

## Acidic processing enhances iron solubility in volcanic ash: a mechanism for increased iron input and organic carbon production upon ash deposition to the surface ocean.

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Marine primary production, driven by photosynthetic phytoplankton, plays a key role in regulating atmospheric carbon dioxide. However, it is limited by a low concentration of dissolved iron (Fe) in approximately 30% of the surface ocean. Atmospherically deposited volcanic ash is increasingly recognised as an intermittent source of Fe to the marine environment which, over geological timescales, may impact the carbon cycle and ultimately the global climate.

A better understanding of the poorly constrained controls on volcanic ash Fe solubility from magma source to ocean sink is crucial for unravelling the impact of ash on the ocean biogeochemical Fe cycle and thus on primary productivity. Research on mineral dust has highlighted that dust Fe solubility is enhanced by interaction with acids during atmospheric transport. Since volcanic ash particles act as cloud condensation nuclei, the same effect may be expected during atmospheric transport of the ash in volcanic clouds containing sulphuric acid. Thus, studies which have measured Fe release from volcanic ash at near-neutral pH may have underestimated its ocean fertilisation capacity.

We investigate ash Fe release under low pH conditions representative of exposure to volcanic cloud acidity. Seven volcanic ash and five volcanic glass samples, ranging from basalt to rhyolite (48-75 wt.% SiO<sub>2</sub>), were exposed to pH 1 sulphuric acid for 336 h in batch reactors. The solution was sampled at regular time intervals and analysed for major element concentrations by optical emission spectroscopy, and for Fe(II)/Fe(III) ratios using the ferrozine method. Changes in sample surface composition were assessed by X-ray photoelectron spectroscopy (XPS), and the surface of selected ash samples was imaged by scanning electron microscopy.

Results indicate that both the glass and mineral phases in ash likely contribute significantly to Fe release at low pH. Element release trends are consistent with silicate leaching and dissolution, and XPS data provide evidence for the formation of a protonated leached surface layer. In contrast to glass, Fe release from ash does not correlate with bulk Fe content. The discrepancy may reflect differences in ash surface reactivity imparted by plume and/or atmospheric processing prior to deposition. Ash from phases I and III of the 2010 Eyjafjallajökull eruption (Iceland) displayed high 1 min Fe release rates (55 and 115  $\mu\text{mol m}^{-2} \text{h}^{-1}$ , respectively). The high reactivity of these samples may be due to in-plume processes, namely formation of Fe (oxyhydr)oxide surface deposits during ash oxidation and surface etching by aqueous and gaseous fluoride, respectively. Initial Fe(II)/Fe(III) values in solution suggest oxidation of the surface relative to the bulk of all ash samples. Knowledge of Fe at the ash surface is critical to understanding Fe release from volcanic ash.