Supplement of The Cryosphere, 9, 1633–1648, 2015
http://www.the-cryosphere.net/9/1633/2015/
doi:10.5194/tc-9-1633-2015-supplement

The Cryosphere
Open Access

Supplement of

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

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S1. Material and Methods

S1.1.Chemical analyses

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

S1.2 Water Isotopes

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

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

The measurements of the total gas content have been performed at LGGE using an original barometrical method implemented with an experimental setup called STAN (Lipenkov et al., 1995). This technique allows a precise evaluation of the pressure and temperature of the air extracted from an ice sample having a mass of 20-30 g by its melting-refreezing under vacuum in a volume-calibrated cell. After correction of the measured pressure for the partial pressure of saturated water vapour and of the calibrated volume for the volume occupied by refrozen bubble free ice, the gas content V is calculated using the ideal gas law. The V values are then corrected for gas loss from air inclusions (i.e. gas hydrates and relaxation features such as gas cavities at depths under consideration) cut at the surface of the sample (Martinerie et al., 1990).

The absolute precision of the STAN measurements has been estimated to be within ±0.6%. However the overall error of obtained *V* values amounts 1% because of the uncertainties in the cut-bubble correction. The replication of the results estimated by repeated measurements in the same horizontal slice of an ice core has been confirmed to be better than 1%.

For CO_2 measurements at the University of Bern, ice samples of about 7 g were pulverized in a cooled and evacuated vacuum chamber using a needle cracker principle. After this dry extraction process, the extracted air was expanded from the vacuum chamber into an infrared laser spectrometer which is used to derive the CO_2 concentration. At the LGGE about 40g of ice were pulverized in a cooled vacuum chamber using a ball mill principle. In this system the extracted air is transferred into a GC in order to derive the CO_2 concentration. A more detailed description of the systems used in Bern and at the LGGE is found in Siegenthaler et al. (2005) and Barnola et al. (1987), respectively. The CO_2 data set shown in this paper has a resolution of about 2.2 m and a precision of 1.6 - 2 ppmv (corresponding to mean Bern and LGGE precision, respectively), whereas up to 8 replicate measurements were performed.

For CH_4 and N_2O measurements, ice samples of about 40 g (University of Bern) or 50 g (LGGE) were melted in sealed and evacuated glass containers. After refreezing of the samples the extracted ancient air is injected into a sampling loop and analyzed by gas chromatography. The gas chromatographs are equipped with a thermal conductivity detector (TCD, for total air amount),a flame ionization detector (FID, for CH_4), and an electron capture detector (ECD) for N_2O (University of Bern only). A detailed description of this melt-refreezing method and the measurement systems can be found in Flückiger et al. (2004) and Chappellaz et al. (1997). The precision of the CH_4 and N_2O measurements is 10 and 5.6 ppbV respectively. Note that the N_2O measurements are potentially affected by in-situ production in the ice leading to elevated values (see Schilt et al., 2010). The mean resolution of the CH_4 and N_2O measurements for the depth interval 3191 to 3259 m is 1.4 and 2.1 m, respectively.

The composition of the oxygen 18 in entrapped air, which gives access to the isotopic composition of the atmosphere,$\delta^{18}O_{atm}$, has been measured at LSCE using the melt-freezing method for air extraction followed by mass-spectrometry measurement as described in Landais et al. (2003) and Dreyfus (2008). The measurement precision for the 2004-2005 dataset is 0.02 ‰ (pooled standard deviation).

S1.4 Crystal size

Crystal sizes in the basal ice were determined in the field, using a simple version of the linear intercept method (Pickering, 1976). In this method, the number (N) of grain boundaries crossed by a random linear traverse of length (N) across the thin section is averaged over many traverses. The mean grain diameter (d) is then estimated as

$d = \bar{N}/\bar{L}$. At NEEM, crystals with cross sections up to 40 cm were observed, with occasional bands of smaller crystals. We therefore simply counted the amount of crystals along a center line of a 3mm thick slab observed through polarized light, and divided by the length of the core (55cm).

S1.5 Dust

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

S2. Validity of the comparison between previous “full glacial” periods and the Clean and Dispersed basal ice facies

As discussed in section 3, we have chosen to compare the chemistry of the Clean and Dispersed basal ice facies to the one of the previous glacial climatic episodes, showing minimum δD values. To achieve this, we have selected these successive “full glacial” episodes by isolating in the δD data set the periods with minimal values, using locations of increasing δ-gradients as cutting points on both sides. Table 1 shows that the δD ranges obtained for the various selected periods are quite similar. However, these various glacial episodes obviously cover different depth and time intervals. Before we discuss and compare the mean values and the variability between those groups and the clean and dispersed basal ice facies, it is essential to show that no artificial “time smoothing” is induced by the methodology. For example, one might expect that, depending on the resolution of the data set, increasing the time window at a given resolution would damp the variability. In figure S1, we have plotted, for each chemical species considered and for each group of samples, their mean (Fig. S1a) and 1σ (Fig. S1b) value as a function of the duration of the period, based on the EDC-3 time scale (Parrenin, 2007, extended for the basal ice layer). Although there is some variability, no clear trend of the chemical signals is seen with duration of the episodes. Furthermore, if “time smoothing” was to occur, it should result in a decrease of the variability, at a given resolution, as we go down the EDC core, which is the reverse of what is observed comparing the clean and dispersed basal ice facies to the “full glacial” episodes above. Finally, the contrast between the signature of different elements within the clean or within the dispersed basal ice facies concerns samples that are strictly from the same time window, at the same resolution, so that it is sound to discuss it.

