Evaluation of Long-Term Impacts of CO₂ Leakage on Groundwater Quality Using Hydrochemical Data from a Natural Analogue Site in South Korea

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Abstract: Three hydrochemical types of CO₂-rich water (i.e., Na-HCO₃, Ca-Na-HCO₃ and Ca-HCO₃) occur together in the silicate bedrock (granite and gneiss) of Gangwon Province in South Korea. As a natural analogue of geological carbon storage (GCS), this can provide implications for the environmental impacts of the leakage of CO₂ from deep GCS sites. By using hydrochemical and isotopic datasets that were collected for previous and current studies, this study aimed to carefully scrutinize the hydrochemical differences in the three water types with an emphasis on providing a better understanding of the impacts of long-term CO₂ leakage on groundwater quality (especially the enrichments of minor and trace metals). As a result, the Na-HCO₃ type CO₂-rich water contained higher Li, Rb and Cs than the Ca-HCO₃ type, whereas Fe, Mn and Sr were higher in the Ca-HCO₃ type than in the Na-HCO₃ type despite the similar geological setting, which indicate that the hydrochemical differences were caused during different geochemical evolutionary processes. The δ¹⁸O and δD values and tritium concentrations indicated that the Na-HCO₃ type was circulated through a deep and long pathway for a relatively long residence time in the subsurface, while the Ca-HCO₃ type was strongly influenced by mixing with recently recharged water. These results were supported by the results of principal component analysis (PCA), whose second component showed that the Na-HCO₃ type had a significant relation with alkali metals such as Li, Rb and Cs as well as Na and K and also had a strong relationship with Al, F and U, indicating an extensive water-rock interaction, while the Ca-HCO₃ type was highly correlated with Ca, Mg, Sr, Fe and Mn, indicating mixing and reverse cation exchange during its ascent with hydrogeochemical evolution. In particular, the concentrations of Fe, Mn, U and Al in the CO₂-rich water, the result of long-term water-rock interaction and cation exchange that was enhanced by CO₂ leakage into silicate bedrock, exceeded drinking water standards. The study results show that the leakage of CO₂ gas and CO₂-rich fluid into aquifers and the subsequent hydrogeochemical processes can degrade groundwater quality by mobilizing trace elements in rocks and consequently may pose a health risk.

Keywords: CO₂ leakage; long-term impact; groundwater quality; trace metal; natural analogue

1. Introduction

Carbon dioxide stored in geological carbon storage (GCS) sites can migrate upwards from a storage reservoir through various paths such as faults, fractures, small cracks in caprocks, and
borehole annulus [1–5]. Even though GCS is a promising technology for substantially reducing CO₂ emissions [6,7], such migration of CO₂ gas and CO₂-rich fluid into freshwater aquifers may lead to the degradation of potable groundwater by total dissolved solids and trace metals, and moreover the leakage itself means the failure of net CO₂ reduction [8–11]. Therefore, accurate monitoring of CO₂ leakage into potable aquifers is crucial for the successful, safe and long-term storage of CO₂. Among various groundwater monitoring methods, hydrochemical and isotopic analyses have been widely used to detect CO₂ leakage and evaluate its potential impact on groundwater quality [9,12–14].

The extent and rate of hydrogeochemical reactions caused by the inflow of CO₂ may differ depending on the geological and geochemical conditions of aquifers [12,15–17]. Therefore, to find a geochemical index for CO₂ leakage detection and to evaluate the impact of CO₂ leakage on groundwater quality, the hydrochemical responses to the inflow of CO₂ into aquifers have been studied in various ways such as in laboratory experiments [1,10,18,19], controlled CO₂ injection field tests [9–12,20,21], and natural analogues [8,15,22–24]. A natural analogue study with CO₂-rich water is the best way to observe the hydrochemical changes caused by a long period of CO₂ supply [8,12]. The hydrochemical and isotopic data of CO₂-rich water improve our understanding of the potential risks associated with the long-term leakage and migration of CO₂ into potable aquifers.

In this study, careful reevaluations of hydrochemical and isotopic data of CO₂-rich water were conducted in a natural analogue site in South Korea (Figure 1) to evaluate the long-term impact of CO₂ leakage on groundwater quality in silicate bedrock areas. In particular, the levels of trace elements were investigated with respect to hydrogeochemical processes depending on water types to understand the relationship between geochemical processes and water quality in GCS sites. It should be noted that CO₂-rich water in the study area has been partly or wholly studied by the current authors [25–27] and others [28,29]. However, the previous studies focused on the identification of geochemical processes causing hydrochemical differences in CO₂-rich water, and did not evaluate the impact of leaked CO₂ on minor and trace elements in CO₂-rich water, although the increases in trace element levels can deteriorate the groundwater quality in potable aquifers [8,24,30].

