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Defining the geochemical composition of the EPICA Dome C ice core dust during the last glacial-interglacial cycle

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[1] The major element composition of the insoluble, windborne long-range dust archived in the European Project for Ice Coring in Antarctica Dome C ice core has been determined by Particle Induced X-ray Emission analyses. The geochemistry of dust from the last glacial maximum (LGM) and from the Holocene is discussed in terms of past environmental changes, throughout the last climatic cycle. Antarctic dust from glacial and interglacial climate clearly reveals different geochemical compositions. The weathered crustal-like signature of LGM dust is characterized by a low compositional variability, suggesting a dominant source under the glacial regime. The close correspondence between the major



element composition of Antarctic glacial dust and the composition of southern South American sediments supports the hypothesis of a dominant role of this area as major dust supplier during cold conditions. Conversely, the major element composition of Holocene dust displays high variability and high Al content on average. This implies that an additional source could also play some role. Comparison with size-selected sediments suggests that a contribution from Australia is likely during warm times, when a reduced glacial erosion decreases the primary dust production and a more intense hydrological cycle and larger vegetation cover inactivates dust mobility in a large part of southern South America, weakening its contribution as a massive dust supplier to Antarctica.

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1. Introduction

[2] Mineral dust is an active contributor to the Earth's climate, and its characteristics, in terms of concentration, chemical composition, and size distribution, are both a function of and a factor affecting climatic changes [e.g., *Satheesh and Krishna Moorthy*, 2005]. Indeed, the production, availability, and geochemical composition of dust is very sensitive to the Earth's climatic and environmental conditions at the dust source, such as moisture balance and vegetation cover, as well as storminess and rate of scavenging during the long-range atmospheric pathways [*Mahowald et al.*, 2006]. The principal natural sources of dust are the arid and semiarid regions of the Earth, where the scarce vegetation cover helps to accentuate the continental aeolian erosion. The locations of the present-day major Earth's atmospheric dust sources were reviewed by *Prospero et al.* [2002].

[3] Glacial climatic conditions should have been even more effective for dust production, in response to a stronger temperature gradient, reduced atmospheric scavenging, and higher wind activity [e.g., *Fischer et al.*, 2007]. In addition, the contribution of sea level lowering, thus exposing wider continental surfaces to wind deflation, is still controversial. Recently, high-resolution chemical measurements in the Dome C ice core indicated that a role of the exposed continental shelf cannot be ruled out during glacial stages [*Bigler et al.*, 2006], while *Wolff et al.* [2006] pointed out the

inconsistent timing of sea level and dust deposition changes, during the last deglaciation. As a response to the higher production, mobility and atmospheric lifetime of dust particles, the dust flux over Antarctica, inferred from ice cores dust measurements, was ~ 25 times higher during the last glacial maximum (LGM) compared to the Holocene [*Petit et al.*, 1999; *EPICA Community Members*, 2004; *Lambert et al.*, 2008]. Ice core archives were widely used in the last decades to study dust depositions and atmospheric loads over different climatic regimes [e.g., *EPICA Community Members*, 2004]. However, except for a few pioneering studies of dust mineralogy [e.g., *Gaudichet et al.*, 1988; *Grousset et al.*, 1992], the geochemical characterization of dust in Antarctic ice cores has been hampered by its very low mass content. Only recently, the Sr, Nd, and Pb isotopic fingerprint [*Delmonte et al.*, 2004; *Revel-Rolland et al.*, 2006; *Vallelonga et al.*, 2005], rare Earth element (REE) composition [*Gabrielli et al.*, 2006], and some single element determinations [*Gaspari et al.*, 2006; *Siggaard-Andersen et al.*, 2007] have provided new constraints on ice core dust provenance, even if a reliable identification of the dust source regions is still a matter of discussion, particularly for interglacial conditions [*Revel-Rolland et al.*, 2006; *Delmonte et al.*, 2007].

[4] In this paper, we present a multielement (Si, Al, Fe, Ti, Ca, Mg, Na, and K) characterization of insoluble dust in ice cores by Particle Induced X-Ray Emission (PIXE). Measurements were per-

formed on selected intervals of the EPICA (European Project for Ice Coring in Antarctica) ice core, drilled at Dome C (further on referred to as EDC, East Antarctic Plateau, 75°06'S; 123°24 E; 3233 m above sea level). Preliminary data obtained by PIXE analyses on Antarctic ice core dust samples were presented elsewhere [Ghermandi *et al.*, 2003; Marino *et al.*, 2004]. In this paper we discuss the PIXE results providing, for the first time, the whole major element composition of dust deposited at Dome C during the last glacial cycle. Because of their sensitivity to chemical weathering processes [e.g., Hawkesworth and Kemp, 2006], major elements can provide useful information on changes in dust chemical composition under different climatic and environmental regimes.

2. Sampling and Methods

[5] The chemical composition of mineral dust found in ice cores is still poorly known because few techniques are available to provide information on the very low amount of dust usually present in polar ice samples (~ 15 ng/g for Holocene and ~ 700 ng/g for LGM [Delmonte *et al.*, 2002]). These low amounts of material discourage the use of common geochemical techniques for major elements determination, such as X-ray fluorescence (XRF) and inductively coupled plasma–atomic emission spectrometry (ICP-AES), and additional analytical limits are set by the small volume of each ice sample (typically 10–20 mL of melted ice) and by the risk of contamination during sample pre-treatment. Here, the geochemical characterization of dust from the EDC ice core was obtained by the PIXE technique (at the National Institute of Nuclear Physics, Legnaro, Italy), applied to 120 ice core samples, spanning the last 30 ka. The temporal resolution is about one sample per 230 years for the Holocene and 300 years for the LGM; samples represent 2–3 years of accumulation for Holocene and 4–5 years for the LGM [Parrenin *et al.*, 2007].

