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To cite this version:

Hélène Hc Castebrunet, C. Genthon, P. Martinerie. Sulfur cycle at Last Glacial Maximum: Model results versus Antarctic ice core data. Geophysical Research Letters, 2006, 33 (L22711), 1 à 5 p. 10.1029/2006GL027681 . insu-00375442

HAL Id: insu-00375442

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Submitted on 25 Mar 2021

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Sulfur cycle at Last Glacial Maximum: Model results versus Antarctic ice core data

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Received 28 July 2006; revised 13 October 2006; accepted 18 October 2006; published 30 November 2006.

[1] For the first time, an atmospheric general circulation and sulfur chemistry model is used to simulate sulfur deposition in Antarctica at the Last Glacial Maximum (LGM). Dimethylsulfide (DMS), emitted by phytoplankton, is the dominant source of atmospheric sulfur in Antarctica. Once in the atmosphere, it is oxidized into sulfur aerosols which are measured in ice cores. Such measurements allow for validating climate and chemistry models for glacial-interglacial changes. Our glacial simulations test the effect of a recent re-evaluation of glacial sea-ice coverage on DMS sources and sulfur aerosol deposition. Using the present-day oceanic concentrations of DMS, the model reproduces observed glacial and interglacial sulfur concentrations in the ice. This result suggests that climate change at the LGM did not greatly impact on DMS production in the oceanic sectors where sulfur aerosols deposited in central East Antarctica originate from. **Citation:** Castebrunet, H., C. Genthon, and P. Martinerie (2006), Sulfur cycle at Last Glacial Maximum: Model results versus Antarctic ice core data, *Geophys. Res. Lett.*, *33*, L22711, doi:10.1029/2006GL027681.

1. Introduction

[2] The Antarctic atmosphere is among the least polluted places on Earth [*Arsene et al.*, 1999]. So far, no significant impact of man-made activities on the sulfur cycle has been detected in the lower troposphere at high-southern latitudes, as illustrated by the absence of a recent trend in sulfate concentrations in Antarctic snow pits and cores [*Jourdain and Legrand*, 2001]. Deep Antarctic ice cores provide information on the atmospheric environment of the remote past, including sulfur concentrations at the Last Glacial Maximum [*Legrand et al.*, 1991; *Udisti et al.*, 2004a]. The high southern latitudes thus offer a test-field to evaluate and understand the natural component of the atmospheric sulfur cycle in relation to climate variability and change.

[3] Understanding this component implies a need to properly evaluate sulfur sources, transport and chemistry in the atmosphere, and finally deposition on the snow surface. Atmospheric General Circulation Models (AGCMs) have been used to simulate the Last Glacial Maximum (LGM) climate [*Joussaume and Taylor*, 1995] including for the Antarctic region [*Krinner and Genthon*, 1998]. Such study of an ice age helps characterize the ability of the models to reproduce and predict climate change. In turn, the AGCMs may be used to better interpret proxies of climate change such as dust, sea-salt and other impurities in ice cores [*Andersen et al.*, 1998; *Krinner and Genthon*, 2003; *Mahowald et al.*, 2006]. Here for the first time, we use an AGCM that includes a sulfur chemistry module to tentatively reproduce the observed present and LGM sulfur concentrations in Antarctic snow and ice cores.

[4] The main source of natural sulfur in the Antarctic region is dimethylsulfide (DMS) emitted by oceanic phytoplankton. DMS is oxidized in the atmosphere into non-sea-salt sulfate (nss SO4) and methanesulfonic acid (MSA) aerosols, which deposit on the ice. Thus, the model has to take into account DMS sources, atmospheric chemistry, transport and deposition. We use an updated version of the model evaluated by *Cosme et al.* [2002] for present-day climate. To run an ice age simulation, boundary conditions for both climate and chemistry are modified. However, because no ice age data are available to prescribe DMS concentrations in the ocean, the same data as for present-day climate are used for the LGM. DMS fluxes to the atmosphere are affected by changes in sea-ice coverage and atmospheric circulation though. The present study concentrates on model results from 2 different representations of sea-ice coverage at the LGM, including a recent re-evaluation of the much used CLIMAP data [*CLIMAP Project Members*, 1981]. Ice core data from different sites on the Antarctic plateau (Vostok, the first Dome C and the EPICA Dome C sites) are used to validate and analyze model results.

