Clim. Past Discuss., 7, 601–633, 2011
www.clim-past-discuss.net/7/601/2011/
doi:10.5194/cpd-7-601-2011

Climate of the Past Discussions

Rare Earth Elements from an ice core in the Atlantic sector of Antarctica indicate a dust provenance change at the end of the last deglaciation

A. Wegner[1], P. Gabrielli[2,3], D. Wilhelms-Dick[1,*], U. Ruth[4], M. Kriews[1], P. De Deckker[5], C. Barbante[2,6], G. Cozzi[2,6], B. Delmonte[7], and H. Fischer[1,8,9]

[1]Alfred Wegener Institute for Polar and Marine Research, Am Alten Hafen 26, 27568 Bremerhaven, Germany
[2]Institute for the Dynamics of Environmental Processes, CNR, 30123 Venice, Italy
[3]School of Earth Science and Byrd Polar Research Center, The Ohio State University, Columbus, OH 43210-1002, USA
[4]Climate Analysis and Consulting, Pfullingen, Germany
[5]Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia
[6]Department of Environmental Sciences, University Ca' Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy

[7]DISAT – Department Environmental Sciences, University Milano Bicocca, 20126, Milan, Italy
[8]Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland
[9]Oeschger Institute for Climate Change Research, University of Bern, Bern, Switzerland
[*]now at: University of Bremen, Klagenfurter Straße, Bremen, Germany

Received: 5 January 2011 – Accepted: 11 January 2011 – Published: 18 February 2011

Correspondence to: A. Wegner (anna.wegner@awi.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

CPD
7, 601–633, 2011

Abstract

We present a Rare Earth Elements (REE) record at decadal resolution determined in the EPICA ice core drilled in Dronning Maud Land (EDML) in the Atlantic Sector of the East Antarctic Plateau, covering the transition from the last glacial age (LGA) to the early Holocene (26 600–7500 yr BP). Additionally, samples from potential source areas (PSAs) for Antarctic dust were analysed for their REE characteristics. The dust provenance is discussed by comparing the REE fingerprints in the ice core and the PSAs samples. We find a shift in REE composition at 15 200 yr BP in the ice core samples. Before 15 200 yr BP, the dust composition is very uniform and its provenance was likely to be dominated by a South American source. After 15 200 yr BP, multiple sources such as Australia and New Zealand become relatively more important, albeit South America is possibly still an important dust supplier. A similar change in the dust characteristics was observed in the EPICA Dome C ice core at around ~15 000 yr BP. A return to more glacial dust characteristics between ~8300 and ~7500 yr BP, as observed in the EPICA Dome C core, could not be observed in the EDML core. Consequently, the dust provenance at the two sites must have been different at that time.

1 Introduction

Mineral dust aerosol in the atmosphere can play a significant impact on the radiation budget of the Earth's atmosphere by scattering and absorbing solar radiation and backscattering IR-radiation from the earth surface (e.g. Sun et al., 2008). In addition, input of aeolian dust particles into the ocean influences the atmospheric CO_2-concentration through iron fertilization of photosynthesizing marine biota (e.g. Ridgwell, 2002). This process is especially important for the high nutrient, low chlorophyll areas in the Southern Ocean, where algal growth is limited by iron supply (e.g. Sarthou et al., 2003). To assess the magnitude of the effect of increased dust input into the Southern

CPD
7, 601–633, 2011

Ocean in the past, knowledge of the dust concentration in the palaeo – atmosphere is critical, but so far a direct measure has not been accessible.

Mineral dust concentration quantified in ice cores from Antarctica is a reliable proxy for dust concentration in the atmosphere over the Antarctic continent over the last 800 000 years (Lambert et al., 2008) and can be considered also to be representative for dust input changes into the Southern Ocean. To interpret changes in ice core dust concentrations in terms of transport and source contributions, it is crucial to know the geographical origin of the dust. In contrast to the concentrations of soluble aerosol proxies, particulate dust in ice cores provides additional parameters. The size and chemical composition of the dust particles can be obtained, and permit the identification of the dust provenance and the impact of changes at the source and variations in transport intensity (e.g. Ruth et al., 2003; Delmonte et al., 2004a,b).

As 98% of Antarctica is covered by ice, most of the airborne dust deposited in the interior of the Antarctic ice cap originates from remote continental sources that surround Antarctica and that is transported through the atmosphere over a distance of thousands of kilometres. However, local Antarctic dust contributions from exposed rocks were likely to affect proximal ice core sites during the Holocene (Delmonte et al., 2010b). Studies about dust provenance in the Atlantic sector of the East Antarctic Plateau are scarce. Marino et al. (2009) identified a common provenance during glacial stages in the two ice cores, Dronning Maud Land (EDML) and Dome C (EDC) drilled in the framework of EPICA (European project for ice coring in Antarctica). Several dust provenance studies were performed on ice from the Indian sector of the East Antarctic Plateau, based on Sr, Nd and Pb isotopic fingerprinting (e.g. Delmonte et al., 2007; Vallelonga et al., 2010), particle induced X-ray emission (Marino et al., 2008) or single element analysis (Siggaard-Andersen et al., 2007). These studies suggested the southern South American continent as the major dust source during glacial times, although minor contributions from Antarctic or Australian sources could not be excluded (Revel-Rolland et al., 2006; De Deckker et al., 2010). A detailed study based on Sr and Nd isotopes revealed the Patagonian region as the major dust source during glacials,

CPD
7, 601–633, 2011

although a slight contribution from high-altitude south American sources located at lower latitudes is also possible (Delmonte et al., 2010a; Gaiero , 2007).

Two major drawbacks of using Sr and Nd isotopes is the large volume of sample needed (ca. 100 µg of dust) and the low sample throughput. Due to the low dust concentration during interglacial stages, the provenance identification is much more difficult, but preliminary evidence points to southern South America becoming less important relative to Antarctic or Australian sources (Revel-Rolland et al., 2006; De Deckker et al., 2010). For peripheral sites as Talos Dome (located in the Indian sector of the East Antarctic plateau), the contribution from local sources becomes important (Delmonte et al., 2010b).

As an alternative approach, Gabrielli et al. (2006) successfully determined Rare Earth Elements (REE) in EDC ice, which are used as tracers for geochemical and cosmochemical processes. REE are the elements following the element lanthanum with atomic numbers 57 to 71, which are characterized by increasing electron occupation of the inner f-orbital and identical outer electron configuration. Thus, REE show (similar to isotopes) very similar chemical behaviour, but still present small although significant differences in physical properties caused by decreasing atomic radius with increasing atomic number (called lanthanide contraction). Additionally, REE show a rather conservative behaviour in the environment caused by their low solubility and immobility in the terrestrial crust. Accordingly, REE compositions of aeolian dust show the corresponding fingerprints of the parental rocks in the source areas. Thus, comparing REE fingerprints of dust entrapped in the ice with those in PSAs represents a promising tool to identify provenances of dust. One advantage of REE compared to, for example, Sr and Nd isotopes is that a 20 times smaller sample volume is required and little sample pre-treatment is necessary. Inductively coupled sector-field mass spectrometry (ICP-SFMS) offers the possibility to quantify REE concentration (Gabrielli et al., 2006) even at very low mass concentrations of dust, typical of ice from the Antarctic Plateau (12 000 yr BP until today, dust concentrations: 10–15 ng mL^{-1}; glacial, 26 000–18 000 yr BP, dust concentrations: 500–1000 ng mL^{-1}; Lambert et al., 2008).

CPD
7, 601–633, 2011

In a recent partner publication of this study using REE in the EDC ice core, the dust provenance in the Indian Ocean Sector of the East Antarctica Plateau was already discussed (Gabrielli et al., 2010). That latter study revealed a persistent crustal-like REE composition during the LGA, which could be produced by one single source or a constant mix of several sources. ~15 000 yr BP, a major change in REE composition was observed, which is explained by multiple sources contributing to the dust fallout to Dome C. A return to more glacial-like conditions was observed between ~8300 and ~7500 yr BP, which is explained by some reactivation of the glacial sources and the shut down of others.

Here, we present a quasi-continuous REE concentration record in the EDML ice core from a set of 398 samples (each sample representing an ice section of 1 m length) covering the depth interval 493–1105 m. The selected depth interval covers the transition from the LGA to the early Holocene (26 600 yr BP to 7500 yr BP; note that dating in this publication is according to Ruth et al., 2007). Each sample represents a time interval of approximately 45 years at 26 600 yr BP and approximately 20 years at 7500 yr BP. In addition, we analysed an extensive suite of samples from PSAs for REE in order to quantify the differences in their REE fingerprint and to assess the Antarctic dust provenance. This forms the first extensive study of dust provenance analysis based on REE in a deep ice core from the Atlantic sector of the Antarctic continent.

