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Raman spectra of plate-like inclusions in the EPICA-DML (Antarctica) ice core

A number of scientists have already warned against the risks of interpreting paleoclimate records without an adequate understanding of the diffusion of relevant chemical traces in deep ice cores (Gow, 1971; Ikeda and others, 1999; Bender, 2002; Faria and others, in press, and references therein). Particularly critical is the formation – either prior to drilling or during ice-core storage – of micro-inclusions such as solid inclusions, microscopic bubbles and plate-like inclusions (PLIs).

PLIs are typical relaxation features of deep ice-core samples. They can be found at most different depths. Essentially, they are small planar polygonal cavities possessing hexagonal symmetry (Fig. 1), i.e. thin negative crystals lying on the basal plane of their hosting ice crystallite. Their typical size ranges from tens to a few hundreds of micrometers, whereas their thickness is estimated to be not more than a few micrometers. New PLIs manifest a remarkable hexagonal symmetry, while older PLIs tend to become rounder and thicker, still preserving a very large aspect ratio (typically larger than 20 : 1). Eventually, most of them collapse into disformed bubbles (see, e.g., fig. 5 of Faria and others, in press).

PLIs were produced in deformation tests by Muguruma and others (1966) and were first reported in Antarctic ice cores by Gow (1971). Since then, while they have been identified in nearly all ice cores, no in-depth investigation of these relaxation features has been made. The aforementioned concerns about the diffusion of chemical traces in deep ice cores and its relation to the formation of relaxation features like PLIs have motivated our investigation.

Here we report the initial results of the first successful study of the chemical composition of PLIs using microfocus Raman spectroscopy, and discuss the possible consequences of this study for the interpretation of ice-core paleoclimate records.

MATERIALS AND METHODS

All polar ice samples used in this investigation were provided by the Alfred Wegener Institute (AWI), Bremerhaven, Germany, in the form of thick sections (50 mm × 100 mm × 4 mm) from the European Project for Ice Coring in Antarctica (EPICA)-Dronning Maud Land (DML) deep ice core. Each section corresponds to the upper centimeter of a 1 m long piece of the core and has been prepared according to the procedure described by Kipfstuhl and others (2006). Two of these sections (from 1294 and 1474 m depth, corresponding to 36.9 and 47.0 kyr BP, respectively) have been selected at random from a set of several samples covering the end of marine isotope stage 2 (MIS2) and the beginning of MIS3.

Screening for suitable PLIs was done using a Leica DMLM optical microscope in a cold room at −20°C. Ice specimens containing the selected PLIs were carefully cut out of the original sections manually into pieces with horizontal dimensions not bigger than 10 mm × 8 mm. They were subsequently microtomed and left for sublimation in the cold room for ~20 hours, in order to obtain clean surfaces for the Raman analyses.

Raman spectra were recorded on a Horiba Jobin Yvon HR800 UV microfocus Raman spectrometer equipped with an air-cooled Ar^+ laser working at 488 nm (laser power <25 mW). The laser beam was focused with an LWD Olympus ×50 objective lens with 0.5 numerical aperture onto a spot size slightly bigger than 1 μm and a confocal hole of ~100 μm. Spectra were collected in the range 200–4000 cm^{-1} with an exposure time of 30 s and a resolution of ~2.2 cm^{-1} using a grating of 600 grooves mm^{-1} and a Peltier-cooled charge-coupled device (CCD) detector (Andor 1024 pixels × 256 pixels). During Raman measurements, the ice sample was kept at −35°C in a Linkam THMS 600 cooling stage. For instrument calibration purposes, air spectra were repeatedly measured.

Photomicrographs of the analyzed PLIs have been produced with the CCD video camera of the Raman microscope.

RESULTS AND DISCUSSION

Typical PLIs observed in the EPICA-DML ice core are shown in Figure 1. Their corresponding Raman spectra are presented in Figure 2, together with the Raman spectrum of the polar ice matrix surrounding them. Owing to the high intensity of the translational lattice, librational and O–H stretching vibrations of ice, we present only the data in the spectral region between 1400 and 2400 cm^{-1}.

Even without any baseline or background correction, two distinctive peaks, at 1557 and 2331 cm^{-1}, are evident in the PLI spectra, which cannot be identified in the spectrum of ice. These two peaks can be assigned to the characteristic stretching modes of oxygen (O_2) and nitrogen (N_2), respectively, since they are very close to the wavenumbers of atmospheric O_2 and N_2 (1556 and 2331 cm^{-1}, respectively; Chazallon and others, 1998).

