

Geochemical characteristics of meltwater and pondwater on Barton and Weaver Peninsulas of King George Island, West Antarctica

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In Antarctica, the geochemical properties of meltwater and pondwater are very sensitive to global warming. Therefore, understanding the geochemical properties of the meltwater and pondwater is crucial to evaluating global climate change. This study was performed to examine the chemical and isotopic compositions of the meltwater and pondwater at the Barton and Weaver Peninsulas of King George Island, Antarctica, to understand their spatial variation and to evaluate factors controlling the surface water chemistry. The meltwater, pondwater and seawater were sampled at 50 sites of the Barton and Weaver Peninsulas during the period from 23 December 2010 to 5 January 2011. The chemical compositions of the meltwater and pondwater were mainly influenced by sea salt. Additionally, the influence of water-rock interaction was observed in some meltwater and pondwater. The LREE/HREE ratios of some of the pondwater in the Barton Peninsula showed a decreasing trend by influence of water-rock interaction. The influences of sea salt and water-rock interaction were more dominant at the Barton Peninsula than the Weaver Peninsula. The $\delta^{18}\text{O}$ and δD of the meltwater and pondwater showed a wide range. Little evaporation losses were observed at the Barton Peninsula but evaporation losses did not occur at the Weaver Peninsula.

Keywords: chemical compositions of meltwater and pondwater, sea salt, water-rock interaction, King George Island, Antarctica

INTRODUCTION

The Antarctic environment is highly sensitive to global warming because of the extreme cold (Knap *et al.*, 1996). Most climate change models predicted that the climate of Antarctica will become warmer and wetter (IPCC, 2001; SCAR, 2009). Recently, ice-free regions in summer have been rapidly expanding in Antarctica due to global warming (Vaughan *et al.*, 2001). Additionally, the collapse of ice shelves and retreat of glacier have occasionally been observed (Vaughan and Doake, 1996; Park *et al.*, 1998). Thus, the monitoring of these environmental changes is important because it is one of the methods used to evaluate global climate change. For this reason, research on monitoring environmental changes has been actively conducted in Antarctica (Knap *et al.*, 1996; King and Turner, 1997; Quayle *et al.*, 2002; Kejna *et al.*, 2013).

The meltwater (MW) and pondwater (PW) in Antarctica are mainly distributed in periglacial environments, where environmental changes due to global warming can be relatively easily observed compared with in other en-

vironments. It has been found that the chemical compositions of MW and PW are mainly controlled by precipitation, sea salt and weathering and are not significantly influenced by anthropogenic factors (Brown, 2002; Borghini and Bargagli, 2004; Hodson *et al.*, 2010; Stumpf *et al.*, 2012). However, the contamination due to heavy metals and organic matters has been reported in some regions, mainly around scientific stations after International Geophysical Year (1957~1958) (Santos *et al.*, 2005; Cai *et al.*, 2012).

The influence of sea salt on MW and PW is significant in the coastal regions of Antarctica because of strong winds (Wagenbach *et al.*, 1998; Kerminen *et al.*, 2000). The concentrations of Na^+ , Cl^- and SO_4^{2-} in MW and PW in the coastal regions were found to be higher than those in inland (Kerminen *et al.*, 2000; Aristarain and Delmas, 2002). Additionally, the Cl^-/Na^+ ratios of snow, streams (MW) and lakes (PW) at the inland stations were found to be lower than those in coastal regions (Wagenbach *et al.*, 1998; Kerminen *et al.*, 2000). Therefore, the concentrations of Na^+ , Cl^- and SO_4^{2-} and Cl^-/Na^+ ratios are used in many areas including Antarctica to evaluate influence of sea salt.

The chemical weathering in Antarctica has been actively discussed to this day. It is generally known that little chemical weathering has occurred in Antarctica (Lee

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et al., 2004; Santos *et al.*, 2007). Chemical weathering was mainly observed in periglacial environments (Levy *et al.*, 2011). The ionic concentrations, including dissolved silica, gradually increase along flow path of stream water. Therefore, these trends have been used with evidence of chemical weathering (Stumpf *et al.*, 2012). In addition, the dissolution of carbonate minerals and the oxidation of sulfide minerals were observed near hydrothermally altered regions of West Antarctica (Jeong, 2003). Nevertheless, the sources of dissolved components in MW and PW are unclear because the fractionation of components in minerals or whole rocks, such as Ca^{2+} , Mg^{2+} , Na^+ and rare earth elements (REE), are induced during water-rock interaction (Webster *et al.*, 1994; Ji *et al.*, 2004).

This study was performed at the Barton and Weaver Peninsulas of King George Island (KGI), West Antarctica. The response to environmental change around KGI has been rapid because the island is located in the marginal area of West Antarctica and the access to KGI is easier than other regions. Therefore, numerous studies in various fields such as environmental change, the petrogenesis of volcanic rocks, soil formation, sedimentation in coastal environments, the isotopic compositions of seawater and dry deposition have been conducted (Khim *et al.*, 1997; Park *et al.*, 1998; Lee *et al.*, 2004; Yeo *et al.*, 2004; Santos *et al.*, 2007; Leal *et al.*, 2008). However, there has been little work on the geochemical properties of MW and PW at the Barton and Weaver Peninsulas. The chemical and isotopic compositions of MW and PW can demonstrate hydrogeological processes such as water-rock interaction, dilution and evaporation. Therefore, this study was executed to examine the chemical and isotopic compositions of MW and PW, to understand their spatial variations and to evaluate factors controlling the water chemistry. The results of this study may further understanding of the hydrogeological processes in the Antarctic environment, and the results can be used as basic data to assess environmental changes in Antarctica.

STUDY AREA

Natural environments

KGI is located in the South Shetland Islands, West Antarctica (Fig. 1). Its surface area is approximately 1,310 km². The fjord morphology of areas such as the Admiralty and Maxwell bays and the Marian Cove has been developed by glaciers (Chang *et al.*, 2003; Santos *et al.*, 2007). The approximately 92% of KGI is covered with glaciers, which have a maximum thickness of 395 m (Leal *et al.*, 2008). However, retreat of glacier rapidly occurs because of climate change (Park *et al.*, 1998). The mean annual temperature shows the increasing trend of 0.02°C/

year during the past several decades, (Kejna *et al.*, 2013). This trend was significantly observed in winter, 0.04°C/year compared with summer (Ferron *et al.*, 2004). The annual precipitation is approximately 500 mm, and slightly decreased by 48.7 mm in 1996 compared with the average of the annual precipitation occurred during the period from 1978 to 1989 (Kejna and Láska, 1999). Then, the snow cover depth ranges 2~73 cm (Kejna and Láska, 1999), and snow mainly melts in summer (November to March) (Wen *et al.*, 1998).