2 Methods

2.1 Analysis of ice core samples

After drilling, the EDML core was logged, packed in PE-bags and transported to AWI, Bremerhaven, Germany, where the ice was cut. A 32 × 32 mm rod of ice from the inner part of the core was melted on a heated melthead, made of gold plated copper for continuous high-resolution chemical analysis (Roethlisberger et al., 2000). The melthead is divided into an inner section, where the innermost clean part of the ice

CPD
7, 601–633, 2011

and the outer section (where the ice is possibly contaminated) are separated. Only the clean innermost part of the ice was used for the determination of the various proxies (for details see Roethlisberger et al., 2000 or Kaufmann et al., 2008).

Part of the meltwater from the inner part was filled into polystyrole (PS) beakers (Accuvettes) and immediately frozen. For the REE determination, the samples were melted at least 24 h prior to the analysis, filled in pre-cleaned sample tubes (low density polyethylene, LDPE, Greiner Bio One), spiked with 100 µl HNO_3 (twofold distilled, 65%, pro Analyse, Merck) per 10 ml and kept refrozen until analysis. All sample handling was performed under class 100 clean-room conditions. Analysis were performed at the department of Environmental Science, Venice, Italy (DES) with an ICP-SFMS (Element2, Thermo Fischer, Bremen) coupled to a microflow/desolvation introduction system (Aridus, Cetac technology) as described in detail by Gabrielli et al. (2006). The Aridus consists of a microflow Perfluoralkoxy-Copolymer (PFA) nebulizer, a heated PFA spray chamber and a heated microporous PTFE membrane. Interferences induced by oxides were highly reduced by this setup. The analysis was performed in low resolution mode (nominal mass resolution of $m/\Delta m \sim 400$).

The calibration was carried out with a set of matrix matched multi-element standards obtained by melting a surface snow sample taken from the surrounding of the EDML drill site and spiked with different concentration of a multi-REE stock solution (Perkin Elmer). The slope of the calibration line was used to calculate samples concentration. Instrumental drift was checked using a 1 µg L^{-1} In solution, analysed at least after every 7th sample. The maximum sensitivity was 3×10^6 counts s^{-1} ln ppb^{-1}. The following isotopes were chosen for the analysis: ^{139}La, ^{140}Ce, ^{141}Pr, ^{144}Nd, ^{151}Eu, ^{152}Sm, ^{158}Gd, ^{160}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu. In Gabrielli et al. (2010), ^{157}Gd was analysed but not used for data evaluation as on mass 157 BaO interferes significantly with Gd. In the presented study ^{158}Gd and ^{160}Gd were used, as no indication of residual interferences emerged.

Procedural blanks were determined using 12 artificial ice cores made of ultrapure water (Millipore, resistance > 18 MΩ cm) and handled in the same way as the samples.

CPD
7, 601–633, 2011

Since two outliers dominated the mean value, whereas all other values had similar levels, the procedural blank was calculated as the median of the 12 artificial samples. The procedural blank was subtracted from the concentration and all samples with a final concentration below the detection limit (LOD) were discarded. (LOD was calculated as 3*SD from ultrapure water analysed every 7th sample).

The samples were analysed in 5 different sets. The typical values for LOD and procedural blank are given in Table 1. Additionally, the mean concentration during warm (~15 200–7500 yr BP) and cold climate (~26 500–15 200 yr BP) are given. The glacial concentrations are, depending on the element, one to two orders of magnitude above the LOD and the procedural blank. The concentrations during the Holocene are up to a factor of 3 higher than the procedural blank and still well above the LOD. However, for 140 Holocene samples, several single REE concentrations were below the procedural blank and therefore were not taken into account. We emphasize that this is a very careful and conservative approach to ensure that only uncontaminated samples were taken into account for interpretation.

Differences in the recovery of samples treated with a full-acid digestion and acid leached samples were carefully investigated in EDC ice (Gabrielli et al., 2010). Acid leached yields only a partial recovery of REE of about 50%. LREE (55%, LREE = light REE, i.e. REE with atomic number 58–61) and MREE (50%, medium REE, i.e. REE with atomic number 62–66) are released slightly more than HREE (40%, heavy REE, i.e. REE with atomic number 67–71), but the recovery is not different between glacial and interglacial ice. Since the estimates of the recoveries themselves are affected by uncertainties, a recalibration would introduce an additional uncertainty. Therefore this recalculation was not performed. As shown in Gabrielli et al. (2010), changes in REE composition during the glacial-Holocene transition are not affected by these findings. Nevertheless, when discussing changes in the dust provenance by comparison with samples from the PSAs, these different recoveries will be kept in mind (see below).

CPD
7, 601–633, 2011

2.2 Analysis of samples from the potential source areas (PSAs)

33 samples from PSAs were analyzed to determine their REE concentration. An overview of the sampling locations is given in Fig. 1. The dust samples collected from the PSAs span a wide size spectrum differing from sample to sample. For this analysis, only the <5 µm fraction was used. This corresponds to the typical size of the particles found in Antarctic ice cores (e.g. Delmonte et al., 2004b). As described by Delmonte (2003), the bulk of the sample (a few grams) was suspended in 45–50 mL of ultra pure water. After 10 min of ultra sonication, the sample was left to separate by settling according to Stokes law. The supernatant was taken with a pipette and the size distribution was checked to achieve a fraction of 95% of the total mass of particles in a size range <5 µm.

The supernatant was treated with a full acid digestion in high pressure PFA beakers using H_2O_2 (suprapure, Fa. SCP Science), HF (subboiled, 40%, suprapure, Merck) and HNO_3 (subboiled, 65%, pro analysi, Merck) to dissolve the sample matrix. The digestion and the analysis of the samples were performed under a clean bench (US Class 100) in the clean room facilities at AWI. To each sample, 10 µg L^{-1} Rh was added to provide an internal standard to correct for instrumental drift during the analysis.

Blanks were prepared using ultra pure water, treated in the same manner as the dust samples and analysed regularly. Also in this case, the median of the blank values was subtracted from the sample concentration. The median was chosen, as a few outliers dominated the mean value. The blank values were less than 0.5% of the mean concentration and less than 10% of the concentration in the lowest PSA sample concentration level. Calibration standards were prepared from multi-element stock solutions (Multielement Calibration Standard 2 and 3, Perkin-Elmer). These analysis were performed at AWI by ICP-QMS (ELAN 6000, Perkin Elmer/Sciex 1997) coupled to a micro concentric nebulizer, made of PFA placed in a heated PFA spray chamber followed by a heated membrane desolvation unit MCN-6000 (Cetac). Here, the solvent is removed with a counter flow gas and oxide formation is minimized (CeO/Ce

CPD
7, 601–633, 2011

was ~0.02% when compared to ~3% of a conventional crossflow nebulizer). The sample uptake was 100 µL min^{-1}. The mean sensitivity obtained during the analysis was ~5×10^5 counts s^{-1} Rh ppb^{-1}, with a variation between two calibrations of ~20% or less. For correction of the instrumental drift, a spike of 10 µg L^{-1} Rh as an internal standard was used. More detailed information about instrumental conditions and analysis settings are given by Dick et al. (2008).

3 Results

3.1 Ice core samples

As an example for the REE-concentration, the La-concentration over the transition is shown in Fig. 2 together with the typical (soluble) dust proxy non sea salt (nss) Ca^{2+} (Fischer et al., 2007) and the corresponding temperature changes as represented by $\delta^{18}O$ (EPICA, 2006). La-concentrations are higher by a factor of 25 during the LGA (26 500–16 000 yr BP) than during the early Holocene (13 300–7500 yr BP). Typically, the LGA-Holocene ratios for the other REE are in the range of 25–35. The lowest LGA-Holocene ratio (15) was found for Lu (see Table 1). This value has to be considered with extreme caution, since Lu is the least abundant REE and, therefore, its concentration was often below the detection limit during the Holocene. Therefore, the mean Holocene Lu concentration is biased towards higher concentrations and has to be taken as an upper limit.

The LGA-Holocene REE increases are slightly higher than the increase for nss-Ca^{2+} concentrations (19) determined by ion chromatography (Fig. 2, Fischer et al., 2007), which can partly be explained by the fact that Ca^{2+}-concentrations in Holocene ice are close to the detection limit of the ion chromatograph and can be taken as an upper limit for the mean concentration.

CPD
7, 601–633, 2011

In the following, the systematic shape of the REE patterns for individual samples is investigated. To this end, all samples were normalized to the typical upper continental crust value (Eq. 1 as an example for La):

$$La^* = \frac{La_{ice}}{La_{UCC}} \quad (1)$$

with La_{ice} the La-concentration in the ice sample, and La_{UCC} the typical La-concentration in the upper continental crust (UCC, Wedepohl, 1995). Although REE concentration in samples from glacial and interglacial periods differ significantly, due to the much higher dust input to Antarctica during glacial times, a source change would affect the shape of the REE fingerprint, independently from the absolute concentration. However, for a better comparison of the shape of the patterns, a second normalization step was applied to eliminate the effect of the concentration values on the absolute values of the ratios (Eq. 2).

$$La_{norm} = \frac{La^*}{\overline{REE^*}} \quad (2)$$

with $\overline{REE^*}$ being the mean value of all REE normalized according to Eq. (1).

