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Hydrochemical Parameters to Assess the Evolutionary Process of CO₂-Rich Spring Water: A Suggestion for Evaluating CO₂ Leakage Stages in Silicate Rocks

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Abstract: Eighteen water samples collected from eight CO_2 -rich springs in the northern part of the Gyeongsang sedimentary basin (GSB), South Korea showed distinct hydrochemistry, in particular, pH, total dissolved solids (TDS), and Na contents, and they were classified into four groups: (1) Group I with low pH (average of 5.14) and TDS (269.8 mg/L), (2) Group II with high TDS (2681.0 mg/L) and Na-enriched (202.9 mg/L), (3) Group III with intermediate Na content (97.5 mg/L), and (4) Group IV with Na-depleted (42.3 mg/L). However, they showed the similar partial pressure of CO_2 (0.47 to 2.19 atm) and stable carbon isotope ratios of dissolved inorganic carbon (-6.3 to -0.6%), indicating the inflow of deep-seated CO_2 into aquifers along faults. In order to elucidate the evolutionary process for each group of CO₂-rich springs, a multidisciplinary approach was used combining stable hydrogen (δ D), oxygen (δ ¹⁸O) and carbon (δ ¹³C), and radioactive carbon (¹⁴C) isotopic, geophysical, and hydrochemical data. The highest δD and $\delta^{18}O$ ratios of water and the relatively young ^{14}C ages in Group I and the lowest δD and $\delta^{18}O$ in Group II indicated the short and long residence time in Group I and II, respectively. The electrical resistivity tomography (ERT) survey results also supported the fast rising through open fractures in Group I, while a relatively deep CO₂-rich aquifer for Group III. Group II had high contents of Mg, K, F, Cl, SO₄, HCO₃, Li, and As, while Group I showed low contents for all elements analyzed in this study except for Al, which exceeded the World Health Organization (WHO) guideline for drinking-water quality probably due to the low pH. Meanwhile Group IV showed the highest Ca/Na as well as Ca, Fe, Mn, Sr, Zn, U, and Ba, probably due to the low-temperature dissolution of plagioclase based on the geology and the ERT result. The levels of Fe, Mn, and U exceeded the WHO guidelines in Group IV, while As in Group II. The different hydrochemistry suggests a distinct evolutionary process for each group. Group I seems to represent a fast discharge from the CO₂-rich aquifer to a discharge point, experiencing a low degree of water-rock interaction, while Group II seems to represent a slow discharge with a high degree of water-rock interaction. GSB is a potential site for geological carbon storage (GCS), and injected CO_2 may leak through various evolutionary processes given heterogenous geology as CO₂-rich springs. The study result suggests that the combined use of pH, Na, K, Li, and Ca/Na are effective hydrochemical monitoring parameters to assess the leakage stage in silicate rocks in GCS projects. Besides, aluminum (Al) can be risky at the early stage of CO₂ leakage, while Fe, Mn, U, and As at the later stage of CO₂ leakage.

Keywords: hydrochemistry; electrical resistivity tomography; CO₂-rich spring; evolutionary process; CO₂ leakage

1. Introduction

Various efforts, including economic incentives and technology development, have been made to mitigate climate change by anthropogenic greenhouse gases (GHGs). Among technologies to reduce the global emissions of GHGs, the geological carbon storage (GCS) is accepted as one of the most promising technologies [1–4]. The global warming potential is estimated to be reduced by 63~82% by GCS based on a life cycle assessment study [5]. However, the geological complexity of GCS sites causes environmental risks, including environmental damages due to CO₂ leakage [5,6], although there has been no harmful leakage at GCS sites until now. The public concern about potential risks of CO₂ leakage from storage sites should be properly addressed for successful demonstration and commercialization of GCS.

Therefore, monitoring and verification (M&V) operations are a key process to gain public acceptance and to sequester CO_2 safely into deep geologic formations. M&V techniques have been proposed to evaluate the response of soil, water, and living resources to injected CO_2 in the shallow subsurface environment at different scales (e.g., laboratory, pilot, or full) and formations (e.g., sedimentary or crystalline) [7–12]. However, the artificial CO_2 injection tests provide limited information about the long-term CO_2 -water-rock interaction and the related changes in the subsurface environment (e.g., groundwater quality, porosity, permeability). Besides, the short history of GCS does not provide enough data to assure the possibility of CO_2 leakage and its causes in GCS projects.

To overcome such limited knowledge from the injected CO₂ tests or GCS projects, natural CO₂ emissions from geologic reservoirs such as CO₂-rich springs have been studied as natural analogues of CO₂ leakage. The natural CO₂ emission has evolved over geological timescales [13–15] and thus provides opportunities to evaluate the potential impacts of a slow and gradual CO₂ leakage and the long-term safety of GCS [14–17] and moreover to suggest effective M&V techniques and parameters [18–22]. In particular, the hydrochemistry of CO₂-rich springs helps to understand the ascending process of injected CO₂ (e.g., rapid leakage through faults, fractures, or abandoned well versus slow leakage along rock discontinuities [15]) and accompanying CO₂-water-rock interactions [23–25]. Specifically, hydrochemical compositions suggest evolutionary processes from deep subsurface to a discharge point [23,26]. Trace elements provide the information on health effects of enhanced water-rock interactions with the CO₂ inflow [23,24]. Besides, stable and radioactive carbon isotopic compositions in CO₂-rich springs have been used to estimate the residence time of CO₂-rich groundwater [23,27] as well as the source of CO₂ [15,28–31].

Recently, electrical resistivity tomography (ERT) has been combined with the hydrochemical and environmental isotopic study to provide an image of near-surface structures and to assess the migration pathway of CO_2 -rich fluids in the sites of both natural emission and artificial injection tests [16,22,32,33]. ERT is a noninvasive technique to image the electrical resistivity pattern of the subsurface [34]. The distribution of the resistivity is related to the geologic, hydrogeologic, and hydrochemical properties, and thus useful to estimate the pathways of fluids with contrast resistivity, including CO_2 -rich water that has relatively low pH and high electrical conductivity (EC) [16,32].

