cambridge.org/aog

The new frontier of microstructural impurity research in polar ice

Nicolas Stoll[1,2,3] (iD), Pascal Bohleber[1] (iD), Remi Dallmayr[2] (iD), Frank Wilhelms[2,4] (iD), Carlo Barbante[1,5] (iD) and Ilka Weikusat[2,6] (iD)

[1]Department of Environmental Sciences, Informatics and Statistics, Ca'Foscari University Venice, Venice, Italy; [2]Glaciology, Department of Geosciences, Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany; [3]Department of Geosciences, University of Bremen, Bremen, Germany; [4]Department of Crystallography, Geoscience Centre, University of Göttingen, Göttingen, Germany; [5]Institute of Polar Sciences, CNR, Venice, Italy and [6]Department of Geosciences, Eberhard Karls University, Tübingen, Germany

Abstract

Deciphering the localisation of solid and dissolved impurities on the micron-scale in glacial ice remains a challenge, but is critical to understand the integrity of ice core records and internal deformation. Here we report on the state-of-the-art in microstructural impurity research by highlighting recent progress in bringing together cryo-Raman spectroscopy and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). We show the potential of both methods and discuss possibilities to improve inter-method approaches aiming for a more holistic understanding of the evolution of impurity localisation throughout the ice column, including post-depositional processes. In this framework, we elaborate on future research priorities such as LA-ICP-MS imaging on firn samples and integrating a large cryo-cell with imaging capabilities.

1. Introduction

As an inherently interdisciplinary field, ice core science has frontiers with several neighbouring research areas, ranging from palaeoclimate studies (e.g. EPICA Community Members, 2004) to material science, e.g. ice deformation, (e.g. Weikusat and others, 2017a) and documenting the human impact on the environment (e.g. McConnell and others, 2022). Ice cores are pivotal to improve our understanding of key features in our climate history, such as the mechanisms behind the mid-Pleistocene transition. This new objective of the ice core community requires the recovery of a 1.5 million-year-old continuous ice core record from Antarctica (e.g. Fischer and others, 2013), making it the prime target of newly emerging international drilling projects, such as the 'Beyond EPICA Oldest Ice' project. However, even if an ice core of such age is obtained, a new level of detail not only in analysis but also process understanding is needed in order to succeed with the Oldest Ice quest. This particularly concerns the investigation of chemical impurities, which make up an important part of the climatic record but are also known to be affected by a number of post-depositional processes that can challenge the preservation of the original climatic signals (Faria and others, 2010). Measurements of the bulk impurity content of ice meltwater using continuous flow analysis (CFA) (e.g. Röthlisberger and others, 2000; McConnell and others, 2002) are a cornerstone to investigating impurity records in today's ice core research. However, melting techniques cannot study in great detail the localisation of solid and dissolved impurities in the (solid) ice matrix. Here, methods analysing solid impurities can provide a more holistic understanding of ice–impurity interactions. A recent example is the investigation of chemical alterations to mineral dust particles in deep ice (Baccolo and others, 2021). On the microstructural scale, post-depositional interactions encompass (1) the impact of impurities on grain growth and ice deformation via Zener pining and the drag of grain boundaries, (2) the dislocation of impurities via grain growth and diffusion, and (3) clustering and chemical reactions of dust particles. A comprehensive investigation of the evolution and preservation of the climate signal with depth in ice cores requires also understanding the original signal formation at the surface and its passing on through the snow-firn column, which adds further to the complexity of this task (Fig. 1). Hence, microstructural impurity research remains a great challenge, not least calling for analysing solid ice with sophisticated analytical methods (Stoll and others, 2021b).

Stoll and others (2021b) provide an in-depth overview of the developments over the last decades regarding microstructural impurity research. Here we aim to present a synthesised update by reporting on the ongoing efforts of two state-of-the-art methods that have individually shown significant potential for studying impurity localisation and ice–impurity interactions in the last years. We highlight the future potential of a multi-method approach particularly for understanding a future 'Oldest Ice' impurity record.