Figure 3 shows the mean REE pattern between 26 600 yr BP and 15 200 yr BP. This pattern is very uniform and shows a mean enrichment of ~20% in MREE and a mean depletion of ~23% in LREE relative to the mean REE concentration and a very light depletion of ~2% in HREE. After 15 200 yr BP, the pattern becomes more heterogeneous (Fig. 3). This shift coincides with the slowdown of the warming trend, which ~14 500 yr BP turns into the Antarctic Cold Reversal (ACR, Blunier et al., 1997). The EDML pattern shows a very similar shape compared to the EDC pattern ($r = 0.98$, excluding Gd) during the glacial time interval (26 600 yr BP–15 200 yr BP), independently supporting the findings of Marino et al. (2009). During the Holocene different patterns occur at both sites ($r = 0.38$, excluding Gd).

CPD
7, 601–633, 2011

At 808.2–808.3 m depth (~14 800 yr BP), the thickest visible ash layer of the whole ice core is recorded. This ash layer dominates the REE pattern of the whole sample 809 (Fig. 3, bottom), which shows a strong enrichment of 45% in HREE and which is also accompanied by a 3–4 times higher sulphate concentration than the background value during that time. Accordingly, the REE pattern of this ice section is not representative of aeolian dust but essentially reflects the REE composition of tephra emitted during an eruption or a set of eruptions. This peculiar REE composition can be explained considering that during the formation of the earth's crust LREE are preferably incorporated in the crust, leaving the magma in the mantle depleted in LREE.

When looking at the low concentration Holocene samples, the blank levels have to be considered very carefully. Table 1 gives the mean REE concentration between 15 900 yr BP and 14 600 yr BP. For Tm and Lu, the concentration is only a factor of 5 and 4, respectively, higher than the blank. However, all the other REE concentrations are well above the blank and are all above the LOD. Consequently, we conclude that the significant changes in the REE fingerprint cannot be due to contamination or concentrations that are too close to the LOD, but report a real change in dust composition in the ice core.

During the Holocene, different patterns occur, the most frequent are shown in Fig. 4 grouped by the similarity of their pattern. The full REE spectrum could not be evaluated for all samples, especially in the case of the lower concentrated Holocene samples. Thus, from the climatically warmer period, postdating 15 200 yr BP, of 227 samples, 86 could be evaluated using the full REE spectrum.

The first pattern, identified 9 times (Type A), is characterized by a 30% enrichment in LREE compared to the mean REE concentration, a positive Ce-anomaly ($Ce/Ce^* = Ce/(0.5 \times La + 0.5 \times Pr)$), with Ce/Ce^* values between 1.30 and 1.87, except for one sample with $Ce/Ce^* = 0.87$) for most of the samples and a very negative Tb-anomaly ($Tb/Tb^* = Tb/(0.5 \times Gd + 0.5 \times Dy)$), with Tb/Tb^* between 0.42 and 0.73. The next pattern (Type B), identified 13 samples that are characterized by a negative Eu-anomaly, with mean Eu/Eu^* ~0.79, ($Eu/Eu^* = Eu/(0.5 \times Sm + 0.5 \times Gd)$) and a strong enrichment in

CPD
7, 601–633, 2011

HREE (~30%). Pattern Type C occurs 4 times and is characterized by a very strong Eu-anomaly ($Eu/Eu^* > 1.85$). Pattern Type D (15 samples) is characterized by a general enrichment in HREE (~20%), together with a negative Ce-anomaly. Pattern Type D is similar to pattern B, although the enrichment in HREE is not as pronounced. The next pattern, Type E, is only found at 541–542 m of depth (8560 yr BP), and is characterized by a strong enrichment (60%) in La, Ce and Pr. Interestingly, the typical glacial pattern, Type F, also occurs frequently (25 out of 86 spanning the entire Holocene REE spectra) during the Holocene.

Figure 5 shows the occurrence of these different patterns over time. There were several samples that could not be classified within the 6 different types. Most of these samples were similar to the glacial type F, but are more enriched in Gd and depleted in Eu and Tb. Before 15 000 yr BP only 4 samples did not show the glacial pattern, between 15 000 and 13 000 yr BP about half of the samples still were characterized by the glacial pattern. Pattern Type A only occured between 12 000 and 8000 yr BP, whereas Type B and D were present contiuously both or at least one of them.

3.2 Samples from the potential source areas

The locations of the sampling sites, where the 33 samples from PSAs were collected, are given in Fig. 1. Figure 6 shows the corresponding patterns, being sorted by continents normalized according to Eq. (2). All PSAs show different features: the samples from the ice free areas on the Antarctic continent (mainly from the dry valleys) are characterized by a variable Eu-anomaly (0.7–1.2) and a slightly enriched LREE (~5%), while the African samples by a 26% MREE enrichment. The samples from Australia mostly originate from the south-eastern part of the continent. These samples are characterized by a LREE depletion of ~20%. On average, the samples from New Zealand exhibit a similar depletion in LREE (~20%) accompanied by an additional enrichment in MREE, up to 35% for some samples. Most of the samples were collected in South America. These samples are characterized by a depletion in LREE (~30%) and a small enrichment in MREE (~13%) as well as HREE (~20%). In addition to these samples,

CPD
7, 601–633, 2011

literature data are also provided for the discussion (Gaiero et al., 2004; Smith et al., 2003). However, a drawback of the latter data is that the analysis were performed on bulk samples, whereas we only used the <5 µm fraction. In Fig. 7, the REE-composition of the samples from the different PSAs is displayed. The field covered by the South American samples is well separated from the Antarctic one, but shows a considerable overlap with South Africa and New Zealand and, to a lesser extent, with Australia. Many South American samples, which are more enriched in HREE, are taken from the literature (Gaiero et al., 2004; Smith et al., 2003) and often are not restricted to the size fraction <5 µm. Furthermore, Australia and Southern Africa are well separated. We note that there is no PSA distinctly separated from all other PSAs.

4 Discussion

4.1 Dust provenances during the LGA and the transition to the Holocene

The REE pattern in the EDML ice core is very consistent throughout the LGA until 15 200 yr BP, which potentially points to one dominant source (or a constant mix of different sources) during this time period, in accord with the findings of Gabrielli et al. (2010). Indeed, comparing the REE from the EDML with those from EDC (Fig. 3), they exhibit the same constant pattern. In both ice cores patterns start to change at approximately the same time (15 200 and ~15 000 yr BP, respectively), indicating a common and stable dust input during the LGA and the first part of the transition. This simultaneous change in EDML and EDC at ~15 000 yr BP is obvious also for the LREE/REE ratio (Fig. 2). During the LGA and until around 15 200 yr BP, the LREE/REE ratio remains rather constant, around 0.22. From around 15 200 yr until 7500 BP, LREE/REE exhibits higher values and much higher variability.

When comparing the REE determined in ice with those in the PSA samples, the already mentioned different analytical recoveries have to be considered.

CPD
7, 601–633, 2011

The glacial pattern is characterized by enrichment in MREE relative to the mean REE and by a slight enrichment in HREE compared to LREE. This is similar to the pattern found for the samples from the South American PSAs. In Fig. 8, the correlation coefficients R^2 of the glacial REE patterns with the mean pattern of each PSA are plotted. R^2 is an indicator for the similarity of the patterns. The highest correlation of the glacial pattern is achieved with those characterizing the samples from the South American PSAs. The differentiation between South America, Southern Africa and Australia (all three showing a higher similarity with the glacial pattern when compared to Antarctica and New Zealand) is obvious. Based on the REE pattern, Antarctica and New Zealand PSAs do not seem to play a major role during the LGA. If the correlation is calculated by taking into account REE concentrations corrected for the lower HREE recovery (see Supplement), still the highest correlations are achieved by the samples from South America and Australia. This finding supports results by Marino et al. (2009) that during the LGA the main dust input to DML originated from South America.