The aim of this study was to characterize the hydrochemistry of CO₂-rich springs and to elucidate their evolutionary process in a natural analogue site in South Korea based on a multidisciplinary approach combining hydrochemical, geophysical, and stable and radioactive carbon isotopic data. Environmental impacts of CO₂-rich water were assessed and useful M&V parameters to evaluate leakage stages were suggested for GCS sites in silicate rocks.

2. Study Area

The study area is located at the northern part of the Gyeongsang sedimentary basin (GSB), South Korea (Figure 1). The GSB is mainly composed of Cretaceous fluvial and lacustrine sedimentary rocks deposited in rivers and temporary lakes and marshes that experienced seasonal drying and repeated wetting events [35]. The sedimentary rocks consist of plagioclase, quartz, K-feldspar, micas and pore-filling minerals such as calcite, dolomite, and chlorite [36]. Cretaceous to early Tertiary Bulguksa granites ubiquitously intruded the sedimentary rocks.



Figure 1. Study area at the southeastern part of South Korea. (a) Geological map with the locations of CO_2 -rich springs (G-1 to G-8; n = 8). The four groups were classified by pH, total dissolved solids, and Na contents in Figure 2. (b,c) show the geophysical survey lines around the G-5 (ERT-1) and the G-1 and G-6 (ERT-2), respectively. In (a), the black lines indicate faults, while in (b,c) the white dashed lines are faults.

In the northern part of the GSB, two Mesozoic granitoids (Yeongdeok and Cheongsong granitoids) occur and are surrounded by Precambrian gneiss and Cretaceous sedimentary rocks (Figure 1a). Both Yeongdeok and Cheongsong granitoids were originated from continental magmatic arcs, while the mixing proportion of crustal components is different: from ca. 20 to 40% in the Yeongdeok granitoid and from ca. 40 to 60% in the Cheongsong granitoid [37]. The Yeongdeok granitoid is biotite-hornblende granite containing K-feldspar megacrysts and mainly consists of quartz, K-feldspar and plagioclase with a minor amount of biotite, hornblende, sphene, zircon, and apatite [38]. The Cheongsong granitoid represents biotite granite with megacrysts of pinkish K-feldspar; includes K-feldspar, plagioclase, quartz, and biotite, with a minor amount of sphene, zircon, and epidote [37]. These two granitoids have older (i.e., Triassic to Jurassic) ages and are emplaced at deeper depths than the Cretaceous Bulguksa granite that is ubiquitously distributed in the GSB [37–39].

Tecto-lineaments appear in several directions within the study area, while the NS-trending faults are the most pronounced, which are thought to have been formed under the influence of the Yangsan fault [38]. Naturally seeping CO₂-rich springs are located along faults mainly in and around the two Mesozoic granitoids in the GSB (Figure 1a). We examined eight springs for this study, of which six springs (G-1, G-4, G-5, G-6, G-7, and G-8) are located in the Yeongdeok granitoid. The spring G-3 is located in the Cheongsong granitoid, while the spring G-2 occurs along the geologic boundary between the Bulguksa granite and the Cretaceous sandstone and red shale. The Bulguksa granite and brecciated andesite intruded the sedimentary rocks in G-2 [40]. Gas bubbles were observed in all eight springs. The origin of CO₂ in the CO₂-rich springs has been reported to be deep-seated such as mantle in the study area [40–43], whereas the hydrochemical evolutionary processes related to the CO₂-water-rock interaction have not yet been fully understood, which motivated this study.

3. Methods

3.1. Sampling and Analytical Methods

A total of 18 water samples were collected from eight CO_2 -rich springs through three sampling campaigns in February 2013 (n = 5), February 2014 (n = 7), and March 2015 (n = 6) for hydrochemical

and isotopic analyses (Figure 1a). Water samples at G-3, G-4, and G-7 were collected since 2014, while the spring G-7 was closed and could not be sampled during the 2015 sampling campaign. Meanwhile, the access to G-8 was not possible after 2013, since the spring G-8 is located on a private estate.

Temperature, pH, redox potential (Eh), EC, and dissolved oxygen (DO) of water samples were measured on-site with a portable multiparameter meter (Orion 1230) within a flow-through cell to minimize the contact with atmospheric oxygen. Alkalinity was also determined on-site by titration with HNO₃ solution (0.5 N or 0.05 N) as soon as the water was collected to minimize CO₂ degassing from the CO₂-rich water. All water samples for laboratory analyses were filtered with 0.45-µm cellulose nitrate membrane filters and stored in high-density polyethylene bottles. Then the samples for major cation and trace element analyses were acidified. Dissolved inorganic carbon (DIC) of water samples was precipitated by adding NaOH and BaCl₂ for the measurement of stable carbon isotopic composition (δ^{13} C) and the radiocarbon dating (¹⁴C). All water samples were maintained at a low temperature (<4 °C) using a cooler or refrigerator until analyses.

