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# Impact of lateral transport on organic proxies in the Southern Ocean

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# Introduction

Well-dated paleoclimate records are unique tools for detecting natural climate variations beyond the instrumental period and to validate climate models that provide past climate scenarios and climate forecasts. Paleoclimate records are often derived from proxies based on sedimentary inorganic and organic matter. Proxies based on inorganic remnants include those based on foraminiferal and diatom assemblages and isotopic and trace element composition of carbonate shell. Organic proxies include the alkenone unsaturation index (e.g. Brassell et al., 1986) based on long-chain unsaturated alkenones synthesized by haptophyte algae and is one of the most thoroughly investigated and widely applied paleotemperature proxies. Recently, new organic proxies have been proposed, based on glycerol dialkyl glycerol tetraethers (GDGTs), i.e. TEX<sub>86</sub> and BIT index. The TEX<sub>86</sub> (TetraEther indeX of tetraethers consisting of 86 carbon atoms) is a paleothermometer based on isoprenoid GDGTs derived from the membrane lipids of marine Crenarchaeota (Schouten et al., 2002). The BIT (Branched and Isoprenoid Tetraether) index is a proxy for soil organic matter (OM) input based on the relative abundance of branched GDGTs derived from bacteria living in terrestrial environments (Weijers et al., 2006) versus a structurally related isoprenoid GDGT "crenarchaeol" produced mainly by marine Crenarchaeota (Hopmans et al., 2004).

The availability of multiple proxies allows the reconstruction of more than one paleoclimatic parameter from a single sediment core.

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# ABSTRACT

Lateral transport of fine-grained organic carbon particles can complicate the interpretation of paleoclimate records based on organic proxies. Here we investigated the effect of lateral transport on newly developed temperature and soil organic matter proxies, TEX<sub>86</sub> and BIT index, respectively, in core MD88–769 recovered from the South East Indian Ridge. Our results show that TEX<sub>86</sub> and BIT records in comparison to diatom and foraminifera records were representative for more local climate changes while alkenones and *n*-alkanes originated from distant areas by oceanic and atmospheric transport, respectively. This suggests that TEX<sub>86</sub> and BIT paleoclimate records are primarily influenced by local conditions and less subjected to long-distance lateral transport than other organic proxies in the Southern Ocean.

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However, it is now broadly recognized that specific proxy signals in marine sediments are not always derived only from overlying water columns but also from remote regions (e.g. Benthien and Müller, 2000; Sicre et al., 2005). In particular, fine-grained particles such as organic carbon and fine-grained inorganic carbon particles are susceptible to resuspension and lateral advection by strong surface and bottom currents, which may have older ages than cooccurring, locally derived sand-sized particles, i.e. planktonic foraminifera (e.g. Ohkouchi et al., 2002, Mollenhauer et al., 2006). Several previous studies have recognized that alkenone sea surface temperature (SST) records are affected by laterally advected allochtonous input (e.g. Sachs and Anderson, 2003; Sicre et al. 2005). Benthien and Müller (2000) also showed that core-top alkenone SSTs in the Argentine basin were affected by lateral advection of re-suspended sediments resulting in cold-biased alkenone SST estimates. This lateral transport effect on alkenone SSTs in the Argentine basin has been confirmed by more recent studies by Mollenhauer et al. (2006) and Rühlemann and Butzin (2006). However, for the GDGT-based organic proxies (i.e. TEX<sub>86</sub> and BIT index) the possibly complicating effect of lateral transport has not been broadly investigated. Recently, Mollenhauer et al. (2007, 2008) found that radiocarbon (<sup>14</sup>C) ages of the GDGT crenarchaeol are younger than those of co-occurring alkenones in continental margin sediments, suggesting that GDGTs are less prone to lateral transport than alkenones.