2. Two examples of state-of-the-art methods in investigating impurity localisation

Recent technological and methodological progress in e.g., cryo-Raman spectroscopy (Eichler and others, 2019; Stoll and others, 2021a, 2022; Kawakami and others, 2023; Stoll and others,
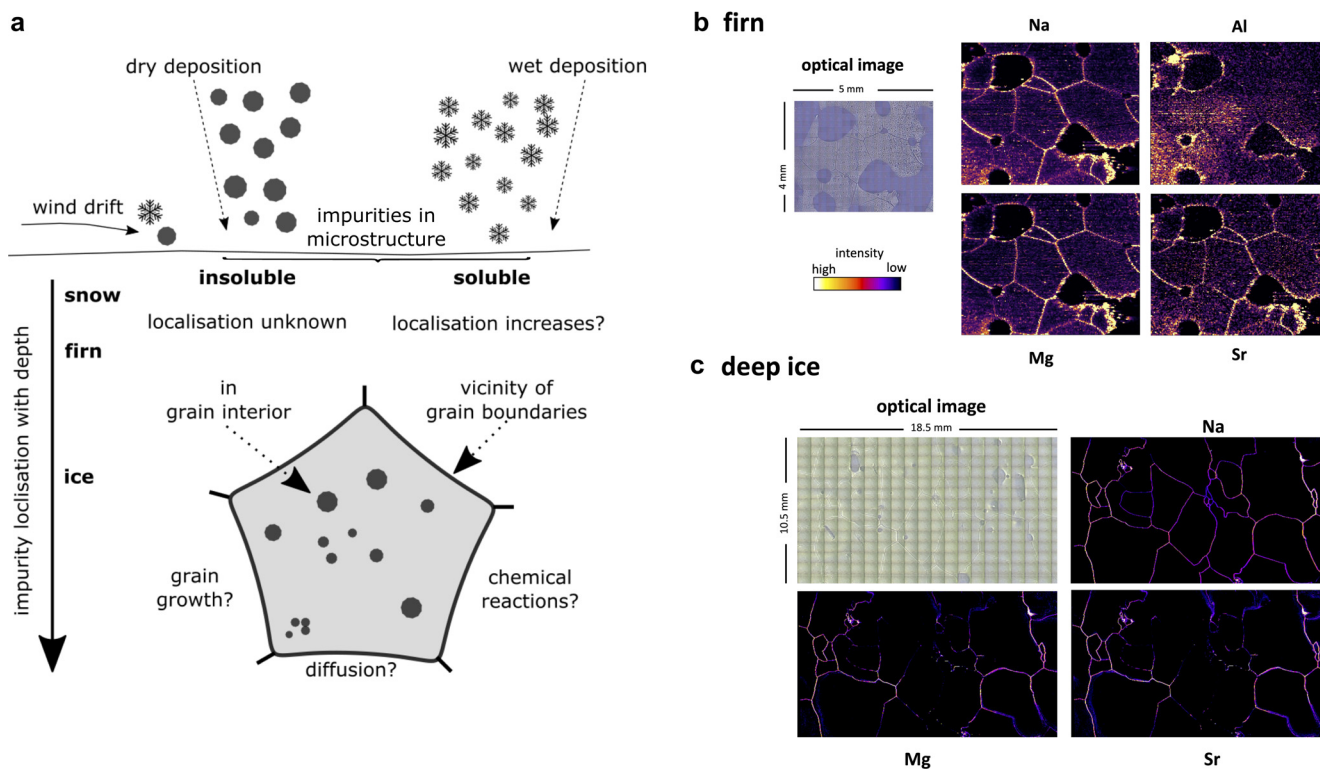
Figure 1. Localisation of impurities in the microstructure of firn and ice. (a) Simplified schemata of impurity deposition on the ice sheet, their localisation with depth and three impacted processes within the ice. (b) LA-ICP-MS 2D imaging of Na, Al, Mg and Sr with a resolution of 20 μm in NEEM S1 firn from a depth of 46.9 m. (c) LA-ICP-MS 2D imaging of Na, Mg and Sr with a resolution of 35 μm in Antarctic ice from a depth of 1700.5 m (Bohleber and others, 2021c).

