

# Elemental composition determined by PIXE analysis of the insoluble aerosol particles in EPICA-Dome C ice core samples representing the last 27000 years

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[1] 107 samples from the first 581 m of the EPICA ice core, Dome C, East Antarctica, representing a 27000 year record, were analysed by the PIXE technique. The concentrations of several elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe) were determined in the insoluble particles, collected by filtration from the melted ice samples. The average elemental ratios for Holocene and LGM are in agreement with continental crust values. The element depositional fluxes, evaluated from PIXE concentration data by means of the EPICA ice accumulation rate, are smaller in the Holocene than during Glacial times, confirming the differences in dust loads in the atmosphere during the contrasting climatic conditions. In Holocene, the fraction of the insoluble particle mass (estimated as the sum of the measured element oxides) agrees well with the total dust mass as determined from Coulter Counter measurements, but during the LGM the particle counting shows a larger dust mass. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1610 Global Change: Atmosphere (0315, 0325); 1827 Hydrology: Glaciology (1863); *KEYWORDS*: Ice Core, Atmospheric Dust, Insoluble Elements, PIXE. **Citation**: Ghermandi, G., R. Cecchi, M. Capotosto, F. Marino, Elemental composition determined by PIXE analysis of the insoluble aerosol particles in EPICA-Dome C ice core samples representing the last 27000 years, *Geophys. Res. Lett.*, 30(22), 2176, doi:10.1029/2003GL018169, 2003.

## 1. Introduction

[2] The most important sources of information about atmospheric composition in the past are the ice cores from the two large ice caps of Greenland and Antarctica, which preserve records of data related to climatic changes over the last few climate cycles. Recent drillings have been done in Greenland (GRIP and GISP2) and in Antarctica (in the Vostok area and at Dome Fuji). These are the basis of important advancements in the knowledge of global paleo-environmental conditions during the Holocene and the late Pleistocene.

[3] The European Project for Ice Coring in Antarctica (EPICA) involves the drilling of a 3300 metre deep ice core on the East Antarctic plateau at Dome C (75°06'S, 123°21'E, elevation 3233 m asl), south of the Indian Ocean. The drilling operation began in 1997, and reached the depth of 3126 m in the field season 2002–2003.

[4] The present work refers to the elemental composition of insoluble aerosol particles from the upper 581 m from the EPICA core, drilled during the 1997/98 and 1998/99 field seasons.

## 2. Material, Methods and Available Records of Data

[5] The 581 m EPICA core was cut into about one thousand sections of 55 cm length in the Laboratory of Glaciology and Geophysics of the Environment (LGGE) at Grenoble (France). 107 of these sections, distributed along the core starting from the depth of 100 m (at intervals ranging from 2.5 m to 5 m, depending on the ice features), were sampled with clean procedures [Delmonte *et al.*, 2002] for successive analyses by Particle Induced X-Ray Emission (PIXE).

[6] The ice samples were kept frozen until required for PIXE target preparation, performed in a clean laboratory in Modena (Italy), by filtration of each melted sample (20 ml volume) through a Nuclepore membrane (polycarbonate 1 mg cm<sup>-2</sup>, pore size 0.4 μm), [Ghermandi *et al.*, 1996].

[7] The PIXE analyses [Ghermandi, 2000] were performed at the National Laboratories of Legnaro (Padua, Italy), using a proton beam accelerated to 1.8 MeV by the AN 2000 Van de Graaff accelerator, with experimental set up and measurement conditions described by Ghermandi *et al.* [1996]. Nuclepore blanks were analysed together with the ice core targets.

[8] Concentrations of Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, and Fe were determined in each sample, by means of previous calibrations [Laj *et al.*, 1997], with measurement errors from 5% to 10%, depending on the element. The error is higher when the mass of material is close to the detection limit and therefore the concentrations of P, V, Cr, Co, Ni, Cu, Br and Zn, determined at trace level, are not presented.