[6] Ice samples were decontaminated following the procedure already described in Delmonte *et al.* [2002, 2004]. After melting the ice, an aliquot of ~ 10 mL was kept for Coulter Counter (CC) measurements, while the remaining part (10–20 mL) was used for PIXE analysis. PIXE targets were prepared by filtering each melted sample through a Nuclepore 0.45 μm membrane, using precleaned filter holders. The possibility to analyze insoluble dust particles directly on the filter surface, without any pretreatment, such as preconcentration, digestion, or precipitation with the addition of chemical

agents, is an important feature of the PIXE technique, thereby reducing possible sample contamination. Procedural blanks were obtained by filtering ultrapure water through a Nuclepore filter: reproducible signals were detectable in blanks for Si and Fe only, due to impurities in the polycarbonate membrane. These low Si and Fe signals accounted for $\sim 2\%$ and $\sim 1\%$, respectively, of their concentration in LGM, and $\sim 10\%$ in Holocene samples for both elements. The average contribution measured in several blanks was subtracted from each sample. Further details about sampling, target preparation and blanks evaluation have been previously presented [Marino *et al.*, 2004].

[7] The typical ice core concentrations detected by PIXE measurements range from ~ 10 (for Ca) to ~ 30 (for Fe) times higher than the corresponding analytical limits of detection (LODs) in Holocene samples and from ~ 20 (for Na and Mg) to ~ 600 (for Fe) times higher in LGM samples. Besides, the analytical error associated with PIXE measurements ranges from 5% (for the more abundant elements Si and Al) to 15% (for Ca) on Holocene samples; in LGM samples error varies from 10% (for Na and Mg) to 3% (for all other elements). In addition, the application of the PIXE technique to measure mineral dust elemental composition in Antarctic ice cores has been recently discussed by Ruth *et al.* [2008], in comparison with other analytical techniques.

[8] Accurate measurements of the eight major constituents of Antarctic ice core dust are discussed; for Holocene samples, Na and Mg concentrations were below or very close to the PIXE detection limit and are not included in this data set.

3. Results and Discussion

3.1. PIXE Oxides Sum Versus CC Dust Mass

[9] Si, Al, Fe, Ca, Na, Mg, K, and Ti are found to be the main constituents of the dust analyzed in the EDC ice core samples, in line with their main continental origin. Mineralogical investigations showed that dust archived in the Vostok ice core is mainly composed of a mixture of silicates and phyllosilicate minerals such as clays, quartz, feldspars, and some minor contribution of pyroxenes, amphiboles, metal oxides, and volcanic glasses [e.g., Gaudichet *et al.*, 1988]. The major elements, closely related to the mineral composition of dust [Pye, 1987], constitute about 99.90% of the Earth's

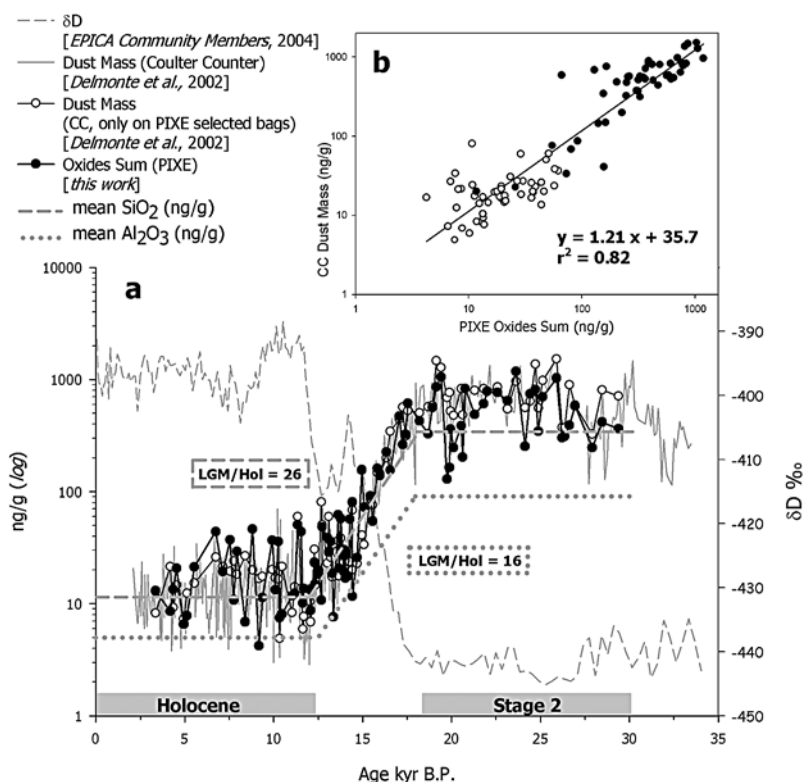


Figure 1. (a) Age profiles of PIXE oxides sum and Coulter Counter (CC) dust mass from *Delmonte et al.* [2002], analyzed in different aliquots of the same EPICA Dome C (EDC) ice core samples; the higher resolution Coulter Counter dust mass record and δD profile [*EPICA Community Members*, 2004] are also plotted to highlight the good correspondence between PIXE and CC records during both the cold last glacial maximum (LGM) and the warm Holocene periods. The mean concentrations of SiO_2 (dashed line) and Al_2O_3 (dotted line) during the Holocene and the LGM are indicated together with their LGM/Holocene ratios (framed boxes); (b) linear correlation between PIXE oxide sum and CC dust mass data: Holocene (gray dots), Deglaciation (white dots), LGM (black dots).