The Barton and Weaver Peninsulas are located in the southwestern areas of KGI. The southwestern coastal areas of the Barton and Weaver Peninsulas in summer season from December to February are ice-free. MW and PW are densely distributed in coastal areas compared with those in inland areas (Fig. 1). At the Barton Peninsula, it is known that the active layer depth was approximately 1 m and that permafrost is present below the active layer (Jeong and Yoon, 2001; Lee *et al.*, 2004). According to climatic data collected at the King Sejong Station in the Barton Peninsula from 1988 to 1996, the Barton Peninsula is warm, wet and windy, with an average annual temperature, relative humidity, precipitation and wind velocity of -1.8°C, 89%, 438 mm and 7.9 m/s, respectively, with winds predominantly from the NW and SW (Lee *et al.*, 1997).

General geology

The Barton and Weaver Peninsulas consist mainly of lavas, pyroclastics and Paleocene to Eocene hypabyssal and plutonic rocks. The lowermost Sejong Formation is distributed along the southern and southwestern coastal area of the Barton Peninsula and is widespread in the central part of the Weaver Peninsula. The Sejong Formation consists of mostly volcanoclastic sediments. Additionally, plant fossils have been observed in the fine-grained sandstone of the Sejong Formation (Yeo *et al.*, 2004). Most volcanic rocks over the Sejong Formation are widely distributed in the Barton Peninsula. Ancient volcanic centers remain with nunataks (Barton, 1965). The volcanic rocks consist of several units ranging from basalt to andesite. Lapilli tuffs are inserted in the volcanic rocks (Yeo *et al.*, 2004). Granodiorite is exposed in the southwestern region of Noel Hill. Hydrothermal alteration is observed at the boundary between the volcanic rock and the granodiorite in the central part of the Barton Peninsula (Lee *et al.*, 2004; Hwang *et al.*, 2011). The altered volcanic rocks contain various secondary minerals, such as hornblende, actinolite, epidote, chlorite, calcite, hematite, ilmenite and pyrite. The pyrite of these minerals has also been observed in fresh volcanic rocks (Hwang *et al.*, 2011). Additionally, various metamorphic minerals, such as quartz, pyrite, illite and kaolinite, have been observed in hydrothermally altered rocks (Jeong, 2003). Pyrite is

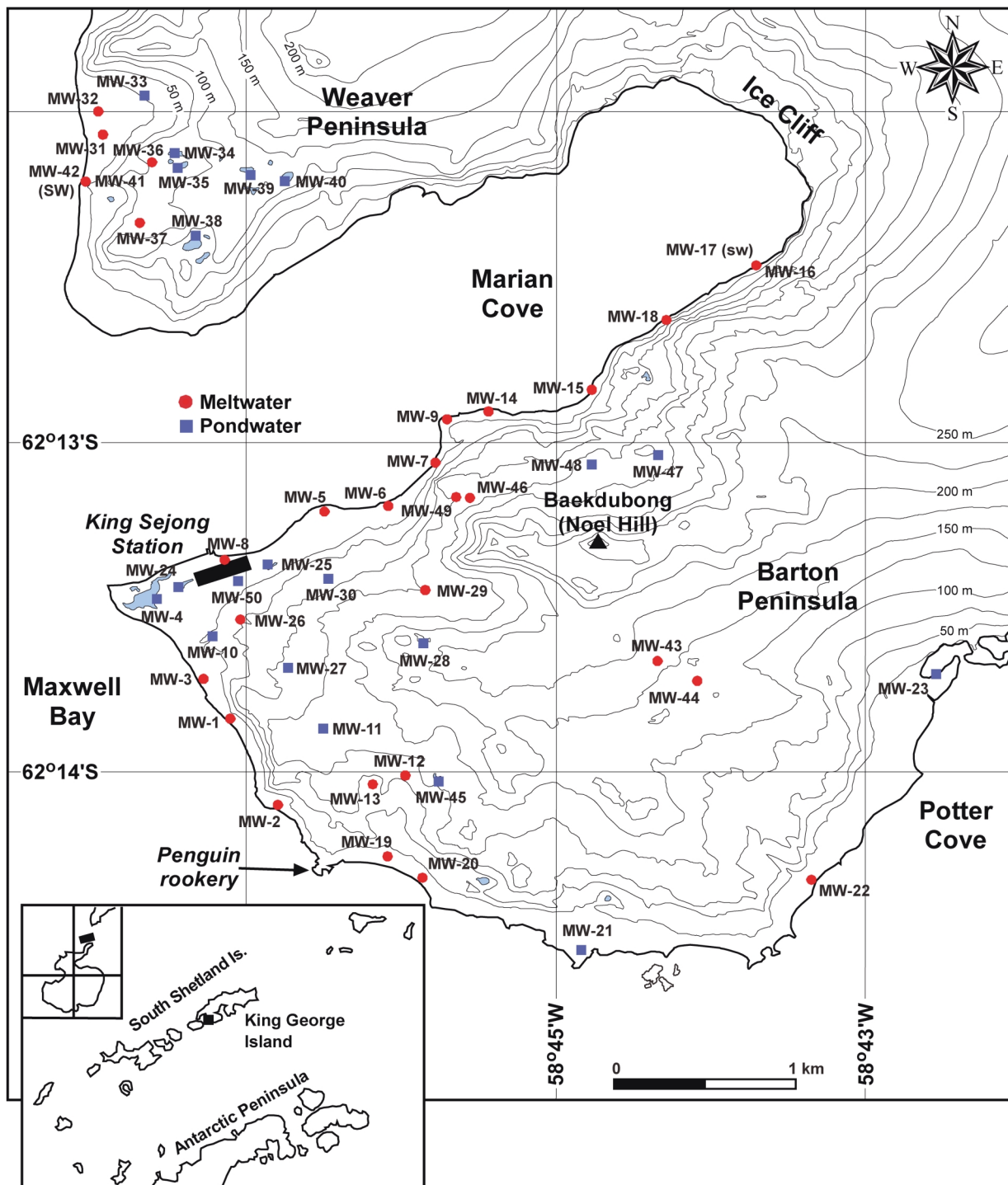


Fig. 1. Location of the Barton and Weaver Peninsulas of the King George Island, Antarctica and sampling sites of the meltwater and pondwater.

especially abundant, and most are highly altered (Jeong, 2003).

