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Micro-investigation of EPICA Dome C bottom ice: evidence of long term *in situ* processes involving acid–salt interactions, mineral dust, and organic matter

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A B S T R A C T

The EPICA Dome C ice core (EDC) reached a final depth of 3260 m, at a maximum height of about 15 m above the ice–bedrock interface in December 2004. We present here data gained from a detailed investigation of selected samples of the deeper part of the core located below 3200 m and referred to as bottom ice. This part of the core has been poorly investigated so far mainly because there are significant challenges in interpreting paleo-records that were very likely modified by long term *in situ* processes. Our study combines high resolution ion chromatography, high resolution synchrotron X-Ray micro-fluorescence (micro XRF), scanning, and transmission electron microscopy. Our aim was to identify the long term physico-chemical processes at work close to the bedrock, to determine how they have altered the initial registers, and, ultimately to extract information on the very ancient Antarctic environment.

The ubiquitous presence of nanometer iron oxide crystals at the surface of wind-borne dust aggregates containing also large amount of organic matter raises the possibility that the consolidation of windborne dust clusters formed during ice recrystallization could be related to microbial iron reduction and, thus, to the progressive reactivation of dormant bacterial activity in warming ice. Inclusions of size and number density increasing with depth observed in the 12 last meters (3248–3260 m) contain liquid and solid species, among them marine biogenic acids, numerous wind-borne dust aggregates and clusters of large reversible calcium carbonate particles precipitated once the inclusion was formed and often covered by secondary gypsum. The refreezing of slush lenses is discussed as a potential cause of the formation of such heterogeneous and complex mixtures. In addition to the very fine micrometer size minerals windborne from extra-Antarctic continental sources and often accreted in large aggregates, single medium size particles (a few to ca 20 μm and among them organic debris) are commonly encountered. Their size, surface shape, and mineralogy suggest that aerosol transport from Antarctic ice-free areas played a significant role at the time EDC bottom ice was formed. Concentrations and concentration ratios of biogenic sulfur species also advocate for the strengthening of peri-Antarctic meteorological patterns that favor the inland penetration of disturbed flow carrying local material. Very large well preserved mineral particles several tens of micrometers in diameter, and biotope relics in deeper ice close to 3260 m likely come from the sub-glacial environment.

1. Introduction

Deep ice cores recovered in central Greenland and on Antarctic sites are considered to be relevant archives of past changes in the climate and the atmosphere's composition for time periods ranging from the last climatic cycle to several hundred thousand years back. While a reliable time–depth relationship is essential to the interpretation of proxy records in terms of paleo-environmental history, ice dating becomes quite uncertain in the lowermost sections of ice cores where time series can be disrupted or altered by flowing ice or by the thermal regime due to the bedrock's proximity. However, and despite the lack of chronology, the exhaustive study of impurities gathered in the deepest layers of polar ice, *i.e.* close to the ice sheet base and generally referred to as bottom or basal ice, can give

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innovative clues for understanding the very ancient polar environment and sub-glacial properties. Moreover, closed or open high pressure–high temperature systems encountered at the bottom of polar ice caps can provide a useful illustration for the study of very long term physico-chemical and possibly biological processes in relation with initial ice content and grain growth conditions.

- Information available from previous deep drilling projects

The few studies conducted to date on Greenland and Antarctic bottom ice provide interesting insights on pre-glacial environments and *in-situ* processes. These are summarized below.

1.1. The basal part of the GRIP (Greenland Ice Core Project) ice core

Dielectric profiling (DEP) measurements providing ice conductance and capacitance at a range of frequencies that span the main dielectric dispersion of ice were performed in the 6 m of the basal silty ice sequence from the GRIP ice core (Summit, Central Greenland) and the detailed profile of the high frequency limit of the conductivity ($\sigma\infty$), the most useful parameter that can be deduced from dielectric measurements, was compared with multi-parameter studies involving water stable isotope, debris content, gas composition of CO_2 and CH_4 and ion concentrations (Tison et al., 1998). These authors concluded that ($\sigma\infty$) was fully explained by the intracrystalline conductivity of pure ice solely disrupted by ammonium impurities in the ice lattice, which may have been initially present as gaseous NH_3. Whilst ammonium peaks in the higher part of the ice core are related to the deposition of biomass burning products, and among them ammonium formate (Legrand and de Angelis, 1995, 1996), carboxylates are largely dominated by oxalate in the basal sequence. The strong correlation between oxalate, ammonium and calcium and the net excess of oxalate compared with what could be expected from uric acid degradation alone led the authors to propose that this basal sequence results from the incorporation of a “local end-term” (firn, permafrost ice) involving local biogenic production by plants and animals that was formed in the absence of the present-day ice sheet.

