Retrieving the paleoclimatic signal from the deeper part of the EPICA Dome C ice core


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Abstract. An important share of paleoclimatic information is buried within the lowermost layers of deep ice cores. Because improving our records further back in time is one of the main challenges in the near future, it is essential to judge how deep these records remain unaltered, since the proximity of the bedrock is likely to interfere both with the recorded temporal sequence and the ice properties. In this paper, we present a multiparametric study (δD-δ18Oice, δ18Oatm, total air content, CO2, CH4, N2O, dust, high-resolution chemistry, ice texture) of the bottom 60 m of the EPICA (European Project for Ice Coring in Antarctica) Dome C ice core from central Antarctica. These bottom layers were subdivided into two distinct facies: the lower 12 m showing visible solid inclusions (basal dispersed ice facies) and the upper 48 m, which we will refer to as the “basal clean ice facies”. Some of the data are consistent with a pristine paleoclimatic signal, others show clear anomalies. It is demonstrated that neither large-scale bottom refreezing of subglacial water, nor mixing (be it internal or with a local basal end term from a previous/initial ice sheet configuration) can explain the observed bottom-ice properties. We focus on the high-resolution chemical profiles and on the available remote sensing data on the subglacial topography of the site to propose a mechanism by which relative stretching of the bottom-ice sheet layers is made possible, due to the progressively confining effect of subglacial valley sides. This stress...
field change, combined with bottom-ice temperature close to the pressure melting point, induces accelerated migration recrystallization, which results in spatial chemical sorting of the impurities, depending on their state (dissolved vs. solid) and if they are involved or not in salt formation. This chemical sorting effect is responsible for the progressive build-up of the visible solid aggregates that therefore mainly originate “from within”, and not from incorporation processes of debris from the ice sheet’s substrate. We further discuss how the proposed mechanism is compatible with the other ice properties described. We conclude that the paleoclimatic signal is only marginally affected in terms of global ice properties at the bottom of EPICA Dome C, but that the timescale was considerably distorted by mechanical stretching of MIS20 due to the increasing influence of the subglacial topography, a process that might have started well above the bottom ice. A clear paleoclimatic signal can therefore not be inferred from the deeper part of the EPICA Dome C ice core. Our work suggests that the existence of a flat monotonic ice–bedrock interface, extending for several times the ice thickness, would be a crucial factor in choosing a future “oldest ice” drilling location in Antarctica.

1 Paleoclimatic signals in basal layers of deep ice cores

Deep ice cores retrieved from the two present-day major ice sheets on Earth, Greenland in the north and Antarctica in the south, delivered a wealth of unique paleoclimatic archives over the last decades. These allowed reconstruction of global climatic and environmental conditions over the last 800,000 years, including unprecedented records of cyclic changes in the composition of greenhouse gases (CO$_2$, CH$_4$, N$_2$O). An important share of that paleoclimatic information is buried within the lowermost sections of those deep ice cores, due to the mechanical thinning of annual accumulation layers with depth. Improving the records further back in time is therefore one of the main challenges of ice core science in the near future (IPICS, 2009). A major concern in this regard is to judge how far down we can trust the paleoclimatic signals stored within the ice, since the proximity of the bedrock is likely to interfere both with the recorded temporal sequence and with the ice properties. This in turn is closely linked to the thermal and hydrological regime at the bottom of the ice sheet, as shown previously in the literature describing basal layers of deep ice cores (e.g. Goodwin, 1993; Gow et al., 1979; Gow and Meese, 1996; Herron and Langway, 1979; Jouzel et al., 1999; Koerner and Fisher, 1979; Souchez, 1997; Souchez et al., 1993, 1995a, b, 2000a, 2002b, 2003, 2006, 1994, 1998; Tison et al., 1994, 1998, Weis et al., 1997). In some cases, where the ice–bedrock interface is clearly below the pressure-melting point (pmp) as, for example, at the GRIP (−9°C) or the Dye-3 (−12°C) ice coring sites in Greenland, single or multiple mixing events between the present-day ice sheet ice and local ice remnants of previous (or even initial) ice sheet configurations are encountered (Souchez, 1997; Souchez et al., 1994, 1998, 2000b; Verbeke et al., 2002). Where the ice–bedrock interface is at the pmp, the meteoric ice has the potential to melt at a rate that would depend on the heat budget at the ice–bedrock interface (geothermal heat flux, internal friction and conduction through the overlying ice). In some cases, where the subglacial topography allows it, like at the Antarctic Vostok site, a subglacial lake will exist. Again, depending on the heat budget but also on the subglacial lake water circulation pattern, lake ice will form at the ice–water interface in substantial amounts (e.g. Jouzel et al., 1999; Souchez et al., 2000a, 2002a, 2003). This ice, evidently, does not carry paleoclimatic information. Furthermore, in the case of large subglacial lakes (such as Lake Vostok) where the ice column above can be considered in full hydrostatic equilibrium buoyancy, re-grounding of the ice sheet on the lee side of the lake will induce dynamical perturbations (such as folds), even in the meteoric ice above, as demonstrated for MIS11 (Raynaud et al., 2005) and for the ice just above the accreted lake ice (Souchez et al., 2002a, b, 2003). A less well-documented case, however, is the one where no significant water body exists at the ice–bedrock interface. If only melting occurs at the interface, with no water accumulation and no refreezing (as, for example at the NGRIP site in Greenland), can we then rely on the paleoclimatic information gathered in the basal layers? The EPICA (European Project for Ice Coring in Antarctica) Dome C ice core potentially provides us with an opportunity to investigate that specific case. In this paper, we are using a multiparametric approach, combining new and existing low-resolution (50 cm) data for the bottom 60 m of ice from the EDC (EPICA dome C) ice core with a new high-resolution (1.5 to 8 cm) chemical data set in order to better understand the processes at work and evaluate how these might have altered the environmental archive.

