

Ernstburkeite, $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$, a new mineral from Antarctica

FATMA ELIF GENÇELİ GÜNER^{1*}, TOSHIMITSU SAKURAI^{2,3} and TAKEO HONDOH³

¹ Process Equipment Section, Process & Energy Department, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

*Corresponding author, e-mail: f.e.genceli@tudelft.nl, egenceli@hotmail.com

² Institute for Laser Technology, 2-6 Yamadaoka Suita, Osaka 565-0817, Japan

³ Institute of Low Temperature Science, Hokkaido University, N19W8, Sapporo 060-0819, Japan

Abstract: The new mineral (IMA 2010-059) ernstburkeite, $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$, occurs as solid inclusions, typically with a grain size up to 5 μm , in an ice core from the Dome Fuji station, East Antarctica. Due to the small crystal size most physical and optical properties cannot be established on natural material. Optically, the mineral is uniaxial (+), ω 1.402(1), ε 1.408(1) (589 nm), and nonpleochroic. Ernstburkeite is trigonal, space group $R\bar{3}$ (no. 148), $a = 9.27150(8)$ Å, $c = 21.1298(4)$ Å, $V = 1572.99(4)$ Å³, $Z = 3$. Strongest X-ray powder-diffraction lines (relative intensities in parentheses) are: 7.04(42), 6.39(39), 4.64(100), 4.41(44), 3.87(89), 3.75(31), 3.74(35). The chemistry of the mineral in the ice core was confirmed by Raman microspectroscopy. The name is for Ernst A.J. Burke, Belgian-born mineralogist at the Vrije Universiteit Amsterdam, Netherlands (1966–2005), chairman of the IMA Working Group on Inclusions in Minerals (1994–1998) and chairman of the IMA Commission on New Minerals, Nomenclature and Classification (2003–2008).

Key-words: Ernstburkeite, new mineral, $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$, magnesium methanesulfonate, Raman microspectrometry, crystal structure, Antarctica.

1. Introduction

Ernstburkeite occurs as small solid inclusions in an ice core from the Dome Fuji station, East Antarctica (77°19' S, 39°42' E), near the summit of the eastern Dronning Maud Land plateau. Deep ice-core drilling at Dome Fuji was started in August 1995, and a depth of 2503 m was reached in December 1996 (Dome-F Deep Coring Group, 1998). The mineral inclusions of ernstburkeite are mostly embedded within Last Glacial Maximum (LGM) ice at a depth of 576.5 m (ice age: approximately 25 kyr B.P., Watanabe *et al.*, 2003a).

The mineral data and name were approved by the IMA Commission on New Minerals, Nomenclature and Classification in February 2011 (IMA 2010-059). The name is for Ernst A.J. Burke, born in Belgium in 1943, in honor of his contributions to the mineralogy of opaque minerals and Raman spectrometry of fluid inclusions. Ernst Burke has worked at the Vrije Universiteit Amsterdam, Netherlands (1966–2005) and has served as chairman of the IMA Working Group on Inclusions in Minerals (1994–1998) and as chairman of the IMA Commission on New Minerals, Nomenclature and Classification (2003–2008).

Some characteristic data of the mineral have previously been mentioned by Williams *et al.* (2011).

Since ernstburkeite occurs as very tiny solid inclusions embedded in ice, it is impossible to remove it from its host

media. Due to the temperature requirements of ice, holotype material is deposited in a cold room (−50 °C) at the Institute of Low Temperature Science at Hokkaido University, Sapporo, Japan, catalogue number 81,616.