METHOD

MW, PW and seawater were sampled from 23 December 2010 to 5 January 2011 at the Barton (38 ea) and Weaver (12 ea) Peninsulas. The collected samples were filtered with a 0.45 μm micropore membrane filter, and part of each filtered sample was acidified with HNO_3 (to approximately $\text{pH} = 2$). All samples were refrigerated for later analysis. The water temperature, pH and electric conductivity (EC) of the samples were measured on site. The dissolved carbon species were calculated from the alkalinity, which was measured according to the Gran method (Wetzel and Likens, 1991), which assumes that dissolved carbon species mainly contribute to the alkalinity. Major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (Cl^- , NO_3^- and SO_4^{2-}) were analyzed using ICP-AES and IC, respectively, at the Sangji University. Rare earth elements (REEs) were analyzed at the Seoul Center of the Korea Basic Science Institute (KBSI). The data quality was evaluated using charge balance. In this study, data showing a charge balance below 30% were used. Oxygen and hydrogen isotopic compositions of samples were analyzed using IRMS at the Ochang Center of KBSI. The analyzed data were reported by δ notation relative to the Vienna Standard Mean Ocean Water (VSMOW). The analytical reproducibility of the $\delta^{18}\text{O}$ and δD was ± 0.1 and $\pm 1\%$, respectively.

RESULTS AND DISCUSSION

Chemical properties

Table 1 shows the water temperature, pH and EC of MW and PW at the Barton and Weaver Peninsulas. The ambient air temperature was well reflected by the water temperature of the MW and PW. The water temperature of the PW was typically higher than that of the MW. At the Barton Peninsula, the pH and EC of the MW ranged 4.38~8.80 and 32.6~390 $\mu\text{S}/\text{cm}$, respectively, and those of the PW ranged 5.00~7.47 and 33.2~27,900 $\mu\text{S}/\text{cm}$, respectively. The variation of the pH and EC in the MW were significantly distinguished from those of the PW. However, the EC of the PW had a range of 33.2~432 $\mu\text{S}/\text{cm}$ in most samples (except MW-4 and MW-23), which is slightly high compared with the MW. The EC was especially high at MW-4 (8,730 $\mu\text{S}/\text{cm}$) and MW-23 (27,900 $\mu\text{S}/\text{cm}$). At the Weaver Peninsula, the pH and EC of the MW showed ranges of 5.11~5.78 and 42.1~98.4 $\mu\text{S}/\text{cm}$, respectively, and those of the PW had ranges of 4.98~5.79 and 69.1~196 $\mu\text{S}/\text{cm}$, respectively. In total, the variation ranges of the pH and EC at the Weaver Peninsula were narrow compared with those of the Barton Peninsula. The

pH of the MW was not distinguished from that of the PW. The EC of the MW was relatively low compared with that of the PW.

The chemical compositions of the MW and PW at the Barton and Weaver Peninsulas are also summarized in Table 1. The values of the standard deviation for each ion showed very wide ranges of 0~1,057. These results are attributed to the vertical and spatial inhomogeneity of snow and glaciers (Maupetit and Delmas, 1992; Fortner *et al.*, 2009). The concentrations of most ions of the PW at the Barton Peninsula were higher than those at the MW, as was especially clear in the Mg^{2+} , Na^+ , K^+ and Cl^- . The average concentrations of Mg^{2+} , Na^+ , K^+ and Cl^- in the PW were higher by approximately 77, 62, 25 and 30 times, respectively, compared with those in the MW. These ions may mainly come from sea salt. The concentrations of Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} in the snow sampled at coastal regions of Antarctica were higher than those inland (Aristarain and Delmas, 2002). Additionally, the average concentrations of Ca^{2+} , SO_4^{2-} , HCO_3^- and H_4SiO_4 in the PW were higher by approximately 3.4, 9.8, 1.4 and 1.5 times, respectively, than those in the MW. These ions are associated with water-rock interaction between carbonate, sulfide and silicate minerals and surface water (Caulkett and Ellis-Evans, 1997; Borghini and Bargagli, 2004; Grasby *et al.*, 2010; Stumpf *et al.*, 2012). Therefore, the influence of sea salt and chemical weathering may be more dominant in the PW than in the MW.

At the Weaver Peninsula, the chemical compositions of the MW and PW did not show difference as large as at the Barton Peninsula. While the average concentrations of Mg^{2+} , Na^+ and Cl^- in the PW increased by approximately 3.4, 2.1 and 1.5 times, respectively, compared with those in the MW, those of Ca^{2+} , SO_4^{2-} and HCO_3^- in the MW increased by approximately 1.1, 1.3 and 1.2 times, respectively, compared with those of the PW. In addition, the average concentration of H_4SiO_4 of the PW was 0.57, but that of the MW did not detected. These results indicate that the influences of sea salt and chemical weathering at the Weaver Peninsula were small compared with those at the Barton Peninsula because of the high altitude and steep slope at the Weaver Peninsula.

The chemical compositions of all samples were plotted on a piper diagram (Fig. 2). The MW was not distinguished from the PW at the Barton and Weaver Peninsulas, respectively. However, the contributions of SO_4^{2-} of the MW and PW at the Barton Peninsula were higher than those at the Weaver Peninsula. These results may be attributed to the influence of alteration of sulfide minerals at the geothermal alterations area of the Barton Peninsula. Most samples were plotted on the area of the Ca-Cl type. MW-4 and MW-23 showing high EC levels were plotted near the seawater. The typical fresh water generally shows Na- HCO_3 or Ca- HCO_3 types in the volcanic

Table 1. Chemical compositions of meltwater and pondwater in the Barton and Weaver Peninsulas of King George Island, Antarctica

Type	pH	T	EC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	H ₄ SiO ₄	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Barton Peninsula												
Meltwater (n = 23)												
Minimum	4.83	0.2	32.6	2.95	0.03	0.81	0.11	0.53	0.49	3.55	2.38	0.61
Maximum	8.80	8.3	390	9.52	1.38	9.71	0.91	9.07	30.2	3.55	43.8	9.15
Mean	6.36	2.3	129	5.67	0.39	3.59	0.50	2.08	13.4	3.55	11.5	3.89
Standard deviation	0.97	1.7	87.0	1.56	0.34	2.13	0.33	0.74	7.00	0	10.4	2.19
Pondwater (n = 14)												
Minimum	5.00	0.2	33.2	3.65	0.14	1.31	0.11	0.45	3.21	—	2.03	0.61
Maximum	7.47	9.2	27,900	99.5	226	2,210	58.3	8.24	3,901	—	816	22.6
Mean	6.00	3.8	2,738	19.3	30.4	222	12.2	3.22	405	—	113	5.30
Standard deviation	0.66	2.6	7,320	27.9	68.3	598	21.2	0.72	1,057	—	223	5.51
Seawater (n = 1)												
	8.12	2.5	42,200	212	642	6,743	179	1.92	13,672	0.61	1,935	54.8
Weaver Peninsula												
Meltwater (n = 5)												
Minimum	5.11	2.0	42.1	4.52	0.08	0.45	—	—	6.42	1.10	3.14	7.32
Maximum	5.78	3.8	98.4	5.53	0.09	3.33	—	—	12.8	1.10	5.70	11.0
Mean	5.43	2.6	69.2	5.04	0.08	1.50	—	—	8.56	1.10	4.50	8.91
Standard deviation	0.23	0.7	19.6	0.32	0.01	1.02	—	—	2.38	0	1.01	1.20
Pondwater (n = 6)												
Minimum	4.98	1.2	69.1	2.65	0.08	1.89	0.32	0.37	1.80	—	2.29	5.49
Maximum	5.79	8.3	196	6.69	0.71	5.85	0.35	0.75	24.9	—	4.04	9.15
Mean	5.35	4.1	122	4.79	0.28	3.14	0.33	0.57	13.1	—	3.36	7.32
Standard deviation	0.29	2.4	51.4	1.18	0.22	1.44	0.02	0.06	8.02	—	0.67	1.22
Seawater (n = 1)												
	5.70	3.4	43,800	281	712	6,997	226	2.37	18,950	—	2,164	67.1