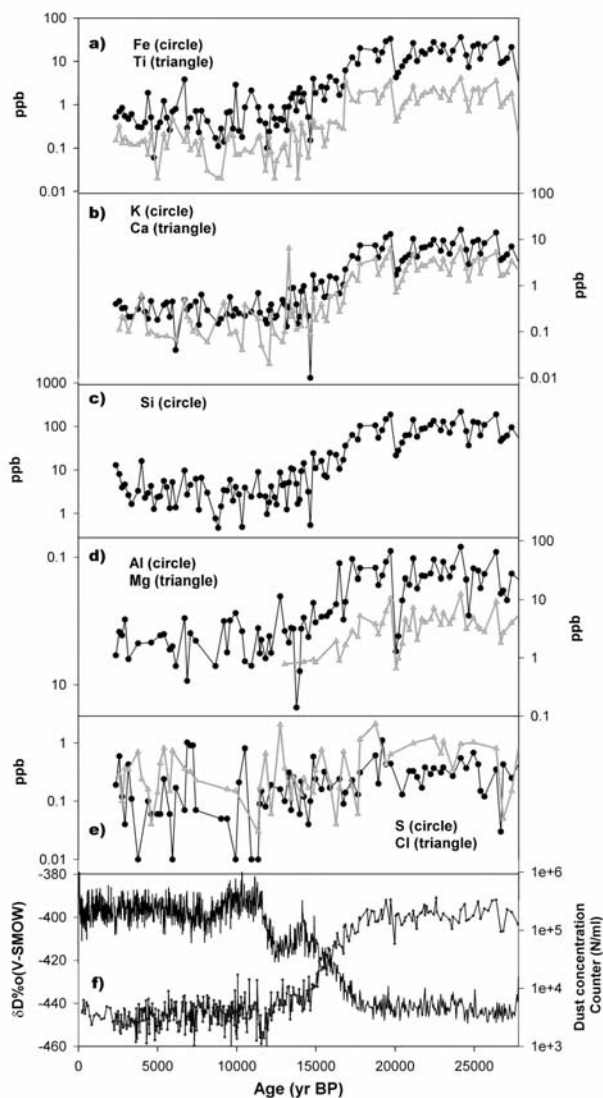
[9] Single-particle analyses of eight of the 107 samples were performed by SEM-EDAX; instruments and working conditions have been described by Laj *et al.* [1997]. Samples were prepared by filtration of 5 ml of sample through a Nuclepore membrane (pore size 0.4 μm). The material collected was subsequently coated with a thin layer of gold to prevent accumulation of charge during analysis.

[10] The insoluble particle number concentration (Figure 1f) and the particle mass records used in this work

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**Figure 1.** Profiles of element concentrations ( $\text{ng cm}^{-3}$ , or ppb) (a–e), of deuterium ( $\delta\text{D}$  (‰)) [Jouzel *et al.*, 2001] (f) and of particle number concentration ( $\text{N cm}^{-3}$ ) [Delmonte *et al.*, 2002] plotted versus age (years before present). The chronology of the core was established by Schwander *et al.* [2001]; the Holocene period, until about 11.4 kyr BP (360 m depth approximately), the isotopic transition, and the Last Glacial Age, from 20 kyr BP (about 480 m depth) can be distinguished in the deuterium profile. The profiles have been plotted on a logarithmic y-scale.

were determined from the Coulter Counter Multisizer IIe particle volume record [Delmonte *et al.*, 2002]. The instrument was set for measurements of particles with diameters from 0.7 to 20  $\mu\text{m}$ .

[11] The drilled core was deposited over a period of approximately 27000 years. The deuterium—age relation is reported in Figure 1f.

### 3. Results and Discussion

[12] The trends of the measured element concentrations ( $\text{ng cm}^{-3}$ ) versus time are shown in Figures 1a–e.

[13] The elements Mg, Al, Si, K, Ca, Ti, and Fe follow a similar behaviour, decreasing with the climate warming. Concentrations of S and Cl are very variable during the Holocene, ranging from below the detection limit to values close to those measured in ice representing the LGM. LGM values are generally higher than in the Holocene. Concentrations of Na and Mn in the Holocene are generally close to the detection limits. Therefore their trends are not shown in Figure 1. The average Na and Mn concentrations in the LGM are  $2.6 \text{ ng cm}^{-3}$  and  $0.2 \text{ ng cm}^{-3}$  respectively.

[14] The K concentrations (Figure 1b) are in agreement with the data given by Hinkley and Matsumoto [2001], for the Taylor Dome ice core (coastal West Antarctica).

[15] The ratio between mean LGM (17.4 ppb) and Holocene (0.7 ppb) Fe concentrations ( $\sim 26$ ), is similar to the value of about 30 reported for Fe in other polar snow and ice by Barbante *et al.* [private conversation, EPICA Report 2001].

