

A method for combined Sr-Nd-Hf isotopic analysis of <10 mg dust samples: implication for ice core science

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Aeolian mineral dust particles below the size of 10-20 μm often experience longer distance transport in the atmosphere, and thus Aeolian dust is considered an important tracer of large-scale atmospheric circulation. Since ice core dust is purely Aeolian in origin, discrimination of its potential source region(s) can contribute to a better understanding of past dust activity and climatic/environmental causes. Furthermore, ice core dust source information provides critical experimental constraints for model simulations of past atmospheric circulation patterns [1,2]. However, to identify dust sources in past dust archives such as ice cores, the mineralogy and geochemistry of the wind-blown dust material must be characterized. While the amount of dust in marine cores or common terrestrial archives is sufficient for different types of analyses and even for multiple repeat measurements, dust content in ice cores is usually extremely low even for the peak dusty periods such as the Last Glacial Maximum (LGM) (5-8 mg dust/kg ice; [3]). Since the most powerful dust fingerprinting methods, such as REE composition and Sr-Nd-Pb isotopic analyses are destructive there is a clear need to establish sequential separation techniques of Sr, Nd, Pb and other REEs to get the most information out of small (5-10 mg) dust samples recovered from ice cores. Although Hf isotopes have recently been added as a robust tool of aerosol/dust source discrimination (e.g. [4,5,6,7]), precise Hf isotopic measurements of small (<10 mg) dust samples are still challenging due to the small Hf amounts (on the order of 1-10 ng) and often compromised by potential problems arising during ion exchange chemistry.

In this pilot study an improved method for chemical separation of Sr, Nd and Hf by Bast et al. [8] was applied, which allows the precise isotope analysis of sub-ng amounts of Hf by MC-ICPMS. This ion exchange chromatography procedure has been combined with established methods of separating and purifying Sr and Nd for subsequent TIMS isotopic measurements. International rock standard BCR-2 (10 mg aliquot) gave $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios of 0.705127 ± 0.000004 (2σ), 0.512625 ± 0.000004 and 0.282853 ± 0.000006 , respectively. These data are in good agreement with the certified values (0.705000 ± 0.000011 , 0.512637 ± 0.000013 and 0.282866 ± 0.000011 ; [9]) demonstrating that the experimental procedures and setup allow for valid ^{176}Lu and ^{176}Yb corrections and results in reliable $^{176}\text{Hf}/^{177}\text{Hf}$ (and also $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$) ratios. Along with the standards 50, 10 and 5 mg aliquots of the fine (<10 μm) fractions of three wind-blown loess sediment samples from Central Europe (NUS), China (BEI) and the US (JUD) were processed (all acetic acid treated for carbonate removal, i.e. aluminosilicate fractions were analysed). Sr isotopic compositions varied between the aliquots within a range of ~ 0.00007 for the three samples. Comparison of these values with previously obtained $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios from the same samples (different acid/sample amounts) reveals that these values are very sensitive to the acetic acid treatment (acid molarity and amount). By contrast, Nd isotopic ratios do not seem to be affected by acid treatment and these signatures are extremely stable both within run (0.000008 variability for the three aliquots, i.e. 0.15 ϵNd unit) and between runs of different laboratories (0.00006, ca 1 ϵNd unit). Hf isotopic compositions varied within 1 (NUS) and 5 ϵHf units (BEI) between the three aliquots, but the BEI sample always gave more positive ϵHf values (mostly below -4.7) than the Central European sample (NUS, above -6.5, mostly around -8). JUD gave two values of -4.9 and -7.9. It should be further studied using other dust samples if the slightly larger dispersion in $^{176}\text{Hf}/^{177}\text{Hf}$ for the different aliquots of BEI is a unique feature or not. Nevertheless, the ca. 3-7 ϵHf unit difference between the Central European and Chinese dust sample provides an opportunity to better discriminate last glacial Greenland dust sources [7] in Nd-Hf space.

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References

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