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Potassium alum and aluminum sulfate micro-inclusions in polar ice from Dome Fuji, East Antarctica

Hiroshi Ohno [a,c,*], Yoshinori Iizuka [b], Shinichiro Horikawa [b,d], Toshimitsu Sakurai [b,e], Takeo Hondoh [b], Hideaki Motoyama [a]

[a] National Institute of Polar Research, 10-3 Midori-cho, Tachikawa, Tokyo 190-8518, Japan
[b] Institute of Low Temperature Science, Hokkaido University, N19 W8, Sapporo 060-0819, Japan
[c] Department of Civil and Environmental Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan
[d] Earthquake and Volcano Research Center, Graduate School of Environmental Studies, Nagoya University D2-2(510), Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan
[e] Institute for Laser Technology, 1-8-4 Utsubo-honmachi, Nishi-ku, Osaka 565-0871, Japan

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Abstract

Water-soluble trace constituents affect the physicochemical properties of polar ice. Their structural distribution provides important insights into the formation history of ice and inclusions. We report the first finding of $KAl(SO_4)_2 \cdot 12H_2O$ (potassium alum) and $Al_2(SO_4)_3 \cdot nH_2O$ (aluminum sulfate) micro-inclusions in the Dome Fuji ice core, East Antartica, using a micro-Raman technique. Eutectic temperatures of these water-soluble species determined using thermal analysis were −0.4 °C for potassium alum and −8.0 °C for aluminum sulfate. Although the formation process of the aluminum-bearing sulfates remains unclear, the occurrence of these salts largely depends on ice depth.

Keywords: Antarctica; Ice core; Aerosol; Potassium alum; Aluminum sulfate

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1. Introduction

Bulk concentrations of water-soluble impurities in polar ice have been relatively well documented as trace constituents of ice cores using various analytical methods, such as ion chromatography (e.g., Legrand et al., 1984). However, these measurements have generally been made on melted samples, which results in a loss of structural and positional information in relation to the water-soluble components. To overcome this limitation, we have developed a technique for analyzing inclusions in ice using micro-Raman spectroscopy (Sakurai et al., 2010a). Moreover, we have determined the microstructural distribution of water-soluble impurities in polar ice (Ohno et al., 2005, 2006; Sakurai et al., 2009, 2010b, 2011). The location and chemical state of water-soluble impurities are important for many aspects of polar ice research, including: (1) understanding the post-depositional

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* Corresponding author. Department of Civil and Environmental Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan. Tel./fax: +81 157 26 9467.
E-mail address: h_ohno@mail.kitami-it.ac.jp (H. Ohno).

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movement of chemical species (i.e., how the modification of climate signals might occur) (Rempel et al., 2001); (2) whether chemical forms might be new climate proxies (e.g., the molecular structures of paleo-aerosols) (Ohno et al., 2006; Iizuka et al., 2012a), and (3) their effect on various physical phenomena in ice sheets, including the electrical conductivity of ice (Wolff et al., 1997), ice grain growth (Durand et al., 2006), ice mechanical properties (Cuffey et al., 2000), and nucleation of air clathrate hydrates (Ohno et al., 2004, 2010).

Using Raman techniques, we have investigated Dome Fuji Antarctic ice and GRIP Greenland ice, and found that a considerable amount of water-soluble impurities exist in the form of salt micro-inclusions (Fig. 1), such as sulfates, nitrates, methanesulfonates, and carbonates (Ohno et al., 2005, 2006; Sakurai et al., 2009, 2010b, 2011). However, the chemical forms of several salt species in ice cores remain unclear. Here we identify unknown sulfates of two types that are observed in the Dome Fuji ice as being $KAl(SO_4)_2 \cdot 12H_2O$ and $Al_2(SO_4)_3 \cdot nH_2O$, and discuss their stability in the ice matrix, origins, and implications for ice core records.

2. Experimental methods

2.1. Micro-Raman spectroscopy

The Raman scattering technique is based on vibrational molecular spectroscopy, which derives from an inelastic light scattering process (Ferraro et al., 2003). Vibrational spectroscopy is an excellent method for substance identification because it provides fingerprint spectra that are unique not only to each molecule, but also to the molecule's local structure and environment (e.g., Haskin et al., 1997). Notably, vibrational spectra of sulfates exhibit various distinctive features depending on their structure and composition (e.g., Fig. 1 of Ohno et al., 2005).

Chemical forms of micro-inclusions in polar ice from Dome Fuji, East Antarctica, were investigated using a Raman spectrometer (T64000; Jobin-Yvon Ltd) with 1800 g/mm gratings (Plane Holographic Package Aberration Correction Grating; Jobin-Yvon Ltd), a CCD detector (Spectraview-2D; Jobin-Yvon Ltd), and a microanalysis system (RSM-500; Jobin-Yvon Ltd). Detailed information on the Dome Fuji ice core is available in Dome-F Deep Coring Group (1998). Experimental procedures for analyzing micro-inclusions in polar ice with the Raman system have been described elsewhere (Ohno et al., 2005; Sakurai et al., 2010a). In brief, ice specimens of approximately 10 × 10 × 3 mm in size were cut from bulk ice cores with a band saw. The upper and lower surfaces of each ice section were then planed with a microtome to prevent irregular light reflection at the surfaces. For Raman analysis, ice specimens were fixed in a cold chamber on a high-resolution (0.1 μm) x–y translation stage of a Raman microscope. Using the confocal optics of the microscope, a micro-inclusion in an ice section was targeted by white light microscopy, followed by laser light (wavelength = 514.5 nm) with power of 20 mW (GLG3280; NEC Corp.) that was focused on the target with a long working distance objective lens with a focal length of 6 mm (M Plan Apo 100×; Mitutoyo Corp.). Backscattered light from each micro-inclusion was corrected with the objective lens and sent to the spectrometer. Raman frequencies were calibrated using neon emission lines. The Raman frequency accuracy was better than $\pm 0.5\ cm^{-1}$. The sample temperature was maintained at $-30 \pm 0.5\ °C$ during measurements by regulating the flow rate of cold N_2 gas in the sample chamber. The laser spot size was approximately 1 μm in diameter. The quantum efficiency (sensitivity to light) of the detector system is

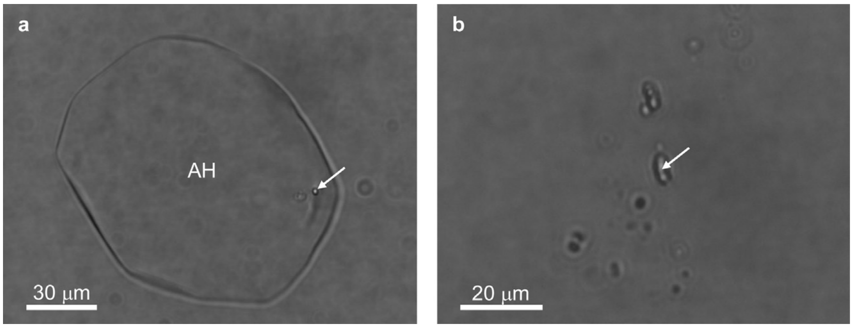

Fig. 1. Optical images of micro-inclusions in the Dome Fuji ice sections. (a) Dome Fuji ice from 1351 m. AH in the image denotes an air hydrate crystal. (b) Dome Fuji ice from 2413 m. White arrows indicate micro-inclusions analyzed by Raman spectroscopy (Fig. 2).