To evaluate the impact of lateral transport on  $\text{TEX}_{86}$  and BIT records, we investigated a core (MD88–769) from the Indian sector of the Southern Ocean over the last 50 ka. This core is located near the Subantarctic Front, a few degrees of longitude eastward of the

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Kerguelen Islands, and is hypothesized to receive material transported from the Kerguelen Islands and Kerguelen Plateau (Dézileau et al., 2000). Changes in oceanic circulation in this region on glacialinterglacial timescales have been documented (Dézileau et al., 2000). A previous study from a nearby core (MD94–103) has shown that the alkenone SST record in this region was affected by laterally advected OM (Sicre et al. 2005), suggesting that this area is well-suited to test the effect of lateral transport on GDGT-based proxies. We reconstructed sea-surface temperatures (SSTs) and soil OM input using GDGTs, foraminifera and diatom assemblages, alkenones, and *n*alkanes and compared the records to each other to evaluate the impact of lateral transport on each proxy.

# Material and methods

Core MD88–769 (46° 04'S–90° 06'E, water depth 3400 m) was retrieved during the APSARA cruise on the western flank of the South East Indian Ridge (SEIR) at the location of the modern Subantarctic

Front (Fig. 1). In this region, the eastward-flowing Antarctic Circumpolar Current (ACC) is controlled by wind stress. Antarctic Bottom Water (AABW) originates along the Adélie Land coast and in the Ross Sea, its rotation is clockwise (e.g. Rintoul et al., 2001). Stratigraphy of core MD88–769 over the last 50 ka is based on 13 AMS<sup>14</sup>C dates obtained from monospecific samples of *Globigerina bulloides* (Crosta et al., 2005).

Diatom counts followed the procedures described by Schrader and Gersonde (1978) and Laws (1983). Samples were taken every 10 cm and summer SSTs were estimated by applying the Modern Analog Technique (MAT<sub>5</sub>201/31 transfer function – 5 analogs, 201 surface sediment samples, 31 diatom species) as described by Crosta et al. (2004). Mean standard error of the MAT for summer SSTs is 1°C. Foraminifera were counted every 2 to 5 cm and summer SSTs were determined using the Modern Analog Technique (MAT<sub>5</sub>225/28 – 5 analogs, 225 surface sediment samples, 28 foraminifera species) described by Salvignac (1998). Mean standard error of the MAT for summer SSTs is 1.4°C.



Figure 1. Map of the study area showing (A) the modern position of the Polar Front Zone and core positions of MD88–769 and MD94–103 and (B) the general bathymetry of the area with circulation patterns of Antarctic Bottom Water (AABW) and the Antarctic Circumpolar Current (ACC) (modified from Dezileau et al., 2000).

For lipid analyses, sediments were sampled at 10-cm intervals. In brief, freeze-dried samples were extracted with an Accelerated Solvent Extractor (DIONEX ASE 200) using a mixture of dichloromethane (DCM):methanol (MeOH, 9:1 v/v). The extract was separated into *n*-alkane, alkenone and polar fractions over an Al<sub>2</sub>O<sub>3</sub> column using hexane:DCM (9:1 v/v), hexane:DCM (1:1 v/v), and DCM:MeOH (1:1 v/v), respectively. For *n*-alkane and alkenone analyses, the internal standard perdeutero-*n*-C<sub>24</sub> alkane was added to the purified hexane:DCM (9:1 v/v) and hexane:DCM (1:1 v/v) fractions, respectively, before gas chromatographic analysis and used as reference for quantification. For GDGT analyses, the polar fractions were filtered using a 0.4 µm PTFE filter and analyzed with a high performance liquid chromatography/atmospheric pressure positive ionization-mass spectrometer as described by Schouten et al. (2007).

The alkenone unsaturation index  $U_{37}^{K'}$  was calculated as defined by Prahl and Wakeham (1987) and converted to temperature, using the culture calibration ( $U_{37}^{K'}=0.034*T+0.039$ , Prahl et al., 1988). The TEX<sub>86</sub> ratio was calculated based on the relative abundance of isoprenoid GDGTs (Schouten et al., 2002) and converted into SSTs using the core-top calibration of Kim et al. (2008a,b) (T=-10.78+56.2\*TEX<sub>86</sub>). Values of BIT index were calculated based on the relative abundance of branched GDGTs versus crenarchaeol according to Hopmans et al. (2004).

