Carbonyl Sulfide Measurements in Antarctic Ice Cores: COS Loss to Hydrolysis Within the Ice Matrix and Implications for Developing Atmospheric Histories

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We measured carbonyl sulfide (COS) in ice cores from Siple Dome and Taylor Dome sites in Antarctica (Fig. 1). Siple Dome measurements are mostly from the Holocene, while the Taylor Dome record covers the last 50 ky (thousand years) before present. Previous ice core data were combined with the firn air and instrumental measurements to provide a continuous and self-consistent COS record for the last 2,000 years. The new measurements expand this existing record considerably, allowing us to explore the stability of COS in ice cores over much longer time scales. At Taylor Dome, where ice temperatures are much colder, the Holocene COS levels are higher than the contemporaneous measurements from Siple Dome, providing strong evidence for COS loss to hydrolysis within the ice core matrix over multi-millennial time scales. Ice core COS measurements cannot be directly interpreted as atmospheric mixing ratios without accounting for the *in situ* loss. We developed Lagrangian temperature histories for the ice core samples from all three sites, using 1-dimensional ice flow and thermal models. The temperature histories are used to correct the COS measurements, assuming the COS hydrolysis in ice cores is described by pseudo first order kinetics. The preliminary corrections to the Taylor Dome data suggest that COS mixing ratios were 10-30 % lower during the last glacial period than they were during the Holocene. The results do not implicate any changes to the existing 2,000-year COS record, which was based largely on measurements in a shallow South Pole ice core (Fig. 1) where mean annual surface temperature is about -51°C, and consequently the COS hydrolysis is negligibly slow. Ice cores from thick ice sheets with cold surface temperatures are ideal for COS measurements, as they may require little or no correction for *in situ* loss to hydrolysis.



Figure 1. Left panel – New ice core data from Taylor Dome (blue) and Siple Dome (red) corrected for the *in situ* loss are compared with the existing South Pole record (gray). Actual measurements from Siple Dome (open red squares) are also shown. No correction has been applied to the South Pole record. Right panel – Same data sets as in the left panel on a 50 ky time scale, except the measured values from Taylor Dome (open blue squares) are shown instead of measured values from Siple Dome. Note that the correction for Taylor Dome is relatively small for the most recent 5 ky.