2 The EPICA Dome C ice core

The Dome C deep ice core (EDC) is one of the two ice cores drilled in the framework of the European Project for Ice Coring in Antarctica (EPICA). It is located at Concordia Station (Dome C – 75°06′04″S; 123°20′52″E), about 1200 km south of the French coastal station, Dumont d’Urville, and 720 km north-east of the Russian Vostok Station. Detailed GPS surface topography and airborne radar surveys were conducted in 1994–1995 in order to optimize the choice for the drilling location (Remy and Tabacco, 2000; Tabacco et al., 1998). These provided clear features of the bedrock and surface topography, showing a set of north–south-trending parallel valleys around 20 km wide and 200–400 m deep in the bedrock, corresponding to smooth elongated undulations a few metres high at the surface.
A final drilling depth of 3259.72 m was reached in December 2004, about 15 m above the ice–bedrock interface (to prevent from eventually making contact with subglacial meltwaters). The ice temperature was −3°C at 3255 m and a simple extrapolation to the bottom indicates that the melting point should be reached at the interface (Lefebvre et al., 2008). The top ca. 3200 m of the EDC ice core have already been extensively studied and provided a full suite of climatic and environmental data over the last 8 climatic cycles (e.g. Delmonte et al., 2008; Durand et al., 2008; EPICA Community members, 2004; Jouzel et al., 2007; Lambert et al., 2008; Loulergue et al., 2008; Lüthi et al., 2008; Wolff et al., 2006). Raisbeck et al. (2006) confirmed the old age of the deep EDC ice by presenting evidence for enhanced 10Be deposition in the ice at 3160–3170 m (corresponding to the 775–786 kyr interval in the EDC2 timescale) consistent with the age and duration of the Matuyama–Brunhes geomagnetic reversal. A coherent interpretation of CO₂ and CH₄ profiles (Lüthi et al., 2008; Loulergue et al., 2008) also established the presence of Marine Ice Stages (MIS) 18 (ca. 739–767 kyr BP) and 19 (ca. 767–790 kyr BP). However, a detailed study of the isotopic composition of O₂ and its relationship to daily Northern Hemisphere summer insolation and comparison to marine sediment records showed potentially anomalous flow in the lowermost 500 m of the core with associated distortion of the EDC2 timescale by a factor of up to 2. This led to the construction of the new, currently used, EDC3 timescale (Parrenin et al., 2007). Note that efforts are still ongoing to refine this timescale, combining multi-site data sets and using δ¹⁸O atm and O₂ / N₂ as proxies for orbital tuning (Landais et al., 2012; Bazin et al., 2013).

As described below, the bottom 60 m of the available core acquired distinctive properties, as a result of processes driven by the proximity of the ice–bedrock interface. We will therefore, in accordance with the previous literature (e.g. Knight, 1997; Hubbard et al., 2009) refer to it as “basal ice”. The last 12 m of the available core show visible solid inclusions (Fig. 1a), which are traditionally interpreted as a sign of interactions with the bedrock. These inclusions are spherical in shape, brownish to reddish in colour, and generally increase both in size and density with increasing depth. They however remain evenly distributed within the ice, therefore qualifying as a “basal dispersed facies” in existing classifications (e.g. Hubbard et al., 2009). Between 3248.30 m (first occurrence of inclusion visible by eye) and 3252.15 m the inclusions are only sparse (0 to 10 inclusions per 55 cm ice core length) and less than 1 mm in diameter. In the lower 8 m, inclusions get bigger (up to 3 mm in the last 50 cm sample) and reach more than 20 individual inclusions per 50 cm ice core length. In several cases, especially for the bigger inclusions, these are “enclosed” in a whitish ovoid bubble-like feature (e.g. upper left corner of Fig. 1a). Careful visual examination of the texture of each individual inclusion suggests that these generally consist of a large number of smaller aggregates although individual particles also occur. In most cases, these inclusions appear to be located at crystal boundaries. A detailed study of the morphology, mineralogy and chemistry of some of these individual inclusions is described elsewhere (de Angelis et al., 2013). Finally, it should be kept in mind that these characteristics are valid for ice collected between 6 and 15 m above the actual ice–bedrock interface. We do not, unfortunately, have any information on the properties of the ice below, the thickness of which was estimated using a downhole seismometer (J. Schwander, personal communication, 2011). The upper 48 m of the basal ice sequence will be referred to as the “basal clean ice facies” (i.e. devoid of visible inclusions), also in line with previous work (Hubbard et al., 2009).
The dispersed facies of the basal ice of the EDC core shows a relatively low debris content, compared to the other deep ice coring sites described in previous studies (Camp Century, GRIP, Dye-3, Vostok), and could therefore be processed in continuity with the cutting scheme used for the EDC ice above. The multi-parametric data set discussed in this paper was therefore obtained applying analytical techniques described in full in previous studies focusing on single parameters. We are summarizing those in the Supplement, referring to the appropriate previous literature for full details.

4 The basal ice properties: a multiparametric approach

Figure 1b and c plot the full δD profile of the EPICA ice core, vs. depth and age respectively (EDC3 timescale, Parrenin et al., 2007). As stated above, we will use the “dispersed ice facies” terminology for the lower 12 m (red open triangles) and qualify the 48 m above as the “clean ice facies” (blue open squares); “basal ice” will refer to the whole 60 m sequence. A combined Vostok-EDC δ18O atm profile (isotopic composition of atmospheric oxygen in ice) vs. EDC3 timescale is shown in Fig. 1d (adapted from Dreyfus et al., 2007; Petit et al., 1999 for the ice above 3200 m). The δ18O benthic record stack of Lisiecki and Raymo (2005) is also plotted as a reference in Fig. 1e. The co-isotopic properties of the EPICA Dome C bottom ice (open squares for clean ice facies, open triangles for dispersed ice facies) are described in Fig. 2a (δD vs. δ18O) and b (deexcess vs. δD) and compared to those of the ice from the last 140 ky (Stenni et al., 2010). Work in progress on the co-isotopic properties of the older ice (down to 3189.45 m) shows that the latter do not differ from the trends seen in Fig. 2 (B. Stenni et al., unpublished data).

