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The application of laser ablation ICP-MS to the analysis of tephra.

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Geochemical characterisation of individual tephra deposits has been widely used in correlation and provenance studies, and requires accurate chemical analyses of the tephra deposits. Most violently explosive, large magnitude eruptions are broadly similar in composition (rhyodacitic) and, in some cases, can be difficult to identify unequivocally using only major element analysis, typically performed on single glass shards by EPMA. Trace element analyses of this juvenile glass component of tephra deposits may, in some cases, be the only way in which they can be distinguished or correlated. Bulk trace element analysis (e.g. INAA, XRF, solution methods) requires a relatively large sample, and the separation of such an amount of material from distal tephras, which are typically thin and prone to contamination, can be awkward if not impossible. ICP-MS is a highly sensitive analytical technique with a small sample requirement, and samples can be introduced for analysis as either a solution or a vapour produced directly from a solid surface. Samples of glass shards separated from tephra deposits weighing as little as 0.025g and digested in HF have been analysed by solution ICP-MS. This method gives accurate data for all elements of petrogenetic significance (typically within $\pm$5%) and precisions (1 σ) are around $\pm$ 3% for the abundant trace elements (e.g. Zr, Rb, Sr) but this deteriorates to about $\pm$20% for rare elements in small samples (e.g. HREE in a 25 mg sample).

Laser ablation (LA) ICP-MS has been used to determine the trace element composition of very small volumes of bulk glass, and also of individual glass shards from tephra deposits. Here a powerful UV laser directly vapourises the sample. An internal standard is required to account for variations in the volume of material ablated and to calibrate the analyses, and in rhyolitic glasses ^{29}Si is used routinely, this being determined by EPMA. For single grain analyses, the EPMA mount is used and the

same grains analysed for major elements are relocated on the LA-ICP-MS and ablated to determine their trace element content. Despite a spatial resolution down to about 5 μm, at present reliable trace element analyses can be produced from shards about 40 μm across, with some 30 elements being determined in a 45-60 second analysis. Laser ablation methods are slightly less accurate (typically $\pm$ 5 to10%) than solution ICP-MS analyses, with precision decreasing from about $\pm$3% at concentrations of a few hundred ppm, to about $\pm$10% at 1 ppm and about $\pm$30% at 0.05 ppm. Detection limits vary, but at laser powers of about 0.8 mJ, used routinely for analysis of glass, Rb has a LLD of 0.8 ppm, Ce has a LLD of 0.3 ppm, and Lu and U have LLDs of about 0.05 ppm. Improvements in instrument sensitivity over the years have reduced these detection limits.

An apparent lack of precision in the bulk analysis of small volumes of bulk glass by LA-ICP-MS often represents within sample heterogeneity (and not analytical error), with inter-shard variation becoming abundantly clear in some tephra deposits when individual glass shards are analysed. In the Minoan eruption of Santorini, for example, Zr varies from about 200-400 ppm between individual shards of glass, a result of fractionation processes within the magma.

Single grain analyses of glass shards provide an accurate analysis of the pure glass phase, which may not be achieved in solution or bulk sample LA-ICP-MS methods because of problems in producing a “clean” glass separate. LA-ICP-MS analyses of individual shards affected by micro-phenocryst phases, such as feldspar or zircon can be easily recognised from their anomalous trace element composition, and can thus be removed from calculations of the glass composition following careful inspection of the data.

Examples will be presented to illustrate the range of methods applied to the analysis of glass from tephra deposits described above. Particularly, data from the analyses of individual glass shards from tephra deposits from USA, Alaska, Santorini and New Zealand will be used to illustrate different applications of this powerful analytical technique, which can assist in the correlation and/or discrimination of individual deposits. Improvements in detection limits on modern instruments hint at a potential reduction in the grain size which can be analysed, and this will be discussed. In addition, the range of internal variation between individual shards evident in some deposits can be related to the eruptive process and fractionation within the parent magma body, variation which would not be observed by a single, bulk-sample, analysis.