upper continental crust (UCC), together with oxygen [*Hawkesworth and Kemp*, 2006]. Therefore, the sum of their oxide masses ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{MgO} + \text{K}_2\text{O} + \text{TiO}_2$) is expected to represent the near total dust mass content in the ice. The PIXE oxides sum and the total dust mass determined by CC measurements, in different aliquots of the same samples, are shown in Figure 1a on a logarithmic scale since the data cover about three orders of magnitude. A similar trend of PIXE oxides sum and CC dust mass is observed in all the concentration ranges, i.e., in warm and cold periods, characterized by low and high dust atmospheric load, respectively, as also indicated by the good correlation ($r^2 = 0.82$) in Figure 1b. Residuals between the two data sets could be explained by differences in analytical uncertainties of PIXE (see section 2) and CC [*Delmonte et al.*, 2002] methods and by the different size range of particles analyzed: PIXE measurements were performed on the insoluble fraction obtained by filtration on a $0.45 \mu\text{m}$ pore size filter

(therefore including also a certain amount of particles smaller than $0.45 \mu\text{m}$); CC dust mass data refer to the 0.7 (first analytical channel)– $5 \mu\text{m}$ size range, where the upper limit is chosen as representative of the dust particle volume (mass)-size distribution for both LGM and Holocene samples [*Delmonte et al.*, 2002]. On the other hand, particles greater than $5 \mu\text{m}$, when present, are included during filtration. In addition, CC mass concentrations are calculated from particle volume measurements, assuming an average density of 2.5 g cm^{-3} [*Ruth et al.*, 2008].

[10] The PIXE data set allows to discriminate the contribution of each oxide to the dust mass during glacial and interglacial conditions. In Figure 1a, SiO_2 and Al_2O_3 mean concentrations account for about 12 and 5 ng/g during the Holocene and 321 and 87 ng/g during the LGM; accordingly, the LGM/Holocene ratios are 26 for SiO_2 and 16 for Al_2O_3 , indicating that the two oxides (chosen as example since they are the main constituents of

Table 1. Major Element Geochemical Composition (Oxides Relative Abundance) of Ice Core Dust Recorded in Holocene and LGM Sections of the EPICA Dome C Ice Core (Mean Values)^a

	Number of Data	SiO ₂ %	TiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %	K ₂ O %	CIA
EDC – Holocene	21	58.97	2.62	26.09	6.31	-	1.78	-	4.23	76
(standard deviation)		(6.26)	(1.03)	(6.29)	(1.95)	(-)	(0.97)	(-)	(1.30)	(9)
EDC Holocene/UCC		0.89	4.12	1.70	1.13	-	0.50	-	1.52	
(standard deviation)		(0.09)	(1.62)	(0.41)	(0.35)	(-)	(0.27)	(-)	(0.47)	
EDC – LGM	36	66.00	1.04	16.64	8.30	2.68	1.41	1.99	2.83	67
(standard deviation)		(3.75)	(0.20)	(4.16)	(1.20)	(0.68)	(0.25)	(0.43)	(0.45)	(8)
EDC LGM/UCC		1.00	1.63	1.09	1.49	1.08	0.40	0.59	1.02	
(standard deviation)		(0.06)	(0.31)	(0.27)	(0.22)	(0.27)	(0.07)	(0.17)	(0.16)	

^aLGM is last glacial maximum and EDC is EPICA Dome C ice core. Ratios with respect to the upper continental crust (UCC) composition used as reference are also reported. The values of chemical index of alteration are indicated in the last column. Standard deviations for each element are also given.

dust) are present with different relative abundances in the dust deposited under different climatic regimes.

[11] In order to investigate changes in the dust geochemical composition during the last glacial-interglacial cycle, we calculated the relative contribution of each element as oxide with respect to the PIXE oxides sum, used as a reliable estimation of the total dust mass, as discussed above. In that way, our results are suitable for comparison with rock and soil geochemical data in the literature. The mean Holocene and LGM oxide percentages are summarized in Table 1 together with their standard deviations (the whole set of data is available as auxiliary material in Table S1).¹ The relative enrichment of each element, calculated against the UCC composition used as a crustal reference, is also reported. Deviations from unity reflect differences in geochemical composition of dust reaching Antarctica and are considered to indicate the chemical nature of source material.

3.2. LGM Dust Composition

[12] The geochemical composition of dust deposited at Dome C during the LGM shows significant deviations with respect to the crustal reference material (Table 1), for some of the lighter elements such as Na and Ca, as well as for Ti and Fe, while the other components (Mg, Si, Al, and K) have abundances close to the UCC mean composition. In particular, Na and Ca are depleted by about 50% with respect to the UCC, while Ti and Fe are enriched by a similar percentage.

[13] Calcium carbonates and bicarbonates, accounting for an important fraction of the Ca percentage in global crustal sediments, are claimed not to reach the Antarctic continent [Delmonte *et al.*, 2004; De Angelis *et al.*, 1992; Legrand and Mayewski, 1997]. Acid-base exchanges of CaCO₃ and Ca(HCO₃)₂ with atmospheric acidic species (mainly HNO₃ and H₂SO₄), leading to the formation of soluble calcium salts, are demonstrated to occur during transport toward Antarctica and, possibly, after deposition [Röthlisberger *et al.*, 2000]. Ca detected by PIXE is the insoluble fraction included in the crystal structure of silicates and other non calcareous minerals. Accordingly, the CaO value obtained in this work (~1.4%, Table 1) is consistent with the value of 1.3% obtained when the UCC is expressed in a carbonate and evaporite-free basis (i.e., UCC exposed to weathering, namely Shale, following Taylor and McLennan [1985]), rather than the UCC value of ~3.6%.

