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Contaminant assessment and removal of volcanic ash in biogenic silica samples from a ca. 50 ka Southern Hemisphere palaeolimnological reconstruction

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The last ca. 50 ka of environmental variability across mid-latitude New Zealand is recorded by the lacustrine sediments of a Late-Quaternary crater maar, Lake Pupuke (36˚47.25'S, 175˚46.25'E; Auckland, NZ). Diatom O and Si stable isotope data (δ^{18}O, δ^{30}Si) show evidence for the timing of MIS 1, onset and termination of MIS 2 and termination of MIS 3.5. Several millennial scale short-term warm, competitive events are marked by relatively high isotope values that correspond to lesser diatom ^{18}O-discrimination.

The presence of tephra isochrons whilst beneficial to chronological modelling resulted in high % contributions to sedimentary biogenic silica (BSi). As even minor ash inclusions can induce marked δ^{18}O variation due to the relatively depleted signatures of tephra compared to BSi (ca. 9 ‰ compared to ca. 35 ‰ respectively) it is essential to remove any tephra present from a biogenic δ^{18}O record. Classical chemical treatments to remove organic residue and carbonates (e.g., H_2O_2, HCl), coupled to traditional purification techniques (e.g., density settling and separation, and magnetic separation) failed to yield sufficient clean diatom silica, ash dominating (min. 40 %) all samples tested (n = 20). A novel split-flow lateral-transport thin (SPLITT) fractionation approach was however successful in separating microfossils and silicate particles (e.g., diatom frustules, sponge spicules, phytoliths, tephra, clays) along a density and diametrical gradient (Rings et al, 2004). 77 clean diatom samples were collected for novel dual stable isotope analyses (δ^{18}O and δ^{30}Si) at the National Isotope Geosciences Laboratory (British Geological Survey, UK).

Scanning electron and optical microscopy provided evidence for high sample purity (>90 % count), limited ash contamination and minor, if any clay/carbonate inclusion in all samples. Application of a novel micro-XRF mass balance model (Brewer et al, 2008) revealed up to 31% contamination in the more heavily contaminated samples. Modelled contamination averaged 10% ± 8% resulting in a mean enrichment of 5.40‰ ± 5.10‰. Nonetheless contamination estimates fluctuate independently of visible tephra isochrons suggesting either (a) reworking of <20 μm original ash layers; and/or (b) failure of a simple 2-end member mixture model to effectively identify tephra from biogenic silica by traditional major oxide and trace element geochemistry.

Comparison of modelled diatom δ^{18}O to bulk geochemical proxies suggests effective removal of tephra δ^{18}O effects during warmer periods and <10 wt.% contribution. Model failures are coincident with periods of greater ash abundance (>10 wt.%) throughout the Last Glacial Period (LGP). Possible reasons for poor model outcomes include:

1. Overlap in major oxide (K_2O, Al_2O_3, Fe_2O_3, TiO_2) and trace element (Ba, Rb) tephra end members (e.g., causing model outputs to duplicate tephra contributions);

2. Uptake of dissolved metals and metal oxides to diatom frustules (e.g., higher abundance of tephra geochemical indicators in the pure diatomite end member);

3. Differences in sample preparation between micro-XRF and IRMS (e.g., removal of readily exchanged outer hydroxyl layers by Step-Wise Fluorination [Leng and Barker, 2006]).

References:

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