other compositions (i.e., rhyolites or basalts) will provide additional data. Mechanical milling of preexisting volcanic deposits may occur during transport of PDCs, lahars, or debris avalanches, sometimes decades or centuries after the initial eruptive activity. Further grain chipping and milling occur during fluvial and aeolian transportation of ash; both of which may occur for decades in many environmental settings. Although these experiments do not replicate conditions in a natural environmental setting, the results pose important implications for not only hazard assessment but also for efforts to understand the potential influence of elements derived from volcanic deposits on various environments. Sudden or sustained input of particular elements into environments over several months to years of deposit disaggregation may alter the chemical characteristics of the environment and may affect a range of flora and fauna by impacting their development and functionality. Consequently, mechanical breakdown of volcanic deposits should be an important consideration when determining the sources of chemical variability and element cycling for particular environments in proximity to active strato-volcanoes of intermediate bulk composition.

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