



## A major glacial-interglacial change in aeolian dust composition inferred from Rare Earth Elements in Antarctic ice

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### ABSTRACT

We present the first Rare Earth Elements (REE) concentration record determined in 294 sections of an Antarctic ice core (EPICA Dome C), covering a period from 2.9 to 33.7 kyr BP. REE allow a detailed quantitative evaluation of aeolian dust composition because of the large number of variables (i.e. 14 elements). REE concentrations match the particulate dust concentration profile over this period and show a homogeneous crustal-like composition during the last glacial stage (LGS), with only a slight enrichment in medium REE. This signature is consistent with the persistent fallout of a mixture of dust from heterogeneous sources located in different areas or within the same region (e.g. South America). Starting at ~15 kyr BP, there was a major change in dust composition, the variable character of which persisted throughout the Holocene. This varying signature may highlight the alternation of single dust contributions from different sources during the Holocene. We observe that the frequent changes in REE composition at the onset of the Holocene (10–13.5 kyr BP) are linked to dust size and in turn to wind strength and/or the path of the atmospheric trajectory. This may indicate that atmospheric circulation dictated the composition of the dust fallout to East Antarctica at that time. Although the dust concentrations remained fairly low, a notable return towards more glacial dust characteristics is recorded between 7.5 and 8.3 kyr BP. This happened concomitantly with a widespread cold event around 8 kyr BP that was 400–600 years long and suggests a moderate reactivation of the dust emission from the same potential source areas of the LGS.

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### 1. Introduction

Ice cores provide compelling evidence that airborne dust from the austral continents reached Antarctica during the past climatic cycles (e.g. Wolff et al., 2006; Fischer et al., 2007; Delmonte et al., 2008). However, dust concentrations in Antarctic ice are extremely

low, ranging from ~15 ng g<sup>-1</sup> during interglacials up to ~800 ng g<sup>-1</sup> during glacial stages. As snow accumulation rates were reduced during cold periods, a glacial/interglacial flux ratio of ~25 was deduced by Lambert et al. (2008). The dust trapped in Antarctic ice is composed of detrital minerals such as clays, quartz and feldspars (Gaudichet et al., 1988). In particular, illite, chlorite, smectite and kaolinite are present at any time but a significantly smaller amount of kaolinite was observed in Last Glacial Maximum (LGM) samples (Gaudichet et al., 1992).

One important question of Antarctic glaciology concerns the provenance of dust trapped in the ice. The answer would provide

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important information on the past atmospheric circulation, serving to validate global circulation models and offering clues on the ancient environmental conditions of the surrounding continents. Sr and Nd isotope studies in East Antarctic ice cores (Delmonte et al., 2008), along with atmospheric circulation modelling (Lunt and Valdes, 2001) have identified South America as a major dust contributor during glacial stages.

During cold periods, weathering and glacial erosion likely played an important role in the dust production in southern South America (Gaiero et al., 2007; Sugden et al., 2009) and a persistent westerly circulation might have allowed the transfer of dust towards the interior of Antarctica (Krinner and Genthon, 2003). However, there is a lack of knowledge concerning the characteristics and the source of the dust transported to Antarctica during interglacial stages. Some preliminary studies suggested that glacial/interglacial changes in dust composition may have occurred (Gabrielli et al., 2005a; Winckler and Fischer, 2006; Siggaard-Andersen et al., 2007; Delmonte et al., 2007; Lanci et al., 2008; Marino et al., 2008). It was also suggested that Australia could be an important contributor of dust for Antarctica during the Holocene (Revel-Rolland et al., 2006) and at present (Li et al., 2008).

Rare earth elements (REE) can provide a robust, specific and versatile tool for the geochemical characterization of the aeolian dust in Antarctic ice. The 14 REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) range in atomic number from 57 (La) to 71 (Lu). From here on, we differentiate between light REE (LREE; La, Ce, Pr, Nd), medium REE (MREE; Sm, Eu, Gd, Tb, Dy, Ho) and heavy REE (HREE; Er, Tm, Yb, Lu). As their atomic mass increases, their radius decreases but they keep the same external electronic configuration. Therefore, their chemical properties remain essentially identical, allowing REE to behave like isotopes. REE are lithophilic refractory elements that, due to their low solubility, are mostly transported in the environment in the particulate phase. All these characteristics prevent REE from being strongly fractionated by weathering and diagenetic processes (except Ce and Eu that might be fractionated by redox processes) and thus they are ideal as geochemical tracers (Henderson, 1984).

The main advantage of using REE is that, as they are 14 elements, they are potentially more suitable for delineating changes in the aeolian dust composition. In addition, REE in polar ice are rarely influenced by sources (e.g. volcanic ash fallout as found by Wei et al., 2008) other than continental rocks and soil dust (Gabrielli et al., 2009).

Here, we show the first record of REE concentrations determined in the EPICA ice core from Dome C in Antarctica (hereafter EDC) from 2.9 to 33.7 kyr BP, which includes the Holocene, the last transition, the LGM and part of the last glacial epoch. Based on these novel dust tracers we provide strong evidence of a large glacial/interglacial change in dust composition that started at ~15 kyr BP and continued through the Holocene, except for an oscillation that occurred ~8 kyr BP which indicates a short return towards more glacial-like dust. In addition, we present a preliminary evaluation of the dust provenance and the linkage between the dust composition and the atmospheric transport.

## 2. Methods

### 2.1. Samples

The samples originate from a deep ice core drilled in Dome C on the East Antarctic Plateau (75°06' S; 123°21' E; altitude 3233 m; mean annual temperature -54 °C) within the framework of the European Project for Ice Coring in Antarctica (EPICA) (EPICA community members 2004). A total of 294 samples were extracted from between 112 and 656 m depth which, according to the EDC3

timescale (Parrenin et al., 2007) spans a period between 2.9 and 33.7 kyr BP. Temporal spacing of the samples is ~60 and ~140 years during the Holocene and the last glacial stage (LGS), respectively. Each sample encompasses 2–3 years in the Holocene and 4–5 years in the LGS. A gap occurs between 21.7 and 27.3 kyr BP where only four samples were available.