2023) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Bohleber and others, 2020, 2021c) opened up new pathways in deciphering the localisation of impurities in ice. We briefly summarise the latest developments and perspectives for combining these methods in the future and ongoing research efforts.

2.1. Cryo-Raman spectroscopy and micro-inclusions

Non-destructive cryo-Raman spectroscopy (e.g. Fukazawa and others, 1997) is an established method to investigate solid impurities in the ice microstructure, enabling new insights into the mineralogy and location of inclusions over the last two decades (e.g. Ohno and others, 2005; Eichler and others, 2019; Kawakami and others, 2023) (for details see Stoll and others (2021b). Stoll and others (2021a) investigated the microstructural location of more than 5700 solid inclusion inside, i.e. 500 um below the surface, 10 solid ice samples from the upper 1340 m of the East Greenland Ice Core Project (EGRIP) ice core. This covered the Holocene, Younger Dryas and Bølling Allerød and revealed that most micro-inclusions are located in the grain interior rather than in the vicinity of grain boundaries. Furthermore, the spatial variability of micro-inclusions is high and localisation patterns range from solitary inclusions to clusters and thick layers.

In a companion study, Stoll and others (2022) identified the mineralogy of almost 800 of the previously located micro-inclusions. Inclusions are mainly composed of dust (quartz, mica, feldspar) and sulphate minerals (gypsum, Na- or Mg-sulphates, bloedite). The upper 900 m exhibit a variety of different (sulphate) minerals while below, mineral diversity decreases, and gypsum is the only relevant sulphate mineral. Both studies and ongoing work show the high complexity of the localisation of solid inclusions in ice and how their chemical composition plays a, not yet well understood, role.

2.2. LA-ICP-MS for 2D impurity imaging

As a micro-destructive technique, LA-ICP-MS has already been established for delivering impurity records at micron-resolution by ablating individual lines along the main core axis (e.g. Della Lunga and others, 2017; Spaulding and others, 2017). Additional important merit comes from introducing state-of-the-art imaging techniques which allow to map the distribution of impurities in the ice matrix (Bohleber and others, 2020). This approach has already revealed a high degree of localisation at grain boundaries for mostly soluble elements like Na, as studied in samples of Antarctic ice cores (Bohleber and others, 2021c). Bohleber and others (2023) extend the analysis to mostly insoluble elements like Al, which reveals clusters of dust particles in an EGRIP sample from the Younger Dryas period. The same sample had already been analysed by cryo-Raman spectroscopy, thereby permitting exploration first pathways in bringing together these two methods.

2.3. Challenges and lessons learned in a multi-method approach

Although still in an early phase, the benefit of the simultaneous investigation of ice samples by both techniques, cryo-Raman and LA-ICP-MS imaging, becomes especially meritful when targeting the co-analysis of (i) the localisation of impurities and (ii) the geochemical investigation of mostly insoluble materials such as dust and micro-inclusions.

