Exploration of elemental details of single mineral dust particles in the EPICA Dome C ice core during interglacial and glacial periods

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Motivation

- The single particle inductively coupled plasma time-of-flight mass spectrometer (sp-ICP-TOFMS, model: icpTOF R from TOFWERK, Switzerland) coupled to the Bern continuous flow analysis (CFA) has demonstrated its ability to resolve signals of individual insoluble particles in the meltwater. This offers valuable insights into the characteristics of mineral dust obtained from the elemental composition of the mineral dust as - in contrast to bulk analyses - it allows deciphering of the complete elemental range of particle composition, which can be a mixture of different minerals (Erhardt et al. 2019).
- Applying this novel technique for the first time to sections of an Antarctic ice core spanning several glacial and interglacial stages, we conducted aerosol chemical CFA measurements on a selection of 18 Antarctic EPICA Dome C (EDC) 55 cm ice core sections, covering both glacial and interglacial periods over the last 800 kyr, using CFA-sp-ICP-TOFMS.
- Through this study, we aim to enhance the understanding of high-resolution elemental analysis with CFA-ICP-TOFMS and its application to ice core samples, which exhibit diverse conditions such as dust contents, ice grain size, and depth.

How we measured

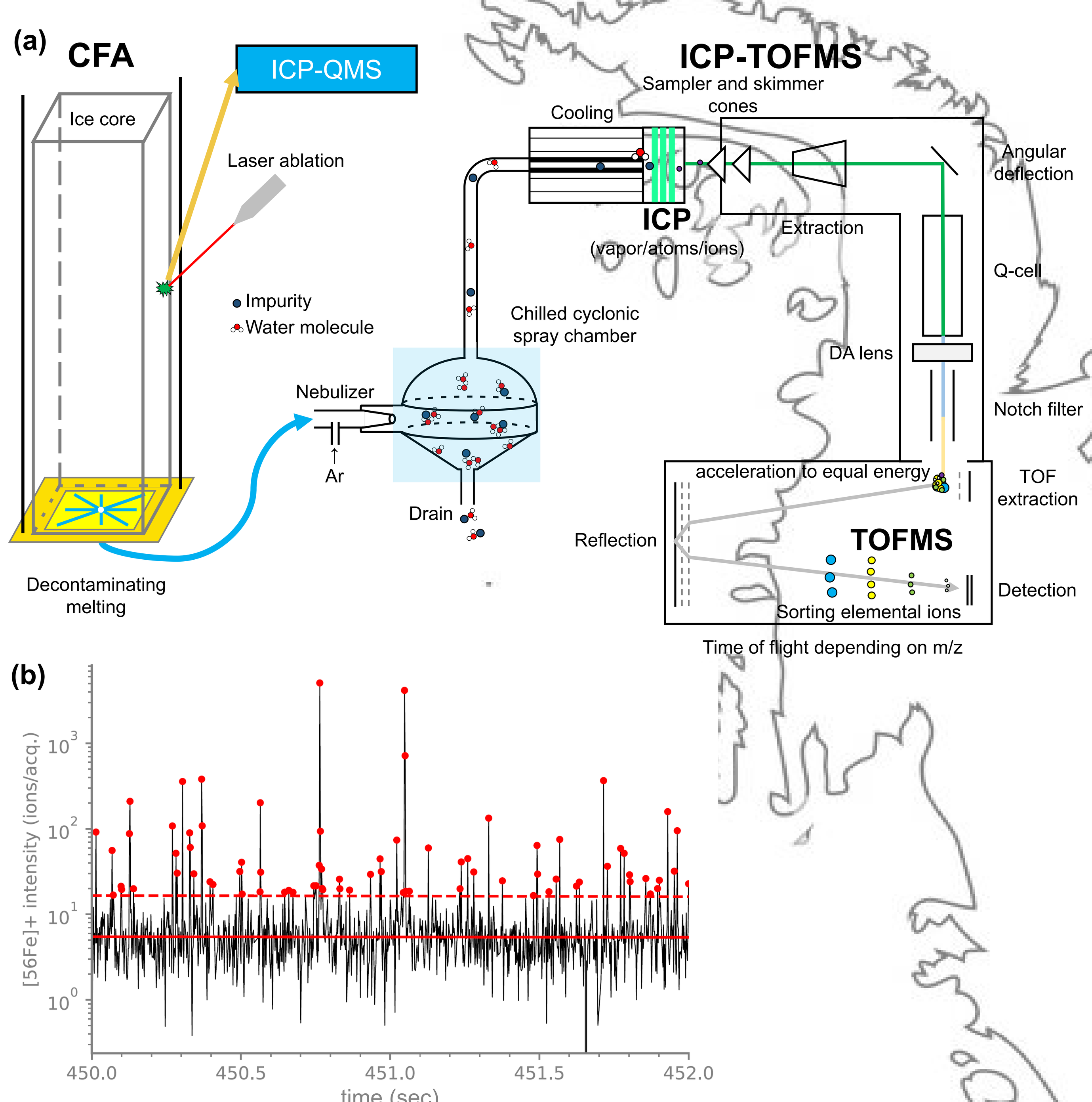

Figure 1. (a) a schematic diagram of sp–ICP–TOFMS (icpTOF R, TOFWERK AG, Switzerland) coupled to Bern CFA. The collaboration using laser ablation–ICP–Quadrupole MS is also illustrated above. **(b)** an example of 56 Fe ion data acquisition of 2 seconds and its single particle identification (Erhardt et al. 2019). The solid line shows the inferred dissolved background and the dashed line shows the threshold over which a signal is defined to be from an ionized particle. Particle signals are marked with red dots.

- The ice core samples of the selected sections were slowly melted on a gold-coated melthead, and their decontaminated inner meltwater samples were continuously supplied to the ICP-TOFMS system (Fig. 1a). The time-of-flight of elemental ions in the TOFMS was translated into their mass, ranging from 23 Na to 238 U.
- The high-resolution data acquisition time of 1.5 ms of TOFMS enabled the capture of spiky signals from analyte ions atop their dissolved background signals (Fig. 1b). Particle-originated ion signals were identified from the continuous data acquisition using a threshold defined by the compound Poisson distribution of signal intensities..