To further distinguish between the different PSAs during the LGA, Fig. 7 shows the relative contribution of LREE, MREE and HREE to REE. In this graph, already published values are also included (Smith et al., 2003; Marx et al., 2005; Gaiero et al., 2004), which are not necessarily restricted to the size fraction <5 µm. The glacial samples (grey dots) form a very uniform "spot", which is located in the area of the South American and African fields. If taking into account the lower recovery of MREE and HREE, this spot moves slightly towards the right into the field covered by the New Zealand PSA samples, but still within the field covered by the PSA from South America. The glacial samples do not overlap with the Australian and the Antarctic fields. The plot in Fig. 7 shows also that southern Africa might have contributed as a dust source to DML during glacial times. However, there are at least two facts that do not support South Africa as realistic PSAs: first, the number of samples from southern Africa is rather small (5). Second, as EDML is located at 0° E and the west coast of southern Africa runs at a longitude between 10° and 20° E, the prevailing westerly winds prevent the transport of large air masses from South Africa to the East and thus to DML. It also

CPD
7, 601–633, 2011

emerges from Fig. 7 that southeastern Australia and Antarctica can be excluded as a major PSA for DML during the LGA.

Studies on Sr and Nd isotopic fingerprinting have been performed by Gaiero (2007), which may allow a discrimination between different source areas in southern South America. A comparison of Sr and Nd isotope data from other Antarctic ice cores, including EPICA Dome C, Talos Dome, Dome B, Vostok and Komsomolskaya, displays a common Patagonian source, which would deliver 70–100% of the dust to the East Antarctic Plateau between 90° E and 180° E during glacial times (Delmonte et al., 2008). REE reveal, with much less analytical effort and by providing a much larger temporal detail, the same overall scenario. Our study shows a constant source or mix of sources, likely being in the South American continent, during the LGA also for DML, which is located closer to Patagonia than the other ice cores drilled on the Antarctic plateau and within the main pathways of air masses transported over the Atlantic sector of the Antarctic Plateau (Reijmer et al., 2002). An overall good correspondence with the other ice core studies indicates the same main dust source throughout the East Antarctic Plateau during the last glacial period.

4.2 Late transition and early Holocene (15 200 to 7500 yr BP)

During the Holocene, the REE patterns are distinct from the glacial ones. The more variable patterns are likely to be caused by various dust sources. By using the conservative approach of sample elimination, the results are not affected by the lower signal/noise ratio of the REE. Even, if not all samples have been evaluated by means of the full spectrum, our study provides the highest resolution dust provenance record available for the Holocene.

In Fig. 2 the ratio LREE/REE calculated for the EDML and EDC ice cores is plotted. As mentioned above a significant change at ~15 200 yr BP is remarkable. From this time, the patterns are much more variable than before (Fig. 3). The EDML record does not show a return to glacial values as it can be observed in the EDC record in the early

CPD
7, 601–633, 2011

Holocene between ~7500 and ~8300 yr BP. Thus, the dust cannot originate from the same sources during that time.

We now discuss the possible contributions of the or multiple PSA for the late transition and the Holocene: The relative majority of the samples (25 out of 86) shows the typical glacial signature (Fig. 6) indicating a possible important contribution (around 30%) from South America also during the Holocene, albeit at a much lower interglacial concentration level. The reduced South American input during the Holocene permits detection of the REE signature of dust from other sources. Together with the glacial-type pattern, the samples showing patterns of Type B and D (Fig. 4) are those occuring most frequently (Type B and D together: 28). These are characterized by enrichment in HREE, which is also seen in the Australian PSA. Alternatively, this pattern also resembles the tephra pattern found at 809 to 808 m depth. However, none of those ice core samples is accompanied by a significantly elevated sulfate concentration, as was seen for bag 809. Accordingly, a volcanic origin seems to be less likely and we conclude that these samples likely reflect a high dust input from southeastern Australia, making this region the second important PSA during the Holocene.

Some of the REE patterns are also characterized by a LREE/HREE-ratio > 1 (Type A, Fig. 4) similar to the pattern of the Antarctic PSA samples (Fig. 6). During the Holocene Antarctic PSA have obviously been active, but this did not likely occur before ~11 800 yr BP. Pattern Type C, shown in Fig. 4, is characterized by an enhancement in Eu, which can only be found in the PSA samples from New Zealand, therefore, indicating this area having occasionally contributed to the Holocene dust input. Of particular interest is the distinct onset of contributions from multiple sources ~15 200 yr BP. The atmospheric dust-concentration, expressed by the nss-Ca-flux, reached 28 ng cm^{-2} yr^{-1} at that time, which is only about 60% higher than the mean nss-Ca-flux during the Holocene (17 ± 18 ng cm^{-2} yr^{-1}) (Fischer et al., 2007). Most of the atmospheric dust concentration variability between glacial and interglacial stages can be explained by a change in the source strength. In fact a variation in transport intensity can explain only an increase in glacial dust fluxes by 40% relative to the Holocene, while an increase

CPD
7, 601–633, 2011

by a factor of 10 was observed (Fischer et al., 2007). Around 15 000 yr BP, a marked change in the dust composition was already observed in the EDC ice core (Gabrielli et al., 2010; Siggaard-Andersen et al., 2007). The time resolution in the EDC REE record is much coarser than in our current study (200 years for EDC compared to 30–50 years in this study). Therefore, the timing of the onset of the change in the geochemical composition of the dust is identified more precisely in our record. Both EDML and EDC ice cores are synchronized by matching records of volcanic signals (Severi et al., 2007) and thus, an error caused by differences in the timescales can be excluded. This clearly indicates, that starting at 15 200 yr BP, dust from other sources can be detected over the East Antarctic Plateau. The decrease in dust input to the East Antarctic Plateau until 15 200 yr BP can be explained by a weakening of the emissivity of the PSA caused by increased vegetation cover or a change in local pricipitation implying wetter conditions. After ~15 200 yr BP, dust from other sources could reach Antarctica indicating a reorganization of the atmospheric circulation. This is supported by earlier studies at EDC (Gabrielli et al., 2010; Siggaard-Andersen et al., 2007; Roethlisberger et al., 2002) but, for the first time in the Atlantic sector of the Antarctic Plateau. Whether other PSAs have always been active cannot be assessed within this study due to the strong dust fallout that dominated the glacial input to East Antarctica.

Interestingly, a clear return to more glacial conditions that is observed in the EDC ice core between ~8300 and ~7500 yr BP, could not be identified at DML. In the EDML ice core, the dust provenance shows several types of pattern. Especially, the Type A, most similar to the Antarctic pattern, occurs during that period. A possible explanation for the absence of a return to a dominant glacial pattern could be the overprint by Antarctic dust in DML that is not onserved at Dome C. In this study, the samples from the ice free areas originate mainly from the Antarctic Dry Valley, located on the opposite site of the Antarctic continent. By collecting and analyzing samples from the mountain range in Heimefrontfjella, located much closer to DML, this hypothesis could be tested.

CPD
7, 601–633, 2011

5 Conclusions

In this study, we investigated the REE composition in the EDML ice over the last climatic transition spanning the period 26 500–7500 yr BP. REE fingerprints in ice core dust samples can help to identify potential source areas, even if the separation of individual source fields is not unambiguous for all PSAs. However, the analytical effort and the small required sample size make it a comparably simple and "cheap" addition to the traditional Sr and Nd isotope studies.

During the LGA and until 15 200 yr BP, the dust composition is uniform and reveals a constant source or a constant mix of sources during that time period. The REE fingerprints in the ice core samples are similar to those extracted from South American PSA samples. From ~15 200 yr BP fingerprints from other source areas, mainly the southeastern part of the Australian continent, can be recognized. However, in about 30% of the ice samples used for this study, the dust reaching Dronning Maud Land still resembles the glacial pattern. A concurrent change in REE composition at Dome C at ~15 000 yr BP suggests a synchronous change of source areas for the entire East Antarctic Plateau. Between ~8300 and ~7500 yr BP, when a return to glacial dust characteristics was observed at Dome C, these seemed unchanged in DML. A weakening of the glacial sources during the first part of the transition and a reorganization of the atmospheric circulation enabled the entrainment of dust from other PSAs to DML during the Holocene. Contributions of southeast Australian dust seem to be the second most frequent one, but also dust inputs from New Zealand and from Antarctic sources appear to have occurred during the Holocene.

Supplementary material related to this article is available online at:
http://www.clim-past-discuss.net/7/601/2011/cpd-7-601-2011-supplement.zip

CPD
7, 601–633, 2011

Acknowledgements. This work is a contribution to the "European Project for Ice Coring in Antarctica" (EPICA), a joint ESF (European Science Foundation)/EC scientific programme, funded by the European Commission and by national contributions from Belgium, Denmark, France, Germany, Italy, the Netherlands, Norway, Sweden, Switzerland and the UK. Anna Wegner thanks DFG for funding.