### 2.2. Analysis

An ultra-sensitive specific methodology was developed for the direct determination of REE in polar ice. This method, extensively illustrated elsewhere (Gabrielli et al., 2006a), is based on Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP SFMS; Element2, Thermo) coupled with a micro-flow nebulizer and a desolvation system. With this setup, REE can be detected down to the sub-pg g<sup>-1</sup> level (1 pg g<sup>-1</sup> = 10<sup>-12</sup> g g<sup>-1</sup>) in ~1 ml of melted ice acidified to pH = 1 with HNO<sub>3</sub> (ultra-pure grade). We will discuss this sample pre-treatment below in section 2.4.

Samples were analysed in low-resolution mode. A desolvation system for sample introduction enhanced the sensitivity and eliminated the spectral interferences. In the course of this analysis, however, a residual interference still affected Gd concentrations, which are reported as upper limits and not used in this study. A matched calibration was used for quantification. The precision (relative standard deviation on ten replicates) ranged from 2% for La, Ce, Pr and Lu, up to 10% for Er, Tm and Yb. Instrumental limits of detection (LOD) ranged from 0.0004 pg g<sup>-1</sup> for Lu to 0.03 pg g<sup>-1</sup> for Gd. To estimate the accuracy, we carried out a recovery test by adding standard spikes of a REE multi-element stock solution to a real sample. The REE concentrations determined in a sample spiked at 0.62 pg g<sup>-1</sup>, were calculated to fall between 95 and 105% of the expected value using the slopes provided by the matched calibration.

Due to the extremely low LOD and the REE concentrations of the blanks (see section 2.3), the relative instrumental standard deviation of the spectra analysed during a run essentially represents the whole analytical uncertainty. For LREE, this is 8% for Holocene samples and 3% for LGS samples. For MREE and HREE, this is higher (25–35% in the Holocene and 5–8% in the LGS samples).

### 2.3. Sample decontamination and blank levels

The determination of REE in EDC is an analytical challenge because of the extremely low concentrations, which range down to the femtogram per gram (10<sup>-15</sup> g g<sup>-1</sup>) level, and because of the consequent risk of contamination (Gabrielli et al., 2006a). Clean procedures and sensitive instrumental techniques are thus required. For REE determination, low density polyethylene bottles (LDPE; Nalgene) were cleaned according to established procedures (Boutron, 1990). The decontamination of the ice samples was performed by means of triple washing with ultra pure water, using clean stainless steel forceps. This process is described elsewhere (Delmonte et al., 2004) and was already successfully used for trace element analysis in ice (Gaspari et al., 2006; Wei et al., 2008).

The procedural blank is defined as the REE content introduced into the samples during their preparation. This was estimated as the difference between the REE concentrations found in an artificial ice core (constructed by freezing ultra pure water in a 2 L Perfluoroalkoxy (PFA) bottle) before and after the decontamination. Although variations at this ultra low level might be relatively large, the REE content introduced by sample handling is undetectable (Table 1). The water and the PFA bottle used to make this artificial ice core were sufficiently clean to provide a REE background that was low enough to allow recognition of a small procedural contamination. However, much lower REE concentrations can

**Table 1**Limit of detection (LOD), typical REE concentrations ( $\text{pg g}^{-1}$ ) in ultra pure water and in an artificial ice core before and after the decontamination process.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Limit of Detection (LOD)	0.004	0.004	0.002	0.008	0.008	0.003	0.030	0.002	0.003	0.001	0.002	0.001	0.002	0.001
REE in ultra pure water	0.01	0.03	<0.002	<0.008	<0.008	<0.003	0.3	<0.002	<0.003	<0.001	<0.002	<0.001	<0.002	<0.001
Artificial ice core	Before processing	0.08	0.11	0.01	0.07	0.08	0.03	0.11	0.002	0.014	0.002	0.005	0.002	0.013
	After processing	0.07	0.10	0.01	0.06	0.08	0.03	0.08	0.002	0.010	0.002	0.004	0.002	0.010

routinely be obtained in ultra pure water that is collected in LDPE bottles used for sample storage (Table 1). Thus the REE concentrations determined in the artificial ice core likely reflect the overall contamination level of the PFA bottle used and were not subtracted from the samples concentration.

The negligible procedural blanks suggest that excellent REE contamination control can be achieved by adopting triple washing in ultra pure water as an alternative to the time-consuming chiselling technique (Candelone et al., 1994). In this way, sample preparation is much faster and the sample analysis rate increases significantly. The confidence in the REE concentrations in samples prepared using this method (Table 2) is confirmed by comparison with very similar concentrations found in other EDC sections cleaned by chiselling (Gabrielli et al., 2006a).

#### 2.4. Sample treatment

In order to understand how various sample pre-treatments impact the REE concentrations and their ratios in EDC, we tested different preparations of melted ice-core samples at low (interglacial) and high (glacial) REE concentrations (Gaspari et al., in preparation). Briefly, these samples were pre-treated in three different ways:

Method 1 (Acid leached): 1%  $\text{HNO}_3$  (ultra-pure grade) acidification. This is the conventional preparation used for trace element determination and was also used in this work.

Method 2 (Pre-filtered acid leached): 1%  $\text{HNO}_3$  (ultra-pure grade) acidification of samples, which had passed through a  $0.2 \mu\text{m}$  filter before acidification. The aim of this test was to obtain information on the REE in the dissolved fraction (particles below  $0.2 \mu\text{m}$  in diameter).

Method 3 (Total): full acid (ultra-pure grade HF and  $\text{HNO}_3$ ) digestion using microwave heating. This test allowed determination of the total REE concentration.