With optical information that permits the identification of individual ice crystals (grains), it is possible to quantify the relative amount of impurities located at grain boundaries, both for insoluble impurities in cryo-Raman analysis and for the total impurity amount in LA-ICP-MS 2D imaging. In an EGRIP sample from the Younger Dryas, both methods found a similar average amount of impurities located at grain boundaries (up to 40%) (Bohleber and others, 2023). Regarding the geochemical

investigation of insoluble material, a direct comparison of individual dust particles is hampered by methodological differences: For LA-ICP-MS, measurements are conducted on a freshly decontaminated surface layer, while cryo-Raman analysis is performed below the surface. Certainly, it is not possible to derive the presence of a mineral purely from LA-ICP-MS data. However, a statistical approach can compare the average composition of detected particles. Especially useful in this regard is a pixel-based classifications of the LA-ICP-MS multi-elemental maps, such as 'Si without Al' and 'Fe without Al' (Bohleber and others, 2023). Here, the former would correspond with the occurrence of quartz (SiO_2) while the latter may indicate minerals such as hematite (Fe_2O_3) or jacobsite ($MnFe_2O_4$). Jacobsite can be additionally distinguished by measuring Mn, which is accessible to LA-ICP-MS imaging (Bohleber and others, 2020). Determining the relative fraction of pixels showing Si or Fe only versus pixels showing either Al or Si (or Fe, respectively) offers a possible indicator of the relative abundance of these minerals according to the LA-ICP-MS maps. This statistical value can then be compared to geological feasibility and to the findings of cryo-Raman analysis in the same area (Bohleber and others, 2023).

3. Future research priorities towards a holistic approach in microstructure impurity research

Covering a broad spectrum of elements is crucial for the simultaneous geochemical characterisation of insoluble material, e.g. using Si, Al, Mn and Fe to distinguish iron-bearing minerals from quartz. However, with a sequential-scanning mass analyser, the LA-ICP-MS imaging technique is typically limited to a handful of analytes per map. Overcoming this limitation becomes possible with a time-of-flight mass spectrometer (TOFMS), which offers in principle the simultaneous acquisition of a full mass spectrum of solid and dissolved impurities. The feasibility of this type of analysis has been demonstrated in a recent pilot study (Bohleber and others, 2021b).

Both the geochemical characterisation and the localisation of impurities at grain boundaries are in principle built on a statistical approach. Hence, this type of comparison still suffers at present from the rather limited physical size of the LA-ICP-MS maps and the comparatively small sample population size of minerals identified by cryo-Raman analysis. Most cryo-cells are limited to small sample sizes (around 10×10 cm). So far, only one instrument worldwide features the possibility to house 100 cm long ice cores for 1D impurity profiling by LA-ICP-MS (Sneed and others, 2015). Integrating imaging capabilities into a chamber for 50–100 cm long samples will enable a fast 2D analysis, and thus overview, of impurity content and localisation in entire ice core segments.

Despite increasing data, cryo-Raman spectroscopy only delivers glimpses into a few dozen solid inclusions. Time-consuming manual work is needed to find inclusions and to focus the laser on them, followed by identifying the measured spectra semi-manually. Developing and applying more automated routines, for the measurements and the identification, would be a big step forward by saving researchers time while increasing the number of performed measurements per sample. To enable this, technical improvement is needed to allow the automated spotting of micron-size particles within the ice matrix. Fluorescence hampers the identification of dozens of inclusions (e.g. Stoll and others, 2022, 2023) and is related to the laser wavelength. Switching between lasers with different wavelengths (e.g. between visible and infrared) could thus help increase the number of identifiable minerals by decreasing the number of unidentifiable spectra due to strong fluorescence. In this context, the development of automated data routines appears to be a shared frontier among both methods, cryo-Raman and LA-ICP-MS imaging. This particularly concerns taking advantage

of modern techniques in computer vision and machine learning, which may yield similar revolutions in data analysis as they have already been introduced to other fields (Bohleber and others, 2021a). As both methods are micro-destructive and laser-based, a combined integration in a single setup could be envisaged for the future. This could open up particularly intriguing semi-automated applications, first using 2D imaging by LA-ICP-MS to detect the localisation of insoluble material and then directing the cryo-Raman analysis to the respective spots for further complementary investigation of a restricted number of solid inclusions. Furthermore, an integration of both methods could solve existing methodological limitations, such as the inability of Raman spectroscopy to identify the, in polar regions abundant, compound NaCl due to its Raman-inactivity. In particular, the origin of the observed localisation of soluble impurities like Na at grain boundaries remains to be fully clarified.