References

Blunier, T., Schwander, J., Stauffer, B., Stocker, T., Daellenbach, A., Indermhle, A., Tschumi, J., Chappellaz, J., Raynaud, D., and Barnola, J.: Timing of the Antarctic Cold Reversal and the Atmospheric CO_2 Increase with Respect to the Younger Dryas Event, Geophys. Res. Lett., 24, 2683–2686, 1997. 611

De Deckker, P., Norman, M., Goodwin, I. D., Wain, A., and Gingele, F. X.: Lead isotopic evidence for an Australian source of Aeolian dust to Antarctica at times over the last 170 000 years, Palaeogeogr. Palaeocl., 285, 205–223, 2010. 604, 605

Delmonte, B.: Quaternary origin and variations of continental dustin East Antarctica, Ph.D Thesis, University of Siena, Siena, Italy, Universite Joseph Fourier-Grenoble I, Grenoble, France, 2003. 609

Delmonte, B., Basile-Doelsch, I., Petit, J.-R., Maggi, V., Revel-Rolland, M., Michard, A., Jagoutz, E., and Grousset, F.: Comparing the Epica and Vostok dust records during the last 220,000 years: stratigraphical correlation and provenance in glacial periods, Earth.-Sci. Rev., 66, 63–87, 2004a. 604

Delmonte, B., Petit, J. R., Andersen, K. K., Basile-Doelseh, I., Maggi, V., and Lipenkov, V. Y.: Dust size evidence for opposite regional atmospheric circulation changes over east Antarctica during the last climatic transition, Clim. Dynam., 23, 427–438, 2004b. 604, 609

Delmonte, B., Petit, J. R., Basile-Doelsch, I., Jagoutz, E., Maggi, V., Sirocko, F., Claussen, M., Sanchez Goni, M. F., and Litt, T.: The climate of past interglacials Late Quaternary interglacials in East Antarctica from ice-core dust records Developments, Quaternary Sci., 7, 53–73, 2007. 604

CPD
7, 601–633, 2011

Delmonte, B., Andersson, P. S., Hansson, M., Schoeberg, H., Petit, J., Basile-Doelsch, I., and Maggi, V.: Aeolian dust in East Antarctica (EPICA-Dome C and Vostok): Provenance during glacial ages over the last 800 kyr, Geophys. Res. Lett., 35, L07703, doi:10.1029/2008GL033382, 2008. 616

Delmonte, B., Andersson, P. S., Schoberg, H., Hansson, M., Aciego, S., Petit, J.-R., Albani, S., Mazzola, C., Maggi, V., and Frezzotti, M.: Aeolian dust in the Talos Dome ice core (East Antarctica, Pacific/Ross Sea sector): Victoria Land versus remote sources over the last two climate cycles, J. Quaternary Sci., 25(8), 1327-1337, doi:10.1002/jqs.1418, 2010a. 605

Delmonte, B., Andersson, P. S., Schoeberg, H., Hansson, M., Petit, J. R., Delmas, R., Gaiero, D. M., Maggi, V., and Frezzotti, M.: Geographic provenance of aeolian dust in East Antarctica during Pleistocene glaciations: preliminary results from Talos Dome and comparison with East Antarctic and new Andean ice core data, Quaternary Sci. Rev., 29, 256–264, 2010b. 604, 605

Dick, D., Wegner, A., Gabrielli, P., Barbante, C., Ruth, U., and Kriews, M.: ICP-Time of Flight-MS as a versatile tool for ultra trace element analysis in Antarctic ice, Anal. Chim. Acta, 621, 140–147, 2008. 610

EPICA Community Members: One-to-one coupling of glacial climate variability in Greenland and Antarctica, Nature, 444, 195–198, 2006. 610, 627

Fischer, H., Fundel, F., Ruth, U., Twarloh, B., Wegner, A., Udisti, R., Becagli, S., Castellano, E., Morganti, A., Severi, M., Wolff, E., Littot, G., Roethlisberger, R., Mulvaney, R., Hutterli, M. A., Kaufmann, P., Federer, U., Lambert, F., Bigler, M., Hansson, M., Jonsell, U., de Angelis, M., Boutron, C., Siggaard-Andersen, M. L., Steffensen, J. P., Barbante, C., Gaspari, V., Gabrielli, P., and Wagenbach, D.: Reconstruction of millenial changes in the dust emission, transport and regional sea ice coverage using the deep EPICA ice cores from the Atlantic and the Indian sector of Antarctica, Earth Planet. Sc. Lett., 260, 340–354, 2007. 610, 617, 618, 627

Gabrielli, P., Barbante, C., Turetta, C., Marteel, A., Boutron, C., Cozzi, G., Cairns, W., Ferrari, C., and Cescon, P.: 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, 2006. 605, 607

Gabrielli, P., Wegner, A., Petit, J.-R., Delmonte, B., De Deckker, P., Gaspari, V., Fischer, H., Ruth, U., Kriews, M., Boutron, C., Cescon, P., and Barbante, C.: A major glacial-interglacial change in aeolian dust composition inferred from Rare Earth Elements in Antarctic ice, Quaternary. Sci. Rev., 29, 265–273, 2010. 606, 607, 608, 614, 618

CPD
7, 601–633, 2011

Gaiero, D. M.: Dust provenance in Antarctic ice during glacial periods: From where in southern South America?, Geophys. Res. Lett., 34, L17707, doi:10.1029/2007GL030520, 2007. 605, 616

Gaiero, D. M., Depetris, P. J., Probst, J., Bidart, S. M., and Leleyter, L.: The signature of river- and wind-borne materials exported from Patagonia to the southern latitudes: a view from REEs and implications for paleoclimatic interpretations, Earth Planet. Sc. Lett., 219, 357–376, 2004. 614, 615

Kaufmann, P. R., Federer, U., Hutterli, M., Bigler, M., Schuepbach, S., Ruth, U., Schmitt, J., and Stocker, T.: An Improved Continuous Flow Analysis System for High-Resolution Field Measurements on Ice Cores, Environ. Sci. Technol., 42, 8044–8050, 2008. 607

Lambert, F., Delmonte, B., Petit, J. R., Bigler, M., Kaufmann, P. R., Hutterli, M. A., Stocker, T. F., Ruth, U., Steffensen, J. P., and Maggi, V.: Dust-climate couplings over the past 800,000 years from the EPICA Dome C ice core, Nature, 452, 616–619, 2008. 604, 605

Marino, F., Castellano, E., Ceccato, D., De Deckker, P., Delmonte, B., Ghermandi, G., Maggi, V., Petit, J., Revel Rolland, M., and Udisti, R.: Defining the geochemical composition of the EPICA Dome C ice core dust during the last glacial-interglacial cycle, Geochem. Geophy. Geosy., 9(10), Q10018, doi:10.1029/2008GC002023, 2008. 604

Marino, F., Castellano, E., Nava, S., Chiari, M., Ruth, U., Wegner, A., Lucarelli, F., Udisti, R., Delmonte, B., and Maggi, V.: Coherent composition of glacial dust on opposite sides of the East Antarctic Plateau inferred from the deep EPICA ice cores, Geophys. Res. Lett., 36, L23703, doi:10.1029/2009GL040732, 2009. 604, 611, 615

Marx, S. K., Kamber, B. S., and McGowan, H. A.: Provenance of long-travelled dust determined with ultra-trace-element composition: a pilot study with samples from New Zealand glaciers, Earth Surf. Proc. Landf., 30, 699–716, 2005. 615

Reijmer, C. H., van den Broeke, M. R., and Scheele, M. P.: Air parcel trajectories to five deep drilling locations on Antarctica, based on the ERA-15 data set, J. Climate, 15, 1957–1968, 2002. 616

Revel-Rolland, M., De Deckker, P., Delmonte, B., Hesse, P. P., Magee, J. W., Basile-Doelsch, I., Grousset, F., and Bosch, D.: Eastern Australia: A possible source of dust in East Antarctica interglacial ice, Earth Planet. Sc. Lett., 249, 1–13, 2006. 604, 605

Ridgwell, A. J.: Dust in the Earth system: the biogeochemical linking of land, air and sea, Philos. T. Roy. Soc. Lond. A, 360, 2905–2924, 2002. 603

CPD
7, 601–633, 2011

Roethlisberger, R., Bigler, M., Hutterli, M., Sommer, S., Stauffer, B., Junghans, H. G., and Wagenbach, D.: Technique for continuous high-resolution analysis of trace substances in firn and ice cores, Environ. Sci. Technol., 34, 338–342, 2000. 606, 607

Roethlisberger, R., Mulvaney, R., Wolff, E. W., Hutterli, M. A., Bigler, M., Sommer, S., and Jouzel, J.: Dust and sea salt variability in central East Antarctica (Dome C) over the last 45 kyrs and its implications for southern high-latitude climate, Geophys. Res. Lett., 29, 1963, 2002. 618

Ruth, U., Wagenbach, D., Steffensen, J. P., and Bigler, M.: Continuous record of microparticle concentration and size distribution in the central Greenland NGRIP ice core during the last glacial period, J. Geophys. Res., 108, 4098, doi:10.1029/2002JD002376, 2003. 604