What we measured

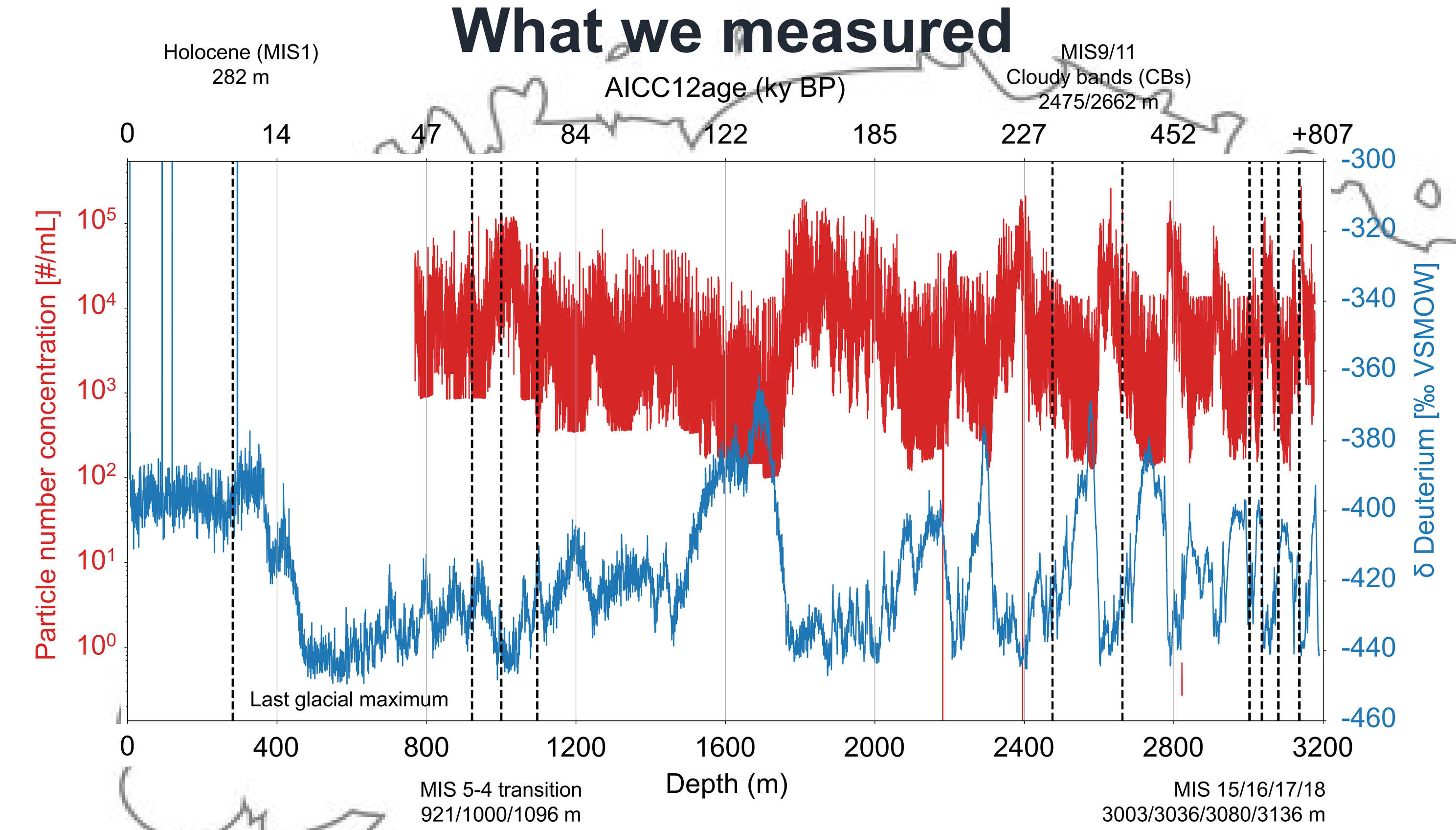

Figure 2. Particle number concentration (red) and δ deuterium (blue) profiles of EDC ice by depth and age (adapted from Lambert et al., 2008; Jouzel et al. 2007). Vertical dotted lines denote the 10 selected ice core sections for this study.

- Ten different ice periods covering various depths, dust contents, and ice grain sizes over the last glacial and interglacial periods were selected. These factors play a crucial role in analyzing impurities in ice cores and interpreting their results