2. Occurrence, associated minerals, and origin

Micrometer-sized (maximum size 5 μm , Fig. 1) ernstburkeite grains are found to be hosted in LGM ice in an Antarctic ice core with gypsum and ice as associated minerals. In LGM ice, methanesulfonate salts form by fixation of $\text{CH}_3\text{SO}_3\text{H}$ on alkaline particles of marine or continental origin during long-range aerosol transport to polar areas (Delmas *et al.*, 2003). During this period, high levels of dust neutralized the acids, greatly reducing their abundance (Röthlisberger *et al.*, 2003; Iizuka *et al.*, 2008). This neutralization of the LGM ice permits the existence of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$. Sakurai *et al.* (2010a) elaborately discussed that $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ might have been formed in the atmosphere and transported as an aerosol. The salt was then deposited on the ice sheet, where it had a chance to survive and be preserved in LGM ice because the acids were neutralized.

In this formation mechanism scenario, dimethyl sulfide (DMS) is emitted by plankton from the open sea to the atmosphere (Saltelli & Hjorth, 1995), and $\text{CH}_3\text{SO}_3\text{H}$ is formed by oxidation of DMS. But also geological processes

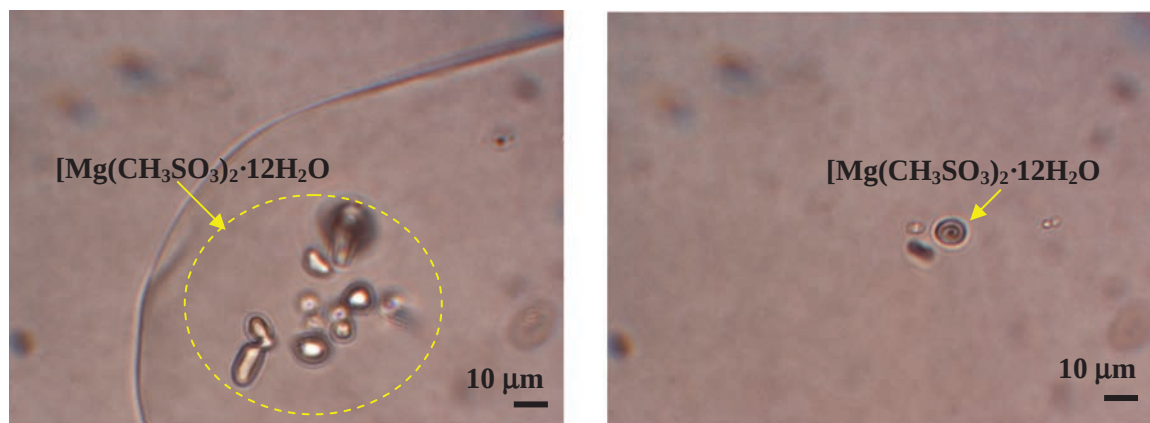


Fig. 1. Optical microscopy of a methanesulfonate salt particle (arrow) found in the ice sample at a depth of 576.5 m (age: 24 kyr B.P.).

are involved in the genesis of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$. By the oxidation of DMS and of CH_3SO_3^- , non-sea-salt-sulfate (nssSO_4^{2-}) is also formed (most of the SO_4^{2-} in the ice core comes from nssSO_4^{2-} and only a little from sea salt). This oxidation occurs outside of sea-water which means that both CH_3SO_3^- and nssSO_4^{2-} are not entirely produced by biological processes (Cosme *et al.*, 2005). Therefore, ernstburkeite must be considered as a mineral, following the criteria in the paragraph on biogene substances in the definition of a mineral (Nickel, 1995).

