Supplementary materials for Short Note

**Sulphur and oxygen isotope signatures of the dissolved sulphate in freshwater from King George Island, Antarctic Peninsula**

Yeongmin Kim1, Insung Lee2, Bernhard Mayer3, Guebuem Kim2, Jong Ik Lee4, Hyoungbum Kim5,\*

1. Research Center for Geochronology and Isotope Analysis, Korea Basic Science Institute, Cheongju 28119, South Korea

2. School of Earth and Environmental Sciences, Seoul National University, Seoul 08826, South Korea

3. Department of Geosciences, University of Calgary, Alberta T2N 1N4, Canada

4. Division of Polar Earth-system Sciences, Korea Polar Research Institute, Incheon 21990, South Korea

5. Department of Earth Science Education, Chungbuk National University, Cheongju 28644, South Korea

\*Corresponding authors: Hyoungbum Kim ([hyoungbum21@chungbuk.ac.kr](mailto:hyoungbum21@chungbuk.ac.kr))

**GEOLOGICAL BACKGROUND**

As shown in Fig. S1, the Barton Peninsula located in the southwestern part of the King George Island is mainly composed of variable volcanic rocks from basalt to andesite, mafic to felsic dike and intrusive rocks, and pyroclastic deposits (Smellie et al., 1984; Yoo et al., 2001; Lee et al., 2002; Yeo et al., 2004). Sejong Formation, the lowermost stratigraphic unit, is a volcaniclastic components with about ~100 m thickness and occurs along the southern coast of the Barton Peninsula, which is overlaid by mafic to intermediate volcanic lavas from basalt to andesite (Yoo et al, 2001; Lee et al., 2002). These widespread volcanic lavas usually contain plagioclase and plagioclase-clinopyroxen phenocrysts with modal contents from 10 to 20% (Lee et al., 2002; Yeo et al., 2004). They are intruded by the calc-alkaline intrusive rocks of granodiorite and diorite at the northern part of the Barton Peninsula (Smellie et al., 1984) where intrusion age was supposed to be during the Eocene (Kim et al., 2000). Several lapilli tuff units are interbedded with volcanic lavas (Fig. S1)

Hydrothermal alterations are pervasively observed in the boundary volcanic lavas and east side of the granodiorite at the northcentral part of the Barton Peninsula, which was related to the granodiorite intrusion (Hwang and Lee, 1998; Hur et al., 2001; Hwang et al., 2011). Various secondary minerals including hornblende, actinolite, epidote, chlorite, hematite, ilmenite and pyrite are observed in the altered volcanic lavas (Hwang et al., 2011). Clay minerals associated with thermal metamorphism such as illite and kaolinite occur with quartz and pyrite in the altered basaltic andesite (Hwang and Lee, 1998; Hur et al., 2001; Hwang et al., 2011).

**SAMPLING AND ANALYTICAL METHODS**

A total of 5 freshwater samples were collected from creeks and small ponds at King George Island for sulphur and oxygen isotope analysis in the dissolved sulphate and ion analysis. 4 samples were from Barton Peninsula whereas the other sample were collected from the Weaver Peninsula (Fig. S1). Several studies suggested that the biological activities by seabirds and animals like seals and penguin could potentially affect the sulphur budget of freshwater system (Xie et al., 2002; Chen et al., 2020; Shen et al., 2021). There were no clear occurrences of habitats of or evidence of biological activities from seabirds and animals near the sampling sites. The sampling sites are described in Table S1. More than 50 L of freshwater was sampled from each site and moved to King Sejong Station.

To pre-concentrate the dissolved sulphate from freshwater samples, anion exchange resin (Amberlite IRA 400) columns (Hong and Kim, 2005) was used at the laboratory in King Sejong Station. Water samples were passed through a 0.45 μm membrane filter and subsequently the anion exchange column at a slow flow rate of less than 4 L per hour. The sulphate filled in the column were eluted using NaCl-rich solution in the laboratory at Seoul National University. After adjusting the pH to 3-4 by concentrated HCl, then 10 % BaCl2 solution was added to the eluted solution for BaSO4 precipitation. The precipitated BaSO4 was filtered through a 0.45 μm membrane filter, washed with Milli-Q water and dried at room temperature. Small volume (< 1 L) of water sample was separately bottled in HDPE without column procedure.