Results and discussion

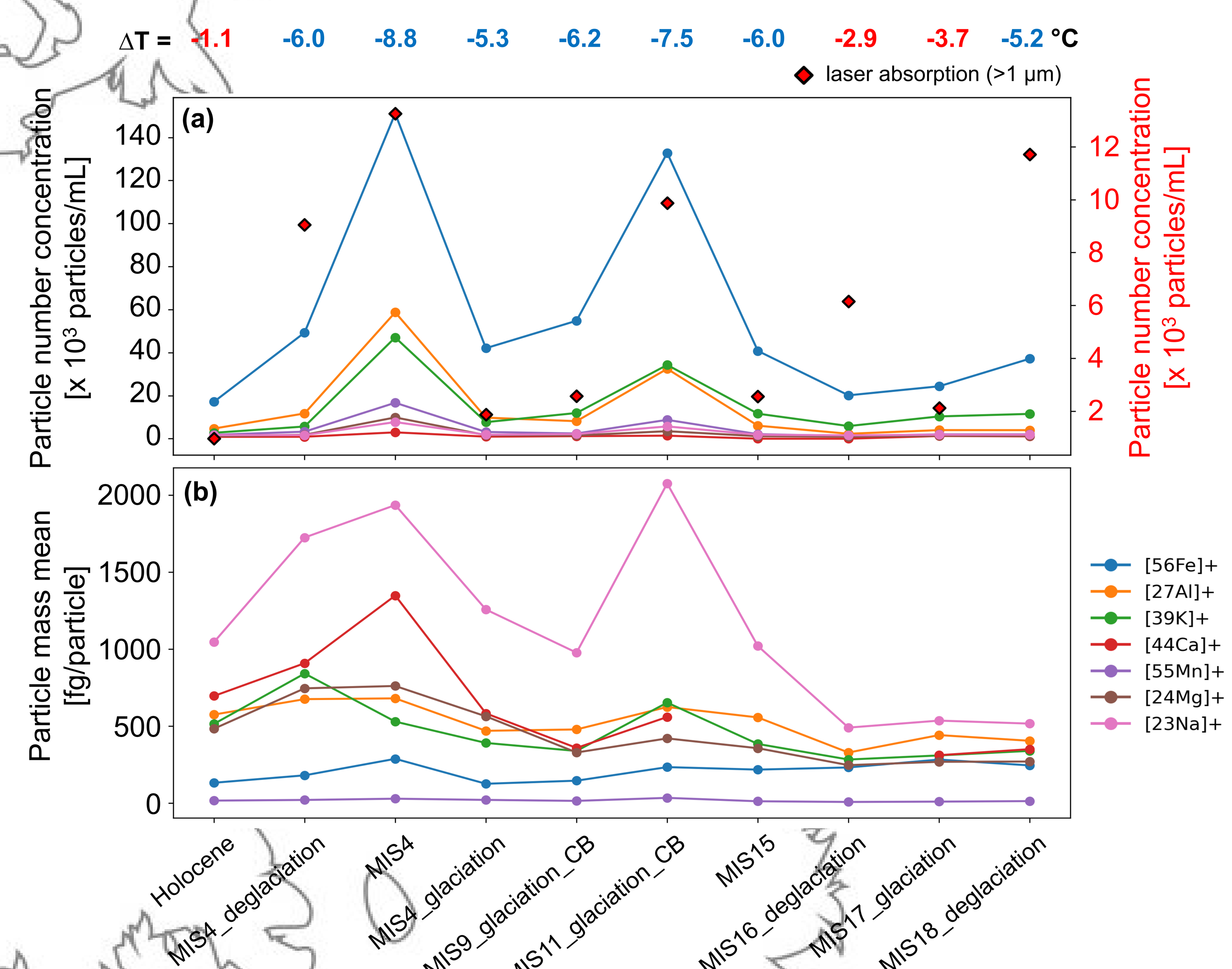

Figure 3. (a) element-bearing particle number concentration (PNC) from sp-ICP-TOFMS and dust PNC from a laser absorption particle sensor (Abakus from Klotz, Germany) and (b) particle mass mean of the detected element-bearing particles over the selected sections of ice. The relative temperature difference compared to the average of the last 1000 years (Jouzel et al. 2007) are shown on the top. The temperature differences colder than -5 °C are indicated in blue, and red for the others.

- The particle number concentrations (PNCs) for all elements and the optically measured PNC showed a strong negative correlation with temperature, indicating a common major source of mineral dust.
- However, a noticeable disparity emerges between the element-bearing particulate number concentration (PNC) and the optically measured PNC within the deep ice core sections. This disparity may stem from a combination of factors, including dust aggregation within the deep ice layers (Lambert et al. 2008) and the divergent size ranges analyzed by the two methods: >1 µm for the laser absorption sensor and a few tens of nm for sp-ICP-TOFMS
- The particle mass mean exhibited a decreasing trend over depth for most elements, except for Fe. This trend may result from englacial acidic oxidative weathering and aggregation of dust (Baccolo et al. 2021).

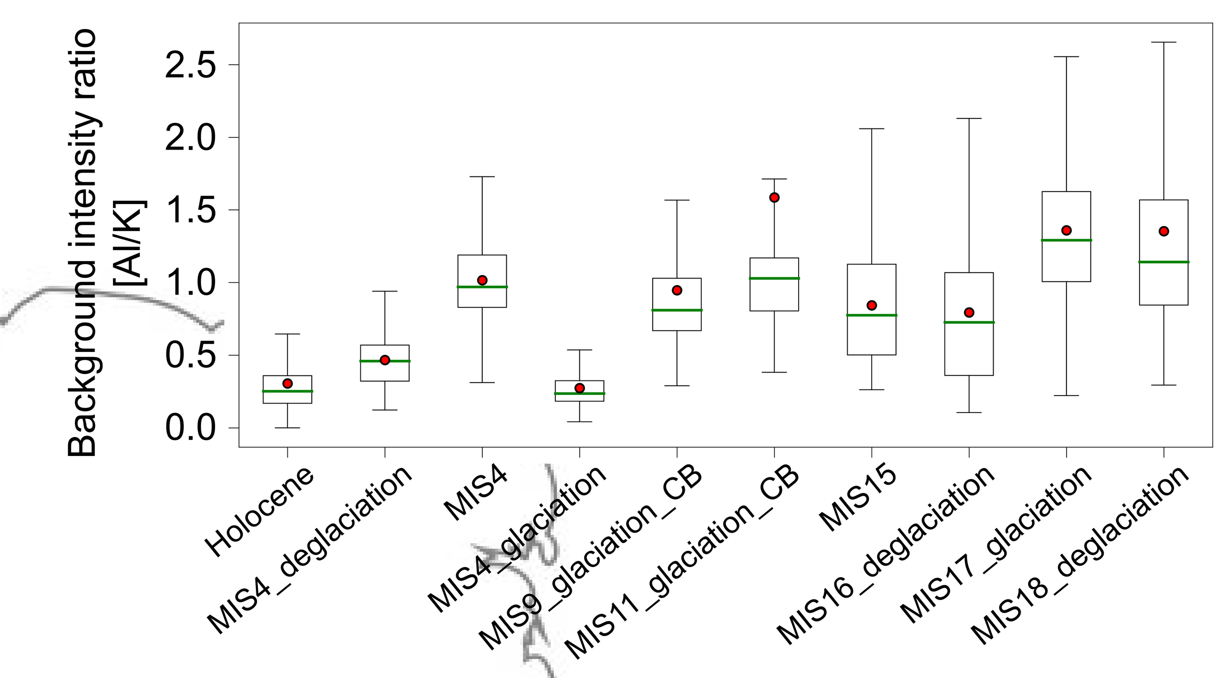

Figure 4. Background intensity ratio distribution of Al to K across selected ice core sections. The average elemental background intensities are highlighted with red dots.