Eutectic temperatures of the methanesulfonate salts were reported (Genceli *et al.*, 2010; Sakurai *et al.*, 2010a) as follows: $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ (-5.0 ± 0.5 °C), $\text{K}(\text{CH}_3\text{SO}_3) \cdot \text{nH}_2\text{O}$ (-17.8 ± 0.1 °C), $\text{Na}(\text{CH}_3\text{SO}_3) \cdot \text{nH}_2\text{O}$ (-29.3 ± 0.2 °C) and $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot \text{nH}_2\text{O}$ (-32.6 ± 0.2 °C). In the first Dome Fuji ice core project, the average temperature at 10 m depth from the surface was -58 °C, and at 2503 m depth from the surface ~ -10 °C (Hondoh *et al.*, 2002). Therefore, at the sampling location of 576.5 m depth, the average ice temperature lies between these temperatures. Since the $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ eutectic temperature is much higher than that of other methanesulfonate salts, the likelihood of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ salt presence and its thermodynamic stability at the sampling location are higher. This phenomenon was confirmed by Sakurai *et al.* (2010a) who did not find any methanesulfonate salts (out of the 758 microparticles that were analyzed) except $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ in LGM ice from Dome Fuji although in previous studies Na^+ was reported to be the most abundant ion while Mg^{2+} and CH_3SO_3^- are minor ions (Watanabe *et al.*, 2003b). The discrepancy is explained by the surface temperature and the acidity of the ice at the time it was formed (Sakurai *et al.*, 2010a).

3. Physical and optical properties of synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$

Ernstburkeite is found only as solid inclusions of a few μm hosted in ice. This creates a number of unavoidable problems since direct measurement techniques cannot be

applied. The mineral being readily water soluble, it is impossible to dissolve the ice to isolate the inclusions. Besides, sublimation of ice under vacuum can also not be an option due to the strong dehydration behavior of the ernstburkeite salt. Since methanesulfonate never reaches a sufficient concentration in sea-water, atmosphere or ice, it is extremely improbable that ernstburkeite will ever be found as hand specimens.

Therefore, most physical and optical properties of ernstburkeite were collected on synthetic material (Genceli *et al.*, 2010). Crystals of ernstburkeite are colorless, have a white streak and waxy luster, and are non-fluorescent. Mohs hardness is estimated to be lower than 2. Cleavage was not observed, fracture is conchoidal, parting good and tenacity sectile. The density could not be measured due to its small grain size. The density calculated from the single-crystal unit cell and empirical formula is 1.364 g cm^{-3} . Optically, the mineral is uniaxial (+), ω 1.402(1), ϵ 1.408(1) (589 nm), and nonpleochroic.

4. Chemical composition

Like the collection of physical and optical properties, it is very difficult to determine directly the chemical composition of daughter mineral phases of ernstburkeite. Extracting these phases or sublimation of the hosting ice under vacuum is virtually impossible. Due to the easy dehydration behavior of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ towards lower hydration levels, application of SEM-EDS analysis caused deformation on the synthetic crystals when vacuum was applied, even at -160 °C. The chemical analysis of the Antarctic ice from the LGM period in the Dome Fuji core was obtained in bulk by dissolving it at room temperature and detecting its composition via ion chromatography (Ohno *et al.*, 2005; Sakurai *et al.*, 2011). Measurement errors of ion chromatography were better than $\pm 0.01 \mu\text{mol/l}$ (Table 1).

In the same study, Raman-spectroscopy frequencies of each salt were presented for the LGM ice (Ohno *et al.*, 2005). In this ice, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sulfate salt with the split

Table 1. Micro-inclusion survey and soluble concentrations in Antarctic ice of the LGM Period in the Dome Fuji core.

N_i (g^{-1})	D_i (μm)	V_i	Constituent ($\mu\text{mol/l}$)						
			Cl^-	MSA^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	Ca^{2+}
$4.3 (\pm 0.4) \times 10^5$	1.4–2.3	$0.6\text{--}2.6 \times 10^{-6}$	5.36	0.19	1.62	2.48 (1.15–5.29)	5.29	0.89	1.55 (1.15–5.29)

N_i : the number concentration (value in parentheses shows the value mean $\pm$ standard error).

D_i : average diameter of micro-inclusions (estimated minimum and maximum values).

V_i : the ratio of total inclusion volume (estimated from N_i and D_i with consideration of their uncertainties) to total ice volume measured with an optical microscope, respectively.

main peak, a compound salt containing SO_4^{2-} and NO_3^- , and methanesulfonate salt signals were detected. Therefore the high Ca^{2+} composition detected by ion chromatography measurements can be explained by the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ salt (gypsum) which is stable at this temperature, having a eutectic temperature of -0.05°C (Kargel, 1991).