Figure 3 and Table S1 in Supplement summarize the available low-resolution gas and insoluble dust concentrations data. CH4, CO2 and N2O are covered for both the clean (squares in Fig. 3a) and dispersed (triangles in Fig. 3a) facies while total gas content (grey dots in Fig. 3a) is only available for the clean ice facies. The full concentration ranges observed for CH4 (Loulergue et al., 2008), CO2 (Lüthi et al., 2008), N2O (Schilt et al. 2010) and total gas content (Raynaud et al., 2007) during the preceding climatic cycles are also shown for reference, as white, dark blue, light blue and grey vertical bars respectively. The limited number of dust concentration measurements available is shown in Fig. 3b (same symbols as above) and also compared to the full range of values observed during the previous climatic cycles (black vertical bar, Delmonte et al., 2008).

Clean and dispersed basal ice facies concentrations of selected chemical species (MSA, SO4, Ca, Mg, Na, K, Cl, NO3) are presented in two complementary ways, in Figs. 4 and 5. In Fig. 4 high-resolution (1.5–5 cm) profiles of discrete sections in the clean (open blue squares) and dispersed (open red triangles) facies are shown, along with the 5–8 cm resolution profile in the ice above 3200 m (black dots, courtesy of the EPICA Chemistry Consortium). In Fig. 5, the same data set is re-arranged as a simple frequency distribution within bins of 5 or 1 ng g−1 depending on the species. Clean facies are plotted as open blue squares on the thick solid blue line and dispersed facies as open red triangles on the thick dotted red line. All data from preceding “full glacial” intervals (i.e. excluding interglacials and complete transitions) are plotted as a background in thin grey lines with incremented symbols (see caption in upper left graph for MSA). Table 1 summarizes the data set used in Fig. 5 in terms of concentration means and 1σ values, with the depth and isotopic ranges associated to each time interval chosen. The “full glacial” intervals were selected on careful analysis of the δD data set, keeping for each glacial period the samples with the lowest values and using the location of increasing isotopic gradient with depth as a cutting point on both sides. We discuss in the supplementary material section why we believe we can compare the results from these various groups of samples shown in Fig. 5 and Table 1, despite the fact that they cover different time windows.
Table 1. Mean concentration and 1σ values (ngg$^{-1}$ or ppb) for selected chemical species in the clean and dispersed basal ice facies of the EPICA Dome C ice core, as compared to those of the previous full glacial periods (see text for details). Depth (m) and δD (‰) ranges are given for each time interval considered.

<table>
<thead>
<tr>
<th>Glacial</th>
<th>Depth range (m)</th>
<th>Isotopic range (δD ‰)</th>
<th>MSA (ngg$^{-1}$)</th>
<th>SO$_4$(ngg$^{-1}$)</th>
<th>Ca (ngg$^{-1}$)</th>
<th>Mg (ngg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
<td>mean</td>
<td>σ</td>
<td>mean</td>
<td>σ</td>
</tr>
<tr>
<td>MIS 2</td>
<td>507.7</td>
<td>583.5</td>
<td>-449.3</td>
<td>-432.8</td>
<td>18.24</td>
<td>7.00</td>
</tr>
<tr>
<td>MIS 4</td>
<td>1007.6</td>
<td>1042.2</td>
<td>-446.4</td>
<td>-430.5</td>
<td>20.94</td>
<td>4.00</td>
</tr>
<tr>
<td>MIS 6</td>
<td>1801.8</td>
<td>1997.0</td>
<td>-447.1</td>
<td>-419.8</td>
<td>18.60</td>
<td>5.00</td>
</tr>
<tr>
<td>MIS 8</td>
<td>2320.0</td>
<td>2398.6</td>
<td>-444.5</td>
<td>-421.5</td>
<td>27.90</td>
<td>6.13</td>
</tr>
<tr>
<td>MIS 10</td>
<td>2599.9</td>
<td>2650.0</td>
<td>-445.0</td>
<td>-425.1</td>
<td>26.77</td>
<td>7.88</td>
</tr>
<tr>
<td>MIS 12</td>
<td>2783.2</td>
<td>2794.9</td>
<td>-440.9</td>
<td>-422.5</td>
<td>23.44</td>
<td>5.04</td>
</tr>
<tr>
<td>MIS 14.2</td>
<td>2915.7</td>
<td>2919.9</td>
<td>-436.4</td>
<td>-429.3</td>
<td>23.75</td>
<td>6.37</td>
</tr>
<tr>
<td>MIS 16</td>
<td>3037.6</td>
<td>3039.8</td>
<td>-441.0</td>
<td>-412.3</td>
<td>32.61</td>
<td>6.95</td>
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<tr>
<td>MIS 18</td>
<td>3137.8</td>
<td>3153.1</td>
<td>-441.4</td>
<td>-423.7</td>
<td>36.40</td>
<td>23.47</td>
</tr>
<tr>
<td>Clean Facies</td>
<td>3201.0</td>
<td>3248.0</td>
<td>-442.5</td>
<td>-427.7</td>
<td>21.50</td>
<td>20.32</td>
</tr>
<tr>
<td>Dispersed Facies</td>
<td>3248.0</td>
<td>-443.2</td>
<td>-436.7</td>
<td>25.27</td>
<td>18.43</td>
<td>139.58</td>
</tr>
</tbody>
</table>

Finally, Fig. 6 plots the mean equivalent crystal radii for the deep and basal ice, as obtained from preliminary measurements in the field, and compare those to measurements using automatic ice texture analyzers as described in Durand et al. (2009). Reliable measurement of crystals radii in the bottom ice using automatic techniques is hampered by the very large increase of crystal sizes, often spanning several individual thin sections. Only “unconventional” measurements such as, e.g. sonic logging (still in development) might allow us to document these properties further in the future.