In Fig. 1a, we display the mass fraction relative to the total content in unfiltered samples (Method 1/Method 3) that are representative of glacial and interglacial stage ice. This is  $\sim 0.55$  for LREE,  $\sim 0.50$  for MREE, and  $\sim 0.40$  for HREE. Thus, LREE does appear slightly over estimated with respect to the fractions of MREE and HREE ( $\sim 9\%$  and  $\sim 27\%$ , respectively) determined by our method. This should be taken into account when comparing the shape of the REE patterns obtained in the ice and in the dust samples collected in potential source areas (as discussed in section 4.2 below).

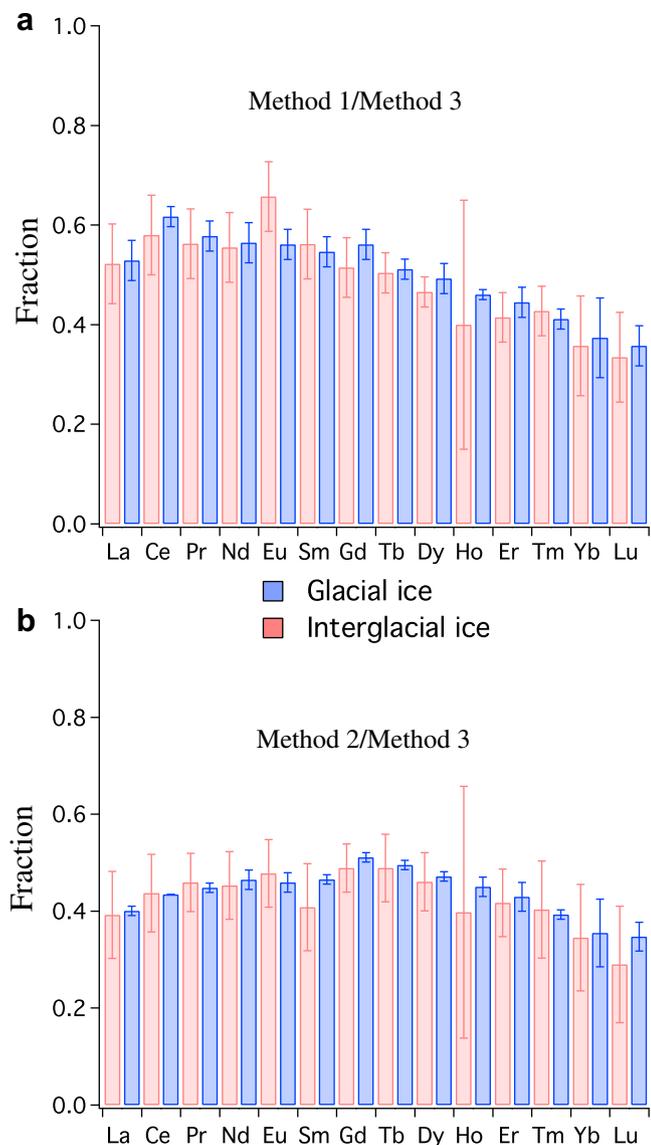
However, we note that the mass fraction determined for each REE is identical within the error bars ( $1\sigma$ ) at low (interglacial) and high (glacial) levels. In general, our experiment suggests that we can compare directly glacial/interglacial changes in dust composition. In fact, as all the samples should show the same LREE enrichment (or HREE depletion), this slight artefact should not affect the glacial-interglacial variations of the REE patterns.

In Fig. 1b, we display the mass fraction determined in filtered samples (Method 2/Method 3). In this case, the mass fraction of MREE ( $\sim 0.50$ ) is over estimated by  $\sim 20\%$  with respect to those of LREE and HREE ( $\sim 0.40$ ). Of course, the REE mass fraction in filtered samples is lower than in unfiltered samples, but this is mainly caused by the decreased contribution of LREE, which strongly suggests that it is essentially the dissolved fraction that is determined by our method. This conclusion is consistent with the idea that the solid (dust) mass fraction for particles  $<0.7 \mu\text{m}$  in diameter is negligible in this ice (Delmonte et al., 2002). Comparison with Fig. 1a suggests that a part of the LREE ( $\sim 0.15$ ) is dissolved in solution only after acidification both at low (interglacial) and high

**Table 2**

Main statistics and enrichment factors (Ce is the crustal reference) of REE in EDC during the Holocene and the last glacial stage.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
<b>Concentrations (<math>\text{pg g}^{-1}</math>)</b>														
Average Holocene	0.39	0.91	0.092	0.31	0.05	0.013	<0.14	0.008	0.043	0.008	0.022	0.003	0.017	0.003
Median Holocene	0.26	0.60	0.065	0.21	0.04	0.009	<0.09	0.006	0.034	0.006	0.017	0.002	0.012	0.002
Average last glacial age	7.6	18.4	2.1	7.6	1.7	0.40	<1.3	0.24	1.3	0.24	0.66	0.089	0.56	0.078
Median last glacial age	6.3	15.0	1.7	6.3	1.5	0.33	<1.0	0.20	1.1	0.20	0.56	0.075	0.47	0.067
Maximum	38	98	11.7	40	9.6	2.2	<9.3	1.4	6.7	1.4	3.6	0.5	3.0	0.43
Minimum	0.022	0.042	0.004	0.019	<0.008	<0.003	<0.03	<0.002	0.006	0.001	0.002	0.001	<0.002	0.001
Average last glacial age/Holocene	20	20	23	25	33	32	-	30	30	30	30	28	34	27
Median last glacial age/Holocene	24	25	27	30	37	37	-	32	32	33	33	31	39	30
<b>Crustal Enrichment Factors</b>														
Average Holocene	0.9	1.0	1.0	0.8	0.8	0.7	-	1.0	0.9	0.8	0.9	0.8	0.6	0.7
Median Holocene	0.9	1.0	1.0	0.8	0.8	0.7	-	1.0	0.9	0.8	0.9	0.8	0.6	0.6
Average last glacial age	0.8	1.0	1.0	0.9	1.1	1.0	-	1.2	1.1	1.0	1.1	1.0	0.9	0.7
Median last glacial age	0.8	1.0	1.0	0.9	1.1	1.0	-	1.2	1.1	1.0	1.1	1.0	0.9	0.7
Average last glacial age/Holocene	0.9	1.0	1.1	1.1	1.4	1.5	-	1.2	1.2	1.2	1.2	1.2	1.5	1.1
Median last glacial age/Holocene	0.9	1.0	1.1	1.1	1.4	1.4	-	1.2	1.2	1.2	1.2	1.2	1.5	1.2
<b>Mean crustal concentrations (<math>\mu\text{g g}^{-1}</math>)</b> (from Wedepohl, 1995)	30	60	6.7	27	5.3	1.3	4.0	0.65	3.8	0.8	2.1	0.30	2.0	0.35