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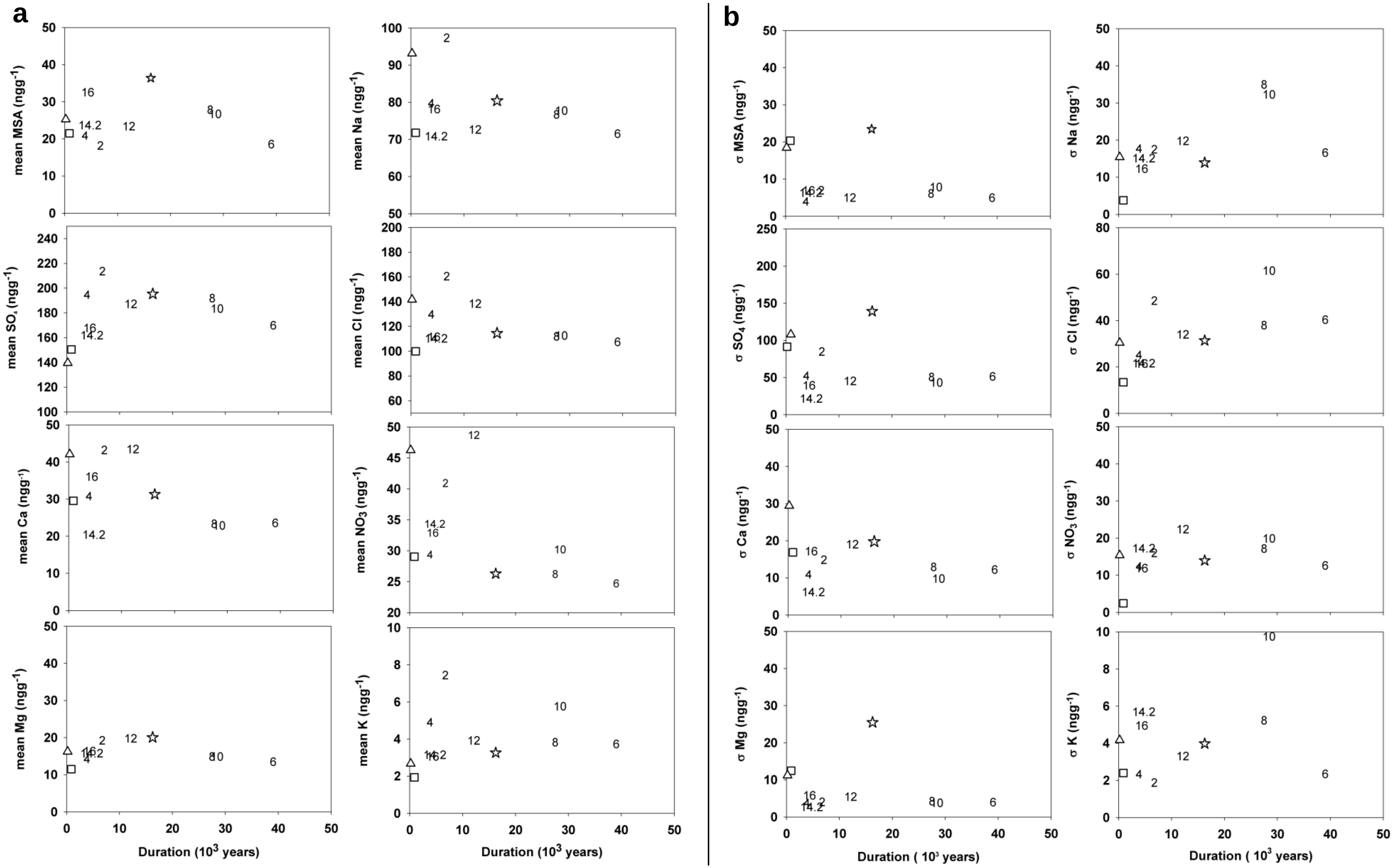
Facies	Total gas Content		CO_2		CH_4		N_20		$\delta^{18}O_{atm}$		$\delta O_2/N_2$	
	Depth (m)	Total gas content ($ml_{air}g_{ice}^{-1}$)	Depth (m)	CO_2 (ppmV)	Depth (m)	CH_4(ppbV)	Depth(m)	N_20(ppbV)	Depth(m)	$\delta^{18}O_{atm}$		$\delta O_2/N_2$
Basal Clean	3190.53	0.10	3191.48	189.10	3191.12	394.30	3191.115	220.70	3190.54	0.17	3190.53	-10.45
	3194.89	0.09	3192.30	189.00	3191.58	376.40	3192.265	263.70	3190.54	0.25	3194.94	-8.75
	3198.88	0.09	3192.73	193.00	3192.27	389.30	3193.315	237.00	3194.94	0.03	3199.34	-12.10
	3203.68	0.09	3193.41	193.20	3192.56	383.30	3195.515	235.30	3194.94	0.05	3203.74	-15.41
	3207.63	0.09	3193.75	197.70	3193.32	409.00	3197.715	236.30	3199.34	0.01	3208.14	-16.60
	3212.08	0.09	3194.68	181.70	3194.89	390.80	3199.915	249.00	3199.34	0.14	3212.54	-10.50
	3216.89	0.09	3195.79	195.00	3195.52	410.00	3202.115	255.00	3203.74	0.17	3216.94	-10.03
	3221.26	0.09	3198.21	192.20	3197.72	410.70	3204.315	266.30	3203.74	0.18	3221.34	-5.70
	3225.28	0.09	3199.08	186.50	3198.88	388.30	3206.588	264.00	3208.14	0.06	3225.74	-9.01
	3230.09	0.09	3200.34	197.10	3199.92	430.00	3208.745	261.70	3208.14	0.15	3230.14	-6.29
	3234.49	0.09	3202.46	200.00	3202.12	430.70	3210.915	262.00	3212.54	0.05	3234.54	-6.42
	3236.70	0.06	3203.48	205.00	3203.68	437.30	3213.165	266.00	3212.54	0.08	3238.93	-9.89
	3242.83	0.09	3204.78	210.80	3204.32	449.00	3215.395	265.70	3216.94	-0.08	3243.34	-6.35
	3247.23	0.09	3207.02	203.90	3206.59	458.70	3217.515	246.70	3216.94	-0.05	3247.74	-8.84
			3207.88	196.70	3207.63	452.10	3219.715	251.70	3221.34	0.06		
			3209.18	203.30	3208.75	468.30	3221.995	237.00	3221.34	0.00		
			3211.35	199.90	3210.92	445.70	3224.115	244.30	3225.74	0.02		
			3212.28	203.10	3212.08	440.30	3226.315	240.30	3230.14	0.08		
			3213.55	197.70	3213.17	448.00	3228.515	236.30	3230.14	0.13		
			3215.83	192.90	3215.40	430.00	3230.715	241.00	3234.54	0.04		
			3216.68	195.20	3216.89	400.50	3232.945	234.70	3234.54	0.05		