The presence of Mg^{2+} and MSA^- in the ion chromatography results supports the detected occurrence of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ in the Antarctic ice.

5. Raman spectroscopy

Raman spectroscopy is the only possible quantitative, indirect method for identifying ernstburkeite by comparing the spectra of the synthetic material to the natural inclusions hosted in Antarctic ice. Since this technique has been successfully applied to the identification of daughter-mineral phases in several fluid and solid inclusions, e.g., ramanite-(Cs) and ramanite-(Rb) (Thomas *et al.*, 2008), and meridianite (Genceli *et al.*, 2009), Raman spectroscopy was also employed for the current characterization. The details of the Raman spectroscopy measurements and the cryostat were given by Sakurai *et al.* (2010b).

To identify the chemistry of the microscopic daughter crystals in the ice core, Raman spectra of the microparticles

(Fig. 1) were compared with the reference spectra of synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ salt crystallized under eutectic conditions. The observed main frequencies (in cm^{-1}) of synthetic magnesium methanesulfonate [$\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$] and ernstburkeite are presented in Fig. 2 and band assignments are listed in Table 2.

To eliminate possible doubts, synthetic methanesulfonate salts of elements detected by ion chromatography (Table 1), ($\text{Na}(\text{CH}_3\text{SO}_3) \cdot \text{nH}_2\text{O}$, $\text{K}(\text{CH}_3\text{SO}_3) \cdot \text{nH}_2\text{O}$ and $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot \text{nH}_2\text{O}$), which may co-exist in the Antarctic ice under eutectic conditions, were also measured by Raman spectroscopy (Sakurai *et al.*, 2010a). With the exception of $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot \text{nH}_2\text{O}$ salt, the Raman spectra of the simple salts are significantly different from those of the Mg salt corresponding with ernstburkeite. The differences are especially evident in the S-O symmetric stretching band (1054 cm^{-1}), CH_3 rocking mode (973 cm^{-1}), C-S stretching (777 cm^{-1}) and SO_3 deformation frequencies (545 cm^{-1}). Besides, Na and K methanesulfonate salts have more splitting peaks around 3000, 2900 and 500 cm^{-1} whereas ernstburkeite and Ca methanesulfonate salts have a single sharp peak. Although the Raman spectra of $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot \text{nH}_2\text{O}$ and ernstburkeite salts are much alike at first sight, the two salts were distinguished through their symmetric and anti-symmetric CH_3 stretching frequencies: 2938.9 cm^{-1} and 3020.9 cm^{-1} for $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$, and 2941.6 cm^{-1} and 3022.6 cm^{-1} for $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot \text{nH}_2\text{O}$. Gaussian fitting

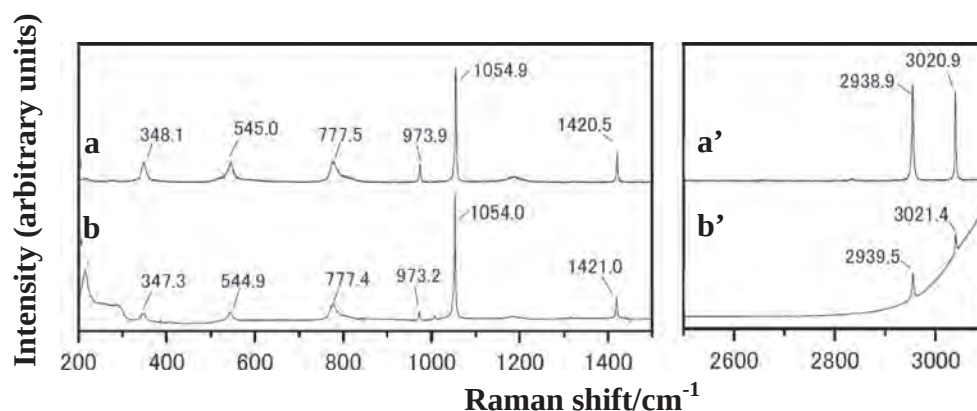


Fig. 2. Raman spectra from 200 to 1500 cm^{-1} (primes: $2500\text{--}3100\text{ cm}^{-1}$) of (a) synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$. (b) ernstburkeite from the Dome Fuji ice core.