- The background intensity ratio of Al to K exhibits an increasing trend with depth, potentially as a result of post-depositional processes. This upward trend could be attributed to the depletion of the dominant Al-bearing mineral, hornblende, in the deep ice (Fig. 5, Baccolo et al., 2021).

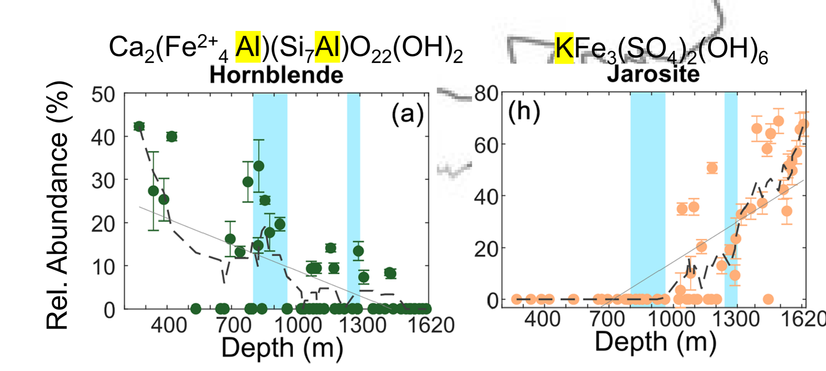

Figure 5. Relative abundance of Al-bearing hornblende and K-bearing jarosite in Talos Dome ice core (Baccolo et al., 2021)

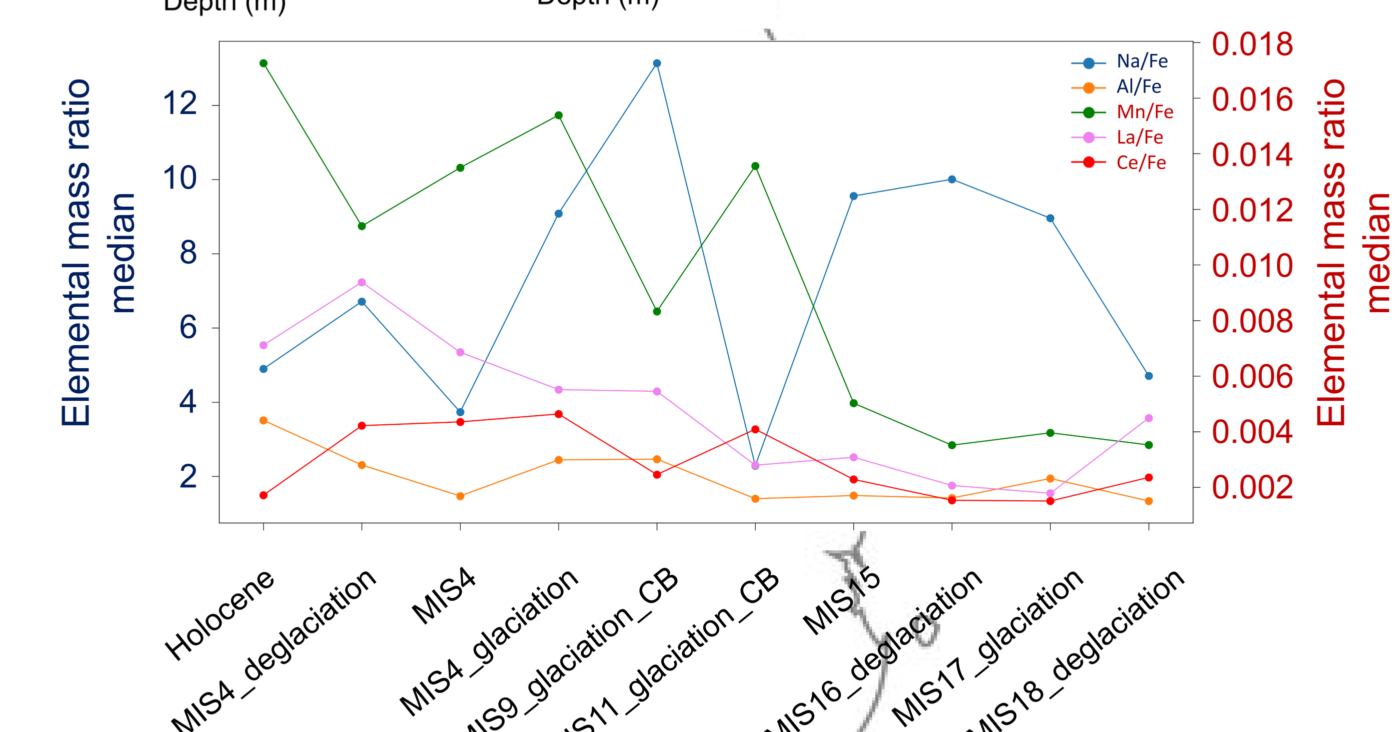

Figure 6. Median elemental mass ratios based on Fe of the detected particles for the selected periods. Ratios with La and Ce as a numerator are plotted on the right y-axis in red.

- The downward trend in the ratios of Al, Mn, La and Ce to Fe with depth may indicate the influence of post-depositional processes such as varying dissolution rates of elements due to acidic weathering. Additionally, atop this relatively consistent trend, the elemental ratios appear to be influenced by the sources of mineral dust.

