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Climate of the Past Discussions

Interactive comment on "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" *by* A. Wegner et al.

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We thank both reviewers for their constructive comments.

General comments to both reviewers:

Better discussion of the analytical aspect for Holocene data:

A major point of the reviewers concerned the possible limits of our procedure when analyzing Holocene samples. This has now been investigated more carefully. Special consideration was given to the remark of the first reviewer, stating that patterns with anomalies for Gd, Tb, Tm or Lu must be explained differently. The most likely reason

for these unexpected anomalies was an overestimation of the blank subtraction. It turned out that no blank correction, (after normalization with the upper continental crust (UCC) values of Rudnick and Gao. 2005) yielded patterns that are coherent with the REE patterns calculated in the more concentrated samples. We conclude that the UPW blank (REE content in MQ-water, resistance >18.2 MΩ cm) did not contribute significantly to the sample concentrations. Indeed MQ water was never added to our samples and thus, in principle, no subtraction of its REE content from that of the sample is needed. The REE amount detected in MQ water must have had a different origin (e.g. from the MQ ion exchange filter columns or the plastic bags that were used to prepare the artificial ice core) while it cannot be linked to any step in the sample preparation (continuous flow melting system, bottling, spiking with acid).

Without blank subtraction, anomalies only occur for Ce, Eu and Tm. While the anomalies of Ce and Eu are well known, the anomaly in Tm is more difficult to be explained and could still be caused by some unidentified contribution (e.g. isotopic interference). However, there are also studies stating that a Tm anomaly could arise from a poorly constrained crustal value, due to the mono-isotopic nature of Tm (Kamber et al. 2005). In conclusion, we cannot really determine whether the Tm anomaly is real or not and thus Tm was conservatively excluded from further discussion. This description is now included in the manuscript in the methods section. This remark was very helpful to improve the manuscript.

By not subtracting the REE content of the MQ water from the samples, the different types of patterns (A-B-C-D-E) can still be clearly distinguished in Holocene samples (but now B and D were combined into one group and the naming of the groups have been changed accordingly. The clear onset of different dust sources at 15 000 yr BP is now less pronounced (Figure 2 was updated accordingly). However, the REE fingerprints still become more heterogeneous at 15 000 yr BP (a time when the ice was still not characterized by low Holocene REE concentrations), indicating that our conclusion that dust from other sources started to reach the EPICA Dronning Maud

Land (EDML) site at 15 000 yr BP, is robust. The manuscript discussion has now been revised accordingly.

Mineralogical composition of the dust:

Glacial dust in the Dome C and Vostok ice cores consist mainly of clays (mostly illite), feldspars and quartz. Kaolinite has (if at all present) very low abundance in Dome C and Vostok ice. (Gaudichet et al. 1986, Gaudichet et al. 1988). For EDML direct mineralogical observations are not available, but since dust characteristics in EDML and EPICA Dome C (EDC) ice are very similar (Marino et al. 2009 and this study) it is likely that the mineralogy is also similar. The state of the art knowledge about the dust mineralogy is now included in the paper in connection with the different recoveries at the end of the methods part.

More noise in postglacial samples due to propagation of the higher analytical uncertainty:

As a consequence of the different reevaluation of the data (see above) the noise is now much reduced for postglacial samples. Still, LREE/REE ratios (linked to the highest and thus most robust REE EDML concentrations) are more variable in postglacial samples, but the strong variability linked to even-odd atomic masses in the Holocene REE patterns is now removed.

Comments reviewer 1:

Use UCC values of Rudnick and Gao (2005) for normalization:

These values have now been adopted in the revised manuscript. Thank you for that remark.

Reason for selecting sites:

All the samples that were made available for this study were used. We do not claim to have a complete data set for potential source areas (PSAs). They rather represent

highlights that provide an indication of zones from which dust may or may not originate. Indeed, it would be beneficial for this study to have more samples from more different locations, especially in Australia.

Several spelling and grammar mistakes mentioned in the manuscript were corrected

Figure 7: Figure caption has been updated

Comment on page 605: would call differences in ionic radii chemical properties.

This is now changed to better specify the incorporation in the lattice.

Comment on page 606: suspect you have not dated your samples but rely on Ruth et al 2007:

Correct. The text was modified according to this suggestion.

Comment on page 607: 157 BaO does not exist: We agree. There is instead an interference on mass 157, which could originate from ^{141}Pr^{16}O. This interference was significant, as ^{157}Gd showed larger values than ^{158}Gd and ^{160}Gd. This passage in the text has now been rewritten accordingly.

Comment on page 608: Blanks will certainly affect some isotopes more than others and the REE patterns will not be well defined in many cases:

Please, see our answer to the general comments.

