Micro-droplets containing sulfate in the Dome Fuji deep ice core, Antarctica: Findings using micro-Raman spectroscopy

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Climatic signals in deep ice cores, particularly from ion concentrations, may be affected by the diffusion of liquid solution along grain boundaries of ice. Such solutions include sulfates. Because of the difficulty of detecting sulfate liquids in the ice matrix, we must infer the phase state of the sulfates from the ice temperature and inclusion properties. In this study, we use micro-Raman spectroscopy to determine the phase state of three sulfate micro-inclusions in the Dome Fuji ice core at 2798.5-m depth. Using a temperature-ramp test, we find a peak position at 984 cm<sup>-1</sup> and a change in the full width at half maximum (FWHM) of the S-O stretching mode that identifies the sulfate in the micro-droplets. Considering the peak position and FWHM of sulfate inclusions, we argue that the sulfate would have existed as a micro-droplet liquid on an air hydrate in the ice. Additionally, the increase in the low frequencies of the Raman spectrum below 30 cm<sup>-1</sup> that we detect can be generally used to identify liquids in natural ice. Our investigation also indicates that the surface of air-hydrates in ice is a preferred location for liquid micro-inclusions. The importance of this finding will be discussed.