EPICA Dome C

Conclusion and outlook

- CFA-sp-ICP-TOFMS provides crucial access to the elemental composition of individual particles, enabling the geochemical characterization of dust impurities beyond the optically measured total dust PNC.
- Deep consideration of post-depositional processes, such as acidic oxidative weathering in Antarctic ice, is essential to avoid misinterpretation in analyzing both insoluble and soluble impurities within deep ice.
- The multi-dimensionality of CFA-sp-ICP-TOFMS offers significant advantages in investigating post-depositional processes by analyzing the elemental composition of mineral dust alongside their background elemental concentrations.
- To enhance confidence in impurity analysis within ice cores, additional analytics such as optical spectroscopy techniques should be employed, and impurities should be investigated from multiple perspectives.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 955750

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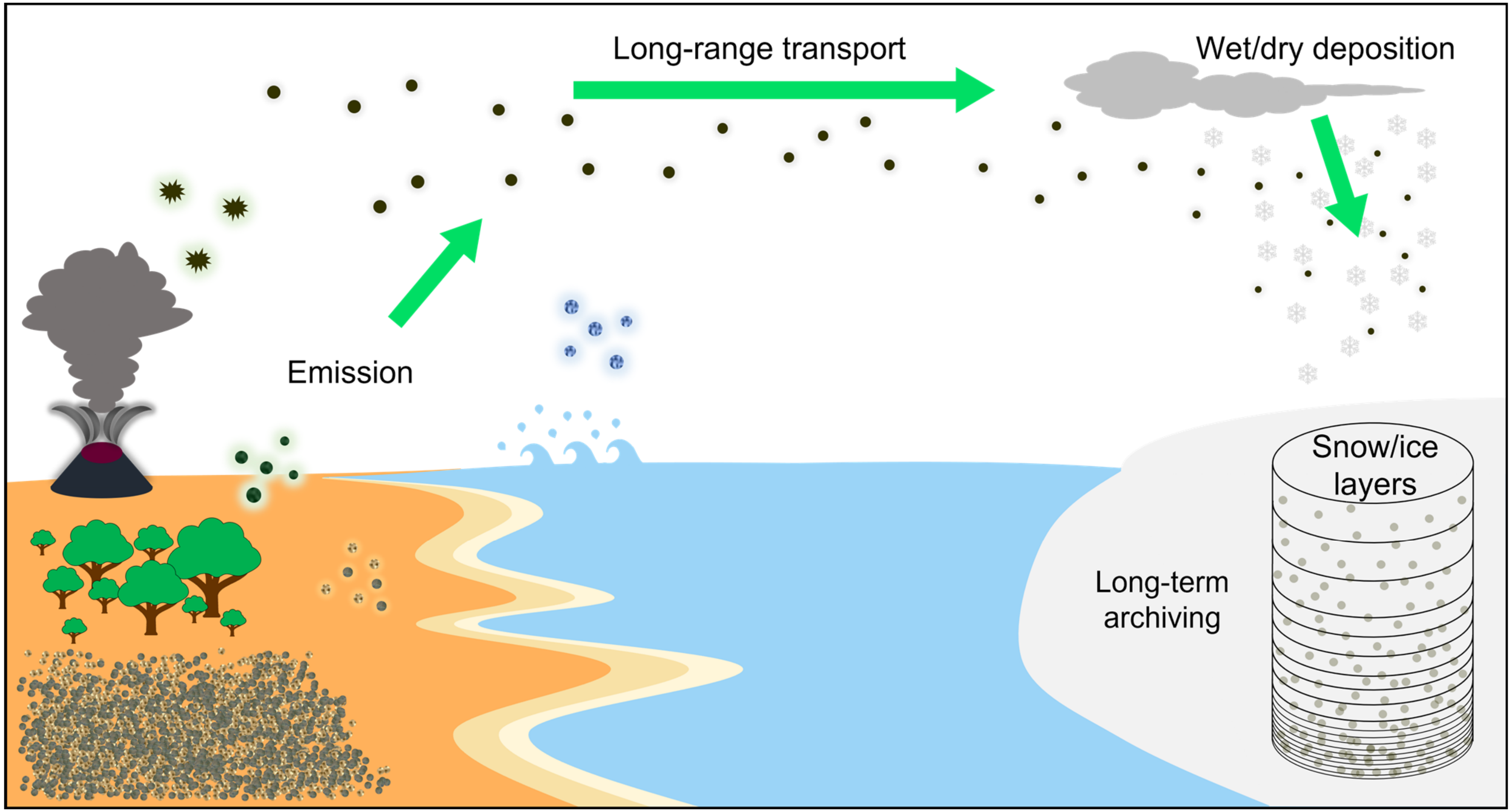
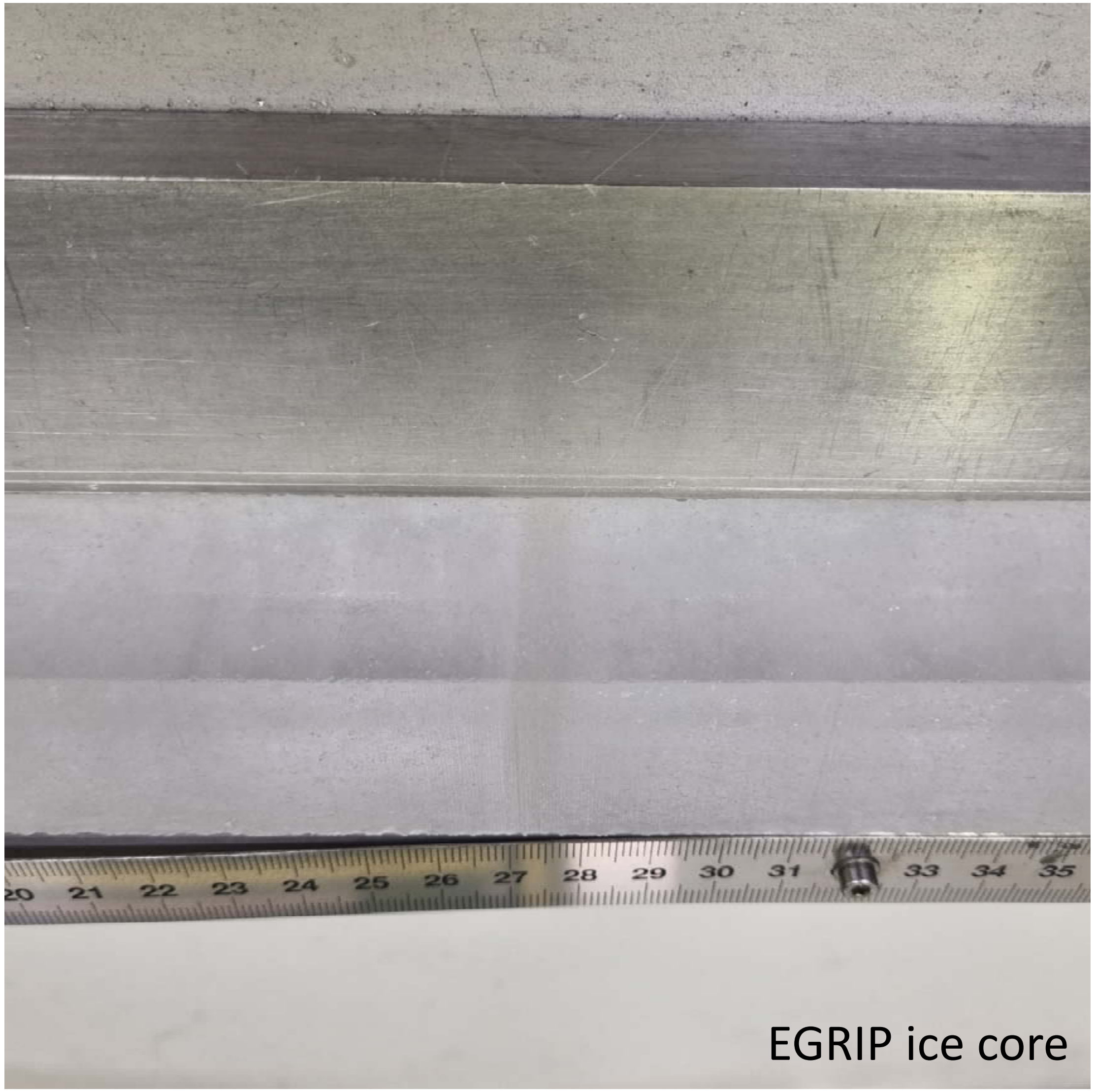
Supplementary 0. Emission, transport, and deposition of aerosols