Water samples with high EC (>1000 μ S/cm) were diluted with a 1:10, 1:30, and 1:100 dilution ratio for cations, anions, and trace elements, respectively before analysis. Then major cations (Na, K, Mg, Ca) and SiO₂ were determined using ICP-AES (Ultima 2, HORIBA Jobin Yvon) at the Korea Basic Science Institute (KBSI), while anions (Cl, SO₄, NO₃, F) were analyzed using IC (Dionex ICS-1100, Thermo Fisher Scientific, Waltham, MA, USA) at the Center for Mineral Resources Research (CMR) of Korea University. Trace elements (Fe, Mn, Al, Sr, Li, Zn, As, U, Ba) were analyzed by ICP-MS (Elan DRC II, PerkinElmer, Waltham, MA, USA) at KBSI. The detection limits were 0.01 ppb for all trace elements analyzed for this study. The alkalinity was converted to HCO_3 (mg/L) because of the pH range (Table 1). Then charge balance errors were within an acceptable range of $\pm 5\%$ for all water samples. The oxygen $(\delta^{18}O)$ and hydrogen (δD) isotopic compositions of water were determined using a stable isotope ratio mass spectrometer (S-IRMS, IsoPrime, GV Instruments Ltd., Wythenshave, Manchester, UK) at KBSI. The δ^{18} O and δ D values were measured relative to the internal standards that were calibrated with the Standard Mean Ocean Water (SMOW) and showed the analytical error of ±0.1‰ and ±1‰, respectively. The δ^{13} C of DIC was determined using an IRMS (Delta V Plus, Thermo Scientific) with $\pm 0.1\%$ precision relative to the Pee Dee Belemnite (PDB) at KBSI. The radiocarbon dating (¹⁴C) was performed using accelerator mass spectrometer (AMS, National Electrostatics Corp., Middleton, WI, USA) at Beta Analytic (Miami, FL, USA). In addition, the partial pressures of CO_2 (P_{CO2}) were calculated based on the physicochemical data measured for this study using PHREEQC software [44].

3.2. Geophysical Exploration

Electrical resistivity was investigated in March 2016 along two 800-m survey lines, i.e., ERT-1 around G-5 (Figure 1b) and ERT-2 around G-1 and G-6 (Figure 1c) to identify the hydrogeological setting (e.g., fault or fracture) around three CO_2 -rich springs and its relationship with hydrochemistry. In Figure 1a, the three CO_2 -rich springs (G-1, G-5, and G-6) occur near the NS-trending faults, which may act as pathways to discharge CO_2 -rich water. Therefore, the survey lines were arranged in the WE-direction perpendicular to the fault direction to detect the pathways of fluids.

The resistivity data acquisition system used for this survey was a Lund Imaging System (ABEM Instrument AB, Sundbyberg, Sweden) equipped with SAS4000 terrameter and ES-10-64c multiplexer, which automatically recorded data using a 41-channel cable (10 m) and 80 electrodes (I type and T type steel sticks). A dipole-dipole array was used because of its high resolution. The length of the survey line and the electrode array used in this study allowed the maximum depth measured by the ERT to be 100 m below the surface. The apparent resistivity data were processed with Res2DInv (Geotomo Software, Gelugor, Penang, Malaysia) electrical resistivity analysis software and the active constraint balancing approach for inversion.

Carrier	Sample ID	Sampling Date	Temp. (°C)	рН	Eh (mV)	EC (µS/cm)	DO (mg/L)	P _{CO2} * (atm)	TDS (mg/L)	Concentration (mg/L)									
Group										Ca	Mg	Na	К	SiO_2	F	Cl	NO ₃	SO_4	HCO ₃
Ι	G-1	February-2013	10.8	4.92	517.6	214	2.3	2.2	328.9	40.19	6.15	19.16	0.63	63.14	0.30	9.54	1.64	4.89	182.08
		February-2014	8.0	5.38	378.5	217	3.6	0.7	280.1	47.43	2.95	13.07	0.67	38.52	0.36	8.31	1.43	4.76	161.70
		March-2015	11.4	5.13	424.9	222	3.2	0.8	200.3	25.36	2.33	14.88	0.57	41.04	0.35	7.63	1.38	4.71	100.68
	Average		10.1	5.14	440.3	217.6	3.0	1.2	269.8	37.7	3.8	15.7	0.6	47.6	0.3	8.5	1.5	4.8	148.2
II	G-2	February-2013	14.3	6.20	490.9	2100	1.0	1.1	2983.8	355.82	114.19	212.51	8.26	72.15	1.37	31.76	0.34	37.19	2144.43
		February-2014	8.7	6.40	299.2	2725	2.2	0.7	2727.5	271.70	87.24	232.93	9.87	57.58	1.27	28.30	0.19	43.35	1989.17
		March-2015	-	6.23	296.0	2588	1.6	1.0	2632.5	249.70	106.55	219.33	8.58	47.56	0.76	25.53	0.17	46.59	1912.95
	G-3	February-2014	9.5	6.44	297.1	2816	1.6	0.6	2575.9	238.25	131.65	171.46	7.60	69.19	1.46	23.75	1.64	29.20	1897.72
		March-2015	-	6.21	285.5	2858	0.9	1.0	2485.2	196.83	130.16	178.17	7.25	73.16	0.41	9.15	0.96	13.14	1861.10
	Average		10.8	6.30	333.7	2617.4	1.4	0.9	2681.0	262.5	114.0	202.9	8.3	63.9	1.1	23.7	0.7	33.9	1961.1
III	G-4	February-2014	12.2	6.08	300.8	1979	1.2	1.0	1838.1	230.14	67.76	87.73	4.36	63.84	0.49	13.92	0.09	15.40	1348.52
		March-2015	-	6.16	340.4	1984	0.8	0.9	2008.5	257.27	74.07	91.06	4.01	66.50	0.01	9.31	0.03	14.02	1479.67
	G-5	February-2013	13.6	6.35	277.7	3240	1.2	0.8	2817.5	318.55	137.89	120.24	4.93	110.20	0.80	16.33	0.73	18.85	2085.38
		February-2014	11.4	6.48	262.8	3190	3.0	0.5	2295.5	297.74	87.60	91.36	5.03	80.06	1.10	16.89	0.71	18.82	1693.41
		March-2015	14.1	6.19	259.9	2980	1.8	1.0	2409.3	301.15	97.82	97.02	4.66	92.11	0.52	12.37	0.27	16.93	1769.67
	Average		12.8	6.25	288.3	2674.6	1.6	0.8	2273.8	281.0	93.0	97.5	4.6	82.5	0.6	13.8	0.4	16.8	1675.3
IV	G-6	February-2013	11.6	6.03	489.0	2046	1.3	1.6	2893.9	544.48	72.28	47.62	1.71	94.37	1.14	12.83	0.05	9.36	2103.73
		February-2014	11.0	6.24	321.4	2125	2.4	0.7	2108.3	396.64	41.39	36.18	1.76	69.16	1.33	13.71	0.37	8.88	1510.17
		March-2015	12.5	5.96	258.8	2007	0.8	1.7	2458.0	460.05	41.31	36.67	1.55	71.61	0.61	9.18	0.05	8.91	1800.01
	G-7	February-2014	8.2	6.08	361.7	1500	2.6	0.7	1381.1	223.73	53.12	19.84	2.47	79.45	0.23	8.96	0.50	5.31	970.17
	G-8	February-2013	5.0	6.30	349.9	908	1.1	0.5	1554.3	266.16	46.91	71.42	2.64	52.75	0.42	11.47	0.57	21.99	1057.12
	Average		9.7	6.12	356.2	1717.2	1.6	1.1	2079.1	378.2	51.0	42.3	2.0	73.5	0.7	11.2	0.3	10.9	1488.2