[14] The depletion in Na (accounting for ~2.0% of the ice core dust mass, Table 1) is due to the dissolution of soluble salts during ice sample melting and filtration. Recently, Bigler *et al.* [2006] emphasized that continental contribution of Na⁺ (coming from halides mobilized from continental evaporite deposits) could be more important than previously assumed over inner East Antarctica, at least during glacial times. However, major ion analysis (Na⁺, Ca²⁺ and Cl⁻) are performed on the soluble fraction, while our determinations exclusively deal with the insoluble content of ice core samples. Similarly, a Na depletion characterizes the Shale composition (Na₂O ~1.2%) compared to the ~3.0% content in the UCC. Hence, the slightly higher Na content found in LGM ice core dust, with respect to the carbonate

¹Auxiliary materials are available in the HTML. doi:10.1029/2008GC002023.

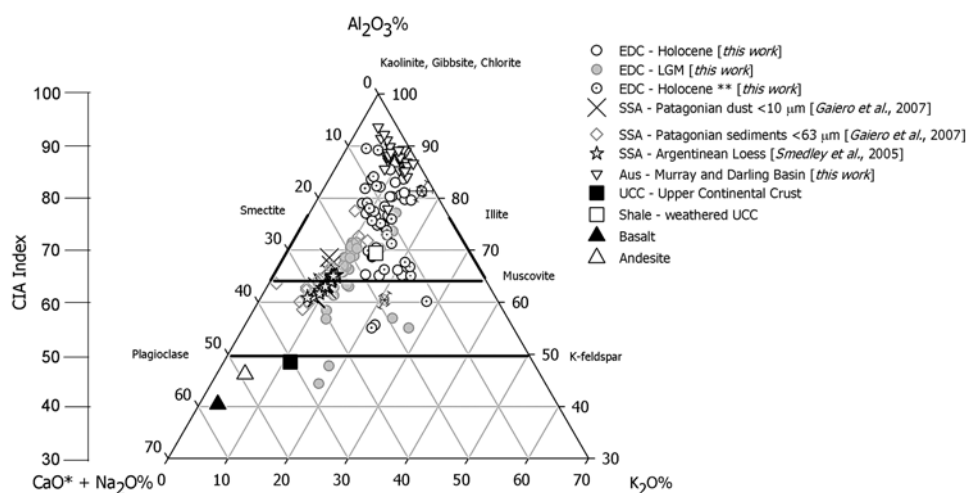


Figure 2. A $(\text{Al}_2\text{O}_3\%) - \text{CN} (\text{CaO}\% + \text{Na}_2\text{O}\%) - \text{K} (\text{K}_2\text{O}\%)$ ternary diagram of EDC Holocene and LGM ice dust compared to reference rock composition and SSA (Argentinean Loess from *Smedley et al.* [2005] and Patagonian sediments from *Gaiero et al.* [2007]) and Australian fine sediments. Data are expressed in mol/mol%. CaO^* values are corrected for the contribution of carbonates, as suggested by *Gallet et al.* [1998] and reference therein. EDC – Holocene** data are obtained by imposing the Na and Mg values of shale used as reference to test the influence of Na and Mg on the CIA index calculation. Typical analytical uncertainties for both Holocene and LGM are applied (as error bars) to one point for each period, to maintain clarity.

and evaporite-free Shale reference, may be related to the nature of the source material. Despite a general enrichment in clay fraction characterizes the far-traveled aeolian dust, its precise final composition relies on the nature of the exposed substrate and the minerals initially present in the source rock [*Pye, 1987; Meunier, 2005*]. In particular, although the effect of size fractionation may affect the Na content, its depletion (or enrichment) with decreasing grain size has been found to be not univocal; the same is true for other alkali and alkaline earth elements such as Ca, Sr, and Ba [*Taylor and McLennan, 1985*].

[15] Other mobile elements, such as Mg and K, do not deviate from their abundance in the UCC ($\sim 2.5\%$ and $\sim 3.2\%$, respectively) and also show similar percentages in the Shale composition ($\sim 2.2\%$ and $\sim 3.8\%$).

[16] Conversely, the positive anomalies of Fe and Ti are taken to reflect the peculiar nature of wind-deflated source material, as discussed below, by comparison with the composition of aeolian sediments from possible dust source regions.

[17] The eight major elements, expressed as oxide molar proportions, allow to calculate the Chemical Index of Alteration (CIA), a measure of the degree of weathering to which sediments have been subjected [*Nesbitt and Young, 1982*]. Because of the dependence of chemical weathering on numerous

factors that can exert a significant control on sediment composition (e.g., temperature and moisture availability), CIA fluctuations can be interpreted as an index of the alteration of source material [e.g., *Dingle and Lavelle, 1998*]; clay-mineral abundance increases in the weathered products, coupled with the depletion of elements having higher geochemical mobility. CIA index is calculated as $[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})]^* 100$, where CaO^* is the amount of CaO in silicate minerals only (i.e., excluding carbonates and apatite). Since the dominant process during chemical weathering of the upper crust is the degradation of feldspars to clay minerals, the CIA index quantifies the ratio of original, primary minerals and secondary (weathered) products, where the proportion of alumina to alkalis typically increases.

[18] The CIA values of Antarctic LGM dust range from 45 to 78 (mean value 67 ± 8 , Table 1), as reported in the triangular plot of Figure 2, together with Holocene dust and values of reference source materials. CIA values are ~ 50 for fresh rocks and increase up to 100, as chemical weathering occurs; therefore, the CIA value for UCC is 50 and the index value for Shale (i.e., weathered UCC) falls between 70 and 75. The CIA mean value obtained for LGM ice core dust agrees with those related to Shale and Loess deposits, corrected for the contribution of carbonates, as suggested in *Gallet et al.*



[1998] and references therein. The close relationship between the composition of the Shale and the multirecycled, well mixed, aeolian material, such as Loess deposits, was already stated by *Taylor and McLennan* [1985] and reinforced by *Gallet et al.* [1998]; these authors suggest several cycles of physical and chemical alteration (i.e., sedimentary differentiation by weathering processes) for loess particles. Accordingly, glacial dust in the EDC ice core reveals a weathered-crustal-like signature.