Unit of water temperature and EC is °C and µS/cm, respectively.
Unit of concentrations of the major ions are mg/L.

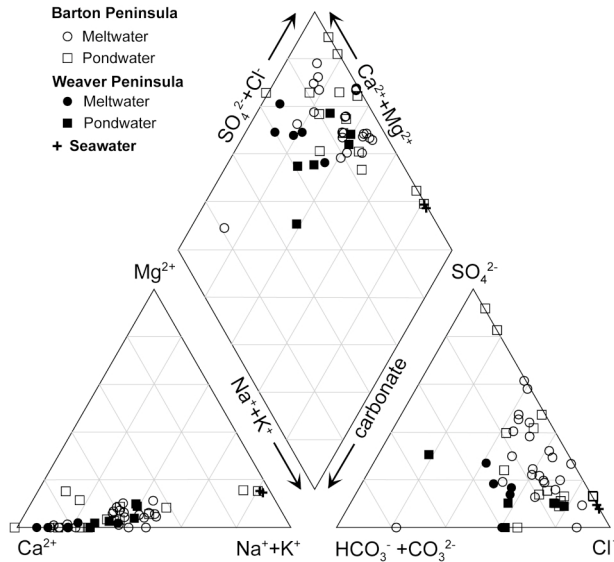


Fig. 2. Chemical compositions of the meltwater and pondwater in the Barton and Weaver Peninsulas.

rock area. However, fresh water affected by sea salt or seawater in a coastal region can be changed to Ca–Cl or Na–Cl types (El Yaouti *et al.*, 2009). Therefore, these results indicate that the MW and PW may be influenced by sea salt.

Rare earth element chemistry

Table 2 shows the concentrations of REEs in the MW and PW at the Barton and Weaver Peninsulas. The standard deviation for concentrations of REEs has wide range from 0.001 to 2.001, which is attributed to vertical and spatial inhomogeneity of REEs of snow and glacier (Bory *et al.*, 2010). At the Barton Peninsula, the average concentrations of REEs of the PW were higher than those of the MW. Ce and Nd were dominant in the MW and PW. Ho, Tm and Lu were not detected in the MW. At the Weaver Peninsula, contrary to the Barton Peninsula, the average concentrations of REEs of the MW at the Weaver Peninsula were higher than those of the PW. Additionally, Eu, Tb, Ho, Er, Tm, Yb and Lu of the MW and PW were not detected. These results indicate that the contributions of the factors controlling the REE levels such as aerosol are different, and the influence of aerosol was predominant in samples at the PW of the Barton Peninsula among the sampling sites. It is known that snow, glacier and surface water at KGI were affected by aerosol from marine spray, particles by weathering and anthropogenic materials occurred around scientific stations (Santos *et al.*, 2005; Leal *et al.*, 2008), and aerosol such as mineral particles can be one of REEs sources in the coastal areas (Bory *et al.*, 2010). To clearly understand

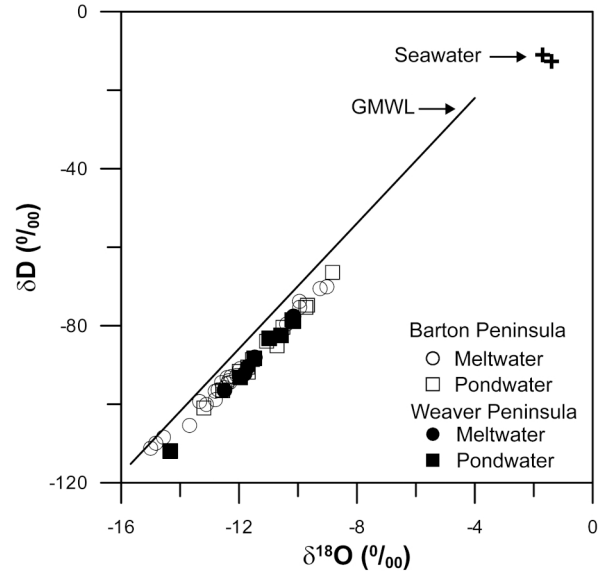


Fig. 3. Oxygen and hydrogen isotopic compositions of the meltwater and pondwater in the Barton and Weaver Peninsulas. GMWL (the solid line) represents global meteoric water line after Craig (1961).

the reasons for these results, additional research on the source identification of the REEs is necessary.

The Ce, Nd, La and Pr of the total REEs of the MW and PW at the Barton Peninsula were 93.7 and 84.5%, respectively, and those of the total REEs of the MW and PW at the Weaver Peninsula were 95.7 and 95.8%, respectively. These results are due to the absence or very low concentrations of heavy REEs (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), in addition to Gd and Dy, at the Weaver Peninsula (Table 2).

Oxygen and hydrogen isotopic composition

Figure 3 shows that the $\delta^{18}\text{O}$ and δD of the MW and PW of the Barton and Weaver Peninsulas did not exhibit mixing trend with seawater. This result indicates that all MW and PW were not directly influenced by seawater. At the Barton Peninsula, the $\delta^{18}\text{O}$ and δD of the MW had ranges of $-14.8\sim-9.0$ and $-111\sim-70\text{‰}$, respectively, and those of the PW had ranges of $-13.2\sim-8.8$ and $-101\sim-66\text{‰}$, respectively. The $\delta^{18}\text{O}$ and δD of the MW and PW showed a wide variation range. These results are due to vertical and spatial inhomogeneity of snow and glaciers (Simões *et al.*, 2004; Wang *et al.*, 2010). The $\delta^{18}\text{O}$ and δD of the PW were slightly enriched compared with those of the MW. Additionally, the regression lines for the MW and PW were $\delta\text{D} = 7.23\delta^{18}\text{O} - 4.26$ ($n = 23$, $r^2 = 0.99$) and $\delta\text{D} = 7.76\delta^{18}\text{O} + 0.72$ ($n = 13$, $r^2 = 0.99$), respectively. The slopes of the regression lines were somewhat different compared with the slopes of the global mete-