Ruth, U., Barnola, J.-M., Beer, J., Bigler, M., Blunier, T., Castellano, E., Fischer, H., Fundel, F., Huybrechts, P., Kaufmann, P., Kipfstuhl, S., Lambrecht, A., Morganti, A., Oerter, H., Parrenin, F., Rybak, O., Severi, M., Udisti, R., Wilhelms, F., and Wolff, E.: "EDML1": a chronology for the EPICA deep ice core from Dronning Maud Land, Antarctica, over the last 150 000 years, Clim. Past, 3, 475–484, doi:10.5194/cp-3-475-2007, 2007. 606

Sarthou, G., Baker, A. R., Blain, S., Achterberg, M., Bowie, A. R., Croot, P., Laan, P., de Baar, H. J. W., Jickells, T. D., and Worsfold, P. J.: Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean, Deep-Sea Res. Pt. I, 50, 1339–1352, 2003. 603

Severi, M., Becagli, S., Castellano, E., Morganti, A., Traversi, R., Udisti, R., Ruth, U., Fischer, H., Huybrechts, P., Wolff, E., Parrenin, F., Kaufmann, P., Lambert, F., and Steffensen, J. P.: Synchronisation of the EDML and EDC ice cores for the last 52 kyr by volcanic signature matching, Clim. Past, 3, 367–374, doi:10.5194/cp-3-367-2007, 2007. 618

Siggaard-Andersen, M. L., Gabrielli, P., Steffensen, J. P., Stromfeldt, T., Barbante, C., Boutron, C., Fischer, H., and Miller, H.: Soluble and insoluble lithium dust in the EPICA Dome C ice core – Implications for changes of the East Antarctic dust provenance during the recent glacial-interglacial transition, Earth Planet. Sc. Lett., 258, 32–43, 2007. 604, 618

Smith, J., Vance, D., Kemp, R. A., Archer, C., Toms, P., King, M., and Zarate, M.: Isotopic constraints on the source of Argentinian loess – with implications for atmospheric circulation and the provenance of Antarctic dust during recent glacial maxima, Earth Planet. Sc. Lett., 212, 181–196, 2003. 614, 615

Sun, D., Lau, K. M., and Kafatos, M.: Contrasting the 2007 and 2005 hurricane seasons: Evidence of possible impacts of Saharan dry air and dust on tropical cyclone activity in the Atlantic basin, Geophys. Res. Lett., 35, L15405, doi:10.1029/2008GL034529, 2008. 603

Vallelonga, P., Gabrielli, P., Balliana, E., Wegner, A., Delmonte, B., Turetta, C., Burton, G., Vanhaecke, F., Rosman, K. J. R., Hong, S., Boutron, C. F., Cescon, P., and Barbante, C.: Lead isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere Potential Source Areas, Quaternary Sci. Rev., 29, 285–295, 2010. 604

Wedepohl, H. K.: The composition of the continental crust, Geochim. Cosmochim. Acta, 59, 1217–1232, 1995. 611

CPD
7, 601–633, 2011

Table 1. Instrumental detection limit (LOD) and procedural blank (PB). Values are given in $pg \cdot g^{-1}$. For comparison, the mean Holocene (13 300–7500 yr BP) and glacial (26 500–16 000 yr BP) concentrations are given. REE concentrations in the Holocene are biased towards higher values, due to the fact that not all the determinations could be evaluated. Additionally, mean concentrations between 15 900 and 14 600 yr BP are given.

	LOD	PB	Mean Holocene	Mean Glacial	Mean Glacial/ Mean Holocene	~15 900 yr BP–14 600 yr BP
La	0.027	0.35	1	25.1	25	5.8
Ce	0.16	0.64	1.94	54.9	28	9.3
Pr	0.005	0.09	0.2	6.68	33	1.21
Nd	0.01	0.27	0.73	23.65	33	4.28
Sm	0.012	0.08	0.17	5.51	33	0.95
Eu	0.005	0.03	0.05	1.15	25	0.21
Gd	0.003	0.08	0.14	4.92	34	0.87
Tb	0.002	0.02	0.03	0.71	25	0.12
Dy	0.002	0.04	0.12	3.95	32	0.8
Ho	0.001	0.01	0.03	0.75	29	0.17
Er	0.002	0.02	0.07	1.99	30	0.48
Tm	0.001	0.01	0.01	0.28	24	0.07
Yb	0.002	0.02	0.06	1.67	30	0.41
Lu	0.002	0.01	0.02	0.23	15	0.06

CPD
7, 601–633, 2011

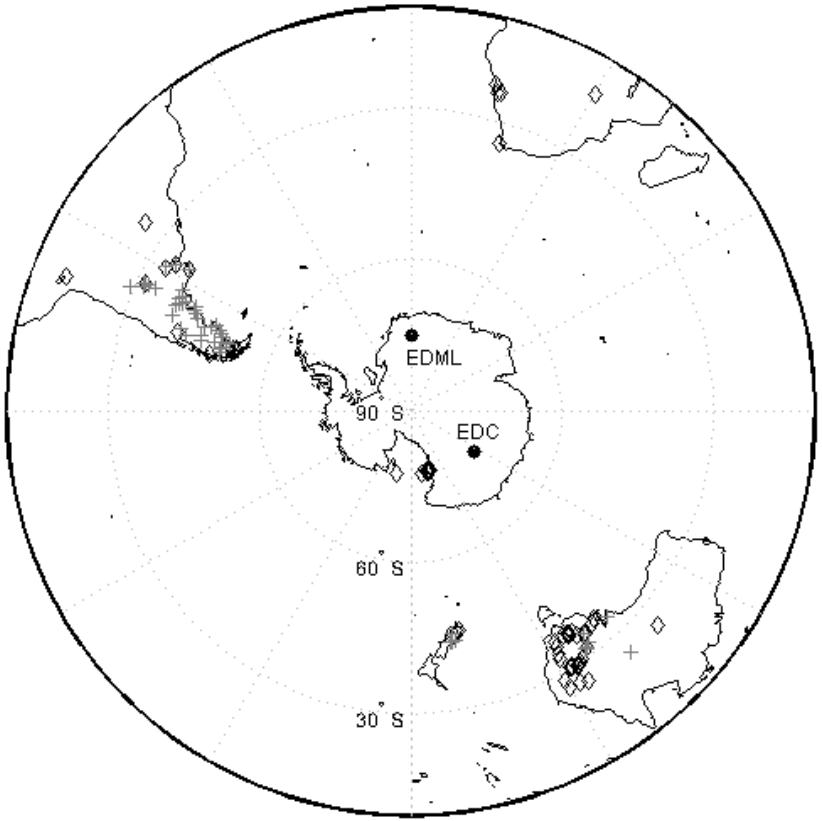

Fig. 1. Map of sample locations. Diamonds indicate samples from this study, and crosses represent already published data (for references see text). EDML and EDC indicate the drill sites for the two deep ice cores drilled within the framework of EPICA in Dronning Maud Land and at Dome C.

CPD
7, 601–633, 2011

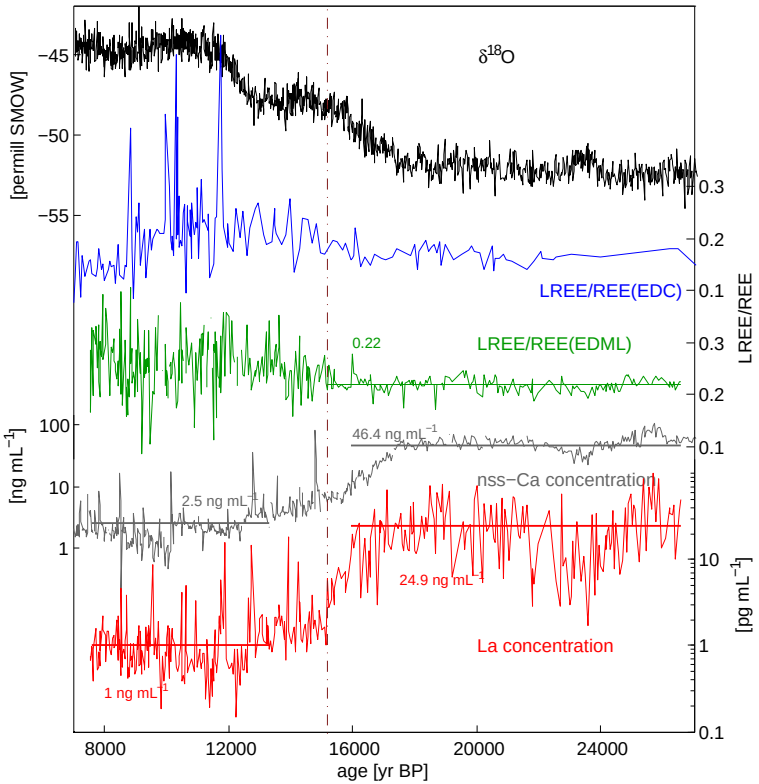

Fig. 2. Different proxies in the EDML ice core over the LGA to Holocene transition: δ^{18}O isotopic composition (top, EPICA, 2006); LREE/REE ratio clearly shows a constant value at 0.22 during the LGA. This changes to higher and more variable ratios at 15 200 yr BP as indicated by the dashed vertical line. The corresponding LREE/REE profile from EDC also shows a change around 15 000 yr BP. Nss-Ca^{2+} concentration is an indicator for the dust concentration (after Fischer et al., 2007); La concentration is an indicator of REE-concentration.