Table 1. Physicochemical data of water samples from the CO₂-rich springs (n = 8) in the northern part of the GSB. The CO₂-rich springs are grouped based on pH, TDS, and Na contents in Figure 2. Group I: dilute and acidic CO₂-rich water; Group II: "Na-enriched" Ca-HCO₃ type water; Group III: "intermediate" Ca-HCO₃ type water; Group IV: "Na-depleted" Ca-HCO₃ type water.

* Calculated based on the physicochemical data measured for this study using PHREEQC (Parkhrust and Appelo [44]).

4. Results

4.1. Hydrochemcial and Isotopic Compositions

The hydrochemical compositions of CO_2 -rich spring water samples were plotted on a Durov diagram to classify water groups and to understand the hydrochemical characteristics of each water group (Figure 2). The temporal variation was ignored because each spring showed similar hydrochemical compositions through the three sampling campaigns (Table 1). All CO₂-rich springs were shown as the Ca-HCO₃ type as in the previous studies [41,43,45,46] and showed relatively low pH values down to 4.92 at G-1 and high EC values up to 3240 µS/cm at G-5 (Table 1). Among them, three water samples from the spring G-1 were much lower in pH, TDS, and HCO₃ (Figure 2; Table 1), and thus classified into a separate group of dilute and acidic (i.e., low TDS and pH) CO₂-rich water (Group I in Figure 2). The other CO₂-rich water samples were further classified into three groups according to the Na content in Figure 2 because of its distinct difference (Table 1; Figure 3c): Na-enriched (Group II; n = 5 from G-2 and G-3) with the highest average Na content (202.9 mg/L), intermediate (Group III; n = 5 from G-4 and G-5) with the moderate average (97.5 mg/L), and Na-depleted (Group IV; n = 5 from G-6, G-7 and G-8) with the lowest average (42.3 mg/L). Group II showed higher TDS than the other groups in the range of 2485.2 to 2983.8 mg/L, while Group III and Group IV had a wide range of TDS from 1838.1 to 2817.5 mg/L and from 1381.1 to 2893.9 mg/L, respectively, whereas pH was similar in the three groups and higher than that in Group I.



Figure 2. Durov diagram showing the hydrochemical compositions of water samples (n = 18) from the CO₂-rich springs (n = 8). They are clustered into four groups by pH, total dissolved solids (TDS), and Na contents, while all show the Ca-HCO₃ type.

The hydrochemical difference between each group is more noticeable in the relationship between TDS and major ions (Figure 3). Group II had significantly higher concentrations of Na, K, SO₄, and HCO₃ than the other groups, while lower Ca concentrations than the water samples with the similar range of TDS in the other groups. Group III had higher Na, K, Mg, and SO₄ concentrations than Group IV. Group I showed the lowest concentrations for all major compositions.



Figure 3. Plots of total dissolved solids (TDS) versus major compositions for water samples: (**a**) Ca, (**b**) Mg, (**c**) Na, (**d**) K, (**e**) SO₄, and (**f**) HCO₃.

The concentrations of trace elements analyzed for this study also varied by groups (Table 2), although they were relatively high in the CO₂-rich springs compared to those in shallow groundwater and surface water in the study area [43,46]. Group I had the lowest concentrations for all trace elements excluding Al. Group II had higher Li and As concentrations than the other groups. Group III usually showed concentrations in the middle of Group II and IV for all trace elements except Sr and U, which showed the lower average in Group III than in Group II and IV. In Group IV, the concentrations of Fe and Mn were significantly higher than those in the other groups, and the concentrations of Sr, Zn, U, and Ba were also higher than the corresponding concentrations in Group II and III.