5 Discussion

5.1 Indicators of an “undisturbed” paleoclimatic record

In this first section of the discussion, we will demonstrate that some of the clean and dispersed basal ice facies properties appear coherent with a climatic signature unmodified by large-scale refreezing processes. As shown in Fig. 1b, c both the clean and dispersed ice facies display δD values typical of a mild to cold glacial period, with respective ranges of −427.7 to −442.5 and −436.7 to −443.2‰ (Table 1), as would be expected for MIS 20 based on more recent glacial data. The δD−δ18O isotope diagram of Fig. 2a, all samples align well with those from the previous climatic cycles, with a slope of 8.5, close to the value of 8.2 for the samples above 3200 m, i.e. in accordance with a meteoric water line. This is very different from the refrozen Vostok lake ice, where the samples were shown to be clearly located on a freezing slope of 4.9, only slightly higher than the theoretical slope calculated from the estimated lake water isotopic value (Souchez et al., 2002a). Also, the $d_{excess}$ values shown in Fig. 2b are within the range of those observed in the more recent glacial, while refreezing processes are known to lower the deuterium excess values (Souchez et al., 2002a; Souchez and Lorrain, 1991). These are first arguments to preclude large-scale refreezing as a plausible process for the bottom-ice formation.

The gas properties of the bottom ice are probably even more indicative of a true climatic signature (Fig. 3a). The total gas content is very stable with a mean value at 0.088 mL air g$^{-1}$ ice, which is identical to the one obtained for the whole 0–400 kyr interval further up in the core (Raynaud et al., 2007). CH$_4$, N$_2$O and CO$_2$ concentrations are also quite
Concentrations (in ppb or ng g\(^{-1}\)) of selected chemical species in the clean (open blue squares) and dispersed (open red triangles) basal ice facies of the EPICA Dome C core, as compared to those of the preceding climatic cycles (black dots, courtesy of the EPICA chemical consortium). Resolution is between 5 and 8 cm above 3200 m depth and between 1.5 and 5 cm in the basal ice below 3200 m. Note the change of depth scale below 3200 m.

Table 1 gives the mean concentration values of the considered suite of chemical species. A systematic comparison of the mean clean and dispersed ice facies values to those of each of the previous full glacial episodes (with similar \(\delta^18O\)/\(\delta^15N\) ranges) shows a very close compatibility, further suggesting that the mean paleoclimatic signal was not modified in the vicinity of the ice–bedrock interface. Indeed, any large-scale regelation process of meteoric ice meltwater would induce significant departure of the chemical composition (both in terms of total impurity content and of chemical speciation) of the refrozen ice from the initial values present in the meteoric ice. De Angelis et al. (2005, 2004) showed that, in the case of refreezing of the Lake Vostok water, away from any sediment source (their ice type 2), the concentrations were significantly lower than those in meteoric ice, in accordance with the efficient rejection of impurities during freezing at very low rates. Conversely, the upper part of the Vostok lake ice, that is thought to have accreted in a shallow bay upstream of Vostok (ice type 1), shows a total ionic content 5 to 50 times higher than meteoric ice, with a specific signature suggesting contamination from salts originating from deeper sedimentary strata, close to evaporites in composition. Nei-
ther of these two signatures are seen in the EDC bottom-ice samples.

5.2 Indicators of a “disturbed” paleoclimatic record

There are however some features of the bottom ice that raise questions about its paleoclimatic significance. First of all, as stated above, the presence of visible-solid inclusion aggregates in the lower 12 m could be the result of incorporation processes of sedimentary material at the ice–bedrock interface (Boulton, 1996, 1979; Cuffey et al., 2000; Gow et al., 1979; Gow and Meese, 1996; Herron and Langway, 1979; Holdsworth, 1974; Iversen, 1993; Iversen and Semmens, 1995; Knight, 1997; Koerner and Fisher, 1979; Souchez et al., 1988, 2000b; Tison and Lorrain, 1987; Tison et al., 1993, 1989). Then, a comparison of Fig. 1c and e reveals a strong discrepancy between the EDC δD record and the benthic record stack of Lisiecki and Raimo (2005) prior to 800 ky, with the lack of MIS21 in the EDC profile, which, instead, displays an unusually long glacial period. Furthermore, the δ18O atm profile of Fig. 1d is also somewhat peculiar in two ways: first it is extremely stable in the bottom ice despite known large fluctuations in the precession and ice volume at the time, to which the δ18O atm was shown to be very sensitive (Bender, 2002; Dreyfus et al., 2007; Landais et al., 2010), and, second, it displays values continuously close to 0‰, which is generally (but not strictly) more typical of full interglacial rather than full glacial conditions.

Finally, although generally coherent with the previous climatic cycles in terms of mean concentration values, individual chemical species can be considered to be two groups with specific and contrasted chemical distribution (Figs. 4 and 5, Table 1). MSA, SO4, Ca and Mg, on the one hand, clearly show increased variability, both in the clean and dispersed ice facies (see left column of Fig. 4 and 1σ values in Table 1), a trend that seems to initiate in MIS18 already. The frequency distributions in Fig. 5 confirm this variability as compared to previous glacials, with a tendency of both skewing towards lower values for MSA, SO4 or Mg and showing outliers at higher concentration, especially in the clean ice facies. On the other hand, Na, K, Cl, and NO3 behave noticeably differently in the clean ice and in the dispersed ice facies (right column in Fig. 4). The clean ice facies (solid line) shows very low variability and narrow frequency peaks in the graphs of Fig. 5, while the dispersed ice facies (dotted line) behaves similarly to the previous glacial, but with a tendency of skewing towards the higher range of concentrations.