[19] The Sr and Nd isotopic composition of glacial dust [*Grousset et al.*, 1992; *Basile et al.*, 1997; *Delmonte et al.*, 2004] suggested South America as a dominant dust source during late Pleistocene glaciations. Here, we compare literature data on elemental composition from southern South America (SSA) loess deposits [*Smedley et al.* 2005] and Patagonian sediments [*Gaiero et al.* 2007], providing further evidence for a close correspondence between the major element composition of glacial ice core dust and SSA sediments (Figure 2). This evidence supports a common origin or similar processes of transport and deposition for Argentine Loess and LGM ice core dust, according to *Gaiero* [2007].

[20] Note that EDC polar dust has a $\sim 2 \mu\text{m}$ centered size distribution [*Delmonte et al.*, 2002]. Actually, the size selection during long-range transport from the source to the sink can occur as a mineralogical selection, with gravitational settling of heavy minerals [*Pye*, 1987]. Consequently, a more reliable comparison with the EDC ice core dust should be carried out by selecting sediments characterized by a similar particle size distribution. Unfortunately, fine fractions of Southern Hemisphere (SH) continental sediments are hardly documented. Patagonian sediments and dust events data, available from *Gaiero et al.* [2007] and used in Figure 2, are not related to a bulk composition but to particles size $< 63 \mu\text{m}$ and $< 10 \mu\text{m}$, respectively; despite these sediments having a coarser size with respect to ice core dust, their low carbonate content and their representativeness of a large geographical area, make them suitable for comparison [*Gaiero et al.*, 2007]. Moreover, the two Patagonian data sets do not show clear differences in their geochemical composition (Figure 2), although grain-size decrease is usually associated to depletion of SiO_2 and a concomitant increase of Al_2O_3 [*Taylor and McLennan*, 1985; *Pye*, 1987].

[21] The only available geochemical data set (major elements) of Australian fine sediments is presented

here for the first time. The Murray and Darling Basin samples come from several locations within a large fluvial system in Southeastern Australia and are representative of a wide catchment area, covering about 10^6 km^2 . These river sediments derive from the erosion and weathering of different source materials, therefore being ideal candidates to represent the southeastern Australian dust sources [*Gingele and De Deckker*, 2005]. In addition, measurements were performed on the $< 2 \mu\text{m}$ grain size fraction, after carbonate removal, making them ideal for a direct comparison with dust in the EDC ice core.

[22] The very different oxide composition of Australian fine sediments indicates that Australia was not the primary dust supplier to Antarctica in the LGM, when the SSA source was dominant.

[23] The close similarity (strong difference) between LGM ice core dust and SSA (Australia) sediment composition in the triangular plot is reinforced by the trend of all major elements shown in Figure 3. It is interesting to note that Ti and Fe show a similar enrichment in source material (SSA) and ice core dust composition (LGM).

[24] Moreover, a uniform geochemical composition for LGM ice core dust is pointed out by the low standard deviation associated with each element (see error bars in Figure 3). This low compositional variability provides further evidence that dust was transported from a dominant source (SSA), with largely unchanged pathways of atmospheric transport from the lower latitudes to the Antarctic Plateau. Furthermore, our results suggest that no significant environmental changes occurred at the dust source during the LGM with conditions allowing for massive availability, intense wind deflation, and long-range transport of dust characterized by steady composition, all through the whole cold period.

3.3. Holocene Dust Composition

[25] When discussing the Holocene dust composition, it is important to note that the low dust concentration found in interglacial ice samples makes geochemical measurements a challenge. Consequently, the evaluation of a reliable geochemical composition of Holocene dust could be affected by a higher level of analytical error with respect to glacial dust archived in ice, mainly for minor components. On the other hand, recent measurements performed on selected ice samples by means of different analytical techniques, such as

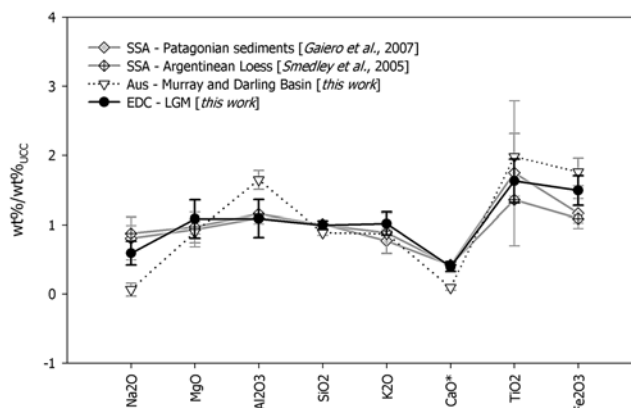


Figure 3. Diagram of LGM ice core data compared to SSA (Argentinean Loess from *Smedley et al.* [2005] and Patagonian sediments from *Gaiero et al.* [2007]) and Australian fine sediments. For each element in the diagram, the ratio between the abundance in the ice core dust (or in the source sediments) and in the UCC [*Hawkesworth and Kemp*, 2006] are plotted. Standard deviations are reported as bars.

PIXE, CC, and HR-ICP-MS, in different laboratories [*Ruth et al.*, 2008], resulted in good agreement both for glacial and interglacial periods.

[26] The composition of the EDC ice dust spanning the entire Holocene is presented in the ternary diagram of Figure 2 and the Holocene mean oxide percentages are summarized in Table 1. It is clearly evident that glacial and interglacial dust measured in the EDC ice core show a distinct signature. The CIA value of Holocene data (76 ± 9) is slightly higher than the value of LGM dust (67 ± 8). Although the difference is still within the error limit and the natural variability, this suggests a possibly higher degree of chemical weathering at the dust source.