			3220.18	199.70	3217.52	433.30	3235.115	220.00	3238.94	0.04		
			3221.08	194.80	3219.72	423.00	3237.315	239.30	3238.94	0.07		
			3222.19	189.10	3221.26	395.60	3239.515	229.30	3243.34	0.00		
			3224.55	192.40	3222.00	418.00	3241.755	231.00	3243.34	0.08		
			3225.48	190.10	3224.12	417.00	3243.965	243.30	3247.74	0.12		
			3226.75	190.70	3225.28	407.70	3246.145	260.70	3247.74	0.03		
			3228.98	198.10	3226.32	420.70						
			3229.88	212.90	3228.52	408.30						
			3231.13	191.70	3230.09	398.10						
			3233.37	189.10	3230.72	417.30						
			3234.28	188.60	3232.95	422.00						
			3235.45	192.90	3234.49	398.80						
			3236.48	192.90	3235.12	413.30						
			3237.74	187.90	3236.70	398.30						
			3240.01	190.90	3237.32	407.30						
			3243.08	191.20	3239.52	401.00						
			3243.89	188.80	3241.76	410.30						
			3247.48	187.90	3242.83	392.30						
					3243.97	430.70						
					3246.15	439.00						
					3247.23	405.40						
Basal Dispersed			3248.81	183.6	3248.315	400.7	3248.315	262.30				
			3250.86	180.9	3250.515	399.7	3250.515	226.00				
			3253.04	178.8	3252.715	438.7	3252.715	257.70				
			3253.9	179.8	3253.865	408.7	3253.865	258.00				
			3257.53	189.2	3257.115	410.7	3257.115	252.30				
					3259.315	450	3259.315	258.00				

Table S1: Gas composition in the EDC basal Clean and basal Dispersed facies. $\delta O_2/N_2$ values are expressed wrt. atmospheric air and corrected for gravitational effects (Landais et al., 2012).



•**Figure S1:** Plot of the mean (a) and 1σ (b) values for the various chemical elements measured in each of the glacial periods considered in this study and for the Clean (open squares) and Dispersed (open triangles) basal ice samples as a function of the duration (in thousand years) of the « full glacial period » selected on the basis of the δD-values. Isotopic Stage 18, which is already thought to show increased variability for some of the elements, is shown as an open star. Duration is estimated from the EDC-3 time scale (Parrenin, 2007).