**Fig. 1.** Fraction of the total REE concentration determined in EPICA Dome C ice samples pre-treated with acidification (Method 1: acid leached; panel a) and with acidification after passage through a 0.2  $\mu\text{m}$  filter (Method 2: pre-filtered acid leached; panel b). Total REE concentrations were obtained by means of a full acid digestion (Method 3: total). Error bars signify the standard deviations linked to three repetitions of the test.

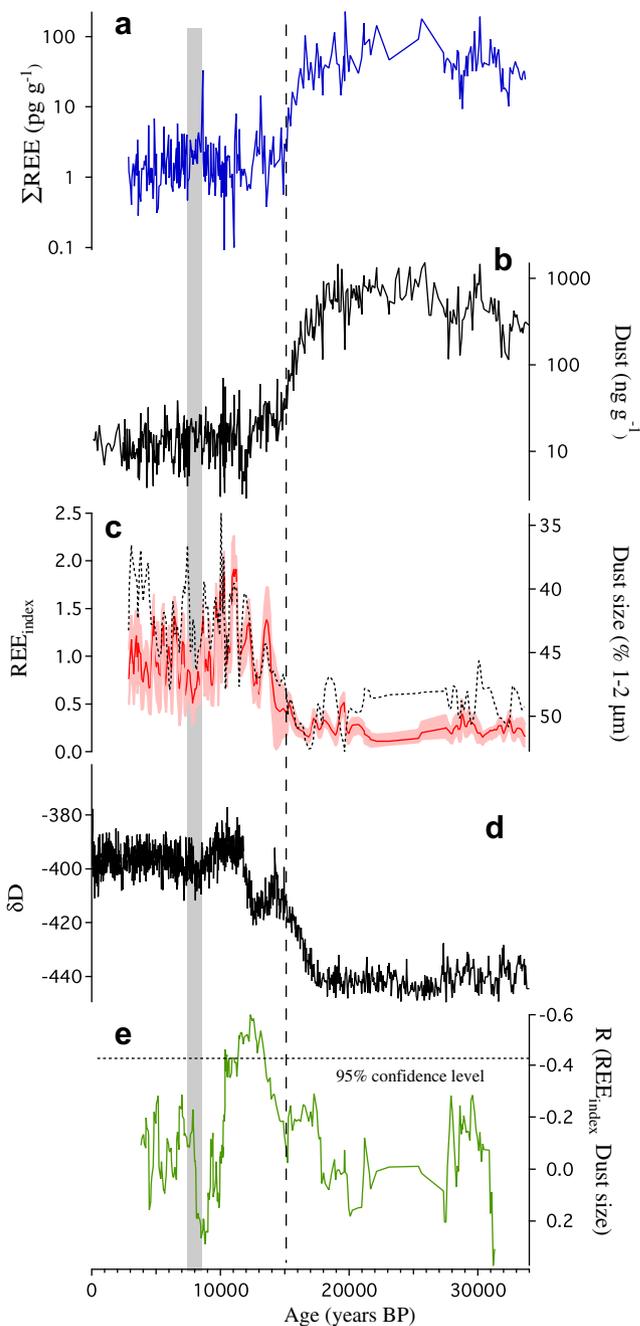
(glacial) concentrations. This provides evidence that particles  $>0.2 \mu\text{m}$  are prone to release more LREE in the acidified solution and are possibly responsible for the slight artefact that is observed.

### 3. Results and discussion

#### 3.1. REE concentrations and enrichment factors

REE concentrations show large variations during the last climatic cycle with lower values during the Holocene (e.g. average La =  $0.39 \text{ pg g}^{-1}$ ; Lu =  $0.003 \text{ pg g}^{-1}$ ) and higher values (20–30 times) during the LGS (e.g. La =  $7.6 \text{ pg g}^{-1}$ ; Lu =  $0.078 \text{ pg g}^{-1}$ ) (Table 2). REE are highly correlated ( $R \sim 0.90\text{--}0.95$ ) and their plotted time series are very similar (Fig. 2a, b).

The REE enrichment factors  $[E_f(\text{REE})_{\text{Ce}}]$  calculated as  $(\text{REE}_{\text{ice}}/\text{Ce}_{\text{ice}})/(\text{REE}_{\text{crust}}/\text{Ce}_{\text{crust}})$ , where Ce is taken as a crustal reference (REE in the terrestrial crust from Wedepohl (1995)), are always



**Fig. 2.** (a) The glacial-interglacial variations of the REE fallout to Dome C are illustrated by the sum of the REE concentrations ( $\Sigma\text{REE}$ ). (b) The Dome C dust concentration profile (Lambert et al., 2008). (c) The  $\text{REE}_{\text{index}}$ , which is a proxy of dust composition (smoothed solid line; the shading indicates  $1\sigma$  analytical uncertainty) is displayed with the dust size data (smoothed dotted line) (Delmonte et al., 2002). The vertical bar highlights dust showing a tendency towards glacial characteristics at  $\sim 8 \text{ kyr BP}$ . (d)  $\delta\text{D}$  is taken as a proxy of past air temperature at Dome C (Jouzel et al., 2007). (e) A one-to-one correlation between the row (i.e. non smoothed)  $\text{REE}_{\text{index}}$  and dust size data is displayed between 13.5 and 10 kyr BP.

close to unity (Table 2). This strongly supports their crustal origin and the absence of significant contamination. We note that the calculation of the  $E_f$  with respect to Mn (Gabrielli et al., 2005b) provides essentially the same result. However, in this latter case, the  $[E_f(\text{REE})_{\text{Mn}}]$  is less precise because Mn was determined during a different session of analysis. Altogether, these results provide strong evidence that REE concentrations in EDC ice represent the aeolian dust composition.

