



The Ice-core Record of Atmospheric Methane: Chemistry-Climate Interactions on Tens to Thousands of Years

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The concentration of methane trapped in Antarctic ice, [CH₄], shows large variations over the last 800kyr that appear to track changes in temperature (ΔT) on orbital timescales. As methane is a potent greenhouse gas and has a strong influence on the tropospheric oxidising capacity, it straddles issues of composition and climate, and explaining past changes in its budget tests our understanding of the Earth system. The most striking (natural) features include: the differences in [CH₄] between glacial and interglacial periods, for example rising from around 360 ppbv at the Last Glacial Maximum (LGM; ~ 21 kyr before present (BP)) to about 700 ppbv in the pre-industrial era (PI; ~ 200 yr BP); and the 100-200 ppbv excursions from the last glacial 'baseline' of 360-460 ppbv, towards interglacial values, during Dansgaard-Oeschger (D-O) events between 21 and 110 kyr BP. Here, we present findings from a series of model studies aimed at better understanding the changes in the methane budget between the LGM and the PI, and across a modelled D-O event.

Our main conclusion is that the rise in [CH₄] between the LGM and the PI was most likely almost entirely source-driven, with the main factors affecting the oxidising capacity—changes in air temperature and humidity, and changes in non-methane volatile organic compound (NMVOC) emissions from vegetation—being responsible for substantial, but roughly equal and opposite, changes in oxidising capacity. We also identify a previously unrecognised cause of glacial-interglacial changes in the carbon-13 content of atmospheric methane, $\delta^{13}\text{C}_{\text{CH}_4}$, that provides a complementary constraint on past changes in the methane budget: circulation-driven changes in the amount of methane oxidised by atomic chlorine in the marine boundary layer. A full, process-based explanation of the methane record will depend upon: direct observational constraints (e.g. [CH₄] and $\delta^{13}\text{C}_{\text{CH}_4}$); data syntheses leading to improved quantification of changes in CH₄ and NMVOC sources; and Earth system models with which to integrate these.