Comment on page 608: Mineralogical composition of the dust; Acid-leaching is "spiking" with 100 μl HNO$_3$?

Acid leaching was performed by spiking with 100 μL HNO$_3$. Gabrielli et al. 2010 extensively discussed the different recovery rates: approximately 50% for acid leached samples with respect to digested samples, as well as slightly higher recoveries for LREE than for HREE as stated in the text. As this is discussed in detail by Gabrielli et al. 2010, we refer to this publication in our text. We have also included in the text a description of different mineralogies in East Antarctic ice cores (see above). As already mentioned, there is so far no study of mineralogy in EDML ice. However, from studies in the Vostok and Dome C cores it was concluded that, due to dissolution, carbonates do not reach Antarctica in a mineral form (Delmonte et al. 2004, Marino et al. 2008, De Angelis et al. 1992). During the Holocene, dust in the Vostok and Dome C core mainly consists of clays, few feldspars and quartz and very low kaolinite content (Gaudichet et al. 1986, Gaudichet et al. 1988).

Comment on page 609: Samples measured in both labs:

Dick et al. 2008 already performed a detailed investigation of EDML samples analyzed for REE in two labs. These data show a good agreement. Since such a detailed study already exists, we no refer to it within the text (end of section 2.2). Additional information is given in the supplement.

Comment on page 609: Outliers in the blanks: Are they also present in the Holocene samples?

To verify the presence of outliers in the Holocene, the samples covering the period from 7500 to 12 000 yr BP were checked. These samples have an approximately constant concentration level. The concentrations for each REE over this time span show logarithmic distributions without any obvious outlier in the sample concentrations. After analysis of the REE patterns, it is most likely that spikes in MQ water did not originate from sample processing but from MQ water production.

Comment on page 610: Use Yb instead of Lu:

In this context we do not understand the meaning of this suggestion. Later in the manuscript we used HREE as a sum of Ho, Er, Tm, Yb and Lu. Thus the weight of Lu (the least abundant of the REE) is limited in the overall HREE balance.

Comment on page 611: Normalization to a mean value of 1:

In Figure 1 La is shown in terms of absolute concentration values. We think this plot is

a good indication of the variability of the determined REE concentrations. If other REE would have had a higher or lower variability than La, this would have emerged in the normalized patterns, but this is not the case. On the other hand, for the calculation of correlation coefficients the use of normalized patterns provides results that are directly comparable, as patterns are not affected by values of different magnitude.

Comment on page 611: approaching the analytical limit:

As explained above, as REE patterns do not show the zigzag pattern anymore, we are confident that the variability in REE concentrations is not due to analytical uncertainties.

Comment on page 612: Pattern Bag 809 is not a peculiar pattern:

This passage was rewritten. In any case Bag 809 is dominated by a volcanic fallout horizon, which is visible and is the thickest ash layer in the entire EDML ice core.

Comment on page 612: You should worry about "anomalies" for elements like Gd, Tb, Tm or Lu and consider that they have other origins:

Please, see our answer in the general comments

Comment on page 613: is marked, but there is no comment

Comment on page 615: Correlation coefficient R instead of R^2; better explanation of the calculation:

R^2 has been replaced with R (Figure 8). However, this does not change the result significantly. In Figure 8 each ice sample from the glacial stage was correlated with the mean value from each PSA. Thus, for each PSA 165 values for R were calculated, which were plotted in the histogram. The crustal normalized values were used for this calculation, according to Eq. 2. The figure caption was also updated.

Comment on page 626: reason for selecting sites:

Please, see our answer to the general comments.

Comment on page 627: more noise in post-glacial samples:

Please see our discussion above.

Comment on page 631:

Headings are now moved into Figure 3 and 6.

Comment on page 632:

Figure caption has been modified with a better explanation.

Comment on page 633: Figure caption has been modified with a better explanation.

Comment reviewer 2:

General comments:

More complete literature list:

The introduction and discussion were modified and the results are better imbedded in the literature (please see also our answers to the specific comments)

Evaluation of the potential of REE as a provenance tool, comparison to results of Sr and Nd isotopes:

A study to compare results from Sr and Nd isotopes was performed. Please see our answers in the specific comments.

Specific comments:

Abstract needs some serious editorial input (e.g. first sentence): The Abstract was rewritten.

Line 8: delete 's' in PSAs Line 10: delete 'to be':

This was modified accordingly in the revised manuscript

Introduction needs work, particularly between line 18 on page 603 and line 11 on

page 905:

The introduction was mostly rewritten with more focus on aeolian dust.

