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Magmatic and fragmentation controls on volcanic ash surface chemistry

Paul M Ayris (1), Spyros Diplas (2), David E Damby (1), Adrian J Hornby (3), Corrado Cimarelli (1), Pierre Delmelle (4), Bettina Scheu (1), and Donald B Dingwell (1)

(1) Department of Earth and Environmental Science, Ludwig-Maximilians-Universität München, Munich, Germany, (2) SINTEF Materials and Chemistry, Oslo, Norway, (3) Earth, Ocean and Ecological Sciences, University of Liverpool, Liverpool, United Kingdom, (4) Earth and Life Institute, Université Catholique de Louvain, Louvain la Neuve, Belgium

The chemical effects of silicate ash ejected by explosive volcanic eruptions on environmental systems are fundamentally mediated by ash particle surfaces. Ash surfaces are a composite product of magmatic properties and fragmentation mechanisms, as well as in-plume and atmospheric alteration processes acting upon those surfaces during and after the eruption. Recent attention has focused on the capacity of alteration processes to shape ash surfaces; most notably, several studies have utilised X-ray photoelectron spectroscopy (XPS), a technique probing the elemental composition and coordination state of atoms within the top 10 nm of ash surfaces, to identify patterns of elemental depletions and enrichments relative to bulk ash chemical composition. Under the presumption of surface and bulk equivalence, any disparities have been previously attributed to surface alteration processes, but the ubiquity of some depletions (e.g., Ca, Fe) across multiple ash studies, irrespective of eruptive origin, could suggest these to be features of the surface produced at the instant of magma fragmentation. To investigate this possibility further, we conducted rapid decompression experiments at different pressure conditions and at ambient and magmatic temperature on porous andesitic rocks. These experiments produced fragmented ash material untouched by secondary alteration, which were compared to particles produced by crushing of large clasts from the same experiments. We investigated a restricted size fraction (63-90 µm) from both fragmented and crushed materials, determining bulk chemistry and mineralogy via XRF, SEM-BSE and EPMA, and investigated the chemical composition of the ash surface by XPS. Analyses suggest that fragmentation under experimental conditions partitioned a greater fraction of plagioclase-rich particles into the selected size fraction, relative to particles produced by crushing. Trends in surface chemical composition in fragmented and crushed particles mirror that partitioning effect, but crucially, disparities between surface and bulk chemistry remain evident. Simple glass-plagioclase mixing calculations suggest that this feature may indicate differences in bulk and surface mineral distributions; future QEMSCAN analysis will investigate this possibility further. Additionally, surface iron enrichments observed in our high temperature experiments suggest that hot oxidation effects can have a near-instantaneous, measurable effect on ash surface chemistry at the nanometre scale. Our preliminary results suggest that the chemical and mineral properties of the source magma, coupled with high temperature fragmentation processes, may have a significant influence on ash surface chemistry and mineralogy, and subsequently, on the post-eruptive alteration of ash particles and their reactivity within biotic and abiotic systems.