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Discussions

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Can we retrieve a clear paleoclimatic signal from the deeper part of the EPICA Dome C ice core?

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1 **Supplementary Material**
2
3 S1. Material and Methods
4
5 *S1.1.Chemical analyses*

6 At the LGGE (Laboratoire de Glaciologie et Géophysique de l'Environnement),
7 preliminary discontinuous samples were rinsed in 3 successive baths of ultrapure water.
8 This decontamination procedure has been proved to be the most efficient even for
9 organic traces in Antarctic ice (de Angelis et al., 2012) but is not suitable for high
10 resolution sampling. Ice lamellae devoted to high resolution studies (both at LGGE and
11 British Antarctic Survey - BAS) were thus decontaminated with a plane and cut into
12 successive samples 1.5 to 2.5cm long, a dry cleaning procedure previously checked
13 and intensively used for analyzing mineral ions in Antarctic firn and ice cores (Littot et
14 al.,2002) . Concentrations were determined by ionic chromatography (IC) with a typical
15 analytical uncertainty varying from 1 to 5%.

16 *S1.2 Water Isotopes*

17 Measurements of the EDC δD and δ^{18}O were conducted on continuous "bag samples"
18 with a depth resolution of 0.55 m, using classical isotope ratio mass spectrometry
19 (IRMS) techniques. The δD measurements were performed in France at Laboratoire
20 des Sciences du Climat et l'Environnement (LSCE) using an automatic injection device
21 and the uranium reduction technique, with a precision of 0.5 per mil. The δ^{18}O
22 measurements of the whole core up to 3189.45 m were performed in Italy at the
23 Department of Earth Sciences of the University of Parma (DST) and at the Department
24 of Mathematics and Geosciences of the University of Trieste (DMG) using the CO_2-
25 water equilibration technique and with a precision of 0.05 per mil. The δ^{18}O
26 measurements of the bottom part have been conducted in Denmark at the Centre for Ice
27 and Climate in Copenhagen using the CO_2-water equilibration technique. The data are
28 reported against VSMOW values. Inter-comparison of reference waters among the
29 involved laboratories were conducted over the analysis period and the same water standard
30 was used in both LSCE and DST/DMG laboratories.

31 *S1.3 Total gas content, Gas Mixing ratios and isotopes*

32 The measurements of the total gas content have been performed at LGGE using an
33 original barometrical method implemented with an experimental setup called STAN
34 (Lipenkov et al., 1995). This technique allows a precise evaluation of the pressure and
35 temperature of the air extracted from an ice sample having a mass of 20-30 g by its
36 melting-refreezing under vacuum in a volume-calibrated cell. After correction of the
37 measured pressure for the partial pressure of saturated water vapour and of the
38 calibrated volume for the volume occupied by refrozen bubble free ice, the gas content
39 *V* is calculated using the ideal gas law. The *V* values are then corrected for gas loss

40 from air inclusions (i.e. gas hydrates and relaxation features such as gas cavities at
41 depths under consideration) cut at the surface of the sample (Martinerie et al., 1990).
42 The absolute precision of the STAN measurements has been estimated to be within
43 ±0.6%. However the overall error of obtained V values amounts 1% because of the
44 uncertainties in the cut-bubble correction. The replication of the results estimated by
45 repeated measurements in the same horizontal slice of an ice core has been confirmed
46 to be better than 1%.
47 For CO_2 measurements at the University of Bern, ice samples of about 7 g were
48 pulverized in a cooled and evacuated vacuum chamber using a needle cracker
49 principle. After this dry extraction process, the extracted air was expanded from the
50 vacuum chamber into an infrared laser spectrometer which is used to derive the CO_2
51 concentration. At the LGGE about 40g of ice were pulverized in a cooled vacuum
52 chamber using a ball mill principle. In this system the extracted air is transferred into a
53 GC in order to derive the CO_2 concentration. A more detailed description of the systems
54 used in Bern and at the LGGE is found in Siegenthaler et al. (2005) and Barnola et al.
55 (1987), respectively. The CO_2 data set shown in this paper has a resolution of about 2.2
56 m and a precision of 1.6 - 2 ppmv (corresponding to mean Bern and LGGE precision,
57 respectively), whereas up to 8 replicate measurements were performed.
58 For CH_4 and N_2O measurements, ice samples of about 40 g (University of Bern) or 50 g
59 (LGGE) were melted in sealed and evacuated glass containers. After refreezing of the
60 samples the extracted ancient air is injected into a sampling loop and analyzed by gas
61 chromatography. The gas chromatographs are equipped with a thermal conductivity
62 detector (TCD, for total air amount),a flame ionization detector (FID, for CH_4), and an
63 electron capture detector (ECD) for N_2O (University of Bern only). A detailed description
64 of this melt-refreezing method and the measurement systems can be found in Flückiger
65 et al. (2004) and Chappellaz et al. (1997). The precision of the CH_4 and N_2O
66 measurements is 10 and 5.6 ppbV respectively. Note that the N_2O measurements are
67 potentially affected by in-situ production in the ice leading to elevated values (see Schilt
68 et al., 2010). The mean resolution of the CH_4 and N_2O measurements for the depth
69 interval 3191 to 3259 m is 1.4 and 2.1 m, respectively.
70 The composition of the oxygen 18 in entrapped air, which gives access to the isotopic
71 composition of the atmosphere,$\delta^{18}O_{atm}$, has been measured at LSCE using the melt-
72 freezing method for air extraction followed by mass-spectrometry measurement as
73 described in Landais et al. (2003) and Dreyfus (2008). The measurement precision for
74 the 2004-2005 dataset is 0.02 ‰ (pooled standard deviation).