### 3.2. A REE index of the dust composition

In order to study the variations in dust composition, a common practice is to normalize REE using a standard. We take as standard the mean REE crustal concentrations ( $REE_{ice}/REE_{crust}$ ;  $REE_{crust}$  from Wedepohl, 1995). In addition, we re-normalize these ratios using Ce, ( $REE_{ice}/REE_{crust})/(Ce_{ice}/Ce_{crust})$ . In this way we obtain REE patterns of comparable magnitude at any REE concentration level. Note that this normalized notation is equivalent to  $(REE_{ice}/Ce_{ice})/(REE_{crust}/Ce_{crust})$ , or  $Ef(REE)_{Ce}$ . Thus, a vector whose single components are  $Ef(i)$  can unequivocally characterize the dust composition of every sample:

$$Ef(REE)_{Ce} = [Ef(La), Ef(Pr), \dots, Ef(Yb), Ef(Lu)]$$

To estimate the difference in dust composition between the Holocene and the LGS, we have calculated the euclidean distance (defined as  $REE_{index}$ ) of the  $Ef(REE)_{Ce}$  linked to each sample from the median  $Ef(REE)_{Ce}$  of the LGS, defined as:

$$Med(REE)_{Ce} = [Med(La), Med(Pr), \dots, Med(Yb), Med(Lu)]$$

This is assumed to be a constant reference. In this way the distance between every glacial  $Ef(REE)_{Ce}$  and the  $Med(REE)_{Ce}$  is expected to be small while, in general, this can be larger when considering the Holocene  $Ef(REE)_{Ce}$ . Thus, glacial/Holocene differences in REE composition will be emphasized and summarized quantitatively as follows:

$$REE_{index} = \sqrt{\sum (Ef_i - Med_i)^2}$$

The proposed  $REE_{index}$  summarizes the REE information and allows the evaluation of the change in dust composition of each sample when compared to the defined glacial stage standard. Rigorous calculation of the error propagation affecting the  $REE_{index}$  shows that its median uncertainty is 29% during the Holocene and 36% during the LGS. The higher relative uncertainty observed over the LGS can be explained by the much smaller difference of each  $Ef(REE)_{Ce}$  from  $Med(REE)_{Ce}$  when compared to the Holocene. However, the absolute uncertainty is larger during the Holocene.

The  $REE_{index}$  is low and constant during the LGS (Fig. 2c), indicating homogeneous glacial dust composition. The  $REE_{index}$  starts to increase at ~15 kyr BP, ~3 kyr after the onset of the last transition, when the increase in Antarctic temperatures and the decrease in dust concentrations commenced (Fig. 2d and 2b). The variation of the  $REE_{index}$  (~400%) from the LGS to the Holocene is much higher than its uncertainty, providing high confidence that the observed shift is not due to the higher analytical uncertainty affecting REE concentrations during the Holocene.

The  $REE_{index}$  peaks at ~11 kyr BP in correspondence with the Antarctic Holocene optimum and the so-called dust minimum (Delmonte et al., 2002), suggesting that the fallout of typical glacial dust was essentially shut down and different dust characteristics could emerge. In general, the dust composition appears very variable during the Holocene with respect to the LGS. A noticeable  $REE_{index}$  minimum for the Holocene occurs between 7.5 and 8.3 kyr BP (Fig. 2c) suggesting the occurrence of dust fallout with a more glacial-like composition around 8 kyr BP. This will be discussed in the next section.

### 3.3. The 8 kyr dust event

A prominent sharp cold climatic event at ~8.2 kyr BP and lasting ~70 years was recorded in Greenland (Johnsen et al., 1992). This was a possible response to a large flood of freshwater (~8.4 kyr BP) to the ocean that slowed the North Atlantic

thermohaline circulation (e.g. Alley and Agustsdottir, 2005). Evidence of a cooling around ~8 kyr has been widely recorded throughout the Northern Hemisphere (Rohling and Palike, 2005) although less strikingly than in Greenland. Despite the slowing of the thermohaline circulation from a large input of freshwater, a corresponding warm event was not recorded in the Southern Hemisphere as a counterpart to the ~8.2 kyr cooling that occurred at the high northern latitudes. This observation evidently contrasts with the bi-polar seesaw concept (Stocker and Johnsen, 2003).

Difficulties in detecting this abrupt event far away from the Arctic might arise from insufficient time resolution inherent in most palaeoclimatic records (Thomas et al., 2007) and because this short climatic event is thought to be embedded in a longer term widespread cooling that spanned some 400–600 years (Alley and Agustsdottir, 2005). This is also suggested by the EDC  $\delta D$  profile (Fig. 2d). Because of the lack of evidence of such a rapid event in the Southern Hemisphere and because of the appearance of the longer term global cooling in EDC at ~8 kyr BP, it is likely more appropriate to attribute the observed REE changes to this long-term cooling.

An increase in rainfall and a fluvial pulse was recorded in south-eastern Australia between 9.5 and 7.5 kyr BP, pointing to unusually humid conditions in this region during the Holocene (Gingele et al., 2007). In South America, glaciers advanced ~8.5 kyr BP, likely as a result of a northward migration of the southern westerlies that caused an increase in precipitation and/or a decrease in temperature at this latitude as suggested by Douglass et al. (2005).