[16] The Al, K, Ca and Mg concentration profiles in continental dust have been presented for the Vostok area by other authors [De Angelis *et al.*, 1992]. The difference between total and fine Vostok concentration profiles provides an estimation of the concentration profiles in coarse (i.e.,  $>0.4 \mu\text{m}$ ) particles. These indirectly-evaluated Vostok concentration profiles may be compared with the concentrations of insoluble particles ( $>0.4 \mu\text{m}$ ) reported in the present work (section 2). For Al and K our concentration values are similar to those of the Vostok data, and our Mg concentrations, whose average value in LGM is less than 4 ppb, are of the same order of magnitude as the Vostok core. The comparison is less reliable for Ca, which is enriched in the soluble fraction. Nevertheless, in the Vostok core the mass ratio of the fine ( $<0.4 \mu\text{m}$ ) to the total Ca varies from 0.7 and 0.9 [De Angelis *et al.*, 1992], and the Ca PIXE data (particles  $>0.4 \mu\text{m}$ ) are comparable to the 10–20 percent of the total Ca from the Vostok core.

[17] We also compare Ca, measured by PIXE in Dome C particles, and the calculated concentrations of essentially insoluble,  $\text{nss-Ca}^{2+}$  given by Röthlisberger *et al.* [2000]. The calculation assumes that  $(\text{nss-Ca}^{2+}) = (\text{Ca}^{2+}) - 0.038 \times (\text{Na}^+)$ ; ( $\text{Ca}^{2+}$  and  $\text{Na}^+$ ) are soluble Ca and Na concentrations measured along the EPICA core by a continuous flow analysis (CFA) technique, and 0.038 is the  $\text{Ca}^{2+}/\text{Na}^+$  seawater ratio [Bowen, 1978]. The comparison clearly indicates large differences in absolute concentration: EPICA  $\text{nss-Ca}^{2+}$ , taken as a proxy for continental dust, ranges from  $\sim 50$  ppb during the glacial age to  $\sim 2$  ppb during the Holocene, whereas our values range from  $\sim 3$  ppb to  $\sim 0.1$  ppb respectively. Nevertheless, the agreement between the LGM/Holocene concentration ratio ( $\sim 25$ ) from  $\text{nss-Ca}^{2+}$  data and from our data ( $\sim 30$ ) is good. Fine particle weathering or dissolution may cause the estimation of Ca concentrations from PIXE analysis to be too low. However, the large difference between the Ca concentrations in the insoluble particles, measured directly by PIXE, and the values calculated from  $\text{nss-Ca}^{2+}$ , indicates that a large fraction of the Ca in continental dust is soluble. This is not surprising, and is in agreement with other studies about the GRIP ice core [Laj *et al.*, 1997].

[18] Cl and S do not closely the behaviour of the other elements. The high uncertainty in Na concentration values hinders the correlation of the marine constituents.

**Table 1.** Average Elemental Ratios Evaluated From PIXE Data for Holocene and LGM Periods Compared With the Same Elemental Ratios in the Continental Crust

	Si/Al	Si/Fe	Al/Fe	S/Cl	Si/K	Si/Ti
Continental Crust <sup>a</sup>	3.62	6.67	1.84	1.48	13.46	72.00
Holocene <sup>b</sup>	2.6 ( $\sigma = 2.3$ )	8.5 ( $\sigma = 9.0$ )	3.0 ( $\sigma = 5.4$ )	0.6 ( $\sigma = 0.8$ )	13.2 ( $\sigma = 6.6$ )	41.1 ( $\sigma = 30.2$ )
LGM <sup>b</sup>	4.3 ( $\sigma = 2.8$ )	5.4 ( $\sigma = 0.5$ )	1.5 ( $\sigma = 0.5$ )	1.2 ( $\sigma = 2.1$ )	13.4 ( $\sigma = 0.7$ )	52.7 ( $\sigma = 3.3$ )

<sup>a</sup>Wedepohl [1995].

<sup>b</sup>Average values of elements concentration ratios obtained in this work and standard deviations ( $\sigma$ ).

[19] The largest Cl and S fraction is expected to be found in the soluble form. Insoluble S particles account for only a few percent of total particles at all depths in the GRIP core [Laj *et al.*, 1997], and the concentrations of soluble and insoluble S are not correlated. Insoluble S probably represents atmospheric sulphur of terrestrial origin. Our average insoluble S concentration is 0.2 ppb in Holocene and 0.3 ppb in LGM, being more abundant during cold periods when accumulation rates are low [Schwander *et al.*, 2001, for LGM Dome C]. Similarly, average insoluble Cl concentrations are 0.1 ppb and 0.3 ppb in the Holocene and LGM, respectively. The occurrence in the continental surface of possible sources of insoluble Cl (mainly apatite) is very low. Our estimation of Cl is probably too high respect to the insoluble Cl provided from these sources. On the other hand, at under-ppb concentration level the PIXE measurement error may be higher.