In this context, imaging the impurity distribution also in firn is important to determine the initial state of the impurity distribution before further evolution in the ice. This could also help to determine the initial distribution to study post-depositional processes, such as diffusion, grain growth and pore close-off. In a recent pilot study analysing samples of NEEM S1 firn, first maps of firn were obtained from a depth of 46.9 m (Fig. 1b), with a spot size of $20\,\mu$m, fluence 3.5 J cm^{-2}, dosage 9 and 300 Hz repetition rate. We found that there are special challenges in obtaining good data from firn, such as the comparatively strong sublimation of the samples under the helium atmosphere in the LA-ICP-MS ablation chamber. Yet, the obtained maps demonstrate that the investigation of firn by 2D chemical imaging is a promising new approach. The images show that not all grain boundaries are fully populated by impurities and also reveal higher impurity content at the interface with air bubbles (Fig. 1b). Similar to findings in ice (Fig. 1c), Al shows little to no association with grain boundaries. Data are still too scarce to discuss in detail any involved processes. Considering what is found in maps obtained at greater depth in Greenland and Antarctic ice suggests that the impurity localisation of soluble impurities like Na develops gradually, but that the involved process starts already in the firn.

A promising next step in this framework is to implement this new observational data into model efforts to simulate the displacement of impurities by various processes. First and foremost this concerns displacement by grain growth but, especially for deeper ice, also diffusion of dissolved impurities in ice cores, which was recently revisited with modelling (Ng, 2021). A next-generation setup combining cryo-Raman and LA-ICP-MS imaging with a large cryo-cell may deliver large (10 cm × 10 cm) images and complementary cryo-Raman mineral characterisation. By this means, new detail at investigating impurity localisation at defined intervals throughout one ice core may get into reach. Models and statistical analysis might serve for scaling up results from specific samples, in order to eventually investigate the evolution of the climatic signal and its preservation against post-depositional processes on the scale of entire ice cores or even ice sheets.

References

Baccolo G and 9 others (2021) Deep ice as a geochemical reactor: insights from iron speciation and mineralogy of dust in the Talos Dome ice core

(East Antarctica). *The Cryosphere* **15**(10), 4807–4822. doi:10.5194/tc-15-4807-2021

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), 2204–2212. doi:10.1039/D0JA00170H

Bohleber P and 5 others (2021a) Ice core science meets computer vision: challenges and perspectives. *Frontiers in Computer Science* **3**, 1–9. doi:10.3389/fcomp.2021.690276

Bohleber P, Roman M, Stoll N, Bussweiler Y and Rittner M (2021b) Imaging the distribution of elements in antarctic ice cores with LA-ICP- TOFMS. *TOFWERK Application Note*.

Bohleber P and 5 others (2021c) 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), 3523–3538. doi:10.5194/tc-15-3523-2021

Bohleber P and 5 others (2023) Geochemical characterization of insoluble particle clusters in ice cores using two-dimensional impurity imaging. *Geochemistry, Geophysics, Geosystems* **24**(2), e2022GC010595. doi:10.1029/2022GC010595

Della Lunga D, Müller W, Rasmussen SO, Svensson A and Vallelonga P (2017) Calibrated cryo-cell UV-LA-ICPMS elemental concentrations from the NGRIP ice core reveal abrupt, sub-annual variability in dust across the GI-21.2 interstadial period. *The Cryosphere* **11**(3), 1297–1309. doi:10.5194/tc-11-1297-2017

Eichler J and 11 others (2019) Impurity analysis and microstructure along the climatic transition from MIS 6 Into 5e in the EDML ice core using cryo-Raman microscopy. *Frontiers in Earth Science* **7**(20), 1–16. doi:10.3389/feart.2019.00020

EPICA Community Members (2004) Eight glacial cycles from an Antarctic ice core EPICA community members. *Nature* **429**(6992), 623–628.