Table 2. Observed main frequencies (in cm^{-1}) of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ and ernstburkeite.

Synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$	Ernstburkeite in inclusions	Assignment
3020.9	3021.4	Y_6 (C-H) symmetric stretching band
2938.9	2939.5	Y_1 (C-H) symmetric stretching band
1420.5	1421	Y_7 vibration (CH_3 deformation)
1054.9	1054	Y_4 (S-O) symmetric stretching band
973.9	973.2	Methyl rocking mode (CH_3 rock)
777.5	777.4	Y_3 (C-S) stretch mode
545	544.9	Y_5 (SO_3 deformation)
348.1	347.3	Sulfonate rocking (SO_3 rock) mode

Band assignments are done according to Barletta *et al.* (2009), Socrates (2001), Thompson *et al.* (1972) and Genceli *et al.* (2010).

was used to estimate the positions and half-band widths of the peaks. The corresponding peaks in Raman spectra obtained from methanesulfonate salt particles in the ice core are located at 2938.9 cm^{-1} and 3020.9 cm^{-1} . The half-band widths of the peaks are $3.9 \pm 0.1 \text{ cm}^{-1}$ and $2.9 \pm 0.9 \text{ cm}^{-1}$, respectively. The peak locations and half-band widths of the $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ reference salt are 2941.6 cm^{-1} , 3023.1 cm^{-1} and $15.8 \pm 0.2 \text{ cm}^{-1}$, $23.7 \pm 3.4 \text{ cm}^{-1}$, respectively. This evidence strongly supports the discovery that the methanesulfonate salt present in the ice core is $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ (ernstburkeite) and *not* $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ (Sakurai *et al.*, 2010a).

For synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ crystals (Genceli *et al.*, 2010), due to the water involvement in the hydrogen bonding, the stretching modes of crystal water in the lattice are manifested as a complex band in the $3000\text{--}3600 \text{ cm}^{-1}$ region with two dominant bands at 3425 cm^{-1} and 3352 cm^{-1} with potential shoulder at 3250 cm^{-1} . In the Raman spectra of natural sample presented in Fig. 2b, a tail of a broad signal (covers also the weak bond appears at 3072 cm^{-1} in the work of Genceli *et al.*, 2010) appeared beyond 3000 cm^{-1} as the effect of the ice surrounding. Therefore, the water band region beyond 3100 cm^{-1} is excluded from Fig. 2a and b. Note that the weak bond recorded at 1120 cm^{-1} in the work of Genceli *et al.* corresponds to SO_3 stretch mode, it was detected neither in synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ nor in natural samples presented in Fig. 2a and b. In natural ernstburkeite inclusions (Fig. 2b) there is a strong ice-stretching band at 216.1 cm^{-1} (Narayanaswamy, 1948) which is not present in synthetic material (Fig. 2a) as expected.

The weak Raman peak seen in the natural sample just above 1000 cm^{-1} was neither detected in the synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ crystals (Genceli *et al.*, 2010) nor in Fig. 2a.

The ideal formula of the mineral is $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$, which requires: Mg 5.64, C 5.58, S 14.89, H 7.03, O 66.86, Total 100.00 wt.%.

