



## Ice core $\delta D(CH_4)$ record precludes clathrate $CH_4$ emissions at the onset of Dansgaard-Oeschger events

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Ice core records show that  $CH_4$  concentrations changed in concert with northern hemisphere temperature during both glacial/interglacial transitions as well as rapid climate changes (Dansgaard-Oeschger events). The stadial/interstadial changes during Marine Isotope Stage 3 (MIS 3) in atmospheric  $CH_4$  concentrations are characterised by strong concentration jumps of 100 to 200 ppbv within a few decades. A concentration gradient with higher values in the northern versus the southern hemisphere during warm stages was reconstructed from ice core methane data from Greenland and Antarctica. This gradient indicates additional sources during warm periods located in the northern hemisphere. However, the underlying processes for these changes are still not well understood. With tropical and boreal wetlands, biomass burning, thermokarst lakes, ruminants, termites, living biomass and marine gas hydrates (clathrates) all contributing to the natural atmospheric  $CH_4$  level, an unambiguous source attribution remains difficult. In addition, marine methane hydrate (clathrate) destabilization events have been proposed to trigger rapid increases in atmospheric methane concentration during the last glacial cycle. Due to the distinct D/H isotopic signature of clathrate emissions,  $\delta D(CH_4)$  extracted from ice cores is well suited to constrain the impact of such catastrophic releases on the global atmospheric methane budget.

We developed a new extraction and gas chromatography-pyrolysis-mass spectrometry technique and measured  $\delta D$  of  $CH_4$  extracted from as little as 500 g ice samples of the North Greenland Ice Core Project with high precision of  $\pm 3.4\%$ . Here we present clear atmospheric  $\delta D(CH_4)$  evidence that clathrates did not provoke atmospheric methane concentration to rise at the onset of Dansgaard-Oeschger (DO) events 7 & 8 (i.e. 34 - 40 kilo years before present). A box model for the methane cycle reveals that boreal wetlands are the dominant additional source strengthening from about 5 to 40 Tg  $CH_4$   $yr^{-1}$  from stadial to interstadial conditions. Modelled clathrate emissions show no increase from stadials to interstadials ( $\sim 30 - 25$  Tg  $CH_4$   $yr^{-1}$ ). Tropical wetland emissions stay rather constant over these climate cycles ( $\sim 90$  Tg  $CH_4$   $yr^{-1}$ ), while biomass burning emissions show a slight increase in interstadials ( $\sim 60$  Tg  $CH_4$   $yr^{-1}$ ) compared to stadials ( $\sim 50$  Tg  $CH_4$   $yr^{-1}$ ). Moreover, our data show a  $\delta D(CH_4)$  drop at the onset of DO 8 that leads the major DO warming by 500 years with boreal wetlands being the most likely explanation. Our high resolution  $\delta D(CH_4)$  data reveal also two centennial scale excursions to heavier values during Interstadial 8, while northern hemisphere temperature and methane concentrations were well at interstadial levels. Their origin remains obscure; however, variations in biomass burning emissions, net to gross  $CH_4$  emissions from wetlands or clathrate contributions may explain these excursions.