Table 2. Concentrations of REEs in the meltwater and pondwater in the Barton and Weaver Peninsulas of the King George Island, Antarctica

Type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Barton Peninsula														
Meltwater (n = 23)														
Minimum	0.378	0.986	0.047	0.567	0.034	0.002	0.021	0.003	0.001	—	0.002	—	0.009	—
Maximum	1.169	2.587	0.275	1.557	0.200	0.041	0.182	0.003	0.088	—	0.043	—	0.028	—
Mean	0.730	1.765	0.141	1.040	0.096	0.014	0.078	0.003	0.024	—	0.016	—	0.017	—
Standard deviation	0.192	0.400	0.055	0.252	0.040	0.016	0.037	—	0.021	—	0.015	—	0.007	—
Pondwater (n = 14)														
Minimum	0.476	1.228	0.068	0.739	0.045	0.007	0.042	0.033	0.003	0.032	0.006	0.012	0.002	0.006
Maximum	3.698	9.264	1.210	6.815	1.329	0.313	1.515	0.132	0.894	0.128	0.413	0.012	0.276	0.006
Mean	1.084	2.750	0.270	1.754	0.240	0.077	0.242	0.082	0.155	0.080	0.113	0.012	0.076	0.006
Standard deviation	0.803	2.001	0.285	1.528	0.329	0.109	0.385	0.049	0.258	0.048	0.145	—	0.100	—
Seawater (n = 1)														
	0.593	1.828	0.134	0.946	0.097	—	0.096	—	0.011	—	0.003	—	—	—
Weaver Peninsula														
Meltwater (n = 5)														
Minimum	0.607	1.509	0.101	0.872	0.066	—	0.050	—	0.003	—	—	—	—	—
Maximum	0.793	1.883	0.146	1.065	0.098	—	0.089	—	0.006	—	—	—	—	—
Mean	0.695	1.699	0.123	0.965	0.083	—	0.068	—	0.005	—	—	—	—	—
Standard deviation	0.068	0.150	0.018	0.077	0.012	—	0.015	—	0.001	—	—	—	—	—
Pondwater (n = 6)														
Minimum	0.541	1.354	0.090	0.777	0.055	—	0.046	—	0.003	—	—	—	—	—
Maximum	0.763	1.828	0.132	1.085	0.119	—	0.076	—	0.010	—	—	—	—	—
Mean	0.650	1.597	0.114	0.921	0.080	—	0.057	—	0.005	—	—	—	—	—
Standard deviation	0.072	0.161	0.017	0.102	0.020	—	0.013	—	0.003	—	—	—	—	—
Seawater (n = 1)														
	0.714	1.828	0.136	1.031	0.097	—	0.073	—	0.011	—	—	—	—	—

Unit of concentrations of REEs is $\mu\text{g/L}$.

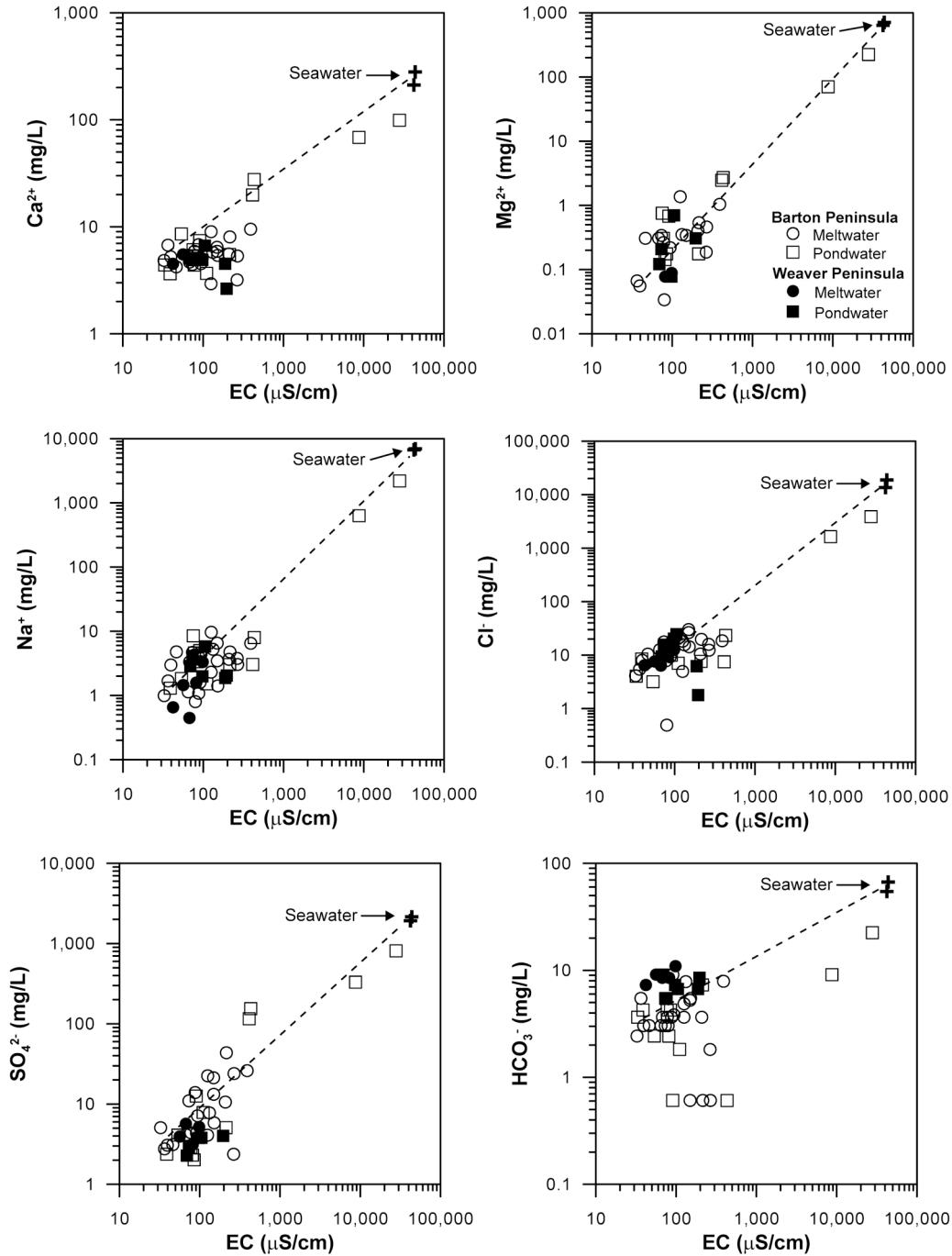


Fig. 4. Relations between the major ions and EC of the meltwater and pondwater in the Barton and Weaver Peninsulas. The dotted lines represent hypothetical lines of mixing reactions between end-member of meltwater and seawater. The end-member of meltwater is MW-43 and MW-44 in inland of the Barton Peninsula.

oric water line (GMWL; $\delta D = 8\delta^{18}O + 10$) (Craig, 1961) and the local meteoric water line of precipitation at Frei Station of KGI ($\delta D = 7.1\delta^{18}O - 2.2$) (Simões *et al.*, 2004).