6. X-ray diffraction

Single-crystal X-ray studies could not be carried out on the inclusions due to their small crystal size. Therefore parameters were refined from synthetic material. X-ray

powder-diffraction data (synthetic material, refined from single-crystal X-ray structure, in Å for $\text{CuK}\alpha_1$), obtained using the Powdercell program (ftp), are given in Table 3. As presented in the work of Genceli *et al.* (2010) single-crystal X-ray diffraction data of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ crystals were collected on a Nonius Kappa CCD

Table 3. Calculated X-ray powder-diffraction^a data of ernstburkeite.

2 Theta (°)	d (Å)]	Rel. Int. (%)	hkl
0.56	7.04	42	003
13.84	6.39	39	10–2
19.13	4.64	100	110
20.11	4.41	44	104
22.95	3.87	89	113
22.95	3.87	69	11–3
23.69	3.75	31	202
23.77	3.74	35	10–5
27.89	3.20	3	20–4
29.72	3.00	31	12–1
30.63	2.92	17	21–2
31.64	2.83	8	107
31.89	2.80	2	11–6
33.45	2.68	5	300
34.04	2.63	10	214
35.86	2.50	5	30–3
35.86	2.50	11	303
36.42	2.47	11	21–5
37.24	2.41	14	20–7
38.31	2.35	23	009
38.82	2.32	13	220
40.71	2.21	6	31–1
42.19	2.14	9	217
44.10	2.05	6	31–4
44.10	2.05	5	134
46.03	1.97	4	315
46.03	1.97	5	13–5
46.89	1.94	6	22–6
46.89	1.94	6	226
52.16	1.75	7	140
52.75	1.73	11	12–10
53.88	1.70	7	14–3
53.88	1.70	5	143
60.34	1.53	6	31–10
61.37	1.51	4	33–3
70.29	1.34	6	600
73.61	1.29	5	250

^a $\text{CuK}\alpha$ radiation, Debye-Waller factor $B = 0$.

diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073 \text{ \AA}$) up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.81 \text{ \AA}^{-1}$ at a temperature of 110(2) K. Integration of the intensities was performed with Eval15 program (Xian *et al.*, 2006). The SADABS (Sheldrick, 1999) program was used for absorption correction and scaling. The crystal structure was solved with Direct Methods using the program SHELXS-97 (Sheldrick, 2008) and refined with SHELXL-97 (Sheldrick, 2008) against F^2 of all reflections. Geometry calculations and checking for higher symmetry was performed with the PLATON program (Spek, 2003).

The magnesium center is located on a crystallographic $\bar{3}$ center (Wyckoff position *a*) and surrounded by six symmetry-related water molecules forming an octahedral coordination geometry similar to the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ motif as found in magnesium sulfate undecahydrate ($[\text{Mg}(\text{H}_2\text{O})_6](\text{SO}_4) \cdot 5\text{H}_2\text{O}$ structure (Genceli *et al.*, 2007). The methanesulfonate ion is not directly coordinated to the magnesium, but acceptor of hydrogen bonds from the coordinated water molecules. The sulfur and carbon atoms are located on a crystallographic threefold axis (Wyckoff position *c*). As the multiplicity of this site is twice the multiplicity of the magnesium site, the stoichiometry is 2:1. The methyl group fulfils the threefold symmetry and is not disordered. The additional uncoordinated water molecule, present in the crystal structure, is located on a general position (Wyckoff position *f*) with a multiplicity six times higher than the magnesium site. The individual residues in the crystal structure of $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ are linked by hydrogen bonds in the crystal packing. The geometries of these bonds are presented elsewhere (Genceli *et al.*, 2010).

The unit-cell of ernstburkeite is trigonal, space group $R\bar{3}$ (no. 148), cell parameters refined from the single-crystal X-ray study are, $a = 9.27150(8) \text{ \AA}$, $c = 21.1298(4) \text{ \AA}$, $V = 1572.99(4) \text{ \AA}^3$, and $Z = 3$. $R = 0.0187$ for reflections with $I > 2\sigma(I)$ (Genceli *et al.*, 2010).