Concentration of major cations including Na+, Mg2+, Ca2+ and K+ in the water samples were measured by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4300DV) at the National Center for Inter-University Research Facilities, and major anions such as Cl-, SO42- and NO3- were determined using an ion Chromatography (IC) system (DIonex/ICS-3000) at the National Instrumentation Center for Environmental Management in Seoul National University.

The BaSO4 powders were converted to sulphur dioxide (SO2) in an Elemental Analyzer (EA) for sulphur isotope analysis and CO in a pyrolysis reactor (Finnigan TC/EA) for oxygen isotope analysis at the Isotope Science Laboratory (ISL) in the University of Calgary. The resultant gases were carried with a He gas to a Mass Spectrometer (Finnigan MAT delta plus XL) in continuous-flow (CF) mode to determine the sulphur and oxygen isotope ratios, respectively. The sulphur and oxygen isotope compositions of sulphate were represented using the δ-notation relative to the Vienna Canyon Diablo Troilite (V-CDT) for sulphur and the Vienna Standard Mean Ocean Water (V-SMOW) using the following equations:

δ34S = 1000 × ((34S/32S)sample – (34S/32S)reference)) / (34S/32S)reference

δ18O = 1000 × ((18O/16O)sample – (18O/16O)reference)/(18O/16O)reference

An average analytical precision (standard deviation on replicate analyses) of the international reference materials (NBS127, IAEA SO5 and IAEA SO6) was 0.3 ‰ for δ34S and 0.5 ‰ for δ18O, respectively.

**RESULTS**

The concentrations of major cations in freshwater samples range from 5.4 to 22.7 mg/L for Na+, from 0.1 to 0.7 mg/L for K+, from 0.1 to 2.0 mg/L for Mg2+ and from 0.6 to 5.7 mg/L for Ca2+ (Table S2). The median concentrations (mg/L) of them show the following order: Na+ (16.3) > Ca2+ (1.9) > Mg2+ (0.8) > K+ (0.7). The median value and range of Cl- and SO42- concentrations are 39.3 mg/L (from 8.8 to 42.1 mg/L) and 10.6 mg/L (from 2.0 to 10.6 mg/L), respectively (Table S2). The concentrations of NO3- were measured to be below the detection limit (1 mg/L).

The sulphur and oxygen isotope values of the dissolved sulphate (δ34Ssulphate and δ18Osulphate) in water at the Barton Peninsula range from 2.6 to 16.3 ‰ with a median value of 14.3 ‰ and from -1.1 to 6.4 ‰ with a median value of 5.0 ‰, respectively (Table S2). The contribution of sea salt sulphate to total sulphate using the measured Na+ and SO42- concentrations could not be estimated because the additional input of Na+ might lead to the overestimation of sea salt sulphate in the study area.

**Additional References**

Chen, Y., Shen, L., Huang, T., Chu, Z., & Xie, Z. (2020). Transformation of sulfur species in lake sediments at Ardley Island and Fildes Peninsula, King George Island, Antarctic Peninsula. *Science of The Total Environment*, *703*, 135591.

Hong, Y. L., and Kim, G., 2005, Measurement of cosmogenic 35S activity in rainwater and lake water. Analytical chemistry, 77, 3390–3393.

Hur, S. D., Lee, J. I., Hwang, J., and Choe, M. Y., 2001, K-Ar age and geochemistry of hydrothermal alteration in the Barton Peninsula, King George Island, Antarctica. Ocean and Polar Research, 23, 11–21.

Hwang, J., and Lee, J. I., 1998, Hydrothermal alteration and mineralization in the granodioritic stock of the Barton Peninsula, King George Island, Antarctica. Economic and Environmental Geology, 31, 171–183.

