Tephra interference during amorphous silica determination - A false environmental signal?

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Amorphous silica (ASi) is a widely applied environmental proxy that had ecological and hydrological interpretations. Volcanic eruptions can eject large amounts of igneous material to the atmosphere. The ash-outfall covers the landscape with continuous ash-deposits called tephra. The rapid weathering of tephra results in the formation of short-range ordered minerals (e.g. allophane, imogolite). The dissolution properties of short-range ordered minerals are believed to be similar to those of ASi. Soil and palaeo-environmental scientists have ignored its contribution during measurment. Nevertheless, evaluation of its exact contribution to ASi measurements or examining its dissolution behavior is lacking. We tested if tephra ASi contributes to ASi measurements during alkaline extraction, and how it interferes with sediment and lake records from the southern hemisphere.

We selected 25 well-known tephra covering a representative range of chemical composition, age, spatial provenance and sample type. A well-studied peat core from Kerguelen was used to verify its interactions with other ecological and hydrological proxies. Samples were analyzed for total ASi using the long-term sequential Na_2CO_3 (0.1M) and continuous NaOH (0.5M) method, as such obtaining detailed dissolution curves.

Amorphous Si content extracted from tephra ranged between 0.19 and 2.92 SiO_2 wt%. The extracted amount was independent of age and weakly related to its chemical composition. Detailed dissolution curves provided a distinct signature for pure tephra compared to other ASi fractions.

Palaeo-environmental studies using elevated ASi levels (> 10 SiO_2 wt%) to indicate environmental changes, encounter limited interference problems. However, our study does not exclude that increased diatom productivity could be caused by tephra weathering rather than a change in environmental conditions.

Metal behaviour during differentiation of subducted-related lavas (Hunter Ridge, SW Pacific)

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The behaviour of key ore-forming metals during magmatic differentiation of typical island-arc lava suites from the Hunter Ridge (i.e. calc-alkaline and adakites) have been investigated using geochemistry of minerals and glass, petrographic observations, and quantitative geochemical modelling. The Hunter Ridge extends from the southern termination of the Vanuatu Trench to the Koro sea near Fiji. Calc-alkaline rocks record a protracted history of magma evolution from the very earliest stages of fractionation (i.e. before volatile loss) to eruption on the sea floor.

Metal partitioning behaviour in the principal magma components was examined (i.e. for olivine, clinopyroxene, plagioclase, magnetite, and melt). Mineral/melt partition coefficients (Ds) for Cu, Zn, V, Pb, Co and Sc were calculated directly from LA-ICP-MS analyses for phenocryst-groundmass/glass equilibrium pairs. For comparison purposes, modelling was also conducted using D values obtained from literature (where available). This approach allows us to examine, in detail, how magma ascent, crystallisation and degassing can lead either to the enrichment or depletion of ore-forming metals.

Our results provide evidence that i) Cu partitions into a H_2O-rich fluid at crustal levels as soon as volatile saturation occurs, ii) arc magmas are likely to exsolve a magmatic hydrothermal fluid before they are able to segregate an immiscible sulphide liquid, due to their higher oxidation states and volatile contents. Thus, a critical step in forming magmatic/hydrothermal ore deposits is concentrating and removing metals (i.e. Cu) from a magma before saturation of an immiscible sulphide liquid occurs. As Cu is incompatible in any of the early crystallizing silicates and oxides, it's concentration in the melt will progressively increase and it will be available to partition into an aqueous fluid phase. Zn and V are strongly controlled by magnetite fractionation. Co and Sc partition into olivine and clinopyroxene from the early stages of fractionation, and magnetite once it enters the liquidus. Pb behaves incompatibly and is concentrated in the melt during magmatic differentiation.

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