CPD
7, 601–633, 2011

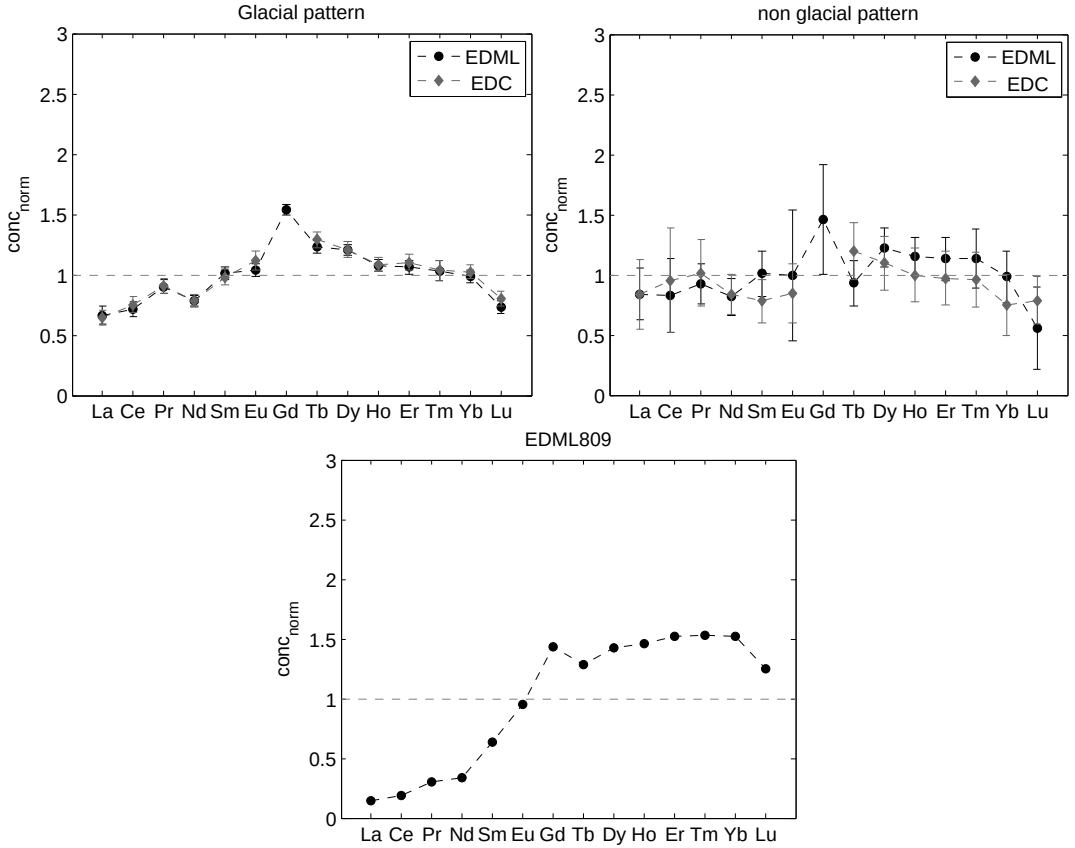

Fig. 3. Mean glacial REE pattern from 27 000 to 15 200 yr BP and 15 200 to 7500 yr BP. Error bars indicate the 1 σ standard deviation of the variability for each rare earth element. Clearly identifiable is the much higher heterogeneity during the Holocene compared the LGA and early transition. The bottom graph shows the pattern from a depth interval, with the thickest volcanic ash layer in the whole EDML ice core showing a strong enrichment in HREE.

CPD
7, 601–633, 2011

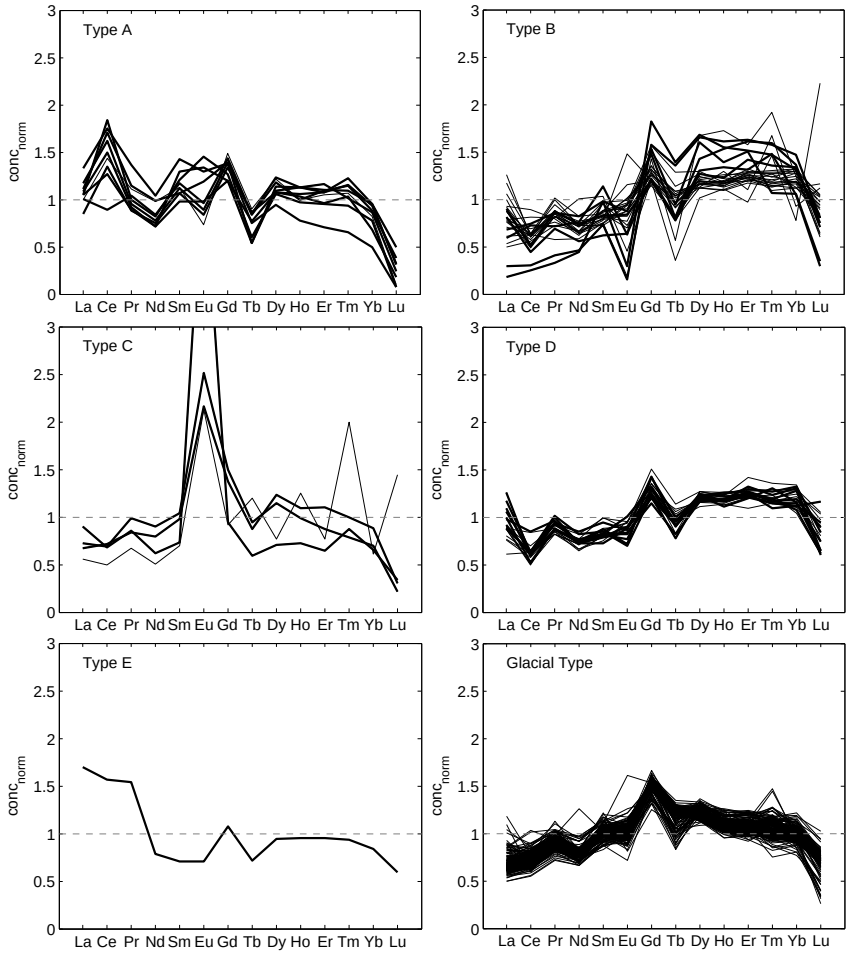

Fig. 4. Typical REE patterns during the Holocene. The characteristic variations in the Eu-anomaly and the HREE/LREE ratios are clearly identified.

CPD
7, 601–633, 2011

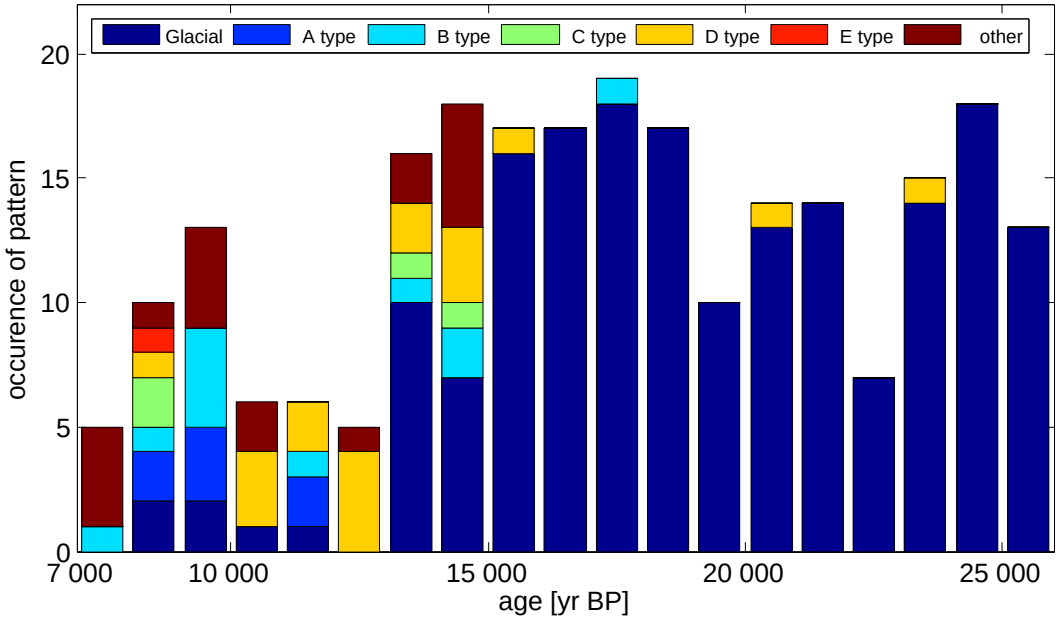

Fig. 5. Occurrence of the different REE patterns over time differentiated by different types. The majority of the samples before 15 000 yr BP are classified as belonging to the glacial pattern; for the period between 12 000 and 10 000 yr BP, very few REE determinations were used.