Kim, H., Lee, J. I., Chose, M. Y., Cho, M., Zheng, X., Sang, H., and Qiu, J., 2000, Geochronologic evidence for early cretaceous volcanic activity on Barton Peninsula, King George Island, Antarctica. Polar Research, 19, 251–260.

Lee, J.I., Hur, S.D., Yoo, C.M., Yeo, J.P., Kim, H., Hwang, J., Choe, M.Y., Nam, S.H., Kim, Y., Park, B.-K., Zheng, X. and Lopez-Martinez, J., 2002, Geological Map of Barton and Weaver Peninsulas, King George Island, Antarctica. Korea Ocean Research and Development Institute, Ansan, 30 p.

Shen, L., Huang, T., Chen, Y., Chu, Z., & Xie, Z. (2021). Diverse Biotransformation of Sulfur in Antarctic Lake Sediments.

Smellie, J. L., Pankhurst, R., Thomson, M. R. A., and Davies, R. E. S., 1984, The geology of the South Shetland Islands: VI. Stratigraphy, geochemistry and evolution. British Antarctic Survey, Cambridge, 87 p.

Xie, Z. Q., Sun, L. G., Wang, J. J., & Liu, B. Z. (2002). A potential source of atmospheric sulfur from penguin colony emissions. *Journal of Geophysical Research: Atmospheres*, *107*(D22), ACH-5.

Yeo, J. P., Lee, J. I., Hur, S., and Choi, B. G., 2004, Geochemistry of volcanic rocks in Barton and Weaver peninsulas, King George Island, Antarctica: implications for arc maturity and correlation with fossilized volcanic centers. Geosciences Journal, 8, 11–25.

Yoo, C. M., Choe, M. Y., Jo, H. R., Kim, Y. D., and Kim, K. H., 2001, Volcaniclastic sedimentation of the Sejong Formation (Late Paleocene-Eocene), Barton Peninsula, King George Island, Antarctica. Ocean and Polar Research, 23, 97–107.

**Table S1.** Description of water sampling sites at King George Island

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | Longitude | Latitude | Lithology | Remark | |
| BMSJW-1 | S62o13'19.6" | W58o46'37.2" | basaltic andesite | Small pond below Seolakbong | |
| BMSJW-2 | S62o13'22.4" | W58o45'58.1" | basaltic andesite | Small pond below Seolakbong |
| BMSJW-3 | S62o14'07.9" | W58o46'01.10" | volcaniclastic sediment | Small pond far from coast and Penguin Village |
| BMSJW-4 | S62o13'38.3" | W58o46'38.6" | andesitic lava | Creek below Kwanakbong and water coming from nearby glacier | |
| BMSJW-5 | S62o12'24.9" | W58o47'24.9" | andesitic lava | Small pond in Weaver Peninsula | |

**Table S2.** The isotopic composition of the dissolved sulphate and major ion concentration of freshwater samples from King George Island. The ‘nd’ indicates not determined

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | δ34Ssulphate (‰) | δ18Osulphate (‰) | Cl- (mg/L) | SO42- (mg/L) | NO3- (mg/L) | Na+ (mg/L) | K+ (mg/L) | Mg2+ (mg/L) | Ca2+ (mg/L) |
| BMSJW-1 | 13.7 | 6.1 | 8.8 | 2.0 | nd | 5.4 | 0.2 | 0.1 | 0.6 |
| BMSJW-2 | 16.3 | 5.0 | 42.1 | 6.9 | nd | 22.7 | 0.7 | 0.8 | 1.9 |
| BMSJW-3 | 2.6 | -1.1 | 20.5 | 5.7 | nd | 11.1 | 0.8 | 1.7 | 2.8 |
| BMSJW-4 | 16.3 | 6.4 | 28.5 | 4.5 | nd | 16.3 | 0.1 | 2.0 | 1.1 |
| BMSJW-5 | 14.3 | 1.9 | 15.4 | 3.1 | nd | 10.3 | 1.1 | 1.7 | 6.0 |

**Figure caption**

**Fig. S1.** Geological map of Barton Peninsula (modified from Lee et al., 2002) and sampling locations.