[27] Since Na and Mg are not measured in Holocene samples (being below or very close to the PIXE detection limit), we tested the shift of Holocene data in the ternary plot (Figure 2) when attributing to ice core dust the Na and Mg values of Shale (used as reference). The position of Holocene samples does not change significantly. These evidences indicate that a peculiar Al contribution characterizes Holocene dust and that weathered secondary products should be dominant.

[28] On average, a certain enrichment of Ti content is found in Holocene ice dust with respect to the UCC (Table 1). Ti rich-heavy minerals such as sphene and rutile, are most unlikely transported by wind over long distances, and *Gaudichet et al.* [1988] reported a minor contribution of amphibole and pyroxene minerals in ice core dust; so samples characterized by high Ti content could be consti-

tuted by a mixture of volcanic inputs and detrital material.

[29] Although the identification of likely source areas of interglacial dust recorded in Antarctic ice cores is still a matter of debate, recent investigations suggest significant differences also in the trace elements (REE [*Gabrielli et al.*, 2006]; lithium [*Siggaard-Andersen et al.*, 2007]) and isotopic [*Delmonte et al.*, 2007; *Winckler and Fischer*, 2006] signatures of glacial and interglacial dust; isotopic composition of interglacial dust points to a possible source mix during warm stages, in which Australia could have played a large role [*Revel-Rolland et al.*, 2006].

[30] Regarding Australia, the fine-grained sediments ($<2 \mu\text{m}$) from the Murray-Darling fluvial system show a major element composition closer to that measured for Holocene ice core dust (Figure 2); particularly, Australian samples have very low values (lower than 1%) for the more mobile elements (e.g., Na and Ca), and high Al content ($\text{Al}_2\text{O}_3\% \sim 25\%$), reflecting their abundance in the clay mineral fraction, largely dominated by Smectite, Illite, and high Kaolinite [*Gingele and De Deckker*, 2005]. Shortly, the peculiar feature of Holocene dust and Australian sediments appears to be their high content of Al_2O_3 that drives the data toward high CIA values (Figure 2). Focusing on SiO_2 and Al_2O_3 , the two main components, Figure 4 points out the geochemical similarity between Holocene dust and the Australian sediments, while significant differences arise from the comparison with Argentine Loess and Patagonian sediment compositions. On the other hand, Figure 4 reinfor-

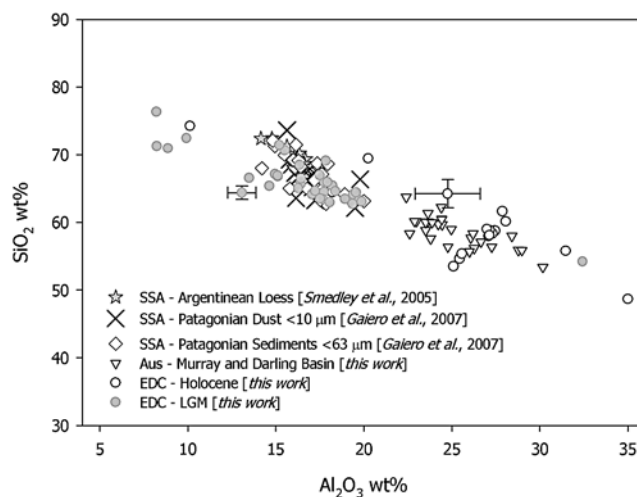


Figure 4. SiO_2 versus Al_2O_3 diagram of dust in Holocene and LGM EDC ice compared to SSA and Australian fine sediments. Typical analytical uncertainties for both Holocene and LGM are applied (as error bars) to one point for each period, to maintain clarity.

ces the previous observations of close similarity with SSA sediments when LGM dust is considered.

[31] Finally, we have to be aware that several components measured in Holocene ice core dust show high variability, as demonstrated by the high values of the standard deviations in Table 1. Moreover, the effects of the analytical uncertainties discussed before (see section 2) are plotted both in Figures 2 and 4; although the uncertainty is clearly higher for Holocene data, analytical errors do not fully explain the Holocene variability. A similar significant data scattering also characterizes measurements reported in the recent literature dealing with Holocene ice core dust [Gabrielli *et al.*, 2006; Siggaard-Andersen *et al.*, 2007; Ruth *et al.*, 2008]. In contrast to the LGM, these results contradict the hypothesis of a single source dominating the dust mix over the whole Holocene. Although up to now investigations on Holocene dust do not depict a definite scenario, the high compositional variability could be a true climatic signal, suggesting a modulate role of the main SH dust sources (Australia and SSA), contributing with changing proportions to the dust mix.

4. Conclusions

[32] The PIXE technique, here applied to the elemental analysis of very low amounts of dust recorded in the EDC ice core during the last climatic cycle, provides accurate records of the eight main dust constituents; since the sum of their oxide masses agrees with the total dust mass

measured by Coulter Counter, PIXE oxides percentages were used to discuss the geochemical composition of ice core dust, against reference materials and potential source sediments. Changes in major element composition of aeolian dust reaching Antarctica have been found for glacial and interglacial climatic regimes.

[33] The geochemical composition of dust recorded in the cold LGM period shows a weathered-crustal-like signature; the close similarity with Argentinean Loess and Patagonian sediments indicates the dominant contribution of SSA for dust transported to Antarctica. Moreover, the low compositional variability with respect to interglacial data, gives evidence of no significant environmental changes at the dominant dust source under glacial conditions.

[34] Conversely, the different major element composition of Holocene dust involves the contribution of additional dust sources. Indeed, a weakening of SSA dust source during the Holocene is consistent with a reduced glacial grinding activity and a more intense hydrological cycle and larger vegetation cover (together with a possible effect of sea level rise), during warm climatic conditions; these different conditions lowered dust mobility and availability decreasing the role of SSA as a massive dust supplier to Antarctica.