The  $REE_{index}$  suggests that the dust shows tendencies towards glacial characteristics between 7.5 and 8.3 kyr BP that was not accompanied by a remarkable increase in dust concentrations. In fact, we note that there was only a moderate increase in median REE concentrations (40–60%) in the 5.3 to 9.3 kyr BP period when compared to the previous and successive 4 kyr periods (Fig. 2a). Overall, our observations suggest a moderate reactivation of the glacial sources (e.g. South America) of Antarctic dust, possibly accompanied by the concurrent suppression of other sources (e.g. Australia) due to more humid conditions.

### 3.4. Atmospheric transport and dust composition

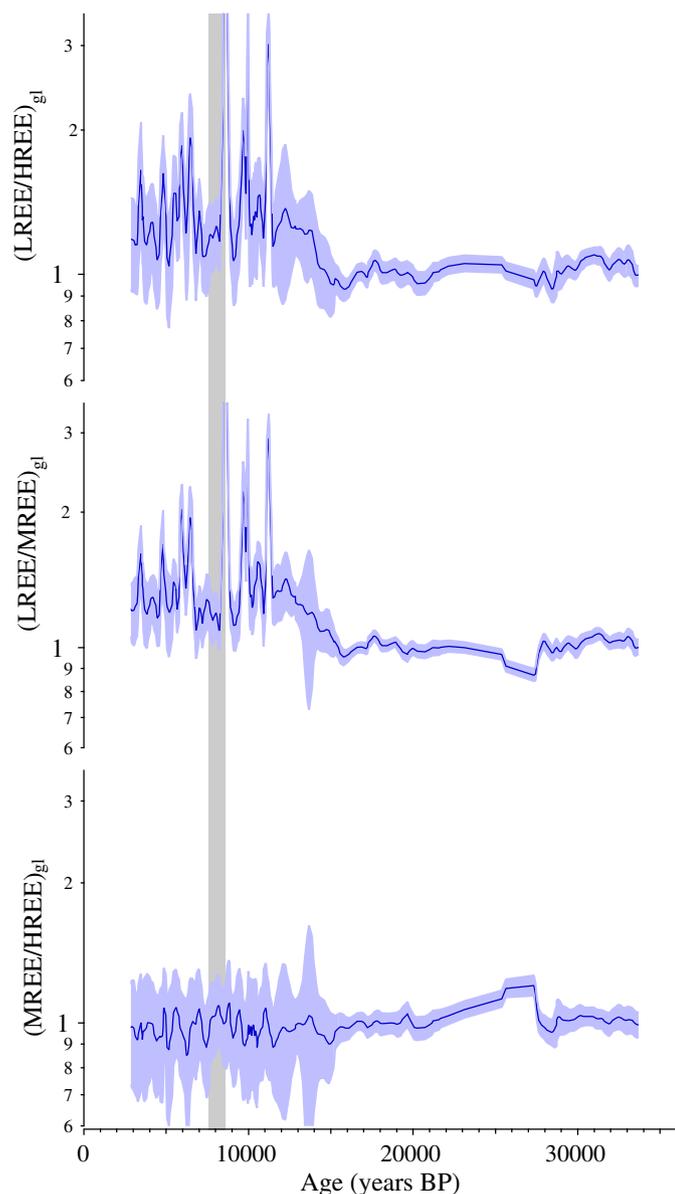
Running correlation coefficients (21-sample window; 95% level of confidence at  $R = 0.44$ ) of  $REE_{index}$  and dust sizes (i.e. percentage of fine dust between 1 and 2  $\mu m$ ) determined in the same samples (Delmonte et al., 2002) are in general not significant but they show an increasing trend from the LGM up to significant values of ~ -0.5 between 13.5 and 10 kyr BP (Fig. 2e). The persistence (~3.5 kyr) of this early Holocene correlation is remarkable considering that it was calculated from the raw data without any smoothing and that the records were detrended from the general large glacial/interglacial temporal variation. This correlation (-0.5) suggests that the fine dust percentage decreases as the REE ratios deviate from the typical LGS pattern. This may highlight a novel direct link between the dust composition and atmospheric circulation. Stronger transport and/or shorter atmospheric paths, possibly producing a reduced mineralogical fractionation, led to a higher percentage of large particles transported onto the East Antarctic Plateau during the glacial-interglacial transition (Delmonte et al., 2002).

At ~10 kyr BP, the correlation between the  $REE_{index}$  and the dust size decreases abruptly. Similarly, these variables are uncorrelated during the LGS until the LGM. In general, this indicates a weak link between atmospheric circulation and dust composition, possibly as a consequence of a different dust regime which was dictated by the sources rather than by changes in the long-range atmospheric circulation (Delmonte et al., 2002; Fischer et al., 2007). Around 8 kyr BP, the dust size/ $REE_{index}$  correlation achieved LGS values

(Fig. 2e), supporting the idea that the observed return to a more glacial-like dust composition was possibly due to a moderate reactivation of the glacial sources at that time.

### 3.5. LREE, MREE and HREE temporal behaviour

To highlight the glacial/interglacial behaviour of the LREE, MREE and HREE, we have normalized their concentrations using the median glacial REE concentrations as a standard. When  $(\text{LREE}/\text{MREE})_{\text{gl}}$ ,  $(\text{LREE}/\text{HREE})_{\text{gl}}$  and  $(\text{MREE}/\text{HREE})_{\text{gl}}$  are plotted versus the age of the samples (Fig. 3), these ratios show a very low variability during the LGS reflecting a fallout of homogeneous dust composition. Only one outlier occurs at  $\sim 27.3$  kyr BP (585.2 m) when Tb (a MREE) is enriched 5 times with respect to its mean crustal composition. One possibility for this anomaly is that this enrichment resulted from a singular volcanic ash fallout.



**Fig. 3.** LREE/HREE ratios (a), LREE/MREE ratios (b) and MREE/HREE ratios (c) were smoothed and plotted versus the age of the ice samples. In this case the REE concentrations were normalized by their own median glacial values. The shading indicates the linked  $1\sigma$  analytical uncertainty. The vertical bar highlights dust showing a tendency towards glacial characteristics at  $\sim 8$  kyr BP, also reported in Fig. 2.