7. Discussion

Since ernstburkeite only occurs as micrometer-sized grains, most of the data necessary for the approval as a mineral, such as physical and optical properties, and X-ray data, could not be carried out on natural material. Although these sample constraints, which are typical of any daughter phase or solid inclusion, limit the ability to obtain these data, in particular unit-cell data, the Raman spectrum of ernstburkeite excellently matches with that of synthetic $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ salt. This shows that the mineral corresponds, at molecular and atomic levels, to this synthetic compound. Macroscopic identification characteristics cannot be provided, but would seem superfluous for a mineral that is highly unlikely ever to occur in hand-specimen size. If, however, it would nevertheless be found as such, it can and will unambiguously be identified with its Raman spectra.

Acknowledgments: The authors acknowledge the supports from STW-NWO (VENI Grant 10680) and Grants-in-Aid for Creative Scientific Research (grant No.

14GS0202) provided by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the Japan Society for the Promotion of Science (JSPS). We thank Dr. Olaf Medenbach (Bochum, Germany) for the optical measurements of the crystals and Prof. Dr. Gerda van Rosmalen for her scientific input.

References

- Barletta, R.E., Gros, B.N., Herring, M.P. (2009): Analysis of marine biogenic sulfur compounds using Raman spectroscopy: dimethyl sulfide and methane sulfonic acid. *J. Raman Spectrosc.*, **40**, 972–981.
- Cosme, E., Hourdin, F., Genthon, C., Martinerie, P. (2005): Origin of dimethylsulfide, non-sea-salt sulfate, and methanesulfonic acid in eastern Antarctica. *J. Geophys. Res.*, **110**, D03302. doi:10.1029/2004JD004881.
- Delmas, R.J., Wagnon, P., Goto-Azuma, K., Kamiyama, K., Watanabe, O. (2003): Evidence for the loss of snow-deposited MSA to the interstitial gaseous phase in central Antarctic firn. *Tellus*, **55B**, 71–79.
- Dome-F Deep Coring Group. (1998): Deep ice-core drilling at Dome Fuji and glaciological studies in east Dronning Maud Land, Antarctica. *Ann. Glaciol.*, **27**, 333–337. ftp://ftp.bam.de/Powder_Cell/
- Genceli, F.E., Lutz, M., Spek, A.L., Witkamp, G.J. (2007): Crystallization and characterization of a new magnesium sulfate hydrate $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$. *Crys. Growth Des.*, **7**, 2460–2466.
- Genceli, F.E., Horikawa, S., Iluzuka, Y., Sakurai, T., Hondoh, T., Kawamura, T., Witkamp, G.J. (2009): Meridianite detected in ice. *J. Glaciol.*, **55**, 189, 117–122.
- Genceli, F.E., Lutz, M., Sakurai, T., Spek, A.L., Hondoh, T. (2010): Crystallization and characterization of magnesium methanesulfonate hydrate $\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$. *Crys. Growth Des.*, **10**, 4327–4333.
- Hondoh, T., Shoji, H., Watanabe, O., Salamatin, A.N., Lipenkov, V.Ya. (2002): Depth-age and temperature prediction at Dome Fuji station, East Antarctica. *Ann. Glaciol.*, **35**, 384–390.
- Iizuka, Y., Horikawa, S., Sakurai, T., Johnsen, S., Dahl-Jensen, D., Steffensen, J.P., Hondoh, T. (2008): A relationship between ion balance and the chemical compounds of salt inclusions found in the Greenland Ice Core Project and Dome Fuji ice cores. *J. Geophys. Res.*, **113**, D07303. doi: 10.1029/2007JD009018.
- Kargel, J.S. (1991): Brine volcanism and the interior structures of asteroids and icy satellites. *Icarus*, **94**, 368–390.
- Narayanaswamy, P.K. (1948): The Raman spectra of water, heavy water and ice. *Proc. Math. Sci.*, **27**, 4, 311–315.
- Nickel, E.H. (1995): The definition of a mineral. *Can. Mineral.*, **33**, 689–690.
- Ohno, H., Igarashi, M., Hondoh, T. (2005): Salt inclusions in polar ice core: location and chemical form of water-soluble impurities. *Earth Planet. Sci. Lett.*, **232**, 171–178.
- Röthlisberger, R., Mulvaney, R., Wolff, E.W., Hutterli, M.A., Bigler, M., de Angelis, M., Hansson, M.E., Steffensen, J.P., Udisti, R. (2003): Limited dechlorination of sea-salt aerosols during the last glacial period: evidence from the European Project for Ice Coring in Antarctica (EPICA) Dome C ice core. *J. Geophys. Res.*, **108**, D16, 4526. doi:10.1029/2003JD003604.
- Sakurai, T., Ohno, H., Genceli, F.E., Horikawa, S., Iluzuka, Y., Uchida, T., Hondoh, T. (2010a): Magnesium methanesulfonate