75   *S1.4 Crystal size*

76   Crystal sizes in the Deep and Basal ice were determined in the field, using a simple
77   version of the linear intercept method (Pickering, 1976). In this method, the number (N)
78   of grain boundaries crossed by a random linear traverse of length (N) across the thin
79   section is averaged over many traverses. The mean grain diameter (d) is then
80   estimated as $d = \bar{N}/\bar{L}$. At NEEM, crystals with cross sections up to 40 cm were
81   observed, with occasional bands of smaller crystals. We therefore simply counted the
82   amount of crystals along a center line of a 3mm thick slab observed through polarized
83   light, and divided by the length of the core (55cm).

84   *S1.5 Dust*

85   At the LGGE), a set of 24 discontinuous 7-cm long samples was selected. Ice was
86   decontaminated through 3 successive baths of ultrapure water. Insoluble dust
87   concentration and size distribution measurements were performed by Coulter Counter
88   Multisizer IIe in a clean room setting. Each data represents the average of three
89   consecutive measurements performed following ultrasonic treatment. A density of 2,5
90   g/cm^3 was assumed for all particles in agreement with earlier studies. Analytical
91   procedure followed in this study is identical to that described in Lambert et al. (2008).

92   S2. Validity of the comparison between previous "full glacial" periods and the Deep and
93   Basal ice layers

94   As discussed in section 3, we have chosen to compare the chemistry of the Deep and
95   Basal ice layers to the one of the previous glacial climatic episodes, showing minimum
96   δD values. To achieve this, we have selected these successive "full glacial" episodes by
97   isolating in the δD data set the periods with minimal values, using locations of
98   increasing δ-gradients as cutting points on both sides. Table 1 shows that the δD ranges
99   obtained for the various selected periods are quite similar. However, these various
100 glacial episodes obviously cover different depth and time intervals. Before we discuss
101 and compare the mean values and the variability between those groups and the Deep
102 and Basal ice layers, it is essential to show that no artificial "time smoothing" is induced
103 by the methodology. For example, one might expect that, depending on the resolution of
104 the data set, increasing the time window at a given resolution would damp the
105 variability. In figure S1, we have plotted, for each chemical species considered and for
106 each group of samples, their mean (Fig. S1a) and 1σ (Fig. S1b) value as a function of
107 the duration of the period, based on the EDC-3 time scale (Parrenin, 2007, extended for
108 the Deep and Basal ice layer). Although there is some variability, no clear trend of the
109 chemical signals is seen with duration of the episodes. Furthermore, if "time smoothing"
110 was to occur, it should result in a decrease of the variability, at a given resolution, as we

111   go down the EDC core, which is the reverse of what is observed comparing the Deep
112   and Basal ice groups to the "full glacial" episodes above. Finally, the contrast between
113   the signature of different elements within the Deep ice or within the Basal ice concerns
114   samples that are strictly from the same time window, at the same resolution, so that it is
115   sound to discuss it.