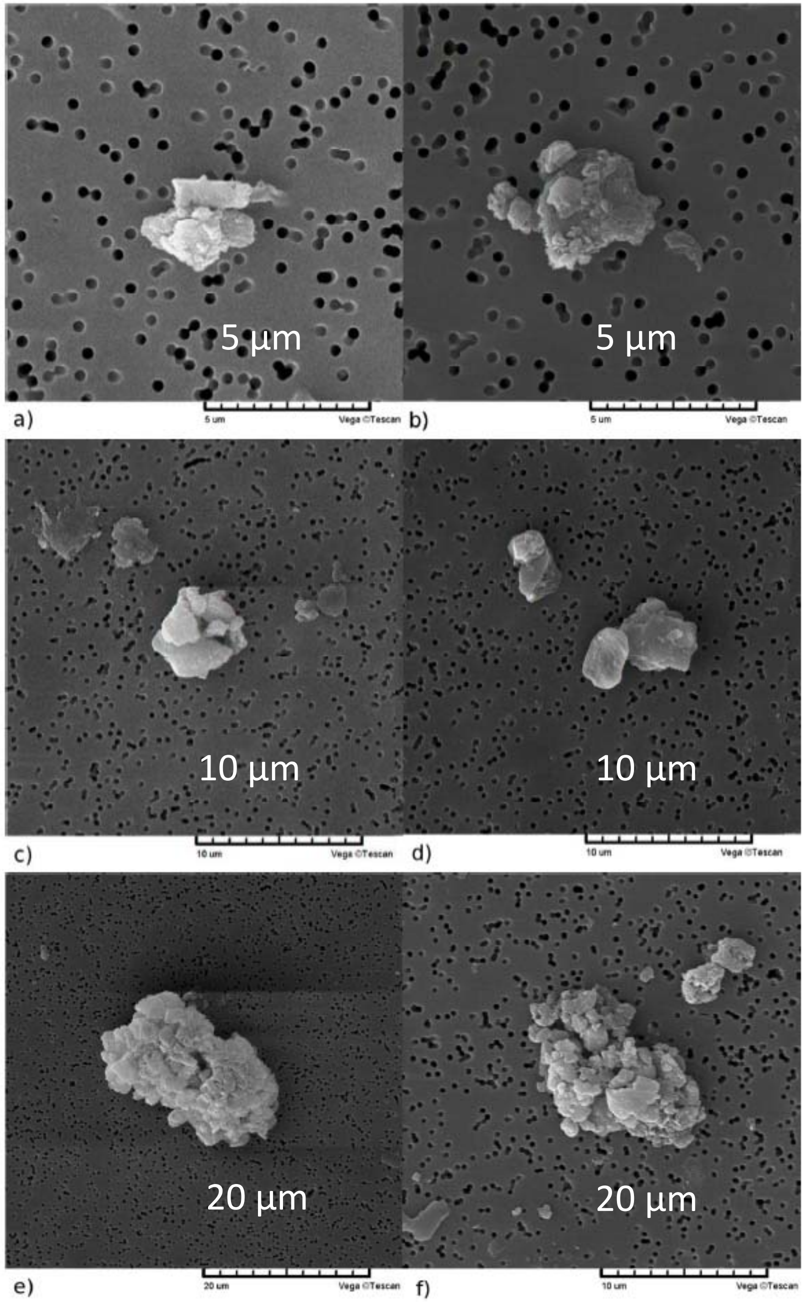


Supplementary 1. Dust layer in polar ice core



Supplementary 2. Dust aggregates in deep EDC ice

SEM images of aggregates in EDC deep ice