5.3 Distribution and relocation of dissolved and solid impurities within ice cores

Ohno et al. (2005) discussed the location and chemical forms of water-soluble salts in ice cores. Initially entrapped between the snow grains that will evolve into firm and then ice under increasing metamorphism, these impurities could therefore be found either within the ice crystals themselves, or within the unfrozen liquid that separates the grain boundaries as a result of “premelting” (Rempe, 2001, 2002; Wetlaufer, 1999), be it veins, nodes or triple junctions. A common view amongst glaciologists is that because those impurities produce strain-energy within ice grains and because trace acids must exist as acid solutions given their very low eutectic point, they will progressively be forced into grain boundaries as grain growth and recrystallization occur (Glen et al., 1977; Rempe, 2003; Rempe et al., 2001, 2002; Wetlaufer, 1999). Although most of the sulfur atoms appear as sulfuric acid in Antarctic ice (samples were observed at triple junctions of grain boundaries in the early days of scanning electron measurements in ice (Mulvaney et al., 1988)), there has been growing evidence that sulfur compounds also exist as sulfate trapped as inclusions within grains (e.g. Baker and Cullen, 2003). Ohno et al. (2005), using micro-Raman spectroscopy, underlined that at shallow depth (185 m) in the Dome Fuji ice core, the fraction of SO4 existing as salts within the micro-inclusions exceeded 50% of the total SO4. Similar fraction values between 30 and 60% were found for Na+, Ca2+ and Mg2+ in discrete samples spanning the 5.6 to 87.8 ky BP interval.

Relocation of impurities under increasing recrystallization is likely to become important in the deeper part of meteoric ice cores, where the ice temperature gets closer to the pressure melting point (pmp) and the temperature gradient generally increases. One of those relocation processes that has been intensively discussed in the recent years is the mechanism often referred to as “anomalous diffusion” (Rempe, 2003; Rempe et al., 2001, 2002). In this process, it is surmised that, as grains slowly grow and recrystallize within ice sheets, most of the impurity molecules are preferentially excluded from the solid grains and enriched in the melt. As the polycrystalline mixture of ice and premelt liquid solu-
tion flows downwards under gravity at velocity $v_1$, it encounters gradual variations in temperature leading to gradients in intergranular concentrations, which, in turn, drive molecular diffusion of solutes relative to the porous ice matrix. The net result is that the bulk impurity profile will move downwards at a rate that differs by a finite “anomalous velocity” $v_a$ from the downward velocity $v$ of the ice itself. A typical modelling case study for the conditions at the location of the GRIP ice core predicts separation of the bulk-impurity profile from the contemporary ice by a maximum amount of about 90 cm in the bottom layers (3028 m). However, Barnes and Wolff (2004) suggested that the anomalous velocity calculated in Rempel’s model is largely overestimated, since the latter mainly surmises that all impurities are located at triple junctions. As underlined by these authors, if impurities are transferred at two-grain boundaries, then $v_a$ would be much lower. Also, Ohno et al. (2005), as discussed above, demonstrated that much of these impurities are distributed within the crystal itself, further potentially hampering the “anomalous diffusion” process, as recognized by Rempel (2003). Another important feature of this migration process is that the amplitude of the concentration changes should not be altered, even in the case of asynchronous initial deposition of different species with contrasted concentration levels (Rempel, 2003). It is therefore difficult to invoke anomalous diffusion to explain the contrasts in species concentration variability observed in our bottom ice at EPICA Dome C (see Sect. 4.2).

Another interesting process discussed by Rempel (2005) is the one in which the density difference between intercrystalline interstitial water (premelt) and ice produces a hydraulic gradient that drives a downward liquid flow. When the temperature rises towards the glacier bed, the associated permeability increase leads to more rapid fluid transport, internal melting supplying the changing flow. Although the author shows that, in the specific case where the lower region of the glacier floats on a subglacial reservoir, a reduction in the hydraulic gradient results from surface energy effects and causes a decreasing transport rate in the lower few tens of centimetres, the process mentioned above provides a potential mechanism for downward migration of the chemical compounds accumulated in the premelt layer as recrystallization at high temperature proceeds.

Finally, it is also worth looking at the few detailed studies on impurity distribution within the accreted lake ice of Lake Vostok (de Angelis et al., 2004, 2005). Although the form (solid vs. dissolved) and origin of these impurities might differ from those found in meteoric ice above, both ice types (bottom meteoric ice at EDC and accreted ice at Vostok) were submitted to intense recrystallization at high temperatures (> −5 °C), potentially involving impurity relocation. Indeed, a strong 10-fold increase of grain size is observed in the EDC bottom ice (Fig. 6), and huge increases (several tens of cm in size-crystals) are reported at Vostok (Montagnat et al., 2001). It is interesting to note that the high-resolution spatial distribution of impurities in both EDC (bottom) and Vostok (lake) ice present striking similarities. Indeed, fine-scale (1 cm) analyses of ion concentration in accreted ice samples at Vostok (e.g. Fig. 5 in de Angelis et al., 2004) show that Cl, Na, F and NO$_3$ have a uniform distribution throughout the samples, while SO$_4$, Ca and Mg are much more heterogeneous. This is clearly the behaviour we underlined in our EDC bottom ice (Figs. 4 and 5): much higher variability in the basal ice than in the meteoric ice above, and much higher variability for SO$_4$, Ca, Mg and MSA (ion absent in Vostok refrozen ice due to lake water concentration) than for Na, K, Cl and NO$_3$ in both the clean and dispersed basal ice facies. In the case of the Vostok accreted ice, de Angelis et al. (2005) observed that Cl, Na and K are incorporated within bubble-shaped structures, very likely brine micro-pockets refrozen during the core extraction, while SO$_4$, Ca and Mg are present in aggregates of insoluble material (initially suspended in the lake water), all impurities being originally randomly distributed within the unconsolidated frazil ice lattice. These authors then surmise that, as consolidation, grain growth and re-crystallization occur at high temperature (−3 °C), brine micro droplets containing soluble salt ionic species like Cl$^-$, Na$^+$ or K$^+$ are not relocated and remain homogeneously distributed throughout the ice lattice, while ions associated to fine solid salt particles, are excluded and gathered with other mineral particles in inclusions of increasing sizes, leading to a greater heterogeneity. Although SO$_4$ salts and associated species clearly could not initially exist as a suspension in lake water in the EDC case (where refreezing of a water body is inconsistent with the isotopic and gas data sets (see Sect. 4.1. above)), they may be formed through in situ chemical reactions and a similar relocation process of atmospheric inputs under recrystallization could have been at work (see sect. 5.4. below).