The description of the methodology should be much reduced and limited to critical details different from Gabrielli et al. 2005:

The methodology has now been rewritten and limited to differences from Gabrielli et al. 2005/2010 (section 2.1)

As mentioned previously, the presentation of the PSA data and a critical evaluation of the data should be a major emphasis of this paper:

The PSA samples available do not cover all the PSAs, but rather represent a selection. We agree that the presentation of PSA data should be extended in furture studies. In the supplement a detailed description of the PSA sample processing and analysis is provided. See also comment 6 on this point.

Comparison of the REE and Sr/Nd study:

Irrespective of how representative the sample selection was, as a first step we can perform a direct comparison between samples that were measured on Sr and Nd isotopes (Delmonte et al. 2004) and REEs in this paper.

Antarctic samples: For the Antarctic samples most similar in their pattern with enriched MREE (mainly Eu and Gd) and depleted HREE are samples 2,3,4,6,8 and additionally 5. In the Sr/Nd study these samples lie at the more radiogenic end. Samples 1 and 10 do not show any sign of enrichment in MREE and fall into the less radiogenic end of the Nd isotopic field. Sample 11 from Terra Nova bay shows a strong negative Eu anomaly dissimilar to all other samples from Antarctica. This sample shows highly radiogenic Sr signature and is thus different to all other Antarctic samples.

South American samples: For the South American samples we investigated the north-south gradient (Figure 9) We find that samples further south are more enriched in

HREE and MREE and more depleted in LREE. Despite this finding, we cannot identify a particular dust source region when evaluating the mean glacial fingerprint from EDML due to the high scatter of the data.

Australian samples: For the Australian samples, the one sample originating from the centre of Australia is slightly more enriched in MREE than the others which all originate from the south east and show very uniform fingerprints. These samples were not analyzed for Sr and Nd before.

To summarize, differences in REE agree with differences in Sr and Nd isotope investigations. Even if Sr/Nd isotope investigations will be the standard tool for provenance analysis, REEs offer a cheap and quick method for preliminary estimates of dust provenance.

Duplicate measurements:

To check the reproducibility of the REE determinations, a sample of recent firn from nearby the EDML drill site was measured regularly during the EDML sample analysis. In total 16 measurements of this sample were conducted. The REE concentration in this sample varied from 13% (for Nd and Dy) up to 26% (for La and Tm).

Additionally 72 samples randomly chosen over the whole record were measured twice, 9 were measured 3 times and one was measured four times, on different days. The mean reproducibility of these replicates was between 19% and 31%. For the Holocene samples this reproducibility is in the same range of the relative standard deviation of a single measurement. The results of the replicates are now included in the manuscript in the methods section.

Comment 1) different LREE/REE ratios in Figure 2:

This was a mistake that occurred when plotting the ratios. The ratio values are now updated over this time interval. Thank you so much for this remark.

Comment 2): Please see our answer in the general comments on analytical aspects

of the Holocene data and the duplicate measurements.

Comment 3) Similarly, the last paragraph on page 612 discusses identification of different types of patterns. How were these patterns selected? Is this done manually or is there a certain algorithm to identify these patterns? Type B, Type D and Glacial Type (or at least subsets of those) seem to be very similar.:

First all patterns differing from the mean glacial pattern were investigated. The difference from the glacial was calculated as the sum of the squared differences between each REE normalized concentration in the sample and the mean glacial value. For the Holocene it was visually clear, that specific patterns occurred when the difference from the glacial pattern was large. Second, these patterns were defined by anomalies or ratios according to these criteria: As Type B and D are very similar, we combined them into one group. The manuscript is updated according to this suggestion and the criteria of the different patterns are included.

Glacial-type pattern: Samples that do not deviate from the glacial mean by more than 0.015 in the mean of the squared differences of each REE from the glacial mean. A-type samples: Ce-anomaly $>$ 1.2, C-type samples excluded B-type samples: HREE/REE $\geq\sim$0.4, C-type samples excluded C-type samples: Eu-anomaly $>$ 1.7 D-type samples. Highly enriched LREE (LREE/REE $>$ 1.3) Unclassified samples (E-type): Samples that cannot be classified into any of the previous categories. This is now included in the results section and in the discussion.

Comment 4) Figure 3. The first order observation is that the post-glacial samples show much higher variability than the glacial samples. However, I don't see much of a difference in REE patterns from glacial to non glacial times. This seems to be especially true for EDML:

Indeed the higher scatter is the most remarkable difference between glacial and post-glacial samples. However, the correlation coefficient between each sample and the mean glacial pattern is on average much higher during the glacial period (i.e. 85%

of the glacial samples highly correlate with the mean glacial, R>0.9. The correlation between the mean post-glacial and the mean glacial pattern is significantly smaller, 0.78, Only 7% of the Holocene samples show a correlation coefficient higher than R>0.9. Also during the current interglacial many samples (97) still show the glacial pattern, although many others show a different pattern indicating a contribution of dust from different sources compared to the glacial. In conclusion, correlation coefficients for glacial samples are higher than for interglacial samples. We acknowledge that some of the observed change in the shape of the Holocene patterns was linked to the analytical bias due to the erroneous subtraction of REE determined in UP water.