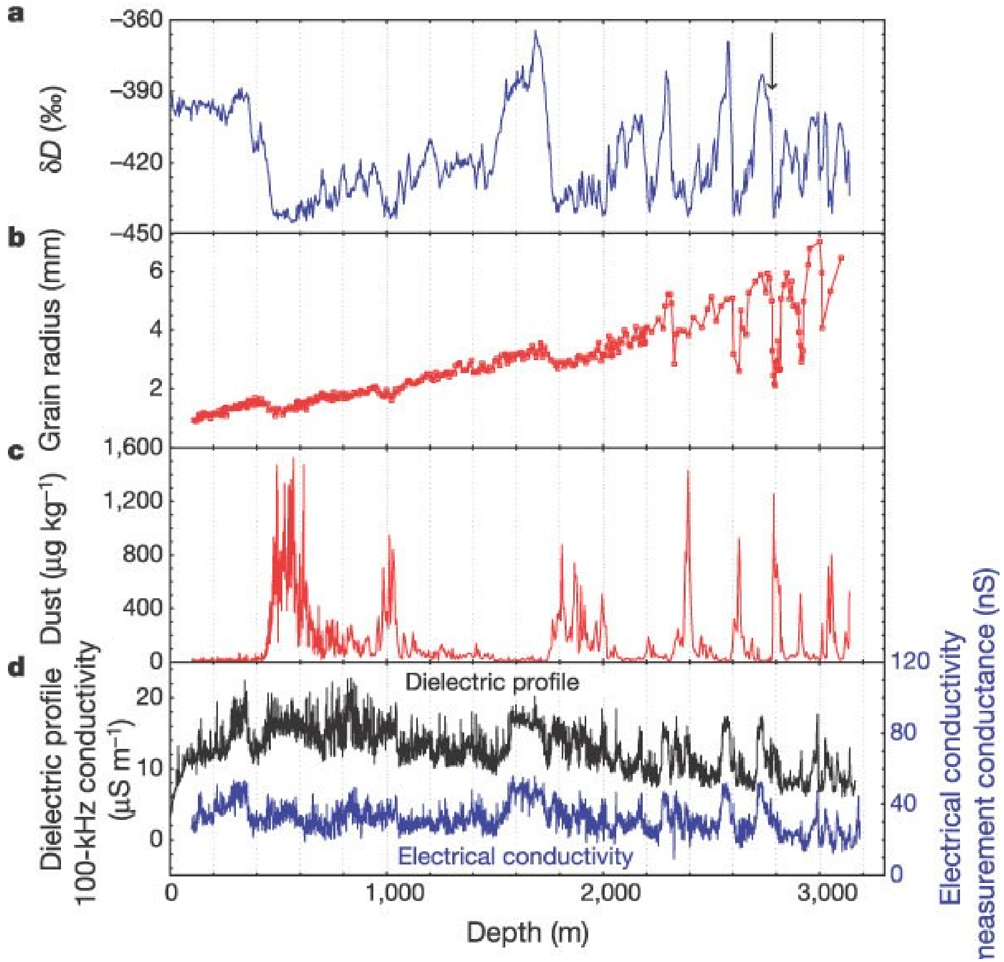
EDC 5768
3171.85 m depth

EDC 5316
2923.25 m depth

EDC 5534
3043.15 m depth

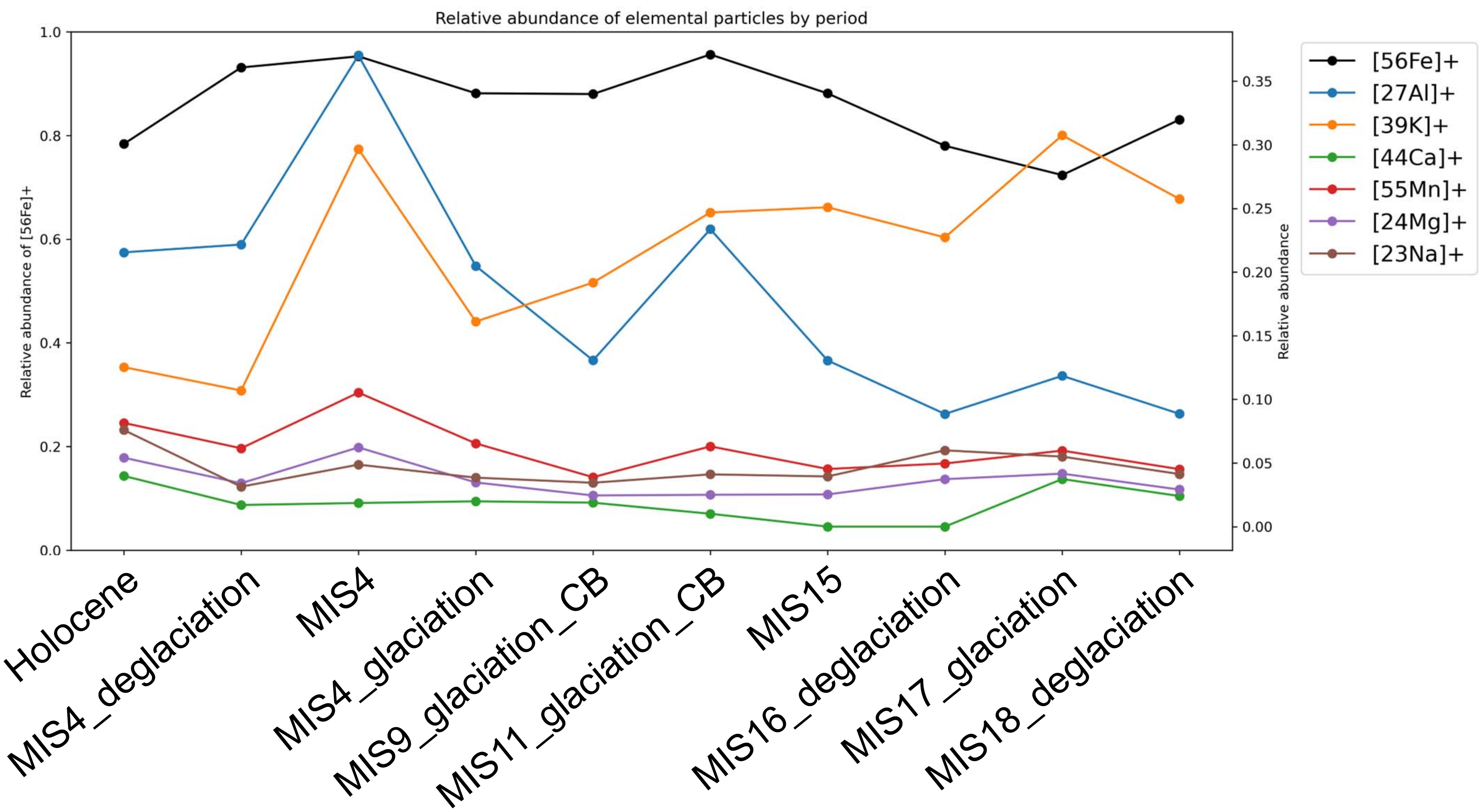
M.A.C. Potenza et al.(2017)