#### Results

# Paleotemperature proxies

SSTs estimates from the various proxies agree to some extent but also differ significantly in some cases.  $TEX_{86}$  SSTs from core MD88–769 (Fig. 2B) were on average 10°C during the last glacial period (marine



**Figure 2.** Paleoproxy records derived from (A)  $\delta^{18}$ O values of *N. Pachyderma* left (% VPDB, from Dézileau et al., 2000), (B) TEX<sub>86</sub> SST (°C), (C) diatom summer SST (°C, Crosta et al., 2005), (D) foram summer SST (°C), and (E) alkenone SST (°C). Black colour indicates MD88–769 records, while red colour MD94–103 records from the study by Sicre et al. (2005). Solid triangles mark <sup>14</sup>C age control points for MD88–769. MIS indicates marine oxygen isotope stage.



**Figure 3.** Paleoproxy records of MD88–769 derived from (A) BIT index, (B) cumulated relative abundances of *Chaetoceros* resting spores and *Thalassiosira antarctica* (%), (C) terrigenous detrital content (%, Dézileau et al., 2000), (D) alkenone concentration ( $\mu$ g/g), and (E) *n*-alkane concentration ( $\Sigma$ ALK<sub>25–33</sub>,  $\mu$ g/g).

oxygen isotope stage (MIS) 3 and 2) and increased gradually to the early Holocene (MIS1) value of 19°C. This warming trend mirrors the global glacial-interglacial pattern as recorded in the  $\delta^{18}$ O of *Neoglo*boquadrina pachyderma left (Fig. 2A). Summer SSTs estimated from diatom assemblages were around 7°C during between 50 and 22 ka and then decreased to about 4°C during the last glacial maximum (Fig. 2C). Temperatures increased abruptly at 17 ka reaching the early Holocene SST value of ~10°C. Temperatures then slowly decreased over the course of the Holocene to reach the modern value of 9°C. Summer SSTs estimated from foraminifera assemblages in core MD88-769 (Fig. 2D) were about 8°C during MIS3 and then dropped to a value of 4°C at 28 ka. Significant oscillations of 2–3°C occurred during MIS2. The foraminifera SSTs increased in the course of the deglaciation, reaching the early Holocene SST values of ~10°C. Summer temperatures stayed stable over the course of the early Holocene. Alkenone SSTs in core MD88–769 (Fig. 2E) showed a warming trend during MIS3 with its highest value of 15°C at 26.6 ka. The alkenone SSTs decreased by about 7°C during the following MIS2 and subsequently increased at 15 ka by about 5°C during the deglaciation, reaching early Holocene value of ~14°C.

#### Soil OM and other proxies

BIT values (Fig. 3A) were close to 0 during the last glacial period (MIS3 and MIS2) suggesting a relatively low input of soil OM, and increased abruptly to a value of 0.12 at 16 ka. For the remaining time period, BIT values were always well above those during the last glacial period. Cumulated abundances of *Chaetoceros* resting spores and *Thalassiosira antarctica* (Fig. 3B), the two main coastal or near-coastal diatom species around Kerguelen Islands (Armand et al., 2008), terrigenous detrital content (Fig. 3C), and alkenone concentrations (Fig. 3D) were in general higher during the last glacial period and dropped abruptly at 16–17 ka towards the lowest values in the early Holocene. The two peaks in coastal diatom relative abundances

centred at ca. 40 ka and 16 ka were synchronous, though shorter-lived, to the two events of highest alkenone concentrations. A homologous series of *n*-alkanes (*n*-C<sub>25</sub> to *n*-C<sub>33</sub>) with a strong odd over even carbon number predominance, typical of terrestrial plant waxes, was detected in the sediments. The summed C<sub>25</sub> to C<sub>33</sub> *n*-alkane concentrations ( $\sum$ ALK<sub>25-33</sub>, Fig. 3E) varied between 0.07 µg/g and 3 µg/g, with higher values in MIS3 and the maximum peak around 27 ka, and lower values in the early Holocene.

