Marine biogenic sulphur in the EPICA ice cores over the last glacial cycle

F. Fundel (1), *H. Fischer (1), **B. Twarloh (1),** U. Ruth (1), E.W. Wolff (2), G. Littot (2), R. Mulvaney (2), M. de Angelis (3), M. Hansson (4) U. Jonsell (4), M. Hutterli (5), P. Kaufmann (5), U. Federer (5), F. Lambert (5), J.P. Steffensen (6), R. Udisti (7), S. Becagli (7), E. Castellano (7), M. Severi (7), C. Barbante (8) and V. Gaspari (8)*

(1) Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany, (2) British Antarctic Survey, Cambridge, UK, (3) Laboratoire de Glaciologie et Geophysique de l'Environnement, Grenoble, France, (4) Stockholm University, Sweden, (5) University of Bern, Switzerland, (6) University of Copenhagen, Denmark, (7) University of Florence, Italy, (8) University of Venice, Italy

ffundel@awi-bremerhaven.de Phone: +49(0)471-4831-1345

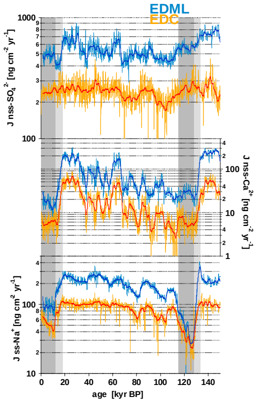
Abstract

With this poster reasons for the observed patterns of the EDML and EDC records of methanesulfonate (MS^-) and non sea salt sulfate (nss SO_4^{2-}) are suggested.

While the EDC MS^- signal seems to be a response to fixation processes due to changed dust levels only, an additional influence of the accumulation rate is observable at EDML during the last glacial. A threshold of about 10 ppb Ca^{2+} was found above which MS^- is mainly independent from impurity changes at both sites.

The unchanged flux of nss SO_4^{2-} at EDC was attributed to an unchanged meridional circulation and marine bio-productivity in the Indian sector of the Southern Ocean (SO). This seems to be not transferable to the Atlantic sector of the SO, as at EDML a small but significant change of the nss SO_4^{2-} flux is observable. Here, a limited iron fertilization effect on the marine phytoplankton during glacial times seems likely.

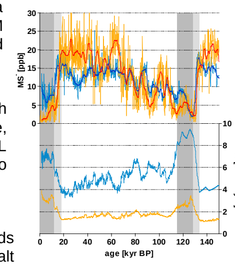
The Records



The fluxes of nss SO_4^{2-} from EDML (blue) and EDC (orange). While the flux is mostly constant at EDC, the EDML flux shows a 50% increase during the LGM and a more pronounced variability than at EDC.

The fluxes of nss Ca^{2+}. Both records show a similar course, however, the dust fluxes to EDML are up to 3 times higher than to EDC.

The fluxes of ss Na^+. Both records show a strong increase of sea salt aerosol from the Holocene to the LGM. Variability in the cold interval is rather low.



Concentrations of MS^- from EDML and EDC. The records show pronounced differences as in e.g. variability and phasing during the terminations.

Accumulation rate estimates.

MS^-

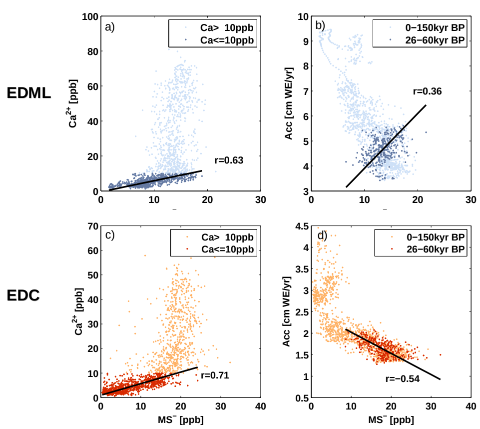


Figure 1: *Ca^{2+} and accumulation rate vs. MS^- in centennial resolution. Ca^{2+} concentrations <=10ppb are marked darker on the left plots. The interval from 26-60kyr BP (covering A0-A4) is marked darker on the right plot. The regression is valid for the dark data points and was found by reduced major axis regression, minimizing the deviation in both variables. The upper row shows the EDML data, the lower row shows the EDC data.*

MS^- from EDC is subject to strong postdepositional processes. As for other volatile species [e.g. Röthlisberger et al., 2003] the main parameter, responsible for the fixation of MS^- in firn is the amount of impurities in firn. For Ca^{2+} (the soluble dust component) concentrations below 10 ppb this can be seen clearly in both records (Figure 1a, c). If the Ca^{2+} concentration exceeds this threshold, MS^- develops independent from the amount of dust. In those periods (mostly the LGM) MS^- at EDC shows the inverse relation to accumulation as expected at sites of dominating dry deposition (Figure 1 d). At EDML, MS^- in this period seems to be conserved better if accumulation is higher (Figure 1b).

The similar threshold of the MS^- dependence on Ca^{2+} levels is also responsible for the shifted decrease of MS^- during Termination I and II (Figure 2). As dust concentrations at EDML are much higher compared to EDC, the threshold is reached later as well and thus causes the lagged decrease of MS^- concentrations at EDML during Transition I and II.