- salt found in the Dome Fuji (Antarctica) ice core. *J. Glaciol.*, **56**, 199, 837–842.
- Sakurai, T., Ohno, H., Horikawa, S., Iizuka, Y., Uchida, T., Hondoh, T. (2010b): A technique for measuring microparticles in polar ice using micro-Raman spectroscopy. *Int. J. Spectros.*, **2010**, 1–7. doi:10.1155/2010/384956.
- Sakurai, T., Ohno, H., Horikawa, S., Iizuka, Y., Uchida, T., Hirakawa, K., Hondoh, T. (2011): The chemical forms of water-soluble microparticles preserved in the Antarctic ice sheet during Termination I. *J. Glaciol.*, **57**, 206, 1027–1032.
- Saltelli, A. & Hjorth, J. (1995): Uncertainty and sensitivity analyses of OH-initiated dimethylsulfide (DMS) oxidation kinetics. *J. Atmos. Chem.*, **21**, 187–221.
- Sheldrick, G.M. (1999): SADABS: area-detector absorption correction, v2.10. Universität Göttingen, Germany.
- Sheldrick, G.M. (2008): A short history of SHELX. *Acta Crystallogr.*, **A 64**, 112–122.
- Socrates, G. (2001): Infrared and Raman characteristic group frequencies: tables and charts, 3rd Edition. John Wiley & Sons Ltd., Chichester. Table 22.1.
- Spek, A.L. (2003): Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.*, **36**, 7–13.
- Thomas, R., Davidson, P., Hahn, A. (2008): Ramanite-(Cs) and ramanite-(Rb): new cesium and rubidium pentaborate tetrahydrate minerals identified with Raman spectroscopy. *Am. Mineral.*, **93**, 1034–1042.
- Thompson, W.K. (1972): The vibrational spectra of caesium and sodium methanesulphonates. *Spectrochim. Acta.*, **28A**, 1479–1484.
- Watanabe, O., Jouzel, J., Johnsen, S., Parrenin, F., Shoji, H., Yoshida, N. (2003a): Homogeneous climate variability across East Antarctica over the past three glacial cycles. *Nature*, **422**, 509–512.
- Watanabe, O., Kamiyama, K., Motoyama, H., Fujii, Y., Igarashi, M., Furukawa, T., Saito, T., Yoshida, N., Uemura, R. (2003b): General tendencies of stable isotopes and major chemical constituents of the Dome Fuji deep ice core. *Mem. Natl. Inst. Polar Res. Spec. Issue.*, **57**, 1–24.
- Williams, P.A., Hatert, F., Pasero, M., Mills, S.J. (2011): IMA-CNMNC Newsletter 8. *Mineral. Mag.*, **75**, 292.
- Xian, X., Schreurs, A.M.M., Kroon-Batenburg, L.M.J. (2006): Eval15: accurate data integration by profile prediction. *Acta Crystallogr.*, **A62**, s92.

Received 14 May 2012

Modified version received 7 August 2012

Accepted 28 August 2012