2. Ice Core Data

[5] Deep ice cores reaching back in time to at least the LGM have been retrieved in various places in Antarctica. On the East Antarctic plateau, the Vostok, Dome C (1978 ice core) and recent EPICA-Dome C cores provide information on glacial-interglacial changes in sulfur species. Concentrations of nss SO_4 and MSA are significantly higher at the LGM than in recent ice, with a larger increase for MSA [*Legrand et al.*, 1991; *Udisti et al.*, 2004a]. However, the rate of snow accumulation was lower at the LGM [*Petit et al.*, 1999; *Schwander et al.*, 2001]. Expressing ice core data in terms of surface deposition flux, which is the product between concentrations in ice and accumulation, allows us to correct for glacial-interglacial changes in the accumulation rate [*Udisti et al.*, 2004b]. Deposition fluxes of nss SO_4 are slightly larger in the glacial than present-day climate, but in fact essentially similar [*Wolff et al.*, 2006] in view of the measurement uncertainties (Figure 1, red circles). On the other hand, MSA deposition fluxes appear much larger, between 2.5 and 5.6 times higher during an ice age (Figure 2, red circles). A differential response of MSA and nss SO_4 to climate change may be interpreted as a differential response of atmospheric S oxidation pathways [*Legrand et al.*, 1991]. Very large glacial-interglacial contrasts in MSA

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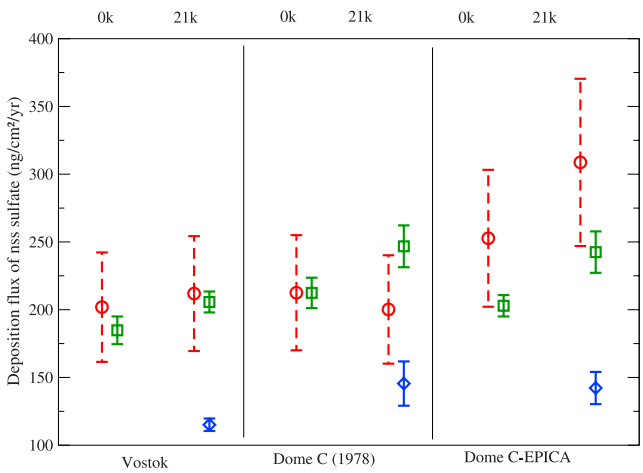

Figure 1. Observed (red circles) and simulated (green squares and blue diamonds) deposition fluxes of nss SO_4 at Vostok, Dome C (1978) and EPICA-Dome C for present day (0 k) and LGM (21 k). Measurements uncertainties (red bars, taking into account uncertainties on both concentration and snow accumulation) and interannual variabilities of the model (green and blue bars) are represented. Simulations 21 k-CLIMAP (blue diamonds) and 21 k-testCG (green squares) allow to compare the LGM *CLIMAP Project Members* [1981] sea-ice lid effect with a test of reduced summer lid, as suggested by *Crosta et al.* [1998] and *Gersonde et al.* [2005].

have been widely quoted in the past as evidence of increased marine biogenic activity in the Southern Ocean during glacial periods [*Wolff et al.*, 2006], in spite of no similar change for nss SO_4. In fact, there is increasing evidence that, under present-day conditions, MSA is not well preserved in snow and ice after deposition [*Wagnon et al.*, 1999; *Pasteur and Mulvaney*, 2000; *Weller et al.*, 2004]. In glacial periods, much more particulate material like mineral dust is present in atmosphere and snow [*Wolff et al.*, 2006]. Higher glacial concentration of MSA in snow probably reflects a better fixation of the MS- ion on this particulate material or an altered deposition mechanism, rather than an increase in DMS production or a major change in atmospheric chemistry [*Wolff et al.*, 2006]. Until processes of attachment on particles, deposition and post-deposition are better understood, MSA in ice cannot be considered as a good and reliable indicator of glacial-interglacial changes, compared to the simpler nss SO_4.

3. Model Description

[6] We use the most recent version of the LMD (Laboratoire de Météorologie Dynamique) AGCM, called LMD4-ZT [*Hourdin et al.*, 2006]. The grid here has 96 longitude $\times$72 latitude points and 19 vertical levels described with a hybrid σ-pressure coordinate. The first level is centered at around 12 m above the ground. The grid is stretched, leading to a resolution of $\sim$100 km in both latitude and longitude [*Krinner et al.*, 1997] over Antarctica. The original sulfur scheme, including emissions, chemistry and deposition, is described in detail by *Boucher et al.* [2002] and *Cosme et al.* [2002]. Oceanic concentrations of DMS are prescribed [*Kettle et al.*, 1999] and ocean to atmosphere fluxes are calculated using the parameterization of *Liss and Merlivat* [1986]. Furthermore, the calculated fluxes are weighted by the fraction of the ocean free of sea-ice, to take into account the lid-effect of sea-ice. DMS is oxidized through various chemical pathways and finally converted into end cycle species, MSA and nss SO_4 aerosols. All species are transported and undergo dry and wet deposition. Prescribed fields from a 3D atmospheric chemistry model (IMAGES [*Müller and Brasseur*, 1995]) are used for photodissociation rates of hydrogen peroxide (H_2O_2) and oxidant concentrations (hydroxyl OH, hydroperoxyl HO_2, nitrate NO_3 radicals and ozone O_3). A comprehensive evaluation and validation of the model for present-day climate in the mid- and high-southern latitudes was carried out by *Cosme et al.* [2002]. The updated version used here yields results very similar to those reported by *Cosme et al.* [2002].