Comment 5) PSA data are an essential part and more data needs to be shared:

Most of the samples were provided by Barbara Delmonte and were already analyzed for their Sr and Nd isotopic composition. All information about these samples is provided by Delmonte et al. 2004. In the supplementary table only the most important information is given, which has now been enlarged. Samples from Australia were mostly provided by Patrick De Deckker.

Comment 6) More critical discussion to evaluate the potential of this method:

As mentioned before, in this study we do not claim to present a complete data set of samples from all the PSAs. The different PSAs cannot be separated completely. The South American samples and the Australian samples show a considerable overlap with the samples slightly enriched in HREE. Note that for most Australian samples the complete HREE spectrum could not be evaluated, thus the enrichment in HREE is based on fewer elements than in the other PSA. When calculating the HREE/REE ratios for the PSA samples the fact of missing elements was not correctly taken into account, resulting in an offset between the literature data and the new data for Australian samples. This has been corrected.

The size-fractionated samples analyzed for this study are more enriched in MREE, indicating a size effect for the analysis. As mentioned earlier, dust in ice cores from

East Antarctica mainly consists of clays, which are depleted in REE compared to quartz or other major silicates (Henderson, 1984), thus the REE content in ice core dust is preserved better than in other minerals.

There are also PSAs that can be separated from each other. For example, the ice free areas in Antarctica show a distinct enrichment in LREE. However, the number of samples is limited and for a concluding interpretation of the EDML dust, samples from the mountain ranges in DML would be beneficial. An exclusive allocation of the ice core samples to an individual PSA is not possible. However, REE are a rather quick and cheap tool for first order provenance analysis.

Comment 7) Discussion of the possibility to distinguish sub-regions within the continents:

Since most of the PSA samples originate from South America a distinction of subregions was performed. If we look along the latitude, we find a tendency of the samples to be more enriched in HREE and MREE with increasing latitude. However, this trend is not so strongly pronounced as to distinguish any distinct source in South America. This is now included in the manuscript in section 4.1 and in an additional Figure (9). For Australia, most of the samples are from South-East Australia. This is due to the fact that unfortunately no other samples were made available for this study.

Comment 8) What is the likely switching (on and off) mechanism of the invoked 're-organisation in atmospheric circulation patterns'?

Most likely a combination of changes in atmospheric circulation and source strength causes different contributions to the Antarctic dust deposition fluxes. Lamy et al found a southward shift of the southern westerly wind belt around 19 000 yr BP at approximately the same time, when the dust concentration at EDML starts to decrease. Thus the decrease could be linked to changes in source conditions due to the changed position of the westerly wind belt. However, a change in the dust provenance could not be observed until ∼15 000 yr BP. Sudgen et al. (2009) describes glaciers terminating into lakes or into outwash plains (around 15 000yr BP and the following millennia) as a possible switching mechanism for shutting on and off very active sources of aeolian dust in Southern South America. This coincides with the time when dust from sources other than South America might have started to play a role at EDML. Additionally, a southward shift of the westerly wind belt observed by Lamy et al. 1999 might have de-activated even more the South American source during the termination. In contrast, during interglacials the coupling between the climate at lower latitudes and Antarctica was found to be weaker (Lambert et al. 2008). The source of dust at the margins of the retreating South American glaciers switched off and the westerly wind belt shifted more south. It is not possible to distinguish in this study if other sources have been active throughout the glacial and were overprinted by the South American signal or were activated through a more southward position of the southern westerly wind belt during the Holocene.

We suggest these to be the most important mechanisms for the occurrence of non-South American dust in EDML after 15 000 yr BP. The manuscript is updated in the discussion section and extended in this part according to the suggestion.

Comment 9) Why could the samples size not be adjusted to analyze larger samples?

Larger samples would not have resulted in a better RSD. The number of spectra (runs x passes) chosen was the minimum to obtain a stabilization of the RSD. Increasing the size would only have improved the RSD if a pre-concentration step had been introduced. This would have resulted in a very time-consuming and sample-consuming method and the high resolution presented in this work would not have been possible. Additionally, one major advantage of using these samples was that they were prepared by using the melting system.

Comment 10) include legend in Figure 7:

Legend is included

Additional Comment: reviewer not familiar with acronym LGA:

LGS for last glacial stage seems more common in the literature. The manuscript was updated according to that remark.

Title seems long and convoluted:

The title is shortened to Change in dust variability in the Atlantic Sector of Antarctica at the end of the last deglaciation

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