	formale ID		Concentration (µg/L)								
Group	Sample ID	Sampling Date	Fe	Mn	Al	Sr	Li	Zn	As	U	Ba
Ι	G-1	February-2013	n.d.	133	197.0	226	9.7	16.5	n.a.	n.a.	166.0
		February-2014	12.6	51	237.2	381	8.2	22.0	n.a.	n.a.	174.2
		March-2015	1.8	91	171.7	429	0.0	14.9	0.3	1.0	189.0
		Average	7.2	91.7	202.0	345.3	6.0	17.8	0.3	1.0	176.4
II	II G-2 Fe		-	1367	2.7	3542	945.0	17.5	n.a.	n.a.	126.0
		February-2014	-	99	32.9	4107	1356.3	30.7	n.a.	n.a.	164.9
		March-2015	6842.0	1023	6.5	5236	997.0	12.1	10.4	15.4	134.1
	G-3	February-2014	-	464	29.3	3047	1147.3	16.9	n.a.	n.a.	253.7
		March-2015	9581.0	869	18.0	3795	955.0	7.8	55.5	18.4	235.3
		Average	8211.5	764.4	17.9	3945.4	1080.1	17.0	32.9	16.9	182.8
III	G-4	February-2014	-	845	23.9	4114	437.0	51.7	n.a.	n.a.	326.9
		March-2015	5390.0	1122	0.7	4290	359.0	8.9	4.5	5.0	303.9
	G-5	February-2013	-	-	1.1	3496	501.0	13.4	n.a.	n.a.	306.0
		February-2014	-	-	73.1	2100	435.8	6.4	n.a.	n.a.	294.2
		March-2015	11,260.0	924	2.5	3520	353.0	13.8	4.0	14.1	426.3
		Average	8325.0	963.7	20.3	3504.0	417.2	18.8	4.3	9.5	331.5
IV	G-6	February-2013	-	2106	10.8	3237	146.0	45.6	n.a.	n.a.	459.0
		February-2014	22,651.4	2082	55.5	3313	131.8	57.1	n.a.	n.a.	565.9
		March-2015	22,070.0	1870	6.3	3278	104.0	24.7	1.1	40.2	591.3
	G-7	February-2014	13,564.0	442	58.0	1650	93.2	25.9	n.a.	n.a.	327.6
	G-8	Feb-2013	7949.0	1228	0.0	12,758	193.0	69.0	n.a.	n.a.	231.0
		Average	16,558.6	1545.6	26.1	4847.2	133.6	44.5	1.1	40.2	435.0
Surface water in the study area ⁽¹⁾			24~300	1~51	1.4~554	32~450	0.6~49.9	0.2~4.2	0.6~1.3	0.1~1.0	5.0~307.0
Shallow §	groundwater in	19~100	n.d.	3.5~9	50~94	0.6~108	2.1~6.3	50.1	n.d.	19.6~28.0	
Guideline Ch	es for Drinking emical Aspects	-	-	-	-	-	-	10	30	1300	
Guideline Acce	es for Drinking ptability Aspec	300	100	100	-	-	4000	-	-	-	

Table 2. Trace element concentrations of water samples from the CO₂-rich springs in the northern part of the GSB. The CO₂-rich springs are grouped based on pH, TDS and Na contents in Figure 2. Group I: dilute and acidic CO₂-rich water; Group II: "Na-enriched" Ca-HCO₃ type water; Group III: "intermediate" Ca-HCO₃ type water; Group IV: "Na-depleted" Ca-HCO₃ type water.

n.d.: not detected; n.a.: not analyzed; -: not determined. ^{(1), (2)} Analyzed by Jeong and Jeong [43] and Jeong et al.; ^{(3), (4)} WHO [47].

The δD and $\delta^{18}O$ of CO₂-rich spring water samples were plotted along the global meteoric water line [48] or local meteoric water line (LMWL; $\delta D = 8.06 \times \delta^{18}O + 12.87$ [49]) in Figure 4a, indicating that all the spring water samples had been recharged from the meteoric water. However, Group I showed the higher values (average $\delta^{18}O = -8.8\%_0$), while Group II had the lower values (average $\delta^{18}O = -9.8\%_0$) than the other groups. Group III (average $\delta^{18}O = -9.2\%_0$) and IV (average $\delta^{18}O = -9.2\%_0$) showed the similar δD and $\delta^{18}O$ (Figure 4a). The ¹⁴C activities of the CO₂-rich springs were considerably low (average 0.2 pMC; Table 3 and Figure 4b) compared to those of soil CO₂ (more than 100 pMC [48]), while Group I showed relatively high ¹⁴C (0.6 and 1.2 pMC).



Figure 4. Isotopic compositions. (a) Plot of δ^{18} O versus δ D values (n = 18). The solid and dashed line are the global meteoric water line (δ D = 8 × δ^{18} O + 10 [48]) and the local meteoric water line (δ D = 8.06 × δ^{18} O + 12.87 [49]), respectively. (b) Plot of ¹⁴C contents versus δ^{18} O (n = 9).

Table 3. Isotopic compositions of water samples from the CO_2 -rich springs in the northern part of the GSB. The CO_2 -rich springs are grouped based on pH, TDS, and Na contents in Figure 2. Group I: dilute and acidic CO_2 -rich water; Group II: "Na-enriched" Ca-HCO₃ type water; Group III: "intermediate" Ca-HCO₃ type water; Group IV: "Na-depleted" Ca-HCO₃ type water.

Group	Sample ID	δ ¹⁸ Ο (‰)	δD (‰)	δ ¹³ C (‰)	¹⁴ C (pMC)	Age (BP)
Ι	G-1	-8.8	-60.8	-1.3	1.2	$35,720 \pm 330$
		-8.7	-58.3	-5.8	n.a.	n.a.
		-8.9	-58.6	-6.3	0.6	$41,\!190\pm560$
II	G-2	-9.4	-64.7	-1.0	n.a.	n.a.
		-9.7	-64.3	-0.6	n.a.	n.a.
		-9.4	-63.1	-3.2	0.0	>43,500
	G-3	-10.2	-68.6	-2.8	n.a.	n.a.
		-10.2	-70.3	-4.8	0.0	>43,500
III	G-4	-9.1	-62.0	-3.8	n.a.	n.a.
		-9.1	-62.6	-2.1	0.0	>43,500
	G-5	-9.2	-62.5	-3.2	0.7	$40,010 \pm 500$
		-9.2	-59.0	-1.8	n.a.	n.a.
		-9.2	-59.5	-2.3	0.0	>43,500
IV	G-6	-9.1	-61.3	-2.9	0.0	>43,500
		-9.0	-58.7	-3.7	n.a.	n.a.
		-9.1	-59.0	-3.1	0.0	>43,500
	G-7	-9.5	-61.4	-4.0	n.a.	n.a.
	G-8	-9.1	-62.1	-4.1	n.a.	n.a.
			, 1	1		

n.a.: not analyzed.

However, the P_{CO2} and the carbon stable isotope ratios of DIC were not different regardless of groups (Figure 5). The P_{CO2} was in the range of 0.47 to 2.19 atm (average $P_{CO2} = 0.97$ atm), which is relatively high compared to the general P_{CO2} in the air (0.0003 atm) and soil (0.003 to 0.01 atm)

and similar to P_{CO2} (0.32 to 2.83 atm) reported in the CO₂-rih groundwater in the GSB [41,46]. The carbon stable isotope ratios of DIC were in the range between -6.3 and -0.6‰ (average $\delta^{13}C = -3.1\%$), which are corresponding to the range of magmatic sources (-8 to -1‰; [48,50,51]).