[7] To simulate the ice age atmospheric circulation, we use modified boundary conditions as recommended by the Paleoclimate Modeling Intercomparison Project (PMIP) [*Joussaume and Taylor*, 1995]. Modified parameters are: the glacial topography [*Peltier*, 1994], sea surface temperatures and sea-ice coverage [*CLIMAP Project Members*, 1981], albedo and roughness derived from Crowley's vegetation [*Crowley*, 1995], ice core CO_2 concentration, and astronomical parameters. The Antarctic LGM climate is reasonably well simulated to the extent of validation data availability (e.g. reduced temperature and precipitation). It is also consistent with LGM simulations by other models (see *Krinner and Genthon* [1998] for a previous version of the LMDZ model and also see *Pollard and PMIP Participating Groups* [2000]).

[8] To our knowledge, it is the first time results of an AGCM including sulfur chemistry are reported for the LGM. Different geophysical parameters modify the sulfur cycle at the LGM compared to present-day. Possibly the least constrained one is the response of marine biology to climate change and its impact on oceanic DMS concentrations. In the absence of a marine proxy tracing past variations in DMS-emitting phytoplankton [*Wolff et al.*, 2006], the same modern sea surface DMS concentration map is used for the LGM and present-day simulations

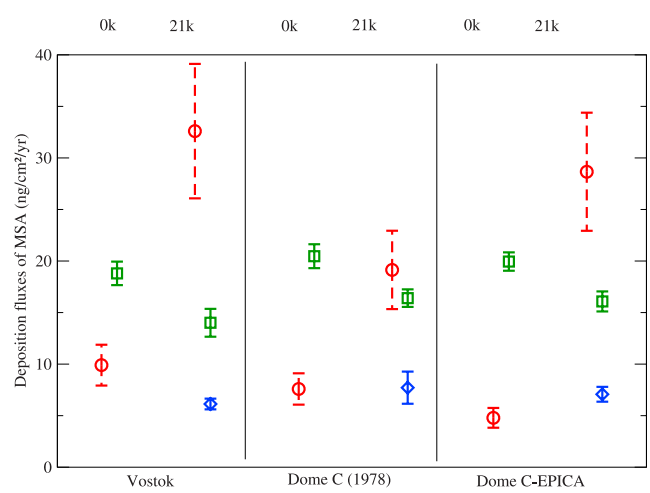

Figure 2. Same as Figure 1, for MSA.

Table 1. Ocean to Atmosphere Fluxes of DMS During Summer and Winter for the Three Simulations in Different Latitudes Bands[a]

	DMS Flux During Summer/Winter, μmol/day/m^2		
	0 k	21 k-CLIMAP	21 k-testCG
50°S–55°S	18.5/2.1	13.8/1.2	21.0/1.9
55°S–60°S	18.0/2.1	8.5/0.6	23.1/1.6
60°S–65°S	14.5/1.3	1.4/0.03	18.6/0.7
65°S–75°S	4.8/0.1	0/0	5.3/0.1

[a]Higher DMS fluxes in summer for 21 k-testCG than for 0 k simulation mainly result from higher wind speeds.

[*Kettle et al.*, 1999]. Sensitivity experiments testing the impact of a change in oceanic DMS concentrations (with spatial distributions unchanged) indicate that in spite of chemical non-linearities, the nss SO_4 deposition flux on the ice sheet is almost proportional to oceanic DMS. Therefore, to a first approximation, any mismatch between the simulated and ice-core deposition fluxes may be translated in terms of glacial-interglacial change in oceanic DMS concentration. By prescribing no change, we make the null hypothesis that climate does not affect oceanic DMS biology, at least in those regions that most directly affect sulfur deposition on the Antarctic plateau.