Supplementary 3. Ice grain size



EPICA community members. Eight glacial cycles from an Antarctic ice core. *Nature* **429**, 623–628 (2004). https://doi.org/10.1038/nature02599

Supplementary 4. Relative abundance of element-bearing particle number



Supplementary 5. Theoretical lognormal size distributions of aerosols particles

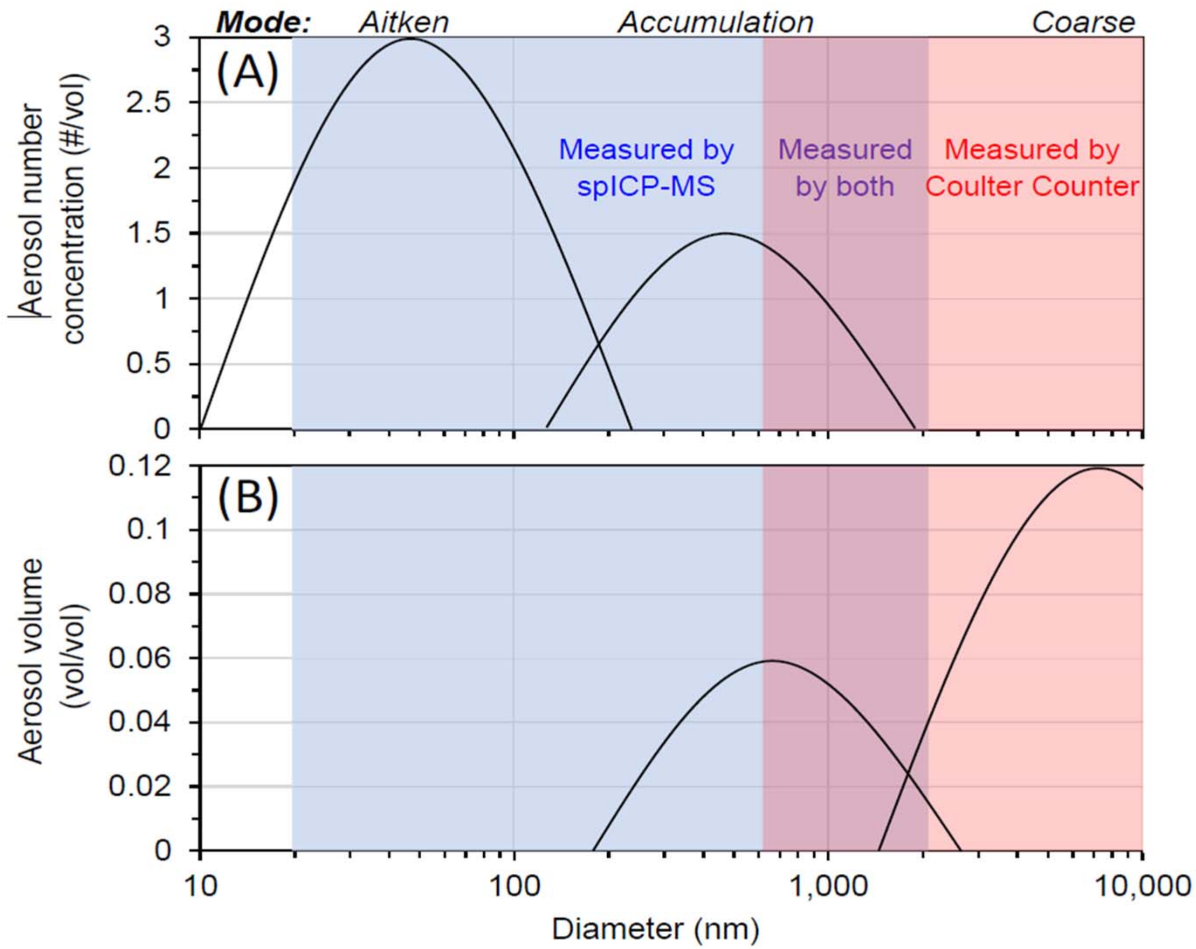


Figure 1: Theoretical lognormal size distributions of aerosol particles measured by spICP-MS displayed as **(A)** a function of number concentration and **(B)** volume/mass. Figure adapted from Seinfeld and Pandis 2006.

Madeleine Lomax-Vogt et al., PAGES science highlights 2023