5.4 Scenarios for the build-up and evolution of the EPICA deep and basal ice

5.4.1 Mixing?

We saw in the previous sections that some of the properties of the EDC bottom ice are consistent with a pristine paleoclimatic record, while other properties raise some suspicion. We also demonstrated that significant net refreezing of a water body at the bottom of the ice sheet can be discarded. Another set of processes that were shown to alter the basal ice properties is mixing or folding under enhanced deformation close to the ice–bedrock interface (Souchez, 1997; Souchez et al., 1995b, 1998, 2003). Among the anomalies in EDC bottom-ice properties, the stability of the δD profile for an unusual period of time, if we trust the EDC timescale and compare our data to the Lisiecki and Raymo benthic record (Fig. 1c, e), is probably the most prominent. Homogenization through mixing is a process that was invoked by Souchez et al. (2002a, b) to explain the isotopic properties of the 3400–
3538 m Vostok depth interval, just above the meteoric-lake–ice interface. They indeed show that the δD values are there bracketed in a tight range corresponding to mean values between glacial and interglacial, and that the deuterium excess variability is also strongly reduced. This was supported by the ionic signature showing a narrow range of concentrations corresponding to ice formed under mild glacial conditions. If this was the case for the EDC bottom ice, we should expect (from the comparison of Fig. 1c and e) that the bottom ice shows mean isotopic values between those of MIS20 and M1S21 in Fig. 2b. However, the bottom ice is truly of glacial signature. Also, samples from the basal ice span the whole glacial deuterium excess range.

Mixing with a local isotopic end member inherited from a previous or initial ice sheet configuration is also unlikely. It was only described for basal ice condition largely below the pmp (see Sect. 1) and generally showed contrasting properties between the present-day ice sheet ice and the local end member, with a whole range of intermediate values in the mixing zone.

5.4.2 Stretching?

If mixing is therefore improbable at EDC, another mechanical way of explaining the abnormal length of MIS20 is relative vertical stretching under changing stress conditions, i.e. alteration of the stratigraphic timescale. Although, given the location chosen for the EPICA Dome C drilling, stress conditions should be (and are) essentially those of vertical uniaxial compression, Durand et al. (2008) indicate that the fabrics in layers of larger mean crystal sizes (about 6 mm) below 2850 m show signs of dispersion of the strong single maximum (which is the rule below 1500 m depth) along a weak vertical girdle. These changes might be the sign of evolving stress conditions near the bottom of the ice sheet, and were recently interpreted so, to explain anomalous flow below 2700 m (Dreyfus et al., 2007) and reworking of sulphate spikes below 2800 m under increased recrystallization (Traversi et al., 2006, 2009).

As seen on the large-scale map of the bedrock elevation in the vicinity of the EDC drilling site (Remy and Tabacco, 2000, their Fig. 4), the ice core bottom location sits at ca. 70 m above sea level, on the eastern flank (200–400 m a.s.l. ridge) of a major S–N trending subglacial valley, with a 400 m a.s.l ridge 15 km across, on the western flank of the valley. The bottom of the central part of the valley is at ca. 50 m below sea level. The next 400 m deep subglacial valley lies about 20 km further to the east.

In Fig. 7, we schematically show what might be the impact of a confining bedrock topography consisting of elongated valleys about 20 km wide and 200–400 m deep (Rémy and Tabacco, 2000) on the stress field and the ice fabric in the bottom ice of EPICA DC. As the ice sinks past the crests of the subglacial valleys, lateral compression on the sides of the valley will progressively combine with the vertical uni-

5.4.3 Enhanced recrystallization and small-scale chemical sorting

In the dynamic context described above (Set. 5.4.2), and relying on our multiparametric results, we can now propose a
plausible scenario for the evolution of the properties of our clean and dispersed basal ice facies at EPICA Dome C, as illustrated in Fig. 8. A changing stress field and the high temperatures, close to the pmp, will trigger sustained migration recrystallization within the bottom layers. Mean crystal size values (up to more than 10 cm) plotted in Fig. 6 are undiscutable proof that recrystallization is indeed very active there. This process will tend to relocate the impurities at grain boundaries and contribute to the build-up of aggregates. Note that Raisbeck et al. (2006) already invoked the formation of aggregates to explain abnormal spikes in $^{10}$Be in the basal ice. Increasing water content in the premelt layer might also slowly initiate downward density-driven migration of the water and of some of the associated impurities. This however, as our data set shows, will only be revealed in a high resolution chemistry approach, since it will not significantly affect the mean concentration values for a given climatic period, but more the frequency distribution within the observed concentration range. It will also behave differently, depending on the species. Detailed SEM (scanning electron microscope) and XRF (X-ray fluorescence) micro-probe elemental analyses of individual aggregates inside the EDC dispersed basal ice facies are described elsewhere and provide further insights in the potential processes at work and environmental implications (de Angelis et al., 2013). They reveal that CaCO$_3$ and CaSO$_4$ are common within these aggregates. These compounds could then be either newly precipitated salts (as observed concentrations are compatible with saturation for, e.g. CaSO$_4$ given estimated vein sizes at those ambient temperatures) or pre-existing solid particles, that were initially present inside the crystals (Ohno et al., 2005). SO$_4$, Ca, Mg and MSA (which can also be associated with salts, Ohno et al., 2005) mean concentrations in the clean and the dispersed basal ice facies will therefore remain within the range of other glacials, but their spatial distribution at the high-resolution scale of sampling will show much greater variability than in meteoric ice as shown above (Figs. 4, 5 and 8, right column).