[20] The suggestion of a common terrestrial source for insoluble S and Cl is supported by the comparison (Table 1) between the average elemental ratios from PIXE data and in the continental crust [Wedepohl, 1995]. Our S/Cl values are close to crustal values. For Al, Fe, Si, Ti and K, relevant constituents of the crustal minerals which are more abundant in insoluble particulate aerosol than in marine materials [Gaudichet *et al.*, 1998], the agreement with continental crust ratios is not surprising. Nevertheless, the uncertainties associated to our elemental ratios are high.

[21] We also evaluate the correlation matrix of the following three parameters: element concentrations, deuterium, and insoluble particle number ( $\text{N cm}^{-3}$ ). Deuterium is highly anti-correlated with the particle number (corr. coeff.  $-0.86$ ) (Figure 1f), and with Si ( $-0.76$ ), K ( $-0.77$ ) and Fe ( $-0.77$ ) profiles.

[22] These trends agree with the decreasing dust concentration in the atmosphere from LGM to the Holocene stage, i.e., at the occurrence of the temperature increase and modification of transport patterns in atmosphere. Moreover, the high correlation of Si with typical crustal elements, as Al (0.94), Ti (0.96) and Fe (0.99), Mg (0.97) and K (0.99) may indicate a decrease through time of the mineral particles containing these elements. In addition, the insoluble Ca (soil tracer) determined by PIXE is well correlated with Si (0.91), K (0.91) and Fe (0.91).

[23] Cl and S (highly correlated with one another, 0.91) are not significantly correlated with other elements. Nevertheless, the average Holocene concentrations are lower than LGM concentrations, and the S/Cl ratios validate the assumption of a crustal origin for insoluble S and Cl aerosol particles. Source areas for S and Cl may be different from those of other insoluble elements, as well as the low frequency occurrence of Cl, highly mobile and easily dissolved after alteration of the rock, and S, mainly from largely soluble sulphate and sulphides. Different particle shapes, partly due to varying mineral habits, may affect susceptibility to atmospheric uptake and transport, and hence cause differences between average chemical composition of source terranes and atmospheric aerosols deposited onto ice.

[24] Insoluble element concentrations were converted into depositional fluxes ( $\text{ng cm}^{-2} \text{y}^{-1}$ ) (Table 2) by means of the ice accumulation rate data (accumulation of snow/ice per year ( $\text{cm y}^{-1}$ )) estimated for the EPICA Dome C ice core [Schwander *et al.*, 2001]. The snow accumulation rate in the LGM ( $1.5 \text{ g cm}^{-2} \text{y}^{-1}$ ) is two times that of the Holocene value ( $2.7 \text{ g cm}^{-2} \text{y}^{-1}$ ) [Petit *et al.*, 1982; Jouzel *et al.*, 2001; Schwander *et al.*, 2001]. Our sampling time frequency along the EPICA core is variable, with mean values of 227 years for Holocene and 299 for LGM.

[25] The ratio of about 11.3 between the mean values of LGM and Holocene iron fluxes (Table 2) is in the range determined by Edwards *et al.* [1998] from the Law Dome (East Antarctica coastal site) ice core ( $\sim 6-19$ ). It is interesting to note that the ratios of Ca fluxes of the LGM and the Holocene, whether evaluated by means of  $\text{nss-Ca}^{2+}$  [based on data of Röthlisberger *et al.*, 2000] or by the method of the present study are about the same ( $\sim 12$  and  $\sim 12.9$ , respectively), assuming snow accumulation rate during the glacial period of about the half that of Holocene [Schwander *et al.*, 2001].

[26] Dust may include insoluble constituents not detectable by PIXE, such as carbonaceous particles, and particles smaller than  $0.4 \mu\text{m}$  not collected in the PIXE target preparation.

[27] The dust mass concentration ( $M_d$ ) obtained [Delmonte *et al.*, 2002] from the insoluble particle volume, assuming an average particle density of  $2.5 \text{ g cm}^{-3}$ , was compared

**Table 2.** Average Depositional Fluxes ( $\text{ng cm}^{-2} \text{y}^{-1}$ ) of Some Elements for **Holocene** and Glacial Stage (**LGM**), Calculated from PIXE Data

Flux ( $\text{ng cm}^{-2} \text{y}^{-1}$ )	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe
Holocene	0.0	0.0	4.5	12.1	0.5	0.4	0.9	0.3	0.3	0.0	2.1
LGM	3.6	5.7	38.2	128.0	0.4	0.4	9.5	4.0	2.4	0.2	23.8

Average values of zero result from element concentrations close to the detection limits.