**Figure 1.** Geological map with cross sections (A-A’ and B-B’) of the northeastern part of Gangwon Province, South Korea, with the locations of CO₂-rich water (circles), shallow groundwater (squares) and surface water (crosses) (modified after Choi et al. [25]). The water types were classified based on the Piper diagram (see below).
2. Study Area

The study area, Gangwon Province, is located in the northeastern part of South Korea (Figure 1). The geology consists mainly of Precambrian gneisses, Jurassic sedimentary rocks and Mesozoic granitoids. The Mesozoic granitoids contain biotite granite, two-mica granite and porphyry, while the Precambrian gneisses occupying the central part of the study area can be grouped into porphyroblastic, banded and leucocratic gneiss [25,31]. The banded gneiss is widely exposed in the study area and shows pytgmatic folding structures and leucocratic gneiss facies [32]. The Jurassic fine-grained biotite granite is present as small intrusions, whereas the biotite granite is intruded into the banded gneiss as a large batholith (Figure 1).

The major geological structures in the study area are the Whocheon fault (in the center of Figure 1), the Woaljeongsa fault (in the southeastern part), the Yeongok fault (in the eastern part) and unnamed faults (Figure 1). The Whocheon, Woaljeongsa and unnamed faults are aligned from northeast to southwest on the Korean Peninsula, formed during the late Cretaceous, and predate the Yeongok fault that is aligned in the east-west direction [25,33]. The study area is characterized by steep mountain slopes. Mt. Sorak and Mt. Odae have an elevation exceeding 1000 m above sea level (Figure 1). The steep topography, with a relief of more than 1000 m between mountaintops and foothills, causes great hydraulic gradients and in turn possibly large circulation depths of groundwater in the study area.

As described by Choi et al. [25], CO$_2$-rich water typically occurs within the biotite granites of the Jurassic period and in the vicinity of the Jurassic biotite granite and the Precambrian gneiss, and the occurrence of CO$_2$-rich water seems to be closely related to faults (Whocheon, Woaljeongsa and unnamed faults) aligned in the northeast-southwest direction (Figure 1). In fact, the CO$_2$-rich water normally flows out as springs adjacent to the valleys formed by such faults [25,26].

3. Sampling and Analyses

Water samples were obtained during several sampling campaigns from August to October in 1998, July 1999, February, September and October in 2000, April in 2002, and November in 2010 for hydrochemical and isotopic analyses. A total of 44 water samples were collected from 14 CO$_2$-rich springs ($n = 32$), four shallow groundwater wells ($n = 6$) and streams ($n = 6$) in the vicinity of the CO$_2$-rich springs (Figure 1). In addition, 16 rock samples were taken from outcrops around the CO$_2$-rich springs for chemical composition analysis to see the geological effect on the hydrochemistry of CO$_2$-rich springs.

Temperature, pH, redox potential (Eh), electrical conductivity (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 impact of atmospheric oxygen. Alkalinity was determined on-site by titration with HCl solution (0.5N and 0.05N) as soon as the water was sampled to minimize CO$_2$ degassing from the CO$_2$-rich water. All water samples were filtered. Then the samples were acidified for major cation and minor/trace element analyses. Dissolved inorganic carbon (DIC) was precipitated using BaCl$_2$ for the carbon isotopic composition ($\delta^{13}$C) analysis of water samples.

Major cations (Na, K, Mg, Ca) and SiO$_2$ were determined using ICP-AES (Shimadzu, ICP-11000 III) at the Korea Basic Science Institute (KBSI). Minor to trace elements (Fe, Sr, Mn, Al, Li, B, Cr, Zn, Rb, Cs, Ba, U) were analyzed by ICP-MS (FISONs, PlasmaTrace) at KBSI. Anions (Cl, SO$_4$, NO$_3$, F) were analyzed using IC ( Dionex, DX-500) at the Korea Atomic Energy Research Institute (KAERI) and the Center for Mineral Resources Research (CMR) of Korea University. Charge balance errors were within an acceptable range of ±10% for all water samples, with most of the samples being <5%.

The $\delta^{18}$O and $\delta$D values of water were determined using a stable isotope ratio mass spectrometer (VG SIRA II and Micromass Optima) at KAERI by equilibrium with CO$_2$ gas [34] and reduction of water [35], respectively. The $\delta^{18}$O and $\delta$D values were measured relative to the internal standards that were calibrated with V-SMOW, GISP and SLAP standards. The $\delta^{13}$C was determined using a VG SIRA II at KAERI. The tritium concentrations of water were measured using an electrolytic enrichment process by a liquid scintillation counter (Packard Tricarb 2770SL/TR) at KAERI. The chemical compositions of rock samples were analyzed using an X-ray fluorescence spectrometer (Phillips, PW 2404) at KBSI.
In addition, the partial pressures of CO$_2$ (P$_{CO2}$) were calculated using PHREEQC software [36]. Principal component analysis (PCA) was performed using IBM SPSS Statistics for Windows, version 23 (IBM Corp., Armonk, NY, USA) to characterize major geochemical processes. PCA transforms a number of correlated variables into a smaller number of uncorrelated variables called principal components. All variables were standardized before PCA to remove the effect of scale differences in variables [37].