Figure 5. Partial pressure of CO₂ versus stable carbon isotopic composition of dissolved inorganic carbon (δ^{13} C) in water from the CO₂-rich springs.

4.2. Geophysical Survey

The ERT results show a wide range of resistivity values from 1 to ca. 3700 Ω ·m (Figure 6). Along the ERT-1, a low resistivity zone of <63 Ω ·m was located from surface to 100 m depth below the spring G-5 (Figure 6a). The low resistivity zone of 23–63 Ω ·m was separated by a relatively high resistivity zone (>126 Ω ·m) around 30 m depth. Low resistivity zones were also seen at a distance of 40 to 100 m and 120 to 200 m on the left end side, while no CO₂-rich spring was found. Excluding these low resistivity zones, the high resistivity zones of 451 to 3715 Ω ·m were distributed in the subsurface along the ERT-1.



Figure 6. The results of electrical resistivity tomography along the survey lines: (**a**) ERT-1 and (**b**) ERT-2 (see Figure 1 for location). In (**b**), G-1 and G-6 are separate by approximately 7 m; the water running above ground at YD-01 is the seepage water affected by the deep-seated CO₂ [52].

On the other hand, a low resistivity zone of 23–63 Ω ·m was observed from 20 to 60 m depth below the springs G-1 and G-6 along the ERT-2 (Figure 6b). In addition, a lower resistivity zone of <23 Ω ·m was observed down to 20 m depth from the surface below the springs. Low resistivity zones of <63 Ω ·m were also found between the distance of 40 and 120 m and between 130 and 170 m, but no CO₂-rich spring has been reported around those regions. Instead, a CO₂-rich surface water sample (YD-01 in Figure 6b) was reported by Kang et al. [52] just above the low resistivity zone at 220 m distance and approximately 40 m left of the G1. To the right of the low resistivity zone below the springs G-1 and G-6, there was a general trend of gradual increase in resistivity with depth without any noticeable low resistivity zones.

It should be noted that the springs G-1 (Group I) and G-6 (Group IV) were hydrochemically distinct (Table 1) and thus classified into the different water group (Figure 2) despite the similar location (i.e., about 7 m separation in Figures 1b and 6b), while ERT could not explain the difference (Figure 6b) probably due to low resolution. Besides, EC in G-5 was higher than that in G-6 (Table 1), while the lower resistivity of 8–23 Ω ·m was observed below G-6, probably because the electrical resistivity is affected by solid materials (e.g., small particles) as well as fluids [53].

5. Discussion

5.1. Source and Discharge Pathways of CO₂

The high P_{CO2} values suggest the influx of external CO₂ (Table 3; Figure 5). The enriched δ^{13} C of DIC (average -3.1%) indicates that the elevated P_{CO2} in the springs might be originated from the reaction between groundwater and deep-seated CO₂ such as magmatic CO₂. The relatively low ¹⁴C activities also suggest the deep-seated CO₂ sources and little impacts of soil CO₂ and carbonates since the CO₂-rich springs excluding G-2 are in the granitoids with scarce carbonate minerals and no sources of ¹⁴C-free DIC except deep-seated CO₂. As for the spring G-2 situated on the sedimentary rock (Figure 1), the main source of CO₂ is also estimated to be the deep-seated CO₂ based on the geological characteristic that the granite and andesite intruded the sedimentary rocks in G-2 [40]. Similarly, previous studies about the naturally occurring CO₂-rich springs in South Korea suggested that the P_{CO2} in these springs were originated from the dissolution of deep-seated CO₂ using noble gases and carbon isotope ratios [40,42,46,52,54]. The gas samples exsolved from CO₂-rich springs in Cheongsong and Yeongdeok granitoids showed the higher ³He/⁴He ratios than the atmospheric and crustal-derived gases, indicating deep-seated sources such as mantle [42,46]. When considering the ${}^{3}\text{He}/{}^{4}\text{He}$ and ${}^{4}\text{He}/{}^{20}\text{Ne}$ ratios altogether, the gas samples obtained from CO₂-rich springs were placed in the mantle origin or in the mixed region of the mantle origin and the atmospheric origin [42,46]. We acknowledge that the δ^{13} C of DIC could be affected by carbonates given the sedimentary rocks in this region (Figure 1), while calcite may precipitate during degassing, affecting the δ^{13} C of DIC in water [51], which needs to be further studied to understand carbon systems.

Faults seem to be related with a discharge pathway of deep-seated CO₂ since all CO₂-rich springs occur within 2 km from the NS-trending strike-slip faults (Figure 1b) and the low resistivity zones were vertically observed below the CO₂-rich springs (Figure 6). We can estimate the low resistivity zones of <126 Ω ·m to be aquifers, with considering the surface geology and features detected from aerial photographs and field works and the locations of the CO₂-rich springs, although the absolute resistivity values corresponding to the properties of the geologic materials are unknown in the study area. Besides, the relatively low resistivity zones of <63 Ω ·m can be considered to be ascending pathways of high-TDS CO₂-rich water because electrical resistivity decreases when CO₂ sources enhance the water-rock interactions and increase EC [32,53,55], although electrical resistivity may increase when a significant amount of CO₂ gas invades into the saturated sediments of an aquifer because the CO₂ migrates to the shallow subsurface along the faults nearby the CO₂-rich springs in the GSB [27,41].

5.2. Hydrochemical Evolutionary Processes

Different hydrochemistry indicates the different hydrochemical evolution of CO_2 -rich springs from the reservoir affected by CO_2 to each spring. Note that the reservoir is not identified in this study, which remains future work.