Starting from  $\sim 15$  kyr BP in the record, the  $(\text{LREE}/\text{MREE})_{\text{gl}}$  and  $(\text{LREE}/\text{HREE})_{\text{gl}}$  ratios increase by  $\sim 20\%$  while becoming more variable. This behaviour persists during the Holocene part of the record (Fig. 3), suggesting a fallout of variable dust composition. We note that the Holocene variability is due to the enrichment of the LREE relative to MREE and HREE because the relative composition of these latter two remains substantially unchanged during the transition. This different behaviour of the REE is possibly due to the occurrence of particles enriched in LREE during the Holocene. Finally, we also note that these REE ratios indicate that the dust shows tendencies towards glacial characteristics between 7.5 and 8.3 kyr BP.

### 3.6. Evaluation of the REE crustal spectra

When plotted against their atomic number, the REE (this time normalized by their mean crustal values; Table 2) allow a visual comparison of the deviation from the mean terrestrial composition of the dust fallout over different climatic stages. When averaged over the LGS (Fig. 4), the REE pattern shows a rather uniform crustal-like signature across the REE spectrum with a slight enrichment in the MREE ( $\sim 12\%$ ) over LREE and HREE.

This is in agreement with glacial stage REE patterns observed in Vostok ice (Gabrielli et al., 2009) and those previously reported for dust filtered from some analogous Vostok and Dome C sections (Basile et al., 1997). As these latter data were obtained by using a full acid digestion, this implies that the slight LREE enrichment as shown by our test did not substantially affected the glacial REE patterns in our samples.

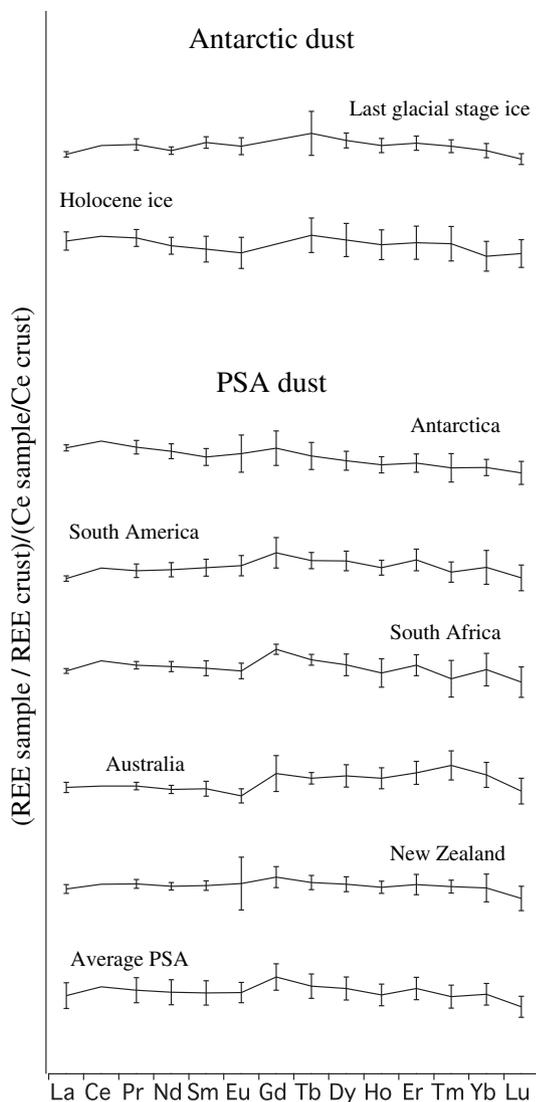
Although the REE average pattern remains close to the average crustal composition during the Holocene, the variability is higher (Fig. 4), indicating an increasing contribution of dust characterized by a more heterogeneous elemental composition. We observe an average slight enrichment of LREE over MREE (8%) and HREE (16%). This might be explained in terms of the slight artefact possibly introduced by our method (see section 2.4). However, although the same analytical procedure was used, this LREE enrichment is not observed in EDC during the LGS neither in the Dronning Maud Land (Antarctica) ice core during the Holocene and the LGS (Wegner et al., in preparation). In conclusion, it remains unclear whether the observed average slight LREE enrichment is real or merely represents a different geochemical response of the EDC Holocene dust to acidification. In any case, this at least provides evidence of the occurrence of dust during the Holocene with significantly different geochemical properties than during the LGS.

## 4. Dust source reconstruction

### 4.1. REE as a tracer of aeolian dust provenance

REE physical characteristics prevent them from being strongly chemically fractionated by environmental processes. However, the literature highlights how REE can be mobilized under certain conditions. A classic experimental work (Balashov and Girin, 1969) shows that 20–95% of the REE in clays are readily leachable and therefore may be available for migration, with the MREE being most susceptible and the LREE least. In particular, REE can be mobilized during both humid and temperate weathering (Balashov et al., 1964).

Our test (see paragraph 2.4) suggests that the REE fraction determined by our method essentially originates from the REE dissolved in the melted ice (Fig. 1). The bulk of the REE in eroded material is contained in clays while quartz and other major silicates are relatively depleted (Henderson, 1984). In particular, clays, as products of weathering of igneous minerals, tend to inherit and



**Fig. 4.** REE average normalized crustal patterns in the EPICA Dome C ice core during the Holocene and the last glacial stage are compared to those obtained from the aeolian fraction of dust collected in potential source areas (PSA). These crustal patterns are re-normalized by Ce to obtain patterns of comparable magnitude. Each pattern is equally constrained between its maximum and minimum values. The error bars ( $1\sigma$ ) represent the natural variability of the samples during the time (EPICA Dome C ice) and in the space (PSA samples).

average the REE distribution of their sources. As a large part of REE in clays is readily leachable, one possibility is that the measured dissolved REE content in EDC primarily reflects the clay content of the aeolian dust and by extension the average REE distribution of the igneous rocks at the potential source areas (PSA).