[35] As a result, the contribution from South America that quantitatively dominated the flux of dust to Antarctica during glacials becomes less important during the Holocene. Under warm conditions, the



lower and constant dust flux from the semiarid lands of Australia, coupled with dust events from southern Patagonia where climate is controlled by the Westerlies wind system [Gassò and Stein, 2007], may have provided the mixture constituting Holocene dust.

[36] Changes in climatic regimes at continental latitudes and transport efficiency to Antarctica are likely able to influence the contribution of the different sources to the dust mix composition during warm periods, so explaining the higher variability observed in the interglacial Antarctic dust with respect to the glacial composition.

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References

- Basile, I., F. Grousset, M. Revel, J. R. Petit, P. Biscaye, and N. Barkov (1997), Patagonian origin of glacial dust deposited in East Antarctica (Vostok and Dome C) during glacial stages 2, 4 and 6, *Earth Planet. Sci. Lett.*, *146*, 573–589, doi:10.1016/S0012-821X(96)00255-5.
- Bigler, M., R. Röthlisberger, F. Lambert, T. F. Stocker, and D. Wagenbach (2006), Aerosol deposited in East Antarctica over the last glacial cycle: Detailed apportionment of continental and sea salt contributions, *J. Geophys. Res.*, *111*, D08205, doi:10.1029/2005JD006469.
- De Angelis, M., N. I. Barkov, and V. N. Petrov (1992), Source of continental dust over Antarctica during the last glacial cycle, *J. Atmos. Chem.*, *14*, 233–244, doi:10.1007/BF00115236.
- Delmonte, B., J. R. Petit, and V. Maggi (2002), Glacial to Holocene implications of the new 27,000-year dust record from the EPICA Dome C (East Antarctica) ice core, *Clim. Dyn.*, *18*(8), 647–660, doi:10.1007/s00382-001-0193-9.
- Delmonte, B., I. Basile-Doelsch, J.-R. Petit, P. Biscaye, V. Maggi, M. Revel-Rolland, A. Michard, E. Jagoutz, and F. Grousset (2004), Comparing the Epica and Vostok dust records during the last 220,000 years: Stratigraphical correlation and provenance in glacial periods, *Earth Sci. Rev.*, *66*(1–2), 63–87, doi:10.1016/j.earscirev.2003.10.004.
- Delmonte, B., J. R. Petit, I. Basile-Doelsch, E. Jagoutz, and V. Maggi (2007), Late Quaternary Interglacials in East Antarctica from ice core dust records, in *The Climate of Past Interglacials*, edited by F. Sirocko, T. Litt, and M. Claussen, pp. 53–73, Elsevier, Amsterdam.
- Dingle, R. V., and M. Lavelle (1998), Late Cretaceous–Cenozoic climatic variations of the northern Antarctic Peninsula: New geochemical evidence and review, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *141*, 215–232, doi:10.1016/S0031-0182(98)00056-X.
- EPICA Community Members (2004), Eight glacial cycles from an Antarctic ice core, *Nature*, *429*, 623–628.
- Fischer, H., et al. (2007), Reconstruction of millennial changes in dust emission, transport and regional sea ice coverage using the deep EPICA ice cores from the Atlantic and Indian Ocean sector of Antarctica, *Earth Planet. Sci. Lett.*, *260*, 340–354, doi:10.1016/j.epsl.2007.06.014.
- Gabrielli, P., C. Barbante, C. Turetta, A. Marteel, C. Boutron, G. Cozzi, W. Cairns, C. Ferrari, and P. Cescon (2006), Direct determination of Rare Earth Elements at the subpicogram per gram level in Antarctic ice by ICP-SFMS using a desolvation system, *Anal. Chem.*, *78*, 1883–1889, doi:10.1021/ac0518957.
- Gaiero, D. M. (2007), Dust provenance in Antarctic ice during glacial periods: From where in southern South America?, *Geophys. Res. Lett.*, *34*, L17707, doi:10.1029/2007GL030520.
- Gaiero, D. M., F. Brunet, J.-L. Probst, and P. J. Depetris (2007), A uniform isotopic and chemical signature of dust exported from Patagonia: Rock sources and occurrence in southern environments, *Chem. Geol.*, *238*, 107–120, doi:10.1016/j.chemgeo.2006.11.003.
- Gallet, S., B. Jahn, B. V. V. Lanoe, A. Dia, and E. Rossello (1998), Loess geochemistry and its implications for particle origin and composition of the upper continental crust, *Earth Planet. Sci. Lett.*, *156*, 157–172, doi:10.1016/S0012-821X(97)00218-5.
- Gaspari, V., C. Barbante, G. Cozzi, P. Cescon, C. F. Boutron, P. Gabrielli, G. Capodaglio, C. Ferrari, J. R. Petit, and B. Delmonte (2006), Atmospheric iron fluxes over the last deglaciation: Climatic implications, *Geophys. Res. Lett.*, *33*, L03704, doi:10.1029/2005GL024352.
- Gassò, S., and A. F. Stein (2007), Does dust from Patagonia reach the sub-Antarctic Atlantic Ocean?, *Geophys. Res. Lett.*, *34*, L01801, doi:10.1029/2006GL027693.
- Gaudichet, A., M. D. Angelis, R. Lefevre, J. R. Petit, Y. S. Korotkevitch, and V. N. Petrov (1988), Mineralogy of insoluble particles in the Vostok Antarctic ice core over the last climatic cycle (150 kyr), *Geophys. Res. Lett.*, *15*(13), 1471–1474, doi:10.1029/GL015i013p01471.
- Ghermandi, G., R. Cecchi, M. Capotosto, and F. Marino (2003), Elemental composition determined by PIXE analysis of the insoluble aerosol particles in EPICA-Dome C ice core samples representing the last 27,000 years, *Geophys. Res. Lett.*, *30*(22), 2176, doi:10.1029/2003GL018169.
- Gingele, F. X., and P. De Deckker (2005), Clay mineral, geochemical and Sr-Nd isotopic fingerprinting of sediments in the Murray–Darling fluvial system, southeast Australia, *Aust. J. Earth Sci.*, *52*, 965–974, doi:10.1080/08120090500302301.
- Grousset, F. E., P. E. Biscaye, M. Revel, J. R. Petit, K. Pye, S. Joussaume, and J. Jouzel (1992), Antarctic (Dome C) ice-core dust at 18 k.y. B.P.: Isotopic constraints and origins, *Earth Planet. Sci. Lett.*, *111*, 175–182, doi:10.1016/0012-821X(92)90177-W.
- Hawkesworth, C. J., and A. I. S. Kemp (2006), The evolution of the continental crust, *Nature*, *443*, 811–817, doi:10.1038/nature05191.
- Lambert, F., B. Delmonte, J. R. Petit, M. Bigler, P. R. Kaufmann, M. A. Hutterli, T. F. Stocker, U. Ruth, J. P. Steffensen, and V. Maggi (2008), Dust-climate couplings over the past