[9] Results from a 2D (zonally averaged) atmospheric model [*Martinerie et al.*, 1995] are used to alter the oxidants fields for the LGM. As Antarctica is broadly axially symmetric, the 2D approximation should not have a strong impact on the results. The zonal glacial-interglacial changes are thus projected as zonal-mean anomalies on the present-day 3D oxidant concentrations of our model. Sensitivity experiments have shown that the resulting glacial-interglacial changes in oxidants have a significant but not dominant impact on sulfur chemistry.

[10] Ocean to atmosphere DMS fluxes depend on surface wind and sea-ice coverage. Through its lid-effect, sea-ice exerts a very strong constraint on DMS sources. Here, the lid effects of two representations of sea-ice coverage are compared. In the widely used LGM sea-ice representation [*CLIMAP Project Members*, 1981], the surface extent of sea-ice around Antarctica is about 10 times greater during the LGM than today in summer, and about 2 times greater in winter. Reconstruction, based on more recent observations [*Crosta et al.*, 1998; *Gersonde et al.*, 2005] suggests increased sea-ice coverage during winter consistently with CLIMAP, but a summer sea-ice quite similar to present-day. The two options are tested here.

[11] Six-year simulations were performed for present (0 k) and glacial (21 k) climate. The first year is used to spin up climate and tracer concentrations, and only the mean of the last 5 years is considered in the following discussion.

4. Results and Discussion

4.1. Model Results for Present-Day Climate

[12] Model results (simulation 0 k) are compared with the Vostok, Dome C-1978 and Dome C-EPICA ice core measurements. The model reproduces present-day concentrations in ice and surface deposition fluxes of nss SO_4 at Vostok, Dome C (1978) and EPICA-Dome C (Figure 1, green squares). Note that model resolution prevents us from reproducing differences between Dome C (1978) and EPICA-Dome C, if real (they fall within experimental uncertainty limits). However, for MSA, the model greatly overestimates present-day concentrations in ice and deposition fluxes (Figure 2, green squares). Yet the modelled atmospheric concentrations of MSA in summer are underestimated at various sites in coastal Antarctica and subantarctic regions [*Cosme et al.*, 2002]. This is probably the consequence of a missing process in the DMS to DMSO to MSA oxidation: the heterogeneous oxidation of DMSO into MSA [*Jourdain and Legrand*, 2001], which competes with the homogeneous reactions taken into account in the model [*Cosme et al.*, 2002]. Because insufficient oxidation of DMSO results in missing MSA but a corresponding excess in DMSO, comparing the sum DMSO + MSA with observations allows to evaluate the branching and relative efficiency of DMS oxidation into nss SO_4 and MSA. This appears reasonably well accounted for in the model [*Cosme et al.*, 2002]. In central Antarctica, modeled summer DMSO concentrations are at least a factor of 10 lower than MSA, thus the impact of the missing heterogeneous reaction should be negligible. Whereas several aspects of the model cannot be comprehensively verified because very few atmospheric observations are available in the Antarctic interior, the fact that nss SO_4 overall, and DMSO + MSA in coastal Antarctica, are fairly well reproduced suggests that the simulated deposition of MSA may be broadly correct. Thus, the model disagreement with ice core data may at least partially confirm a poor preservation of MSA in snow and ice as discussed in section 2. Therefore, the following discussion is mainly focused on nss SO_4. As the dominant product of DMS oxidation - deposition fluxes are about 10 times higher than those of MSA - nss SO_4 should be much less affected by uncertainties in the DMS oxidation scheme.

4.2. Model Results for Ice-Age Conditions

[13] Under ice age conditions, and using the *CLIMAP Project Members* [1981] sea-ice extent to calculate ocean-atmosphere DMS fluxes (simulation 21 k-CLIMAP), the model strongly underestimates deposition fluxes of nss-SO_4 aerosols (Figure 1, blue diamonds). This is not fully unexpected as back transport studies have shown that much of the S that reaches the Antarctic plateau originates from the 50–60° S latitude band [*Cosme et al.*, 2005], and the sea-ice coverage at LGM extends way beyond these latitudes, even in summer according to CLIMAP. Indeed, DMS source regions retreat by as much as 1000 km compared to present day (Table 1). Part of the differential response of nss SO_4 and MSA to climate change appears to be related to this source effect. Table 1 shows that in the model, DMS fluxes during glacial periods are strongly reduced at high latitudes. Even if changes in atmospheric circulation and chemistry also contribute to the model results, the sea-ice related source effect has the main impact. According to this simulation, assuming the CLIMAP sea-ice coverage, DMS concentrations in Surface Ocean should have been about a factor two higher during the LGM to counteract the sea-ice lid effect.