Defining exactly to what extent REE are conserved in aeolian dust with respect to their source is clearly beyond the scope of this work. However, given that REE are only slightly fractionated by chemical processes and are possibly transported mainly by clay particles, the REE composition in comparable mineralogical fractions at the source and at the sink can be compared to trace back the dust deflated from the source. For this reason, great care must be taken in selecting the appropriate dust size of samples from the PSA. In our case, however, one should also take into account that our methodology could be slightly biased towards a slight LREE enrichment. In conclusion, great precautions must be taken in using REE as tracers of dust provenance.

#### 4.2. REE patterns comparison

In order to attempt a preliminary reconstruction of the dust provenance using the REE, their patterns determined in EDC ice were compared with those obtained from the aeolian dust fraction collected at the PSA (Supplementary material) according to the criteria described in Delmonte et al. (2004). Briefly, the samples were collected from loess, silts, sands, fluvio-glacial sediments, aeolian deposits and moraines: four from the Pampas in northern South America, five from Patagonia and Chile in southern South America, three from South Africa, one from New Zealand, and eight from the Dry Valleys and Victoria Land in Antarctica. For these samples, the dust fraction  $<5\ \mu\text{m}$  was extracted (Delmonte et al., 2004) and analysed for REE (Wegner et al., in preparation). Twenty seven samples of fine grained sediments ( $<2\ \mu\text{m}$ ) from several rivers (mostly obtained as overbank deposits) were also collected from the Murray Darling Basin in south-eastern Australia (Gingele and De Deckker, 2005) and analysed. Complementary REE data from eleven New Zealand and six Australian bulk samples were obtained from Marx et al. (2005).

During the LGS, the slight enrichment in MREE suggests a Patagonian origin (as indicated by Basile et al., 1997) because this pattern resembles those from volcanic rocks sampled in this region (Gaiero et al., 2004) and those shown by our South American dust samples (Fig. 4). However, this homogeneous crustal-like signature is also consistent with an aeolian dust originating from a well-mixed pool of various sources located in different areas or within the same region (e.g. southern South America; see Gaiero et al., 2007). We also note that sedimentary processes are also recognized to be the cause of homogenization of the REE fractionation, which occurs during the formation of igneous rocks (Henderson, 1984).

During the LGS, aridity on Earth was quite widespread and a synchronous change in atmospheric dust occurred at low and high latitudes in the Southern Hemisphere (Winckler et al., 2008). Thus the homogeneous REE composition found in East Antarctic ice during the LGS may also reflect a “background” that was homogeneous in dust composition, as a result of different influxes from multiple areas located in the Southern Hemisphere. One consequence is that it might not be possible to trace back the dust sources during the LGS. However, this emerging hypothesis of a large-scale homogeneous compositional background will need to be verified using other dust proxies and modelling studies.

REE patterns point to a more variable dust composition (Fig. 4) indicating multiple dust contributions from various sources during the Holocene. A slight average enrichment in LREE during the Holocene may reflect a different geochemical response of the aeolian dust to acidification during interglacials. A similar LREE enrichment was also observed in some Vostok interglacial ice sections (Gabrielli et al., 2009). However, we note that the local Antarctic dust sources also show enrichment in LREE. Assuming that Holocene REE EDC patterns are reliable, this LREE enrichment would point to Antarctica as a possible source contributing to the dust budget in Antarctic ice during the Holocene.

Today about 2% of Antarctica is free of ice. These deglaciated areas occur sporadically around the coast of East Antarctica, in the Transantarctic Mountains, and in the Antarctic Peninsula. Aeolian dust trapped in Antarctic ice has a higher Isothermal Remanent Magnetization (IRM) during the Holocene and a relatively higher IRM in EDC than in Vostok ice (Lanci et al., 2008). A high IRM points to a local source of higher density dust particles (iron oxides). This idea is consistent with a Holocene local volcanic dust contribution to Dome C (Vallelonga et al., 2010) and with the higher super-chondritic fluxes of siderophilic elements to East Antarctica during the Holocene (higher in EDC than in Vostok ice) (Gabrielli et al., 2006b).

In conclusion, a LREE enrichment would support several independent lines of evidence pointing to Antarctica itself as a dust source during the Holocene. However, the larger variability in dust composition during the Holocene allows us to observe similarities of several individual Holocene REE patterns (not shown) with Australian, New Zealand and South African signatures. This may support the idea of multiple dust contributions from various sources during the Holocene and does not allow the exclusion of any major PSA in the Southern Hemisphere.

## 5. Conclusions

REE prove to be sensitive indicators of changes in aeolian dust composition trapped in Antarctic ice during the last climatic cycle. The dust shows a persistent crustal-like REE composition during the LGS that was possibly produced either by the atmospheric mixing of the abundant emissions derived from multiple source areas or by the averaging of individual heterogeneous sources within one single region (e.g. South America). If confirmed by further developments in the REE analysis, the LREE enrichment found in EDC ice during the Holocene might support several independent lines of evidence that point to Antarctica as an important dust source during the Holocene. For this purpose, a routine ultra clean full acid digestion should be developed.

Starting at ~15 kyr BP, we observe a major variation in dust composition, whose variable character persists throughout the current interglacial. Likely contributions from multiple sources emerged after the high deposition of glacial dust started to decrease at ~15 kyr BP. Interestingly, the dust composition might have been dictated by the atmospheric transport at the onset of the Holocene (10–13.5 kyr BP). In contrast, the dust composition might have been regulated by environmental changes that occurred at the sources during the other periods. In particular, a return to more glacial-like dust characteristics is apparent between 7.5 and 8.3 kyr BP, probably as a consequence of a modest reactivation of the glacial sources.

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## Appendix Supplementary information

Supplementary information associated with this article can be found, in the online version, at doi:10.1016/j.quascirev.2009.09.002

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