At the Weaver Peninsula, the $\delta^{18}O$ and δD of the MW had ranges of $-12.5 \sim -10.2$ and $-96 \sim -78\text{‰}$, respectively,

and those of the PW had ranges of $-14.3 \sim -10.2$ and $-112 \sim -79\text{‰}$, respectively. The $\delta^{18}O$ and δD were slightly depleted and showed narrow variation ranges compared with those of the Barton Peninsula. In addition, the regression lines for the MW and PW were $\delta D = 8.18\delta^{18}O +$

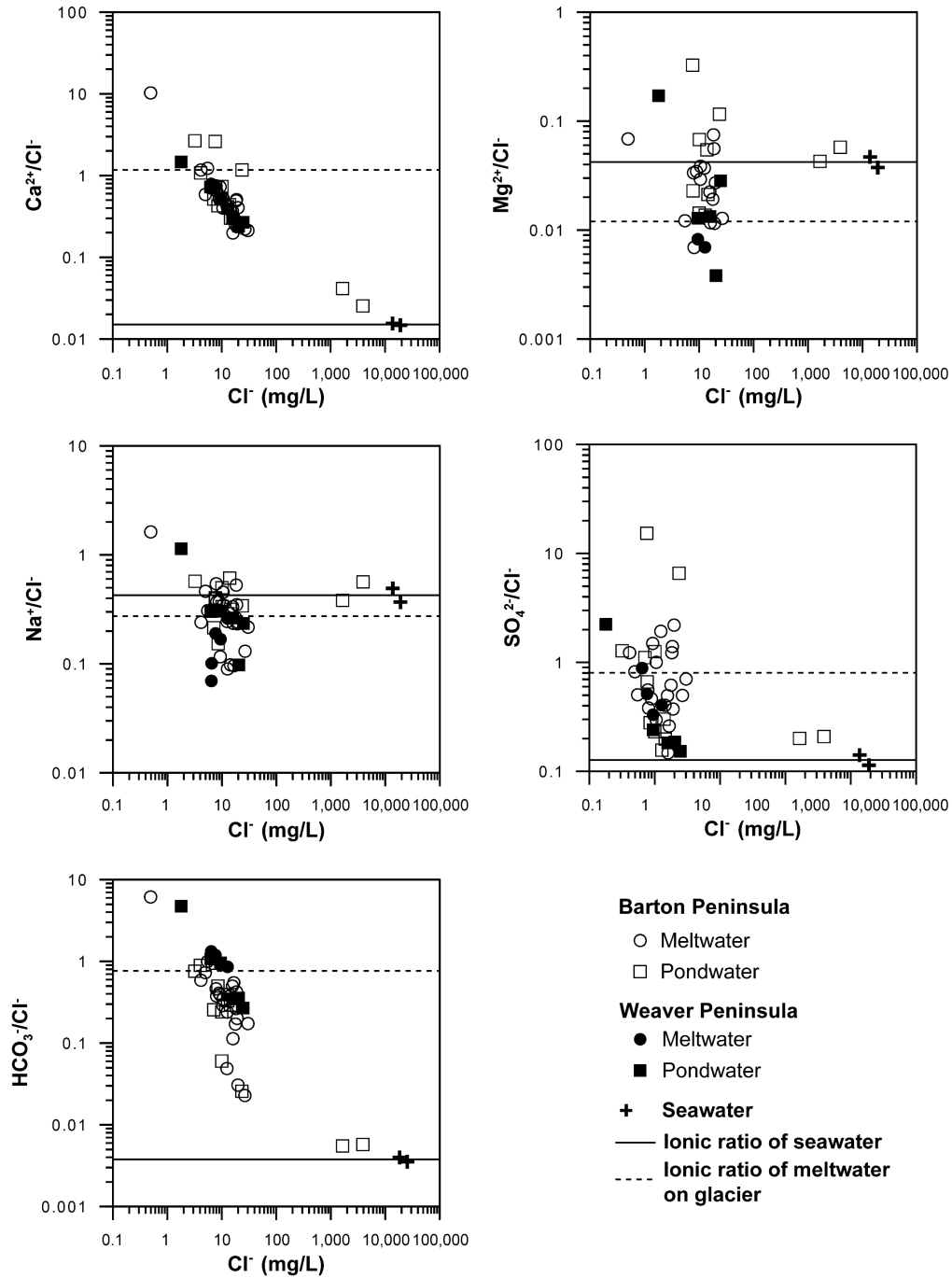


Fig. 5. Ionic ratios of the major ions for Cl^- of the meltwater and pondwater in the Barton and Weaver Peninsulas. The end-members calculating the ionic ratios of the meltwater are same in Fig. 3.

5.34 ($n = 5$, $r^2 = 0.99$) and $\delta D = 8.02\delta^{18}\text{O} + 3.28$ ($n = 6$, $r^2 = 0.99$), respectively. The slopes of the regression lines were similar to those of GMWL, but showed large values compared with those at the Barton Peninsula. These results suggest that the MW and PW at the Barton Peninsula may undergo little evaporation losses because the

MW and PW at the Barton Peninsula were plotted near the GMWL. However, the MW and PW at the Weaver Peninsula did not undergo the evaporation losses.