5.2.1. Group I and II

Group I seems to represent a relatively fast rising through open fractures, while Group II seems to represent slow rising along rock discontinuities and extensive CO2-water-rock interactions over a long residence time as in Figure 7 based on the following results: First, the δD and $\delta^{18}O$ values of Group I were the heaviest, whereas those of Group II were the lowest (Figure 4a), which suggests the shortest and longest recharge pathway, respectively. The previous studies of CO₂-rich springs in South Korea showed that the lighter isotope ratios of CO_2 -rich water indicate the higher recharge altitudes and longer residence times [24,27,56–58]. A study using groundwater samples from various depths in the GSB also revealed that groundwater with a lighter water isotope has a relatively longer residence time and more water-rock interactions [59]. Second, Group II contained high pH, TDS, and contents of Na, K, F, and Li, which are well-known indicators of water-rock interactions in silicate bedrock [59,60], while Group I showed low pH and TDS indicating the impact of CO₂ sources but little water-rock interactions. Third, ¹⁴C was not detected in Group II, while Group I showed higher ¹⁴C contents than the other groups, implying the mixing with relatively young groundwater unlike the other groups. In addition, NO₃⁻, which is the indicator of anthropogenic activity, was high in Group I, which suggests the effect of both recently recharged groundwater and fast rising CO₂-rich fluid in Group I. Fourth, the relatively narrow and vertical distribution of low resistivity zones below the CO₂-rich springs G-1 and G-6 suggested a separate pathway for G-1 similar to for YD-01 (Figure 6b) since the G-1 and G-6 showed the different hydrochemistry (Table 1) despite the similar location (i.e., about 7 m separation in Figure 6b). According to Kang et al. [52], YD-01 was not surface water but CO₂-rich groundwater discharging to the surface and had similar hydrochemical and isotopic characteristics to G-1. It appears that the high-EC CO₂-rich groundwater rising from the depth of 60 m is divided into two (i.e., YD-01 and G-1) by the high resistivity zone at 220–250 m distance.



Figure 7. Evolutionary processes suggested for each group.

Highly connected open fractures seem to cause a fast movement of deep-seated CO₂ at G-1 and YD-01, shortening the residence time and making little water-rock interaction. A hydrochemical evolving process can be suggested for Group I as: CO₂ ascends to a shallow aquifer along a conduit (i.e., NS-trending fault and fracture in this study), is dissolved in groundwater, lowering pH and increasing P_{CO2} , while the water-rock interaction is less advanced, causing low pH and EC. There have been several studies that reported CO₂-rich springs with low pH and TDS as Group I in similar geologic conditions [23,57,58,61], which showed that the low pH and TDS in CO₂-rich springs resulted from the continuous inflow of deep-seated CO₂ to shallow aquifers, causing high PCO₂ (average 0.8 atm) and heavy carbon isotope ratios of DIC (average -7.1%), but short residence times (<35 years) based on the tritium data.

The highest concentration of aluminum (Al) exceeding the guideline for drinking-water quality of the World Health Organization (WHO) [47] in Group I suggests the aluminum can be risky at the early stage of CO_2 leakage to groundwater, probably due to its high mobility at low pH [62]. Aluminum is immobilized in the pH range of about 6 to 8, while mobilized as cations and anions at pH below and above the range, respectively. The pH of Group I was as low as 5.14 on average, and thus the Al might exist in the form of $Al(OH)_2^+$, increasing the Al concentration, whereas the pH of the other groups was in the range of 5.96 to 6.48, in which Al is precipitated and immobilized.

Meanwhile the evolutionary process for Group II can be suggested as in Figure 7: groundwater acidified by CO₂ travels along less connected fracture networks and undergoes a water-rock interaction over a long residence time. The Fe, Mn, and As concentrations in Group II exceeded the WHO guidelines. Group II showed highest As as well as Li (Table 2). Arsenic is a representative chalcophile element [63,64] and known to have good affinity with sulfur. It can be considered that arsenic contained in sulfide minerals was eluted during extensive CO₂-water-rock interactions given high sulfate concentrations in Group II (Table 1; Figure 3). Besides, Group II occurs at different geology from the other groups (Figure 1), which might affect the high As concentrations.

5.2.2. Group III and IV

Group III and IV showed the similar δD and $\delta^{18}O$ between Group I and II (Figure 4a), implying the similar recharge altitudes and had similar hydrochemical composition to Group II with high TDS (Figure 2). ¹⁴C concentrations were not detected except a sample in Group III (Figure 4b). Thus, Group III and IV also seem to have a longer residence time in the subsurface than Group I (Figure 7). Similarly, Kang et al. [52] suggested long residence times of G-6 (Group IV) by slow upward movement of CO₂-rich groundwater through narrow or less-connected fractures unlike G-1 (Group I). However, there were different hydrochemical properties between Group III and IV (Figure 3; Tables 1 and 2). In particular, Group IV had lower Na and K concentrations than Group III, while higher concentrations of Ca, Sr, Zn, Ba, Fe, Mn, U, and thus Ca/Na (Figure 8), although the levels of Fe, Mn, and U exceeded the WHO guidelines in both groups (Table 2).

The difference in hydrochemistry between the two groups from the same bedrock geology (Yeongdeok granitoid) is presumed to be due to different degrees of water-silicate rock interaction. In particular, the dissolution of plagioclase, which is the major component of the Yeongdeok granite, can account for the hydrochemical difference. At low temperature conditions, the different solubility of albite and anorthite causes the enrichment of Ca in water and thus increases the Ca/Na ratio as the dissolution of plagioclase proceeds [65]. However, the solubility difference between albite and anorthite decreases dramatically with increasing temperature [66]. Thus, the Ca/Na ratio in water tends to decrease at high temperature conditions. For instance, the calculated Ca/Na ratio of a water sample in equilibrium with plagioclase containing 20 wt % of anorthite was estimated to be 700 at 25 °C, while the ratio decreased to ca. 70 and 20 at 50 °C and 75 °C, respectively in [66]. In the field, the Ca/Na ratio can be lower than the estimation due to calcite precipitation at high temperature.