We have measured altogether 16 different PLIs with a total of 63 measurement points. The number of points measured inside each PLI (at different positions) varied between 1 and 12. The N_2 and O_2 peak intensities were numerically integrated, and errors estimated on the basis of Gaussian fits to the vibron peaks. The resulting N_2/O_2 ratios vary between the extreme values of 0.82 with an error of 0.09 and 2.49 with an error of 0.38. While the observed ratios for the PLIs (not the individual points) span the whole range given above, they are mainly concentrated in the range 1.0–1.9, with typical errors in the order of 0.3–0.4. This range covers ~80% of the observations.

We conclude that all N_2/O_2 ratios measured in PLIs significantly deviate from the expected value of air (3.7), indicating a general oxygen enrichment that is similar to O_2 enrichments reported for air hydrates in the bubble–hydrate transition depth zone of polar ice cores (first reported by Nakahara and others, 1988, and later explained in terms of

Fig. 1. Typical PLIs observed in the EPICA-DML ice core. All PLIs shown here are from the 1474 m depth sample. PLI1 is the thinnest (~1–2 μm thick), while PLI2 and PLI3 are no thicker than 5 μm.

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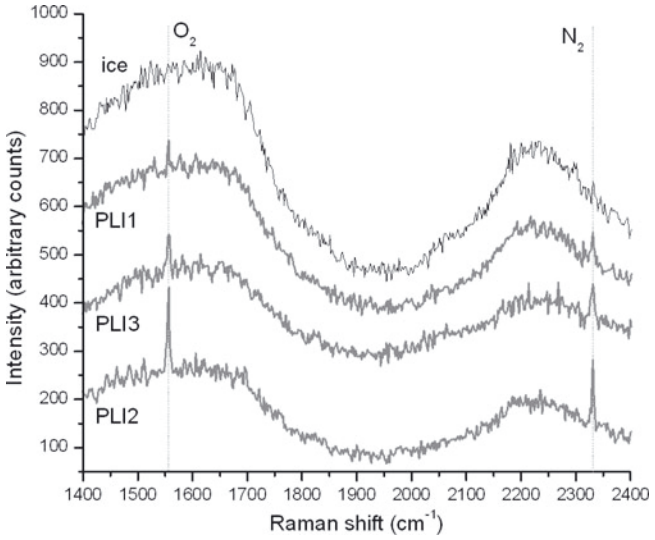

Fig. 2. High-resolution Raman spectra (raw data) of the PLIs shown in Figure 1. For clarity, the spectra are offset with respect to each other. The characteristic spectrum of polar ice in the same range has been included for comparison.

molecular diffusion by Ikeda and others, 1999). These results seem to lend support to the current hypothesis that O_2 diffuses faster than N_2 through the ice matrix (Ikeda-Fukazawa and others, 2001, 2005; Severinghaus and Battle, 2006). Indeed, according to the current belief (Mae, 1968; Gow, 1971; Faria and others, in press), PLIs are initially formed as voids (containing only small amounts of water vapor, since perfect vacuum would be thermodynamically unstable) by aggregation of vacancies driven by pressure relaxation of the ice core. According to this view it makes sense to suppose that gas molecules dissolved in the ice matrix may end up in PLIs and fill progressively these initially almost empty cavities; apparently O_2 is the faster diffusing species in this process. Nevertheless, a definitive corroboration of this hypothesis requires further investigation, since other potential causes (e.g. a heterogeneous distribution of dissolved O_2 and N_2 molecules in the ice matrix) cannot be excluded.

Even in this incipient state, our findings suggest that gases dissolved or entrapped in ice cores may diffuse through the ice matrix during the period of storage, i.e. within a period of several years. The intensity of such diffusive processes, in particular their dependence on time, temperature and pressure, is currently under investigation, in order to estimate their effect upon the accuracy of high-resolution paleoclimate records of polar ice cores. At this stage the possibility that dissolved O_2 (or N_2) may concentrate at certain defects, causing a heterogeneous distribution of dissolved air molecules, cannot be discarded.

CONCLUSION

By means of microfocus Raman spectroscopy we show that the ice-core relaxation features known as plate-like inclusions (PLIs) contain a considerable amount of atmospheric gases (more precisely O_2 and N_2) in their interior. These results suggest that the diffusion of chemical traces in the ice matrix may not be negligible, at least locally, on a timescale of a few years. Future Raman investigations will clarify the relation between the size and age of PLIs and the amount of gas they may contain. Experience tells us that the ice-core storage temperature has a decisive role in the formation of relaxation features like PLIs, but their connection to diffusive processes in the ice matrix requires further investigation.

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