Influence of sea salt

The MW and PW of the coastal regions of Antarctica

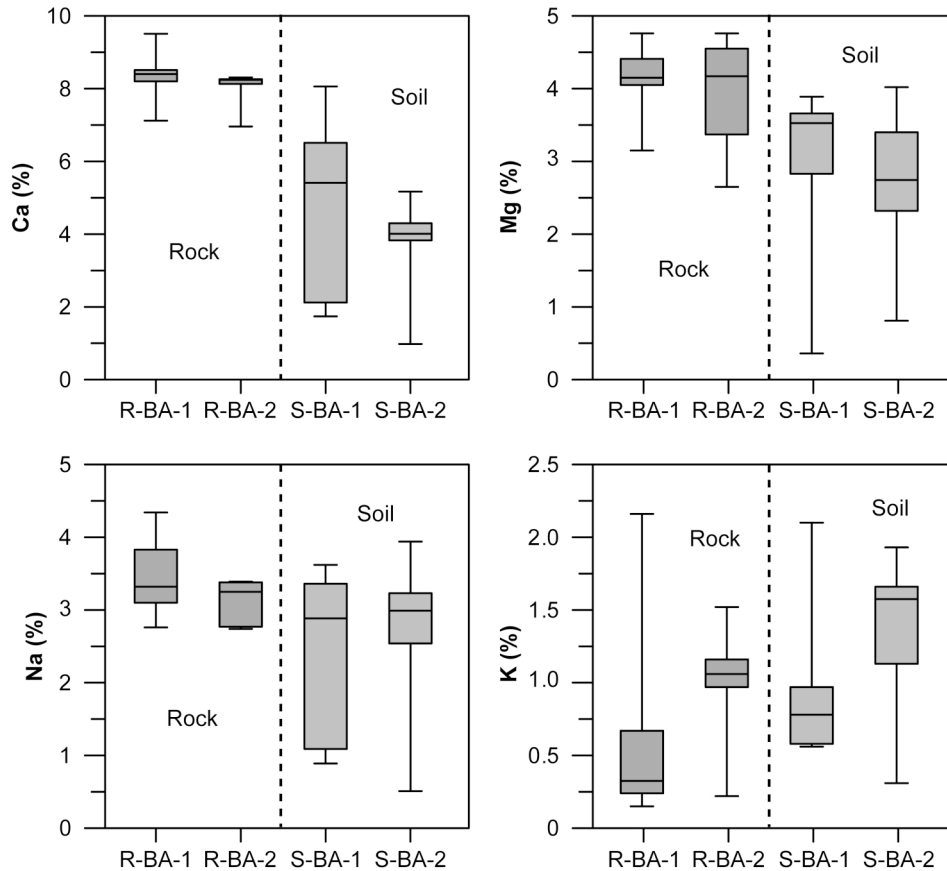


Fig. 6. Comparison of chemical compositions of rocks with those of soils in the Barton Peninsula. The chemical compositions of rocks and soils are collected from Yeo *et al.* (2004) and Lee *et al.* (2004), respectively.

can be generally influenced by sea salt transported by strong winds (Hall and Wolff, 1998). To assess the influence of sea salt on the MW and PW, MW-43 and MW-44 were considered with the end-member of MW uncontaminated by sea salt. The sampling sites of these end-members are located inland of the Barton Peninsula, and they showed very low EC levels (33 and 37 $\mu\text{S}/\text{cm}$, respectively).

Figure 4 shows the relationship between the ECs and major ions. In Fig. 4, the dotted lines represent hypothetical mixing lines for each ion. Most major ions, except HCO_3^- of MW-4 and MW-23 with high EC levels (8,730 and 27,900 $\mu\text{S}/\text{cm}$, respectively), showed a thorough mixing trend between the freshwater and seawater. The influence of seawater was significantly observed at the MW-4 and MW-23. The Mg^{2+} , Cl^- and SO_4^{2-} of many of the samples were plotted around hypothetical lines of the mixing trend. These trends were more dominant at the Barton Peninsula than those at the Weaver Peninsula. Cl^- and SO_4^{2-} were mainly supplied from sea salt in the coastal areas (Kerminen *et al.*, 2000; Aristarain and Delmas, 2002). However, Ca^{2+} , some of Mg^{2+} , Na^+ and

HCO_3^- did not show significant mixing trends. These results indicate that sea salt is not main factor supplying Ca^{2+} , some Mg^{2+} , Na^+ and HCO_3^- . It is known that Ca^{2+} , Mg^{2+} and HCO_3^- are associated with the dissolution of carbonate minerals. The water-rock interaction will be explained in next section.

Generally, the ionic ratios of major ions have been used to identify sources because the ratios are conservative parameters (Hall and Wolff, 1998; Borghini and Bargagli, 2004). Figure 5 shows the ionic ratios of the MW and PW at the Barton and Weaver Peninsulas. The $\text{Ca}^{2+}/\text{Cl}^-$ (1.203), $\text{SO}_4^{2-}/\text{Cl}^-$ (0.868) and $\text{HCO}_3^-/\text{Cl}^-$ ratios (0.798) of the end-member were higher than the $\text{Ca}^{2+}/\text{Cl}^-$ (0.015), $\text{SO}_4^{2-}/\text{Cl}^-$ (0.128) and $\text{HCO}_3^-/\text{Cl}^-$ ratios (0.004) of the seawater. The Na^+/Cl^- (0.275) and $\text{Mg}^{2+}/\text{Cl}^-$ ratios (0.012) of the end-member were lower than the Na^+/Cl^- (0.431) and $\text{Mg}^{2+}/\text{Cl}^-$ ratios (0.042) of the seawater. If sea salt and glaciers were the main factors controlling the chemistry of the MW and PW, all samples should be distributed between the end-member of the fresh water and the seawater. Most samples from the Weaver Peninsula were distributed in the mixing area between

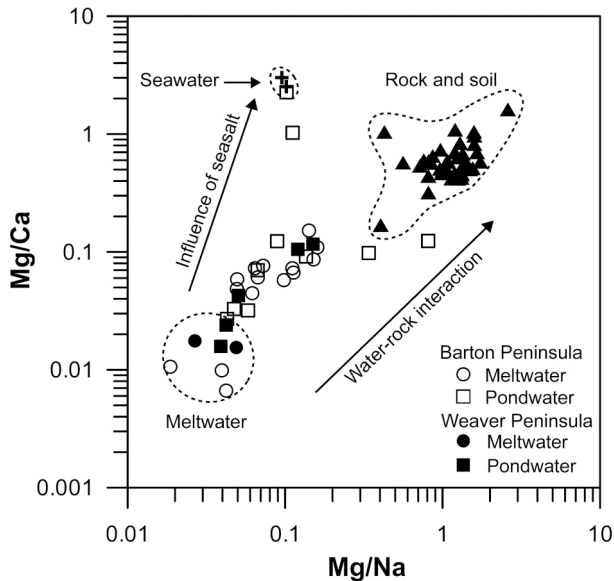


Fig. 7. Mg/Na vs. Mg/Ca for the meltwater, pondwater, rocks and soils in the Barton and Weaver Peninsulas. The end-members calculating Mg/Na and Mg/Ca of the meltwater are same in Fig. 3. The chemical compositions of rocks and soils are from Yeo *et al.* (2004) and Lee *et al.* (2004), respectively.