Figure 8. Useful hydrochemical parameters: Li, K, and Ca/Na.

In the study area, the Ca/Na ratio of Group III (average 1.65) was about three times lower than that of Group IV (average 5.12) similar to Group I (average 1.42) (Figure 8), which can be explained by the different reaction temperature based on the different depth of low resistivity zones of <63 Ω ·m (Figure 6), with assuming that the low resistivity zones represent the reservoirs of CO₂-rich groundwater with relatively high EC since EC of the fluid is inversely proportional to the electrical resistivity [53]. Specifically, the low resistivity zone (<63 Ω ·m) widely distributed below 40 m depth in Figure 6a suggests that the spring G-5 (Group III) has a large CO₂-rich reservoir extending to a depth of >100 m. Whereas the ERT-2 showed the low resistivity zones of <63 Ω ·m down to 60 m depth below G-6 (Group IV). In particular, the low resistivity zone of <23 Ω ·m at a depth of 0–20 m distributed at 250–290 m distance along ERT-2 can be considered to be a reservoir for Na-depleted high-TDS CO₂-rich water (i.e., Group IV).

Given the average geothermal gradient of the study area of 28.3 °C/km (http://kredc.kier.re.kr) and assuming 100 m difference in the reservoir depth, the difference in reaction temperature between the two groups would be 2.8 °C similar to the difference in measured temperature between Group III and Group IV (3.1 °C) in Table 1. Due to the low reaction temperature in the reservoir for Group IV probably at shallow depths, the Ca/Na ratio increases mainly as a result of dissolution of anorthite, while Li is low since Li is mobilized by the albite dissolution [67]. Subsequently, the significantly high concentrations of divalent metal ions (Sr, Zn, Ba, Fe, and Mn) in Group IV can be explained with their affinity with Ca [63,67]. In addition, it is known that the mobility of U is enhanced when the Ca content is high because the formation of calcium uranyl carbonate complexes (e.g., $Ca_2UO_2(CO_3)_3$) inhibits the sorption of U ions to the mineral surface [68–70].

Namely, an evolutionary process for Group IV can be suggested as in Figure 7: groundwater is reacted with CO_2 in a relatively shallow and low-temperature aquifer similar for Group I, but slowly moves along less connected fractures unlike for Group I, thus shows high TDS. Group III may have a deep and high-temperature reservoir and move slowly from the reservoir to the discharge point.

5.3. Useful Hydrochemical Parameters

The study results indicate that the rising and dissolution of deep-seated CO_2 and subsequent CO_2 -water-rock interaction in the silicate bedrock can cause various hydrochemical compositions in groundwater depending on the evolutionary process as in Figure 7. Based on the study result, hydrochemical parameters such as pH, TDS, Na, K, Mg, SO₄, HCO₃, Li and their ratios as Ca/Na were

useful indicators to trace the evolving process of groundwater triggered by CO₂ leakage (Figures 3 and 8), despite the similar P_{CO2} and δ^{13} C. δ^{18} O and δ D were also useful, reflecting the length of reaction pathways, while ¹⁴C addressed the impact of recently recharged groundwater.

Specifically, the significantly lower pH and higher P_{CO2} than the surrounding groundwater but little change in TDS indicate the early stage of CO₂ leakage. When CO₂ leaks as in Group I (Figure 7), the pH decreases and P_{CO2} increases as CO₂ dissolves in groundwater, but the reaction time is short, and thus the reaction with surrounding aquifer sediments or rocks does not much proceed. For this reason, the ionic concentrations of groundwater do not increase noticeably. However, Al can be risky due to the low pH. In contrast, the later stage of CO₂ leakage can be determined by high TDS, Na, K, and Li as in Group II because of extensive water-rock interactions. In general, the contents of monovalent ions such as Na, K and Li increase as the water-rock interaction proceeds [67]. Besides, the Ca/Na ratio is effective to distinguish the reaction depth between CO₂ and groundwater as for Group III and IV.

6. Conclusions

Naturally occurring CO₂-rich springs were classified into four groups according to the hydrochemical compositions. Then the evolutionary process of each CO₂-rich spring group was assessed based on the combined result of hydrochemical, environmental isotopic, and geophysical studies. Hydrochemical, ¹⁴C, and hydrogen and oxygen isotopic results as well as the ERT survey result suggest that Group I (low pH and TDS) is formed by fast ascending of CO₂ along faults and/or fractures and experiences the CO₂ dissolution into shallow groundwater but little water-rock interactions, whereas Group II (Na-enriched and high TDS) ascends through less-connected fracture networks and experiences extensive CO₂-water-rock interactions. According to the same geology and similar ¹⁴C concentrations and hydrogen and oxygen isotopic compositions, Group III (Na-intermediate and high TDS) and IV (Na-depleted and high TDS) have similar recharge altitudes, while different reaction temperatures may cause hydrochemical differences, in particular Ca/Na between two groups. Group IV seemed to have a shallower reservoir than Group III based on the higher Ca/Na and shallower depth of low resistivity zone of <63 Ω ·m, although we did not identify the reservoir affected by deep-seated CO₂ in this study.

The study result suggests that the combined use of pH, TDS, Na, K, Li, and Ca/Na are effective hydrochemical M&V parameters to assess the leakage stages in silicate rocks in GCS projects. A decrease in pH is noticeable at the beginning of the CO_2 leakage, and the Ca/Na ratio decreases while the Na and Li content and TDS increase with extensive CO_2 -water-rock interactions. However, if the groundwater affected by CO_2 is shallow, the Ca/Na ratio can be higher than the estimation in silicate rocks, and divalent metal ions are also enriched with increasing Ca. Besides, this study reveals that the groundwater quality can be degraded by Al contamination in the early stage of CO_2 leakage, and by high levels of Fe, Mn, and U in the later stage or arsenic depending on the geology.

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