Imaging the Distribution of Elements in Antarctic Ice Cores with LA-ICP-TOFMS

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Polar ice cores are invaluable to paleoclimate research, archiving a unique variety of proxies, including aerosol-related atmospheric impurities, over timescales from decades to hundreds of millennia. To reliably decipher the oldest part of the ice core impurity record, comprised in the deepest and most highly thinned layers, it is key to employ high-resolution analysis in concert with understanding the interaction of impurities with the ice crystal matrix.

Being a high spatial resolution, high sensitivity and micro-destructive technique, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has unique potential in this regard and was recently refined for state-of-the-art 2D impurity imaging [2]. This revealed that many impurities in the deep ice are preferentially located in the interstitial volumes between adjacent crystals, the so-called "grain boundaries", which may have broad impact on the interpretation of LA-ICP-MS signals from deep ice [1]. Using a sequential-scanning mass analyzer, such as a quadrupole ICP-MS (LA-ICP-QMS), imposes fundamental limitations on the number of analytes that can be recorded within a single imaging run. In contrast, time-of-flight mass spectrometers (TOFMS) provide quasi-simultaneous acquisition of the entire mass spectrum.

Designed as a first proof-of-concept, we demonstrate the capabilities and advantages of the icpTOF in combination with a fast-washout laser ablation system for the investigation of elemental impurities in ice cores by LA-ICP-TOFMS.

Experimental Setup

An Analyte G2 excimer laser (193 nm) equipped with a HelEx II cell (Teledyne CETAC Technologies, USA) and a custom-designed cryogenic sample holder was used in the experiments [2]. An Aerosol Rapid Introduction System (ARIS) was used to achieve fast washout of the ablated material (< 20 ms signal duration from single laser pulse). The laser fluence was 4.0 J/cm^2, the laser spot size was 35 µm, and the repetition rate was 80 Hz.

The special cryostatic sample holder in use for LA-ICP-MS ice core analysis at Ca' Foscari University of Venice was transported to TOFWERK's facilities in Thun, Switzerland and installed into the Analyte G2's HelEx II cell. Following closely the approach to LA-ICP-MS ice core imaging developed at Venice University [2], ice core samples were freshly decontaminated by scraping prior to analysis.

The TOFWERK icpTOF 2R was run in CCT mode (using a H_2-He mixture in the collision/reaction cell) collecting ~ 21,700 mass spectra per second that were further integrated into one mass spectrum per pixel. Imaging was performed in spot-resolved mode, implying that each pixel in the image represents the signal from a single laser shot with minimal overlap of neighboring pixels [3]. Here, the laser was fired at a dosage of 2, so that neighboring pixels overlap by 50%, to increase spatial resolution in x-direction. Image acquisition was performed with TOFWERK's TOFpilot software, allowing real-time display of the images.

A sample from the Holocene period in the EPICA Dome C ice core in Antarctica was chosen for the pilot analysis. Interglacial periods in Antarctica are characterized by extremely low bulk concentration of impurities. The rationale was to select a sample with generally low impurity content to benchmark it against the sensitivity of the icpTOF 2R. In addition, samples from this core were already successfully analyzed by 2D impurity imaging with a quadrupole ICP-MS system in Venice [1].

Results/Conclusions

An image area of 4 x 7 mm was selected and imaged within 21 minutes. The image recorded by icpTOF imaging at a spatial resolution of 35 µm reveals clear signals for a broad range in analyzed masses, encompassing Na to Pb (Figure 1). The analytes Na, Mg, Sr, which were previously studied in LA-ICP-MS imaging, show the already known distinct localization along grain boundaries [1]. This feature also applies to K, Ca and Zn. In contrast, metals such as Al, Fe, Ni, Cu, Ba and Pb, also feature significant intensity from the grain interiors.