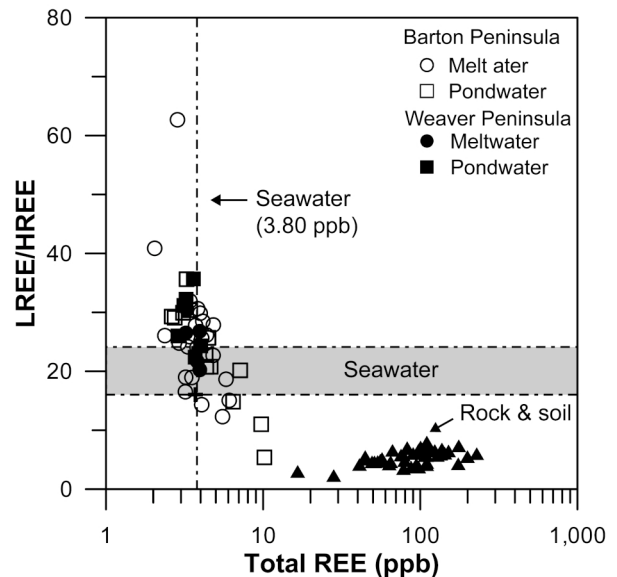


Fig. 8. Evaluation of the water-rock interaction using REEs of the meltwater, pondwater, rocks and soils in the Barton and Weaver Peninsula. The chemical compositions of rocks and soils are from Yeo *et al.* (2004) and Lee *et al.* (2004), respectively.

two end-members, but some samples from the Barton Peninsula were distributed outside of mixing areas. These trends are distinctly shown in the SO_4^{2-}/Cl^- ratios of the samples from the Barton Peninsula. These results indicate that the chemistry of the MW and PW at the Weaver Peninsula is greatly influenced by sea salt. However, the chemistry of the MW and PW at the Barton Peninsula is mainly controlled by sea salt and is only slightly influenced by other factors, which may be the water-rock interaction and dry depositions. An additional study on sources of dissolved components in the MW and PW will be necessary to clearly understand them.

According to previous works (e.g., Borghini and Bargagli, 2004), Na^+/Cl^- ratios show a positive relation with distance from the coast line because sea salt is mainly transported by wind. However, these trends were not obviously observed in this study because the study area is small, and most sampling sites are influenced by wind. Therefore, the influence of sea salt on the MW and PW may be controlled more by the exposure time to air than by wind in the study area.

Evaluation of the water-rock interaction

According to the previous works, there has been little chemical weathering in the Barton Peninsula (Lee *et al.*, 2004), and the clay minerals in the soil were mainly formed by the glacial erosion of rocks (Jeong *et al.*, 2004). However, chemical weathering evidence such as carbon-

ate mineral dissolution and the alteration of plagioclase, in thin sections (Jeong, 2003). Therefore, this study evaluated of the water-rock interaction using the chemical compositions of the rock, soil and surface water (MW and PW). Figure 6 shows the chemical compositions of the basaltic andesite (data from Yeo *et al.*, 2004) and the soils on the basaltic andesite (data from Lee *et al.*, 2004) at the Barton Peninsula. The average concentrations of Ca, Mg, Na and K were 4.21, 2.88, 2.72 and 1.24%, respectively, in the soils and 8.19, 4.05, 3.28 and 0.76%, respectively, in the rocks. The concentrations of the Ca, Mg and Na of the soils were lower than those of the rocks. This result may be associated with carbonate mineral dissolution and alteration of silicate minerals (Tranter *et al.*, 2002; Wadham *et al.*, 2007). However, the K concentrations of the soils were higher than those of the rocks, which may be attributable to the accumulation of K^+ from sea salt. Additionally, Jeong (2003) did not observe the alteration of K-feldspar in the bedrocks of the Barton Peninsula. Additionally, H_4SiO_4 concentrations were very low (0.37~9.07 mg/L), which indicates that the alteration of silicate minerals did not occur actively. Therefore, the influence of the water-rock interaction on the MW and PW was evaluated using the Mg/Ca and Mg/Na of the MW, PW, seawater, soils and rocks. In Fig. 7, the Mg/Ca and Mg/Na of end-member of the MW were relatively low compared with those of the seawater, soils and rocks. Additionally, the Mg/Na of seawater was relatively low

compared with that of the soils and rocks because Na^+ is more abundant in the seawater than in the soils and rocks. Therefore, if the influence of sea salt increases gradually, the Mg/Ca of the MW and PW will show a gradually increasing trend. In addition, if the influence of the water-rock interaction increases gradually, the Mg/Na and Mg/Ca of the MW and PW will have a gradually increasing trend together. Figure 7 shows that the MW and PW chemistry was controlled by sea salt and the water-rock interaction. The water-rock interaction dominantly occurred in the PW of the Barton Peninsula.

In Fig. 8, the heavy REEs (HREEs) and light REEs (LREEs) represent La and Nd and Gd and Yb, respectively. The LREE/HREE ratios of the seawater ranged from 16.1 to 24.0 and those of the soils and rocks ranged from 3.07 to 7.40. Most samples are plotted near the seawater or above (Fig. 8). Additionally, REE mobility is mostly influenced by weathering condition and stability of mineral bearing REE (Aubert *et al.*, 2001). Therefore, REEs of the MW and PW may be mainly supplied from sea salt rather than water-rock interaction. However, the LREE/HREE ratios of some of the samples from the Barton Peninsula were lower than those of the seawater, perhaps due to the influence of the water-rock interaction. These ratios were especially low in MW-24 (5.43) and MW-48 (11.1).

CONCLUSIONS

In this study, the geochemical properties of the MW and PW at the Barton and Weaver Peninsulas were demonstrated, and the water-rock interaction was evaluated using Mg/Ca , Mg/Na and REEs. The MW and PW at the Barton and Weaver Peninsulas showed the Ca-Cl type by the influence of sea salt. The influence of sea salt was more obvious in the PW than in the MW and at the Barton Peninsula compared with the Weaver Peninsula. However, some of the Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} , HCO_3^- and REEs may be released by the water-rock interaction. According to previous works, the water-rock interaction does not occur significantly at KGI, and the soils were mainly formed by glacial erosion. Additionally, there has been little research on the water-rock interaction in the MW and PW at the Barton and Weaver Peninsulas. However, some of the Ca^{2+} , Mg^{2+} and Na^+ in the MW and PW are controlled by sea salt and the water-rock interaction, including carbonate mineral dissolution and the alteration of sulfate minerals. Additionally, REEs of some PW (MW-24 and MW-48) at the Barton Peninsula were influenced by the water-rock interaction. The water-rock interaction was more distinctly observed at the Barton Peninsula than the Weaver Peninsula. However, the water-rock interaction was not the main factor controlling the surface water chemistry at the Barton and Weaver Peninsulas. The $\delta^{18}\text{O}$

and δD of the MW and PW showed a wide range because of the inhomogeneity of the glacier and snow. The MW and PW of the Barton Peninsula underwent evaporation losses but those of the Weaver Peninsula did not undergo.

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