As discussed above, the other group of species (Na, Cl, K, NO$_3$) shows two important features in the frequency distribution of Fig. 5 (right column): (a) although the whole data set is spanning the range of the previous glacial, the concentration mode is lower for the clean ice facies and higher for the dispersed ice facies and (b) the frequency distribution in the basal ice facies is generally single-modal and narrow, while it is bi-modal in the dispersed ice facies with the first mode in the basal ice facies range and the second mode skewed towards the high side of the range observed in other glacial. The contrast in concentration level between the clean ice facies and the dispersed ice facies could simply reflect the slightly colder conditions (thus higher impurity content) at the time the ice of the dispersed basal facies was formed at the surface of the ice sheet, as suggested by the lower $\delta$D values compared to the clean ice facies (Fig. 1b). Although this contrast is less obvious for the first group of chemical compounds, it might have been over-written by invoked aggregation and new in situ precipitation processes. Alternatively, the observed contrast in behaviour of Na, Cl, K, NO$_3$ between the clean and dispersed ice facies might reflect the signature of the premelt migration process as theoretically proposed by Rempel (2005). These species would indeed remain in the dissolved state within the premelt layer, and eventually partly and more easily migrate downwards, resulting in the left skewing mode in the clean ice facies...
and the bimodal distribution in the dispersed ice facies (low concentration mode corresponding to the remaining fraction in crystals as salts micro-inclusions and high concentration mode to the fraction that migrated in the premelt). Note that the process of upward pulling of liquid from the underlying reservoir discussed by Rempel (2005), if it exists, provides a means to prevent expulsion of the premelt from the basal ice, and therefore preservation of this bi-modal frequency distribution. Basal melting would potentially counteract this effect but the two basal ice facies would then migrate upwards into the ice column. Unfortunately, as underlined before, the available data set is missing the lower 6–15 m of the basal ice section to the ice–bedrock interface, where further arguments might have been found to (in-) validate this premelt migration hypothesis.

The large inclusions visible in the bottom 12 metres of basal ice are principally located at grain boundaries. Theoretical considerations from Alley et al. (1986, Eq. 21) suggest a high velocity ice grain boundary migration regime with decoupling of the grain boundaries from the particle aggregates because of their relatively large sizes and very low volume fraction. However, as underlined by these authors, this is probably no more valid for the “warm” (EDC bottom) ice, in a full migration recrystallization process, where the increased water content in the vein network will favour Ostwald ripening as the temperature of the ice-impurity system rises above the melting point of the impure grain boundaries. Another feature to consider here is that the particle aggregates might also behave very differently from single particles in terms of drag force on the grain boundaries. Also, as discussed in de Angelis et al. (2013), the significant contribution of organic compounds (such as exopolymeric substances – EPS) to the impurity load might also strongly affect the inclusion/grain boundary geometrical relationships.

5.4.4 Water isotopes, gases and dust

We focused until now on a plausible explanation for the peculiarities of the chemical signature of our two basal ice facies at EDC. How do the water isotopes signature, gas and dust properties fit into the proposed mechanism? Although the water co-isotopic signature of our basal ice facies does not show large-scale signs of modification, the recent work of Pol et al. (2010) suggests that it might not be the case at the crystal size scale, thereby providing some independent support to the interpretation of our chemical data set. These authors indeed used high-resolution (cm scale) δD measurements to depict abnormal isotopic diffusion which they attributed to water circulation at grain boundaries (premelt) for large crystals which spent more than 200 000 years at temperatures > −10 °C. The diffusion length diagnosed from the data is about twice as large (40 cm) as expected from solid state diffusion in ice, and it is also suggested that the process might start as early as in MIS 11 (Pol et al., 2011).

Why would the relocation process invoked for the chemical impurities not show up in the total air content or the CH₄ and CO₂ concentrations? First of all, it should be noted that the resolution of our gas data sets is much lower than the one we achieved for the chemical species. Also, one should remember that the gas molecules are exclusively present as clathrates at these depths and little is known on the behaviour of those during small-scale phase changes under large overburden pressures. If the glacial MIS20 “stretching” hypothesis is valid, it is not surprising to observe a stable δ¹⁸O atm signal. Landais and Dreyfus (2010) provide an in depth analysis of the potential drivers for the millennial and orbital variations of δ¹⁸O atm and show the strong impact of Northern Hemisphere monsoon activity on the observed values, in response to precessional and millennial shifts of the Intertropical Convergence Zone (ITCZ). Intervals where δ¹⁸O atm is close to 0‰ correspond in that context to episodes where precession favours warm Northern Hemisphere summers with a strong East-Asian monsoon. In Fig. 1f, we plotted the values for the integrated summer insolation at 30° N, for various thresholds τ, as calculated by Huybers (2006). This integrated summer insolation can be defined as the sum of the diurnal average insolation on days exceeding a specified flux threshold (τ). As can be seen from the comparison between Fig. 1f and d, high values of δ¹⁸O atm concur with high integrated summer insolation associated with very high diurnal average insolation thresholds (e.g. for τ = 450 (green curve) to 500 (red curve) Watt m⁻² in Fig. 1f), which is the case for our basal ice sequence. This relationship is enlarged in Fig. 9a, where one can clearly see that maxima in δ¹⁸O atm are well coupled to maxima in integrated summer insolation (to the exception of a missing peak around 750 ky). It can also be suggested that larger δ¹⁸O amplitudes correspond to larger summer insolation values and vice versa, with a threshold around roughly 2 GJ. In Fig. 9a we attempted to use the synchronicity of small-scale oscillations of the δ¹⁸O atm signal (however well above the precision of measurements −0.015‰), to the summer insolation one (tie points 1 and 2 in Fig. 9a) to derive the amount of stretching of the basal ice sequence. This produces a factor of about 2, which allowed us to reconstruct a new timescale for the basal ice, assuming linear stretching also applying to the bottom ice, for which δ¹⁸O atm are not available. Unfortunately, this does not resolve the discrepancy with the Lisiecki and Raymo curve (Fig. 9b), and suggests that the amount of stretching is probably much larger, with an initial time frame for the basal ice of only about 10 000 years. To build our 60 m of basal ice sequence in ca. 10 000 years would require an “in situ” annual layer thickness of 6 mm, which is 10 times the value observed during the previous glacial, following the recently published AICC2012 climate record (Bazin et al., 2013, Supplement). This seems too extreme, and suggests stretching might have been supplemented by other processes such as dynamical thickening in the lee of bedrock obstacles or stacking up of several glacials, with missing interglacials. The latter is how-
Figure 9. Attempting to reconstruct the timescale for the basal ice sequence: (a) zoom on the $\delta^{18}O_{atm}$ curve vs. integrated summer insolation at 30° N (see Fig. 1c) and (b) comparison of the benthic $\delta^{18}O$ curve (open circles) to the EPICA $\delta^{18}O$ profile (black dots), where the basal ice timescale was linearly “compressed” using tie points 1 and 2 in (a) (see text for details).