- 800,000 years from the EPICA Dome C ice core, *Nature*, 452, 616–619, doi:10.1038/nature06763.
- Legrand, M., and P. Mayewski (1997), Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, 35, 219–243, doi:10.1029/96RG03527.
- Mahowald, N. M., D. R. Muhs, S. Levis, P. J. Rasch, M. Yoshioka, C. S. Zender, and C. Luo (2006), Change in atmospheric mineral aerosols in response to climate: Last glacial period, preindustrial, modern, and doubled carbon dioxide climates, *J. Geophys. Res.*, 111, D10202, doi:10.1029/2005JD006653.
- Marino, F., V. Maggi, B. Delmonte, G. Ghermandi, and J. R. Petit (2004), Elemental composition (Si, Fe, Ti) of atmospheric dust over the last 220 kyr from the EPICA ice core (Dome C, Antarctica), *Ann. Glaciol.*, 39, 110–118, doi:10.3189/172756404781813862.
- Meunier, A. (2005), *Clays*, 472 pp., Springer, Berlin.
- Nesbitt, H. W., and G. M. Young (1982), Early Proterozoic climates and plate motions inferred from major chemistry of lutites, *Nature*, 299, 715–717, doi:10.1038/299715a0.
- Parrenin, F., et al. (2007), The EDC3 chronology for the EPICA Dome C ice core, *Clim. Past*, 3, 485–497.
- Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, 399, 429–436, doi:10.1038/20859.
- Prospero, J. M., P. Ginoux, O. Torres, S. E. Nicholson, and T. E. Gill (2002), Environmental characterization of global sources of atmospheric soil dust identified with the NIMBUS 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product, *Rev. Geophys.*, 40(1), 1002, doi:10.1029/2000RG000095.
- Pye, K. (1987), *Aeolian Dust and Dust Deposits*, 334 pp., Academic, London.
- Revel-Rolland, M., P. De Deckker, B. Delmonte, P. P. Hesse, J. W. Magee, I. Basile-Doelsch, F. Grousset, and D. Bosch (2006), Eastern Australia: A possible source of dust in East Antarctica interglacial ice, *Earth Planet. Sci. Lett.*, 249, 1–13, doi:10.1016/j.epsl.2006.06.028.
- Röthlisberger, R., M. A. Hutterli, S. Sommer, E. W. Wolff, and R. Mulvaney (2000), Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core, *J. Geophys. Res.*, 105(D16), 20,565–20,572, doi:10.1029/2000JD900264.
- Ruth, U., et al. (2008), Proxies and measurement techniques for mineral dust in Antarctic ice cores, *Environ. Sci. Technol.*, 42, 5675–5681, doi:10.1021/es703078z.
- Satheesh, S. K., and K. Krishna Moorthy (2005), Radiative effects of natural aerosols: A review, *Atmos. Environ.*, 39, 2089–2110, doi:10.1016/j.atmosenv.2004.12.029.
- Siggaard-Andersen, M.-L., P. Gabrielli, J. P. Steffensen, T. Strömfeldt, C. Barbante, C. Boutron, H. Fischer, and H. Miller (2007), Soluble and insoluble lithium dust in the EPICA DomeC ice core - Implications for changes of the East Antarctic dust provenance during the recent glacial–interglacial transition, *Earth Planet. Sci. Lett.*, 258, 32–43, doi:10.1016/j.epsl.2007.03.013.
- Smedley, P. L., D. G. Kinniburgh, D. M. J. Macdonald, H. B. Nicolli, A. J. Barros, J. O. Tullio, J. M. Pearce, and M. S. Alonso (2005), Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina, *Appl. Geochem.*, 20, 989–1016, doi:10.1016/j.apgeochem.2004.10.005.
- Taylor, S. R., and S. M. McLennan (1985), *The Continental Crust: Its Composition and Evolution*, 312 pp., Blackwell Sci., Oxford.
- Vallelonga, P., P. Gabrielli, K. J. R. Rosman, C. Barbante, and C. F. Boutron (2005), A 220-kyr record of Pb isotopes at Dome C Antarctica from analyses of the EPICA ice core, *Geophys. Res. Lett.*, 32, L01706, doi:10.1029/2004GL021449.
- Winckler, G., and H. Fischer (2006), 30,000 years of cosmic dust in Antarctic ice, *Science*, 313, 491, doi:10.1126/science.1127469.
- Wolff, E. W., et al. (2006), Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles, *Nature*, 440, 491–496, doi:10.1038/nature04614.