[14] However, the CLIMAP reconstructions of LGM sea-ice extent around Antarctica date back to the early 1980s and are based on very few ocean sediment cores data [*Crosta et al.*, 1998]. Recent reconstructions [*Crosta et al.*, 1998; *Gersonde et al.*, 2005] suggest that while the

winter LGM sea-ice coverage was about 2 times larger than today, in broad agreement with CLIMAP, summer coverage was similar to today, in strong contrast with CLIMAP. To quantify the sea-ice cover/S relationship, the model was rerun (simulation 21 k-testCG) with the same LGM climate boundary conditions (thus the LGM atmospheric circulation is strictly the same as in the previous simulation), but the lid effect of sea-ice was altered so that DMS could escape in the atmosphere as if the summer sea-ice cover was the same as today. In winter, on the other hand, the full lid effect is retained. This experiment is meant to simply evaluate the impact of LGM reduced summer sea-ice coverage, as suggested by *Crosta et al.* [1998] and *Gersonde et al.* [2005]. It focuses on the consequence of the sea-ice lid effect on DMS sea-air fluxes. As expected, a very significant increase in S deposition on the plateau is obtained. This results from a strong increase in the DMS emission fluxes (Table 1) compared to 21 k-CLIMAP simulation. The model now reproduces correctly the observations of nss SO_4 at Vostok and Dome C, within measurement uncertainties and model interannual variabilities (Figure 1, green squares). Again, the model can not realistically discriminate between Dome C (1978) and EPICA-Dome C and reproduce a significant difference between the two sites. MSA deposition is also very significantly increased (Figure 2, green squares), although still between 0.4 and 0.5 short of the ice core reports, but this may be due to unresolved deposition and preservation issues with MSA (section 2).

5. Conclusion

[15] An AGCM was used for the first time to simulate the atmospheric sulfur cycle during an ice age. Of the 2 aerosol end-products of DMS oxidation recorded in ice cores, nss SO_4 is the best indicator of glacial-interglacial S changes. The model disagreement with ice core MSA data seems to confirm that deposition and post-deposition processes of MSA in snow and ice are not fully understood. The model successfully reproduces the present-day deposition flux of nss SO_4 in central Antarctica. Prescribing LGM sea-ice coverage according to PMIP recommendations [*Joussaume and Taylor*, 1995], the model cannot reproduce the observations unless the concentrations of DMS in the surface ocean are doubled compared to present. However, a recent re-evaluation of the LGM sea-ice suggests that in summer, its coverage and extension was hardly more important during LGM than today [*Crosta et al.*, 1998; *Gersonde et al.*, 2005]. In that case, the model reproduces the LGM ice core nss SO_4 (and the MSA within a factor of 2) without resorting to increasing DMS oceanic concentrations. Through its lid-effect on sea-air DMS fluxes, sea-ice thus exerts a major constrain on the atmospheric S cycle and its response to climate change. If both the model and the recent reconstructions of sea-ice coverage are correct, then the biology of DMS production in the high-southern latitude oceans shows little sensitivity to climate change, at least in the oceanic sector where nss SO_4 deposited in central East Antarctica originates from.

[16] A biological forcing of climate has been postulated [*Charlson et al.*, 1987] through the effects of temperature and sunlight on phytoplankton populations and DMS production. A feedback may result from DMS production and sea-air exchange affecting the cloud albedo through the abundance of aerosols, and thus cloud condensation nuclei. Whether such feedback thermo regulates or destabilizes climate is unknown. Ice core data have been used to tentatively demonstrate a response of oceanic DMS biology to climate [*Legrand et al.*, 1991], mainly through the MSA data, but this is called into question by the model results we report here. Besides uncertainties in the modeled atmospheric circulation and chemistry, and in the interpretation of MSA ice core data, our simulations show that the sea-ice is the key factor that determines the response of Antarctic S to glacial-interglacial changes. To proceed further and refine these results, it is important to better constrain sea-ice at the LGM with additional proxies, in particular in the Pacific sector, and to improve the transfer functions used to retrieve perennial and seasonal information [*Gersonde et al.*, 2005]. A modeling study of ocean biology at LGM could also bring additional constraint to the atmospheric S cycle, provided that adequate data are available for model validation.

[17] **Acknowledgments.** We acknowledge support from the Programme National de Chimie Atmosphérique (PNCA). We are grateful to Eric Wolff for helpful comments and discussions. We thank the reviewers for suggesting significant improvements of the manuscript.

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