Quantitative Insights on Impurities in Ice Cores at the Grain Scale

Pascal Bohleber\textsuperscript{1,2}, Piers Larkman\textsuperscript{2}, Nicolas Stoll\textsuperscript{2}, David Clases\textsuperscript{3}, Raquel Gonzalez de Vega\textsuperscript{3}, Martin Šala\textsuperscript{4}, Marco Roman\textsuperscript{2}, and Carlo Barbante\textsuperscript{2,5}

\textsuperscript{1}Alfred-Wegener-Institute Helmholtz Zentrum für Polar- und Meeresforschung, Bremerhaven, Germany
\textsuperscript{2}Ca'Foscari University of Venice, Italy
\textsuperscript{3}Nano Micro LAB, Institute of Chemistry, University of Graz, Graz, Austria
\textsuperscript{4}Department of Analytical Chemistry, National Institute of Chemistry, Ljubljana, Slovenia
\textsuperscript{5}Institute of Polar Sciences, CNR, Venice, Italy.

Understanding the spatial variability of impurities in glacier ice on a quantitative level has importance for assessing the preservation of paleoclimatic signals and for the study of macroscopic deformational as well as dielectric ice properties. Two-dimensional imaging via laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) can provide key insight into the localization of impurities in the ice matrix: Employing the relatively recent advances in LA-ICP-MS featuring fast wash-out devices and single laser shot resolution, state-of-the-art LA-ICP-MS imaging has revealed snapshots showing a close association between grain boundaries and some impurities as well as dispersed clusters in dust-rich ice. So far, these findings are mostly qualitative and gaining quantitative insights remains challenging. Accurate calibrations rely on matrix-matched standards which ideally show the same ablation behavior as the sample. Previous studies successfully prepared ice blocks on glass slides as calibration standards at a resolution of a few hundred microns. State-of-the-art LA-ICP-MS imaging fully reveals the imprint of the ice matrix on the impurity distribution at the grain scale, which also introduces the need for new adequate quantification strategies and consequently, the design of new calibration standards. Here, we present different quantification methods, which provide a high level of homogeneity at the scale of a few microns and, which are dedicated to imaging applications of ice core samples. For this purpose, we use small µL volumes and fast freezing techniques. One of the proposed methods has a second application, offering laboratory experiments to investigate the displacement of impurities by grain growth, with important future potential to study ice-impurity interactions. Standards were analyzed to enable an absolute quantification of impurities in selected ice core samples. Calibrated LA-ICP-MS maps indicate similar distributions of impurities in all samples, while impurity levels vary distinctly: Higher concentrations were calibrated in glacial periods and Greenland, and lower levels in interglacial periods and samples from central Antarctica. These results are consistent with known ranges from bulk meltwater analysis. Further comparison with bulk meltwater analysis calls for a more sophisticated representation of the ice chemistry across spatial scales, for which the calibrated LA-ICP-MS maps now also introduce the quantitative domain.