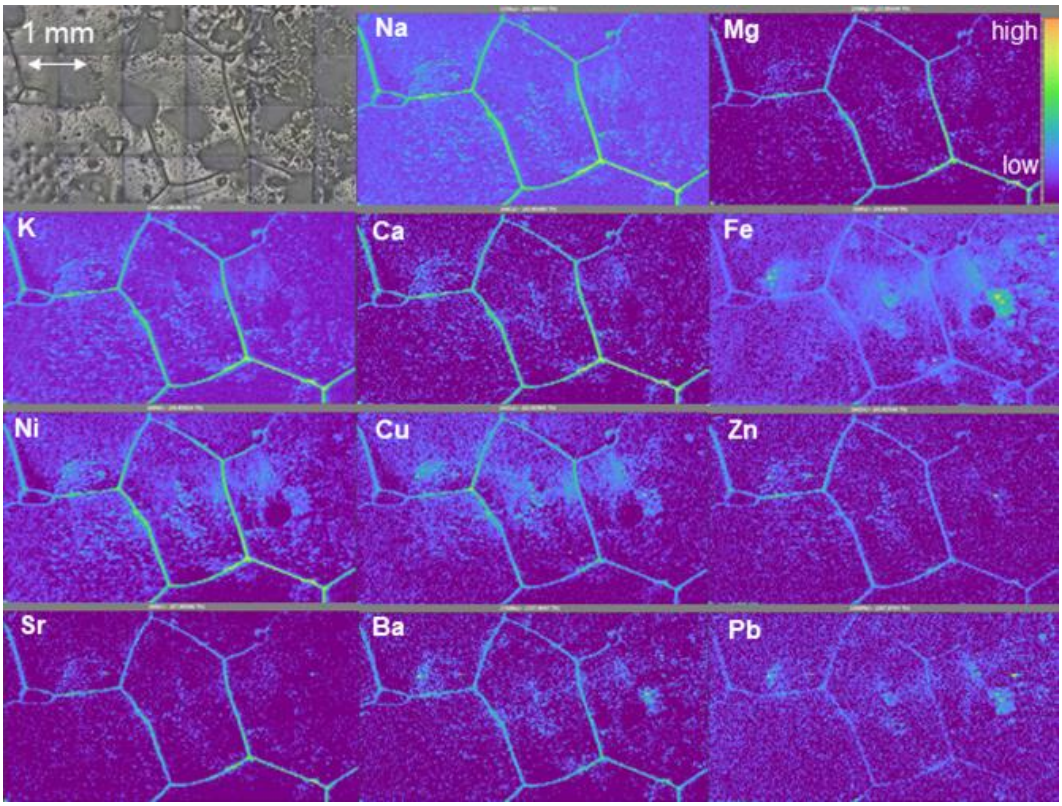

Figure 1. *LA-ICP-TOFMS images of impurities spatial distribution in Antarctic ice (EPICA Dome C core) from the Holocene time period. The color-scale refers to the raw signal intensity recorded by the icpTOF 2R. Image dimension is 4 mm by 7 mm. The top left corner shows a mosaic of optical images taken with the integrated camera from the same region of interest, where dark lines correspond to the grain boundaries, large dark spots to air bubbles.*

It becomes evident that the icpTOF 2R clearly provides sufficient sensitivity to detect signals in low-concentration polar ice cores, with the unique added value of providing a complete glacio-chemical characterization from a single image. Regarding the future target of employing LA-ICP-MS imaging in deep samples of polar ice cores, ice grains are expected to be substantially larger than in the sample analyzed here, potentially several cm in diameter. This will introduce the need to enlarge the size of the images and analyzed sample areas accordingly. Even with a fast-washout, high-repetition rate laser ablation system, the recording of such large images is expected to require a substantial amount of time (i.e., hours), and thus millions of fired laser shots. If more than a few impurity species are the target, analysis with a LA-ICP-QMS system would require several replicate runs of the same region of interest. Evidently such an approach has strong limitations with regards to practicality and feasibility. Eliminating these restrictions makes the icpTOF the natural partner of fast-washout, high-repetition rate laser ablation systems to

truly capitalize on LA-ICP-MS imaging in the next-generation of ice core analyses.

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References

[1] Bohleber, P., Roman, M., Šala, M., Delmonte, B., Stenni, B. and Barbante, C., 2021. Two-dimensional impurity imaging in deep Antarctic ice cores: Snapshots of three climatic periods and implications for high-resolution signal interpretation. The Cryosphere, 15(7), pp.3523-3538.

[2] Bohleber, P., Roman, M., Šala, M. and Barbante, C., 2020. Imaging the impurity distribution in glacier ice cores with LA-ICP-MS. Journal of Analytical Atomic Spectrometry, 35(10), pp.2204-2212.

[3] Bussweiler, Y., Borovinskaya, O. and Tanner, M., 2017. Laser Ablation and inductively coupled plasma-time-of-flight mass spectrometry—A powerful combination for high-speed multielemental imaging on the micrometer scale. Spectroscopy, 32(5), pp.14-20.