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## Hafnium (and Sr-Nd) isotope analysis of mineral dust: from sample digestions to mass spectrometry

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Mineral dust in ice cores provides insight into past atmospheric circulation patterns provided that the source(s) of these aerosols can be identified. Isotopes of strontium, neodymium and lead are frequently used for source discrimination in ice cores, while those of hafnium much less so. This is because of the extremely low (1-5 ng) amounts of Hf present in 5-10 mg dust samples usually available for isotopic analyses from the dustiest periods of past glaciations, e.g. the Last Glacial Maximum. The use of <sup>176</sup>Hf/<sup>177</sup>Hf isotopic ratios in dust fingerprinting is crucial in situations when Sr-Nd isotopes are inconclusive in source identification.

The overall Hf budget is dominated by the heavy mineral zircon in silt-sized, wind-blown material, while it is significantly depleted in the finer (<5 µm) fractions and the effects of other minerals (apatite, sphene, monazite, xenotime and clay minerals) become increasingly important. Since the major hosts of Hf are refractory heavy minerals, the complete digestion of dust material is crucial in determining reliable Hf isotope ratios.

Here we introduce a closed vessel ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) digestion method (220 °C), which is a fast and low blank (0.5 ng for Sr, 0.2 ng for Nd, and <25 pg for Hf) technique for dust dissolution, prior to column chemistry for combined Hf-Sr-Nd isotope analyses. Repeated measurements of the Hf isotope ratios of USGS geological reference materials (AGV-2, BCR-2 and GSP-2) demonstrate that raw, non fractionation corrected <sup>176</sup>Hf/<sup>177</sup>Hf ratios are accurate within 5-50 ppm, while the JMC-475 fractionation corrected values are accurate to 5-10 ppm, compared to reference values using our ion exchange chemistry setup. This methodology also allows separating Sr and Nd from the same samples, and analysing the <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd isotopic compositions. Here we discuss mass spectrometry issues (including sensitivity) of TIMS and two different MC-ICP-MS instruments, and major limitations on dust sample size for Hf-Sr-Nd isotope analyses. Furthermore, the mineralogical background of Hf isotopic compositions, including zircon

depletion effects and clay mineralogy (illite) control will be demonstrated. Hf isotope data obtained from four NorthGRIP ice core samples will be presented.

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