(for the 107 samples examined in this work) with the concentrations of the particle mass fraction ( $M_{\text{ox}}$ ), calculated as the sum of the masses of the oxides of the insoluble elements ( $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{SO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_3$ ) detected by PIXE per  $\text{cm}^3$  of melted sample. These oxides are the major constituents of the continental crust [Wedepohl, 1995]. Most carbonate and sulphate-containing particles are very soluble, so we did not take them into account.

[28] The  $M_d$  and  $M_{\text{ox}}$  series are well correlated (0.89), but the correlation coefficients become smaller as time passes, from the LGM to the Holocene period. The  $M_d$  average value [Delmonte *et al.*, 2002] in the Holocene is  $15 (\pm 7) \text{ ng cm}^{-3}$  and does not differ strongly from the  $M_{\text{ox}}$  mean value of  $16 \pm 11 \text{ ng cm}^{-3}$ . In the Glacial period, the average values are  $790 (\pm 290) \text{ ng cm}^{-3}$  for  $M_d$  and  $368 (\pm 204) \text{ ng cm}^{-3}$  for  $M_{\text{ox}}$ .

[29] The difference between  $M_d$  and  $M_{\text{ox}}$  is also shown by the comparison of the particle numbers (Figure 1f), for which the mean value in the LGM is at least 50 times greater than in the Holocene. On the other hand, the Coulter data are very imprecisely converted to mass, both because of the assumptions about particle shape, and because the densities are imprecisely known.

[30]  $M_d$  was obtained from particle counting measuring all particles larger than  $0.7 \mu\text{m}$  (see section 2.), whereas  $M_{\text{ox}}$  was calculated from PIXE analysis (summed oxides) of the particles larger than  $0.4 \mu\text{m}$ . The implication may be that during glacial time the large dust mass  $M_d$  is due to the presence of abundant particles larger than  $0.7 \mu\text{m}$  whose constituents are not detected by PIXE, such as carbonaceous particles. It may suggest different sources for the atmospheric dust in the glacial period respect to Holocene.

[31] An indication of the presence of insoluble constituents in the core, not detectable by PIXE, may be provided from SEM-EDAX analysis of EPICA samples: four Holocene and four LGM samples were analysed by SEM-EDAX. Given the very low number of particles in the samples (mainly in the Holocene ones), any quantitative estimation results are not significant. The investigation would require the availability of more numerous and larger volume samples.

[32] Given the numerous sources of uncertainties, the difference between  $M_d$  and  $M_{\text{ox}}$  might be partly expected. Nevertheless, this difference is not yet fully understood: adequate SEM-EDAX analyses would allow us to investigate the hypothesis of different dust sources for Holocene and LGM.

#### 4. Conclusions

[33] The examination of 107 samples from the EPICA ice core, covering the last 27000 years, provides the concentration profiles for a group of elements detected by PIXE in the insoluble particles.

[34] The element concentrations agree satisfactorily with literature data. Correlations and average element ratios indicate the dominantly crustal origin of the elements measured (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe). Different source areas and differences in uptake and transport efficiency of different particles of differing mineral identity, size, density, and habit may explain the variability

in elemental proportions and abundances through the core profile.

[35] Fluxes are greater in the Glacial time than in the Holocene, confirming long-held assumptions of dust enrichment in atmosphere in the last Glacial period, related to the higher continental aridity. Elemental analysis by PIXE and particle counting by Coulter Counter both confirm this relation.

[36] For the Holocene, sums of elemental oxides from PIXE analysis of particles filtered from ice agree well with the dust mass concentration record obtained from particle counting measurements. In contrast, the agreement is less good for the time of the Last Glacial Maximum. In future work, SEM-EDAX analyses must be coupled to PIXE to perform a complete study of the dust mineralogy, in order to investigate the differences of the atmospheric dust composition in the Holocene and the LGM.

[37] Finally, PIXE technique is a promising tool for measuring element concentrations in insoluble atmospheric particles. PIXE provides direct measurements of element concentrations in dust particles, with high sensitivity. Furthermore, the multi-element capability of PIXE analysis allows the simultaneous and rapid determination of multiple elements in a single analytical run. The possibility of measuring the concentration of Si, a crustal reference element not determined by others in the insoluble dust particles from the EPICA ice core, represents a further advantage of the present application of PIXE technique.

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