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Raman spectroscopy of bubbles and microbubbles in EDML antarctic ice core

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Air bubbles entrapped in ice cores give the unique opportunity to measure and reconstruct the composition of palaeo-atmospheres, which is mandatory for climate change interpretations for our warming planet. However, the processes which occur during e.g. the entrapment of the air during the firn-ice-transition, the hydrate formation due to pressure increase and processes during deformation of the ice as well as relaxation after retrieval of an ice core, are still poorly understood. One of the dangerous pitfalls in ice core interpretation, which is sometimes underestimated by glaciologists, are the processes occurring after the retrieval of the core due to pressure release and temperature changes during processing, transport and storage. The identification and analysis of secondary relaxation features (such as microbubbles or the so-called *plate-like inclusions* [1]) is thus an ongoing topic of high importance. Detailed analyses of microstructure and associated micro-chemical composition of inclusions in the ice can improve our understanding of these post-depositional mechanisms.

Modern micro-Raman spectroscopy allows for the identification and quantification of N_2/O_2 mixing ratios inside individual gas inclusions (bubbles, microbubbles, clathrates) in ice cores. As N_2 and O_2 are the most important components in the Earth's atmosphere, changes of the N_2/O_2 mixing ratios can be used as a proxy for the evolution of other gases (*e.g.* CO_2). The benefits of this method to the understanding of small-scale fluctuations in palaeo-atmospheric signals have been demonstrated (*e.g.* [2]).

In the study presented here, N_2/O_2 mixing ratios of bubbles and microbubbles from several depths of the EPICA DML ice core (Antarctica) were measured by Raman spectroscopy. Comparative measurements were made for ice just below the firn-ice transition and also from the bubble-clathrate transition zone. The results show that bubbles with diameters smaller than $\sim$200 μm are enriched in O_2 compared to larger bubbles. The amount of O_2-enrichment is clearly correlated with the size of the microbubble, where the smallest bubbles show the highest relative O_2 contents. Given the distinctly larger diffusion constant for O_2 compared to N_2 in ice [3], our results indicate that these microbubbles are secondary features produced by relaxation of the ice core during storage. The same samples used for Raman spectroscopy were additionally characterized by micro-CT measurements, giving the opportunity to calculate mass balances and visualize the bubble/microbubble distribution.

[1] A. Nedelcu et al., Raman spectra of plate-like inclusions in the EPICA-DML (Antarctica) ice core. Journal of Glaciology, 2009, 55, 183-184

[2] T. Ikeda-Fukazawa et al., Variation in N_2/O_2 ratio of occluded air in Dome Fuji antarctic ice. Journal of Geophysical Research, 2001, 106, 17799-17810

[3] T. Ikeda-Fukazawa et al., Effects of molecular diffusion on trapped gas composition in polar ice cores. Earth and Planetary Science Letters, 2005, 229, 183-192