# Discussion

## Impact of lateral transport on the TEX<sub>86</sub> paleothermometer

In general, summer SSTs derived from foraminifera (Salvignac, 1998) and diatom (Crosta et al., 2005) assemblages co-varied and were in the same range (i.e. 4-12°C). The early Holocene values are similar to the modern summer SSTs at the core site ( $\sim 10^{\circ}$ C) (Conkright et al., 2002). The temporal evolution of TEX<sub>86</sub> SSTs is comparable to those of foraminifera and diatom SSTs, showing the typical global glacial-interglacial warming, albeit with a ca. 10°C magnitude of change. The higher TEX<sub>86</sub> SST values compared to diatom and foraminifera estimates are likely due to the calibration problem of TEX<sub>86</sub> in polar oceans where TEX<sub>86</sub> is not linearly correlated with SSTs (Kim et al., 2008a,b). Despite this uncertainty in the TEX<sub>86</sub> calibration resulting in unreliable absolute temperature estimates, the TEX<sub>86</sub> accurately depicts the glacial-interglacial climate variation in the Southern Ocean. Remarkably, the temperature trends of these proxies differ completely from that of the alkenone SST record. Alkenones indicate much warmer SSTs between 30 and 20 ka compared to all other SST estimates considered in this study. Anomalously warm glacial alkenone SSTs were previously attributed to a strong advection of detrital alkenones produced in warmer surface waters from the Agulhas region to the SEIR (Sicre et al., 2005). Our new alkenone SST results from core MD88-769, located few degrees eastward of core MD94–103, confirm this earlier finding and are in agreement with the stronger supply of warm waters from the Agulhas region to the SEIR by a strengthened ACC during the last glacial (Dézileau et al., 2000).

The similarity between the TEX<sub>86</sub> SST record and the foraminifera and diatom SST records and dissimilarity with the alkenone SST record in the SEIR suggests that lateral transport effect on TEX<sub>86</sub> SST was likely negligible in the SEIR and that TEX<sub>86</sub> therefore likely represents the local SST variations. This finding is consistent with core-top TEX<sub>86</sub> data from the Argentine basin, recording no cold-biased SSTs in contrast to alkenone SSTs (Kim et al., 2008a,b). This is probably due to an ineffective transport mechanism of isoprenoid GDGTs compared to that of alkenones, which prevents GDGTs to be transported over long (>1000 km) distances. This idea of preferential preservation of alkenones during lateral transport is derived primarily from the relatively younger <sup>14</sup>C ages of crenarchaeol compared to those of alkenones in the same sediment layer (Mollenhauer et al., 2007, 2008).

## Impact of lateral transport on the BIT index

The BIT values close to 0 during the glacial period indicate that soil OM input to the SEIR was negligible at that period in agreement with the open marine setting and remoteness from nearby continents (Hopmans et al., 2004). Alternatively, relatively high crenarchaeol productivity during the glacial period might have resulted in such low BIT values. However, this latter interpretation cannot be tested adequately at this stage due to a lack of accumulation rate data. The BIT values abruptly increased in the course of the deglaciation, suggesting transport of soil OM from land to the core site. Although the BIT values are relatively low (0.08 to 0.16) these values are still substantially higher than those commonly observed for open marine settings (<0.02; Hopmans et al., 2004), suggesting the presence of small but significant amounts of soil OM. Clues towards the origin of

the soil OM can be derived from diatom assemblages. Coastal diatoms, Chaetoceros resting spores and T. antarctica, are more abundant around the Crozet-Kerguelen islands than in the open ocean (Armand et al., 2005). Higher occurrences of these species at our core site indicate either stronger eastward advection from the Crozet-Kerguelen islands by the ACC-Circumpolar Deep Water (CDW) sweeping the island shelves or greater northward transport from the Antarctic coast by the AABW during the last glacial period, which have widespread effects on sediment transport and accumulation in the SEIR (Dezileau et al., 2000). A previous study on terrestrial detrital contents, rareearth element (La/Tb ratio), and other trace element (Th/Sc ratio) in core MD88-769 (Dezileau et al., 2000) showed distinct sources of the terrestrial material. One terrestrial sediment source is the volcanic oceanic islands (the Crozet-Kerguelen islands), from which higher terrigenous particles were transported via the ACC-CDW during the last glacial period (Fig. 3C). Another terrestrial source is the sediment from the old Antarctic continental craton, from which particles were transported by the AABW during the early Holocene. Mapping of the focusing factor data also showed an increased lateral supply at the foot of the SEIR during the last glacial period, suggesting an increase in speed of the ACC-CDW (Dezileau et al., 2000). Additionally, higher alkenone concentration during the last glacial period supports the hypothesis of stronger ACC-CDW at that period.