1.2. Accretion ice from the Vostok core

The first comprehensive study of the ionic composition of accretion ice of Lake Vostok, the largest Antarctic sub-glacial lake, combined with additional isotopic and iron measurements suggested that sedimentary sequences with a composition close to evaporite contribute to the lake chemistry (De Angelis et al., 2004). The second step was to investigate accretion ice using high resolution synchrotron X-Ray micro-fluorescence (De Angelis et al., 2005). Liquid brine micro-droplets (3–10 μm) were observed, that coexist with large irregular sulfur-rich aggregates (10–800 μm) containing gases and a mixture of very fine particles. Most of these objects were sequestered inside large ice crystals that grew slowly after ice formation. Their structure and composition provides evidence of hydrothermal activity at the lake bottom and of haline water pulses carrying fine solid debris perhaps biota from a deeper evaporitic reservoir into the lake. The presence of both reduced and oxidized sulfur forms tightly associated in solid inclusions was particularly interesting regarding potential bacterial activity. The coexistence in ice lattice of relatively scarce large inclusions with regularly scattered micro-droplets can be explained by relocation processes: at high temperature (−3 °C for accreted ice, under *in situ* conditions), the minimization of grain boundary free energy induces abnormal grain growth, leading to grain boundaries of high crystalline quality (Montagnat et al., 2001). At the beginning of the grain growth process, solid particles initially homogeneously distributed in the ice lattice are probably caught up in moving grain boundaries, in order to reduce free surface energy. However, particles aggregate with progressive grain growth and, when large enough, the aggregates remain in the ice lattice. Considering its high salinity, the brine is likely in a liquid state at −3 °C. Interaction between grain boundaries and liquid inclusions is probably similar to the interaction between ice and water, which means that brine bubbles can remain in the ice lattice.

- The EPICA Dome C core:

The EPICA Dome C ice core (EDC) is one of the two ice cores drilled in the framework of the European Project for Ice Coring in Antarctica (EPICA). The drilling site is located on the East Antarctic Plateau at Concordia Station (75°06′04″S; 123°20′52″ E, 3233 m above sea level), about 1200 km inland. The core reached a final depth of 3260 m estimated to be about 15 m or less above the ice–bedrock interface, based on seismic sounding in the drill hole (Schwander, personal communication). Detailed information on bedrock and surface topography were gained by altimeter and airborne radar surveys conducted in 1994–1995 (Rémy and Tabacco, 2000) and from 1995 to 2001 (Forieri et al., 2004). The most notable bedrock features in the 50 km × 50 km enlargement of the Dome C central area include sub-glacial highlands, a set of north–south-trending parallel valleys tens to hundreds of meters deep and a few cirque bowls. The detailed description of the bedrock under the drilling site provided by Forieri et al. (2004), highlights a topographic depression surrounded by hills on the order of 50–100 m high. Rémy and Tabacco, 2000, and Forieri et al., 2004, concluded that the bedrock topography below the Dome C area developed before the East Antarctic ice cap and was not significantly modified by subsequent glacial erosion, mountain ridges being very likely of tectonic origin while the valleys may have been formed by erosion by wet-based mountain glaciers, weathering of granitic rocks, or karstification of limestone.

While high resolution multi-parameter analyses performed along the upper 3140 m of the core have provided a wealth of paleo-environmental data over the last 8 climatic cycles (see for instance EPICA Community Members, 2004, 2006; Loulergue et al., 2008; Delmonte et al., 2008; Lüthi et al., 2008; Kaufmann et al., 2010; Wolff et al., 2006, 2010), the deeper part of the core has remained poorly investigated. The ionic content associated with very sharp sulfate spikes observed between 2800 and 3140 m, was determined by Traversi et al. (2009). Compared with volcanic events recorded in the upper part of the core, these spikes seemed anomalous, with unusually low acidity, high Mg^{2+} concentrations, high Mg^{2+}/Ca^{2+} ratios, and significant Mg^{2+}–SO_4^{2-} correlation. The authors suggest that long term rearrangement of impurities via migration in the vein network led to the formation of soluble magnesium sulfate particles in liquid film at grain boundaries. The dust size profile is not available below 2900 m because of the presence of particle aggregates of unknown origin (Lambert et al., 2008). The first data gained between 3200 and 3260 m reported in Jouzel et al. (2007), show a much lower than expected signal variability of water isotope and deuterium excess records, shared by the oxygen 18 of O_2 in air and preliminary dust mass, CH_4, and CO_2 data, that are however in the range of concentrations found in ice formed under full glacial conditions. Air content comparable to shallower values led these authors to dismiss large scale melting and refreezing as a plausible explanation of the profiles they observed and to suspect that this part of the core has been affected by flow disturbances due to stretching of the ice sequence or mixing of layers of different origins. Based on radiometric ages provided by ($^{234}U/^{238}U$) activity ratios for a set of samples taken along the EDC core, Aciego et al., 2011, observed a marked change