The results of field measurements and laboratory analyses of water samples are shown in Tables 1–3, while the results of the chemical analysis of representative rock samples are shown in Table 4. It should be noted again that some datasets for a few water and rock samples were utilized by the current authors for previous studies with different research purposes. The sources of previously used data are clearly given in each table as captions.
Table 1. Physicochemical data of water samples in the Gangwon Province of South Korea. CO2-rich water is grouped based on the Piper diagram (see Figure 3).

| Sample No. (1) | Sampling Date | Temp. (°C) | pH | Eh (mV) | EC (µS/cm) | DO (mg/L) | TDS (mg/L) | Log P CO2 (atm) (2) | Na (mg/L) | K (mg/L) | Mg (mg/L) | Ca (mg/L) | SiO2 (mg/L) | Cl− (mg/L) | SO4 2− (mg/L) | NO3 − (mg/L) | F− (mg/L) | Alk. (3) |
|----------------|---------------|------------|----|---------|------------|----------|------------|----------------|-----------|---------|-----------|-----------|-------------|----------|-------------|--------------|---------|--------|
| CO2-rich water (Na-HCO3 type) | | | | | | | | | | | | | | | | | | | |
| KW-1(a) | Sep-01-98 | 19.4 | 6.04 | 318 | 1345 | 2.6 | 1629 | -0.02 | 345.0 | 23.0 | 1.6 | 31.5 | 79.6 | 7.0 | 12.9 | 0.1 | 7.5 | 1117 |
| KW-1(b, c) | Jul-07-99 | 18.5 | 6.24 | 326 | 1348 | 3.1 | 1773 | -0.21 | 419.0 | 25.0 | 2.1 | 44.6 | 87.7 | 8.3 | 13.8 | n.d. | 7.7 | 1159 |
| KW-2(a) | Apr-08-02 | 9.6 | 6.38 | 264 | 1469 | 4.2 | 1641 | -0.36 | 377.3 | 18.7 | 1.4 | 36.6 | 68.2 | 6.8 | 11.0 | 0.4 | 5.0 | 1113 |
| KW-3 | Mar-01-98 | 14.5 | 5.52 | 254 | 725 | 2.4 | 714 | 0.15 | 71.4 | 4.5 | 7.3 | 76.1 | 32.5 | 6.7 | 16.2 | 16.1 | 0.3 | 2.4 | 488 |
| KW-3′(a) | Apr-08-02 | 14.3 | 5.85 | 335 | 1956 | 1.2 | 1846 | 0.21 | 455.0 | 13.0 | 5.2 | 54.0 | 61.0 | 8.3 | 8.0 | 0.1 | 4.9 | 1233 |
| KW-4′(a) | Jul-07-99 | 19.8 | 6.43 | 343 | 1871 | 1.5 | 1921 | -0.35 | 457.0 | 10.5 | 5.1 | 53.2 | 60.1 | 8.6 | 7.3 | n.d. | 4.8 | 1312 |
| KW-5′(a, c) | Apr-08-02 | 9.8 | 6.65 | 237 | 1713 | 0.5 | 1947 | -0.56 | 484.4 | 7.6 | 4.0 | 46.3 | 48.1 | 8.1 | 6.1 | n.d. | 3.1 | 1334 |
| KW-5′′(a) | Nov-19-10 | 9.7 | 6.62 | 280 | 1837 | 1.2 | 1903 | -0.54 | 433.7 | 13.0 | 4.6 | 57.8 | 59.5 | 21.7 | 8.8 | n.d. | 6.9 | 1304 |
| CO2-rich water (Ca-Na-HCO3 type) | | | | | | | | | | | | | | | | | | | |
| KW-5 | Jul-01-98 | 14.5 | 5.52 | 254 | 725 | 2.4 | 714 | 0.15 | 71.4 | 4.5 | 7.3 | 76.1 | 32.5 | 6.7 | 16.1 | 0.3 | 2.4 | 488 |
| KW-5′(a) | Jul-07-99 | 16.2 | 5.70 | 357 | 778 | 2.1 | 775 | 0.00 | 91.8 | 4.0 | 8.6 | 88.4 | 37.9 | 2.1 | 12.7 | n.d. | 2.6 | 519 |
| KW-5′′(a, c) | Apr-08-02 | 17.2 | 5.67 | 287 | 695 | 1.9 | 675 | 0.33 | 91.1 | 2.1 | 6.4 | 71.2 | 24.3 | 6.7 | 12.0 | n.d. | 1.9 | 473 |
| KW-5′′′(a) | Nov-18-10 | 10.4 | 5.91 | 398 | 990 | 1.3 | 982 | -0.12 | 106.6 | 6.7 | 10.3 | 120.9 | 40.5 | 33.3 | 13.0 | n.d. | 6.5 | 653 |
| KW-7(b, c) | Apr-08-02 | 13.5 | 6.45 | 237 | 894 | 2.1 | 967 | -0.66 | 89.7 | 2.4 | 11.9 | 134.2 | 37.5 | 11.2 | 7.9 | 5.4 | 2.7 | 656 |