In the case of elevated ACC-CDW during the last glacial period, one would expect higher BIT values compared to those found during the early Holocene, similar to the patterns of the enhanced coastal diatom abundance and detrital content from these islands. However, during the glacial period Crozet-Kerguelen islands were largely covered by glaciers and air temperatures were much lower than during the Holocene (Hall, 1984). Similar extension of glacial ice was recorded on Heard Island at 53°S (Balco, 2007) and on Marion Island at 45°S (Hall, 1979) in the Indian Ocean. Soil formation, needed for sufficient production of branched GDGTs, thus might have been hampered on the Crozet-Kerguelen islands during the last glacial period. When climate on the Crozet-Kerguelen islands ameliorated during the early Holocene, soil formation was enhanced and thus increasing amounts of branched GDGT were transported from land to our core site, causing higher BIT values. Indeed, initial soil development on the Kerguelen Islands was mainly due to high precipitation on glacier forelands where mechanical weathering, frost-heaving, and particle translocation occurred (Frenot et al., 1995). Accordingly, a climatically controlled soil production rather than a climatically-controlled oceanic circulation could thus possibly explain the observed pattern in BIT values in core MD88-769.

The predominance of C<sub>27</sub>, C<sub>29</sub>, and C<sub>31</sub> *n*-alkanes indicate that *n*alkanes in our record were derived predominantly from terrestrial sources, i.e. higher land-plant epicuticular waxes (Eglinton and Hamilton, 1967; Mazurek and Simoneit, 1984). In contrast to branched GDGTs, which are associated with fluvially transported soil OM (Hopmans et al., 2004; Kim et al., 2008a,b; Walsh et al., 2008), nalkanes in open marine settings are usually derived from longdistance eolian transport (e.g. Poynter et al., 1989; Simoneit et al., 1991). Dust transport from Argentine loesses (Patagonia) to the Indian sector of the Southern Ocean was much more intense during the last glacial period (Basile et al., 1997; Andersen et al., 1998). Given that nalkane concentrations do not follow the record of diatom abundance, detrital content and alkenone concentration patterns, the origin of *n*alkane during the last glacial period is more likely Patagonia, instead of the Agulhas region and the Crozet-Kerguelen islands. We hypothesize that *n*-alkanes were transported mainly by wind to our core site in agreement with higher dust concentrations in the Vostok (Petit et al., 1999) and EPICA Dome C ice cores (Delmonte et al., 2002) during the 30-19 ka period.

Interestingly, the timing of the highest peak of *n*-alkane concentration at 27 ka (Fig. 3E) fits the alkenone SST maximum during the last glacial period (Fig. 2E). This indicates that the wind stress and thus

the ACC-CDW was strongest around 27 ka. Despite stronger wind conditions in combination with stronger ACC-CDW during the last glacial period, BIT values were lower than those during the early Holocene. This further strengthens the idea that the BIT record primarily reflects climate-related changes in soil production on the Crozet–Kerguelen islands in the Southern Ocean.

# Conclusions

The TEX<sub>86</sub> SST estimates from the Southern Ocean show a parallel trend to diatom and foraminifera SSTs, with an expected glacialinterglacial pattern, albeit with a substantial SST offset. In contrast, alkenones record anomalously warm SSTs for the last glacial period, confirming the previous finding that detrital alkenones were transported from the Agulhas region to the SEIR during that period (Sicre et al., 2005). Diatom, terrigenous detrital content, and alkenone records also show higher allochtonous material input to the SEIR during the last glacial period, reflecting more intense lateral transport. The BIT record conversely shows a reversed glacial-interglacial pattern with lower soil OM input to the SEIR during the last glacial than during the early Holocene. This pattern may be linked to greater soil production in the Kerguelen-Crozet source area during the early Holocene. Our results show that GDGT-based records of climate change are dependent primarily on GDGT production/availability in the source area and that the impact of long-distance (>1000 km) lateral advection is relatively low.

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