Faria SH, Freitag J and Kipfstuhl S (2010) Polar ice structure and the integrity of ice-core paleoclimate records. *Quaternary Science Reviews* **29**(1–2), 338–351. doi:10.1016/j.quascirev.2009.10.016

Fischer H and 29 others (2013) Where to find 1.5 million yr old ice for the IPICS 'Oldest-Ice' ice core. *Climate of the Past* **9**(6), 2489–2505. doi:10.5194/cp-9-2489-2013

Fukazawa H, Suzuki D, Ikeda T, Mae S and Hondoh T (1997) Raman spectra of translational lattice vibrations in polar ice. *The Journal of Physical Chemistry B* **101**(32), 6184–6187. doi:10.1021/jp963161r

Kawakami K, Iizuka Y, Matoba S, Aoki T and Ando T (2023) Inclusions in ice layers formed by melting and refreezing processes in a Greenland ice core. *Journal of Glaciology* **69**(276), 790–802. doi:10.1017/jog.2022.101.

McConnell JR and 14 others (2021) Hemispheric black carbon increase after the 13th-century Māori arrival in New Zealand. *Nature* **598**(7879), 82–85. doi:10.1038/s41586-021-03858-9

McConnell JR, Lamorey GW, Lambert SW and Taylor KC (2002) Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry. *Environmental Science & Technology* **36**(1), 7–11. doi:10.1021/es011088z

Ng FSL (2021) Pervasive diffusion of climate signals recorded in ice-vein ionic impurities. *The Cryosphere* **15**(4), 1787–1810. doi:10.5194/tc-15-1787-2021

Ohno H, Igarashi M and Hondoh T (2005) Salt inclusions in polar ice core: location and chemical form of water-soluble impurities. *Earth and Planetary Science Letters* **232**(1–2), 171–178. doi:10.1016/j.epsl.2005.01.001

Röthlisberger R and 6 others (2000) Technique for continuous high-resolution analysis of trace substances in firn and ice cores. *Environmental Science and Technology* **34**(2), 338–342. doi:10.1021/es9907055

Sneed SB and 9 others (2015) New LA-ICP-MS cryocell and calibration technique for sub-millimeter analysis of ice cores. *Journal of Glaciology* **61**(226), 233–242. doi:10.3189/2015JoG14J139

Spaulding NE and 7 others (2017) A new multielement method for LA-ICP-MS data acquisition from glacier ice cores. *Environmental Science & Technology* **51**(22), 13282–13287. doi:10.1021/acs.est.7b03950

Stoll N and 5 others (2021a) Microstructure, micro-inclusions, and mineralogy along the EGRIP ice core – part 1: localisation of inclusions and deformation patterns. *The Cryosphere* **15**(12), 5717–5737. doi:10.5194/tc-15-5717-2021

Stoll N, Eichler J, Hörhold M, Shigeyama W and Weikusat I (2021b) A review of the microstructural location of impurities and their impacts on deformation. *Frontiers in Earth Science* **8**, 615613. doi: 10.3389/feart.2020.615613.

Stoll N and 5 others (2022) Microstructure, micro-inclusions, and mineralogy along the EGRIP (East Greenland Ice Core Project) ice core – Part 2: implications for palaeo-mineralogy. *The Cryosphere* **16**(2), 667–688. doi:10.5194/tc-16-667-2022

Stoll N and 6 others (2023) Chemical and visual characterisation of EGRIP glacial ice and cloudy bands within. *The Cryosphere* **17**, 2021–2043. doi:10.5194/tc-17-2021-2023.

Weikusat I and 10 others (2017) Physical analysis of an Antarctic ice core – towards an integration of micro- and macrodynamics of polar ice. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **375**(2086), 20150347. doi:10.1098/rsta.2015.0347