CPD
7, 601–633, 2011

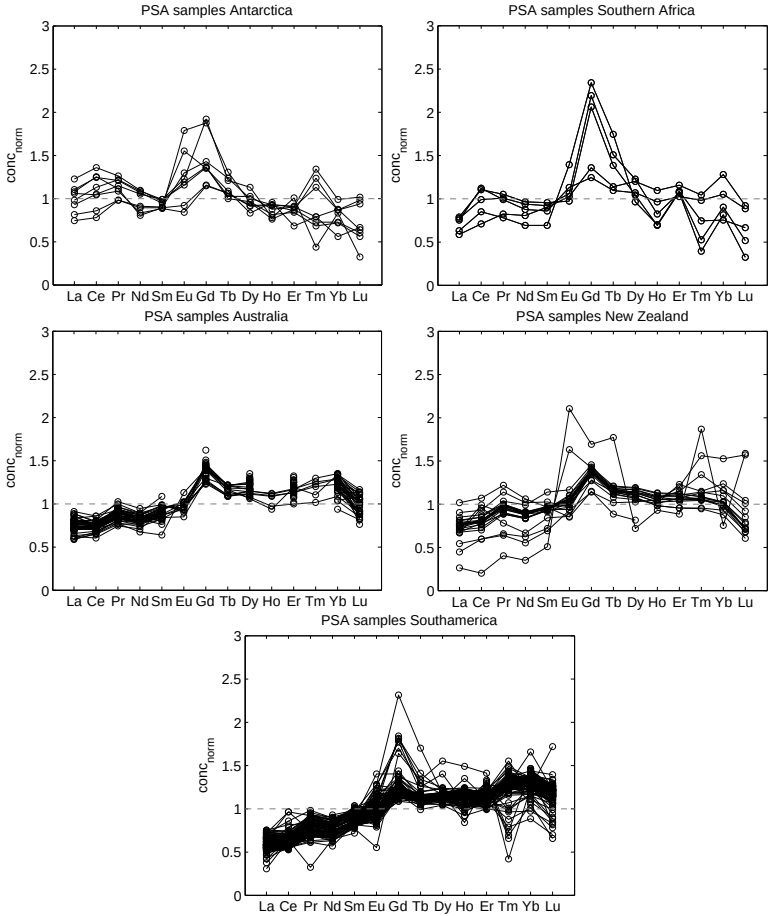

Fig. 6. REE patterns in the samples from the PSAs.

CPD
7, 601–633, 2011

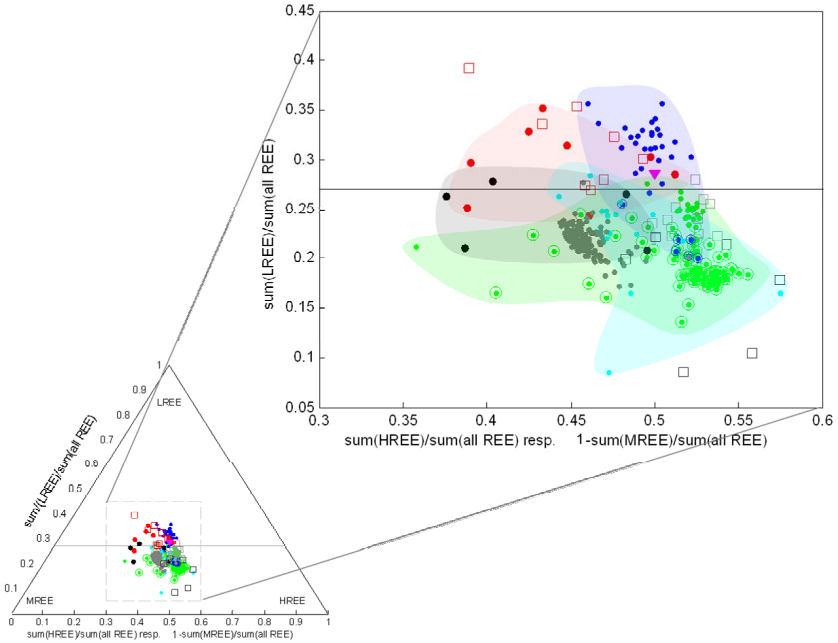

Fig. 7. Plot of the ratios of LREE, MREE and HREE. The samples from the PSAs are indicated as follows: South America: green dots, southeastern Australia: blue dots (for Australia and South America, the samples for this study (<5 µm) are indicated with circles around the dots), Antarctica: red dots, southern Africa: black dots, New Zealand: light blue dots. The shaded areas give the areas covered by the different potential source areas. Glacial EDML samples are indicated with grey dots. All other ice core samples are indicted with squares: Type A red, Type B dark grey, Type D light grey. For a description of the different types, see Fig. 3 and the text. The horizontal line at LREE = 27% indicates the differentiation between South America and Australia with respect to the ratio of LREE. The glacial samples are clearly located in the area covered by the South America samples. The magenta triangle indicates the mean UCC values used for normalization.

CPD
7, 601–633, 2011

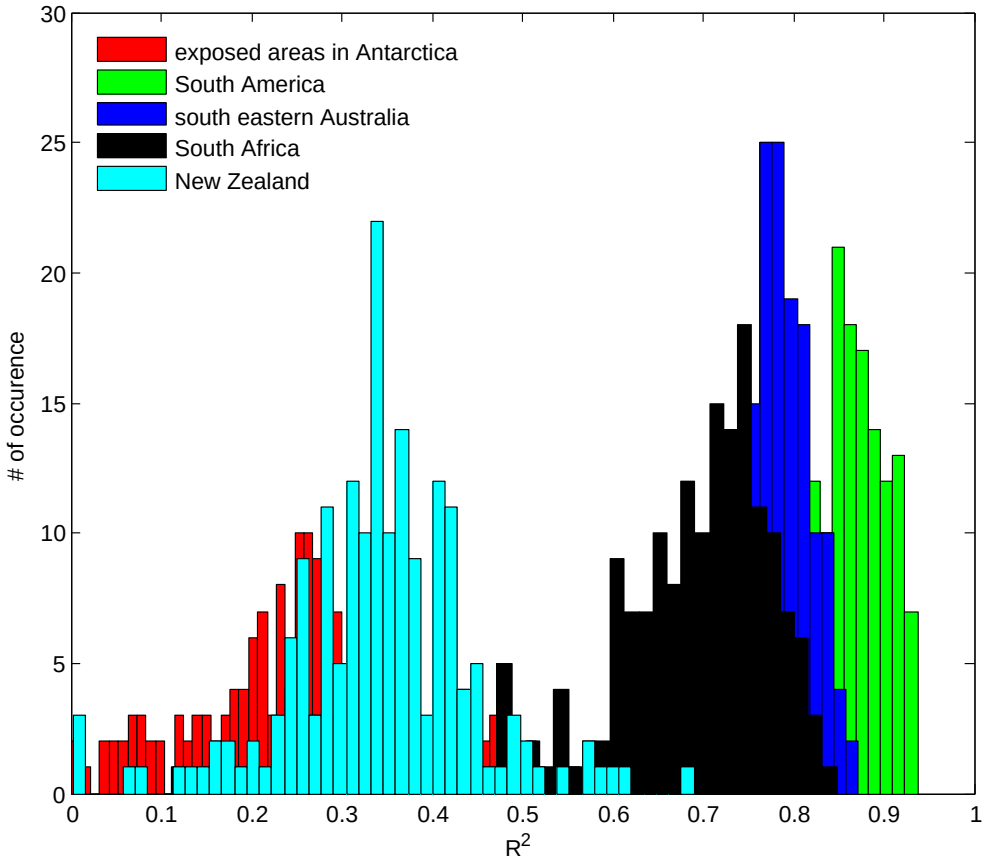

Fig. 8. Histogram of the correlation coefficient R^2 of the REE pattern of each sample between 26 500 and 15 200 yr BP and the mean REE pattern of each PSA (red: exposed areas in Antarctica, green: South America, blue: south eastern Australia, black: south Africa, light blue: New Zealand).

CPD
7, 601–633, 2011