ever unlikely, since interglacial ice is usually harder to deform due to lower impurity content and larger crystal size (Dahl-Jensen et al., 2013). Finally, as demonstrated in de Angelis et al. (2013), the detailed analysis of individual inclusions supports the occurrence of in situ bacterial activity. To our knowledge, it is not known so far if these might have potential impact on the $\delta^{18}O_{atm}$ of the neighbouring gas phase. It is however unlikely that it might be significant given the observed low CO$_2$ mixing ratio (Fig. 3a), in line with atmospheric values at glacial times.

Despite the very poor resolution of the dust record in our bottom ice the large variability of the data within the glacial range could also result from our increased relocation scheme. Moreover, below 2900 m, a significant shift of particle size towards large diameters is in agreement with the formation of aggregates.

### 6 Conclusions

We used a multiparametric approach to discuss the plausibility of recovering an unaltered paleoclimatic signature from the basal ice of the EDC ice core. We showed that some of the data ($\delta^{18}D$ values, total air content, gas composition, dust content, mean chemical species concentrations) suggest a pristine meteoric glacial signature while other data (length of the glacial, $\delta^{18}O_{atm}$, visible inclusions, variability of the chemical species distribution) suggest mechanical and compositional alteration of the bottom ice. Ice stable isotopes and total air content rule out large-scale refreezing processes of a water reservoir as the origin for the bottom ice. Mixing, be it internally (as in Vostok MIS11) or with a local ice remnant of previous or initial ice sheet configuration (as in GRIP and Dye-3) can be equally discarded.

Using a new high resolution data set for selected chemical species in the basal EDC ice and remote sensing information on the general setting of the Dome C area, we propose a mechanism in which the confining bedrock topography contributes to a downward change in the stress field from uniaxial vertical compression to longitudinal extension along the valley axis. This stress configuration change results in a potential relative vertical stretching of the ice layers, which explains the abnormal length of MIS20. Combined with an ice temperature close to the pmp it also favours rapid migration recrystallization, as witnessed by the large increase in grain size. This, in turn, induces relocation of impurities, with accumulation of newly formed salts and already existing solid particles in the premelt layer, forming aggregates. Those become visible about 12 m above the bottom of the core and increase in size and number downwards. The basal inclusions thus mainly consist of reworked existing material; they do not represent the incorporation of allochthonous material from the ice–bedrock interface. However some potential candidates for the latter (large, single, mineral inclusions) were detected in the last meter layer (de Angelis et al., 2013). Although the mean concentration values were not significantly different from those observed in the previous full glacial periods, some chemical sorting is apparent, especially for those species that are not involved in salt formation. We suggest this might result from a slow process of downward migration of the premelt layer under the hydraulic gradient resulting from the density difference between ice and interstitial water, although the lack of data from the last 6–15 m to the ice–bedrock interface prevents us from further validating this hypothesis. The ice isotopic and gas properties are apparently not affected by these small-scale processes that, however, only become detectable at high-resolution sampling (sub-crystal size), where they are involved in smoothing processes. The apparent discrepancy in the $\delta^{18}O_{atm}$ signal is resolved if one considers potential stretching of a glacial time span during which precession favours warm Northern Hemisphere summers, as happened temporarily in each of the previous glacial isotopic stages.
We conclude that the paleoclimatic signal is only marginally affected in terms of global ice properties at the bottom of EPICA Dome C, but that the timescale was considerably distorted by mechanical stretching due to the increasing influence of the subglacial topography. It is interesting to note that MIS18 already shows signs of isotopic smoothing, chemical relocation and increased variability for the species involved in salt formation (MSA, SO4, Mg and, in a lesser extent Ca), before the timescale (EDC3) got significantly distorted. Along the same line the anomalous flow detected below 2700m, that led to the change from the EDC2 to the EDC3 timescale, might already find its roots in this subglacial topography distortion, although possible changes in the Dome position with time need also to be considered (e.g. Urbini et al., 2008). Many interior ice divides are indeed migrating today, and this could also be the case for the EDC location. Given the rough bed topography, it takes a migration of only a few ice thicknesses to change the bedrock elevation by ca. 200 m. The basal ice may therefore have experienced vertical stretching due to flow from the bedrock ridge to the current valley position, with recent migration of the divide at the top. Today, lively discussions exist and preliminary actions are undertaken within the ice core community to select a suitable location for a new deep drilling targeting the “oldest ice” (above 1 million years old, IPICS, 2009). Our work shows that the location of the EDC ice core on the flank of a valley-type subglacial topography has considerably affected the inference of deep timescales. We conclude that the retrieving of reliable paleoclimatic signals down to a few metres from the ice–bedrock interface would probably be thinkable on a flat monotonic bedrock, for distances several times the local ice thickness, although small-scale reworking of some of the proxies should be expected. It is however not clear yet why the gas content and composition is so well preserved at EDC, and not at other deep basal ice location. The presence of a liquid water layer at the interface might partly explain that discrepancy, although this could not be verified here.

Future work on the EPICA DC bottom ice will involve high resolution gas measurements in selected areas and an in-depth analysis of the crystallographic properties below 3200 m. Hopefully, these will allow us to validate and refine the general mechanism discussed here.

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References


