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Title: A deglacial ice core record of clumped isotopes of oxygen: implications for enhanced biomass burning and its effects on the tropospheric ozone budget

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The clumped-isotope composition of oxygen, denoted as Δ_{36}, measures the proportional abundance of two heavy oxygen isotopes, i.e., $^{18}O^{18}O$ bonds in molecular oxygen, and is sensitive to the photochemical and thermal properties of the atmosphere. Ozone photochemistry in the atmosphere controls Δ_{36} values via isotope exchange reactions, which yield a higher abundance of $^{18}O^{18}O$ than would be expected for a stochastic distribution of isotopes (i.e., a positive Δ_{36} value). Colder temperatures increase this preference for $^{18}O^{18}O$ formation at equilibrium by 0.01-0.024‰/K. If tropospheric ozone mixing ratios and stratosphere-troposphere exchange fluxes remain the same, changes in free-tropospheric temperatures would then be recorded by O_2 clumped isotopes to provide a high-resolution ice core record of high-altitude temperatures on glacial-interglacial timescales.

However, the atmosphere is dynamic and ozone concentrations in the troposphere change in response to a multitude of factors: primary among them being changes in the concentration of ozone precursors in the troposphere. In this work, we present an ice core record of Δ_{36} values measured in the West Antarctic Ice Sheet Divide ice core (WDC06A) spanning the last deglacial from 20,000 – 10,000 years before present (BP). Our data suggest that the mean Last Glacial Maximum (LGM, 18-21 ka BP) ice-core Δ_{36} value reflects a colder free troposphere and a slightly smaller tropospheric ozone burden compared to the late preindustrial Holocene. After the onset of deglaciation 18-17 ka BP, a decrease in atmospheric Δ_{36} value is observed, which unexpectedly reaches and stabilizes at preindustrial values by ~14 ka BP. The preindustrial Δ_{36} value is reached when global-mean surface air temperatures are still ~3-4°C colder than those of the late Holocene. This decoupling of the atmospheric Δ_{36} value from climate suggests that tropospheric chemistry must be exerting a strong influence on the Δ_{36} trend during this time. Our preliminary investigation indicates that this 18 – 14 ka decrease in Δ_{36} value is coeval with a global increase in biomass burning documented in sedimentary charcoal records, particularly those from the extratropics. A plausible explanation for the decrease observed in Δ_{36} values is thus an increased tropospheric ozone burden associated with a global-scale increase in ozone precursors emitted from biomass burning.