However, there is strong indication that neither at EDML nor at EDC MS^- is able to give any information about changing biological productivity in the Atlantic or Indian sector of the SO.

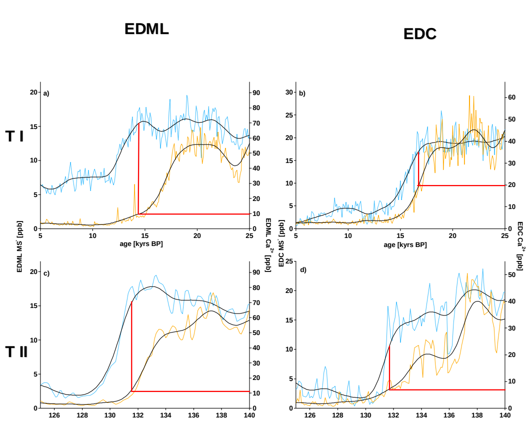
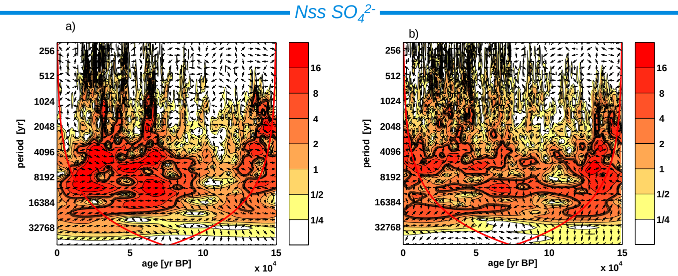


Figure 2: *MS^- (blue) and Ca^{2+} (orange) records from EDML (a) and c)) and EDC (b) and d)) over Transition I (a) and b)) and Transition II (c) and d)). The data are shown in 100 yr resolution superposed by a 20 points Gaussian low pass filter. The moments, when MS^- starts to decrease from glacial to inter-glacial concentrations are indicated by the vertical red lines. The according Ca^{2+} concentrations are marked by the horizontal red lines.*

Nss SO_4^{2-}



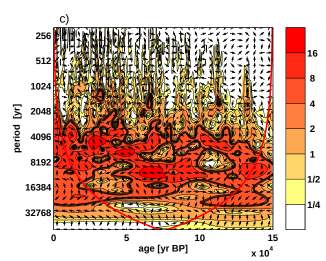


Figure 3: *Cross wavelet transform [Grinsted et al. , 2004] of J nss SO_4^{2-} and J nss Ca^{2+} (a) and J nss SO_4^{2-} and J ss Na^+ (b) fluxes and J nss SO_4^{2-} and the accumulation rate (c). The arrows indicate the phase shift between the records with no phase shift when pointing to the right. The thick black line shows the 95% significance level assuming a red noise background spectrum. The cone of influence (thick red line) shows where the cross wavelet transform is influenced by side effects.*

Nss SO_4^{2-} seems to be the more reliable proxy for biological productivity of the SO. Throughout all ages, nss SO_4^{2-} very likely was the main biogenic sulfur component [*Legrand and Pasteur*, 1998], additional sources are short-lived or of minor importance only and no significant postdepositional effects exist.

As shown by *Wolff et al.,* [2005], the constant flux observed at EDC is a strong indication for unchanged bio-productivity and transport efficiency of nss SO_4^{2-} in the Indian sector of the SO. This is not necessarily true for EDML as well. The proximity to the source of dust causing up to three times higher dust fluxes at EDML than at EDC [*Fischer et al.,* 2005] might have as well a stronger effect on bio-productivity by relaxing iron limitation.

In fact, the nss SO_4^{2-} flux measured at EDML shows a 50% higher level during the LGM and a much higher variability than observed at EDC. The increase in mean concentrations might be the consequence of errors in the accumulation estimate although this seems unlikely. However, the higher variability relatively to EDC is significant.

The assumption of an iron fertilization effect in the Atlantic sector of the SO is affirmed by the cross wavelet transform of the nss SO_4^{2-} and nss Ca^{2+} fluxes. There is a significant, in phase, phase locked variability in the millennial band can be found in both records (Figure 3a). This correlation only breaks down in warm stages, where the dust input was very low as well.

Variability in sea ice shows no effect on the millennial scale variability of the nss SO_4^{2-} flux. This can be seen in the cross wavelet transform of the nss SO_4^{2-} flux and the ss Na^+ flux (as proxy for sea ice production [*Wolff et al.*, 2003]) (Figure 3b). Although both records share variability on the same scale, it is not phase locked. Therefore, a physical cause is excluded.

The same holds for the accumulation rate (Figure 3c), significant shared variability exists, but not in a constant phase relation. Thus, the observed pattern in J nss SO_4^{2-} can be excluded to be caused by the flux calculation using the accumulation rate.

An effect of meridional transport efficiency on the flux of nss SO_4^{2-} towards EDML is unlikely, as model Studies show a mostly unchanged or even reduced meridional circulation in the LGM [*Krinner and Genthon,* 2003*; Lunt and Valdes,* 2001].

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