CO2-rich water (Ca-HCO3 type)
Table 1. Cont.

| Sample No. | Sampling Date | Temp. (°C) | pH | Eh (mV) | EC (µS/cm) | DO (mg/L) | TDS (mg/L) | Log P_{CO2} (atm) (2) | Na | K | Mg | Ca | SiO_2 | Cl^- | SO_4^{2-} | NO_3^- | F^- | Alk. (3) |
|------------|---------------|------------|----|---------|------------|-----------|------------|----------------------|----|---|----|----|-------|------|----------|-------|-----|--------|
| KW−16      | Jul−01−98     | 20.2       | 6.56 | 379    | 125        | 5.8       | 86         | −2.11                | 15.1 | 1.1 | 1.5 | 5.3 | 12.3  | 11.2 | 8.0       | 1.4   | 2.3 | 27     |
| KW−16'     | Feb−17−00     | 6.8        | 6.78 | 342    | 101        | 6.5       | 78         | −2.51                | 9.8  | 0.6 | 2.4 | 5.4 | 11.0  | 14.8 | 11.6      | 4.1   | 0.3 | 18     |
| KW−16"     | Oct−16−00     | 22.0       | 6.13 | 317    | 268        | 7.5       | 181        | −1.47                | 36.7 | 1.3 | 0.52 | 7.2 | 23.1  | 25.8 | 39.0      | 1.7   | 0.2 | 45     |
| KW−17      | Sep−05−00     | 25.7       | 6.75 | 405    | 234        | 6.0       | 208        | −1.75                | 36.4 | 1.2 | 1.12 | 18.7| 15.8  | 9.5   | 17.4      | 8.1   | 2.7 | 98     |
| KW−18(a)   | Jul−01−98     | 13.7       | 6.49 | 452    | 69         | 7.0       | 63         | −2.09                | 6.0  | 0.7 | 1.6 | 3.7 | 19.4  | 4.8   | 1.4       | 0.4   | 0.4 | 24     |
| KW−20(a)   | Jul−07−99     | 17.1       | 6.27 | 378    | 35         | 6.3       | 39         | −2.07                | 3.1  | 0.5 | 0.6 | 3.5 | 10.1  | 0.9   | 2.5       | 2.3   | 0.2 | 15     |
| KW−55      | Jul−01−98     | 14.5       | 6.75 | 366    | 94         | 9.4       | 56         | −2.35                | 6.9  | 1.7 | 1.4 | 3.7 | 7.5   | 3.7   | 3.4       | 2.4   | 0.5 | 24     |
| KW−8S      | Oct−30−98     | 13.4       | 7.77 | 354    | 53         | 9.4       | 52         | −3.36                | 2.1  | 0.5 | 0.9 | 6.8 | 9.9   | 1.0   | 4.1       | 1.4   | 0.0 | 25     |
| KW−9S      | Oct−30−98     | 13.0       | 7.46 | 384    | 47         | 9.1       | 46         | −3.16                | 3.3  | 0.6 | 0.7 | 5.1 | 10.1  | 1.2   | 4.3       | 1.4   | 0.1 | 19     |
| KW−10S     | Oct−30−98     | 10.2       | 6.86 | 389    | 60         | 9.6       | 50         | −2.46                | 1.9  | 0.5 | 0.1 | 8.1 | 8.4   | 0.9   | 4.5       | 1.0   | 0.1 | 24     |
| KW−13S     | Aug−01−98     | 15.2       | 6.87 | 366    | 29         | 6.4       | 29         | −2.89                | 1.8  | 0.4 | 0.6 | 3.3 | 6.4   | 0.7   | 2.2       | 4.2   | 0.1 | 9      |
| KW−14S     | Jul−01−99     | 17.2       | 6.89 | 358    | 46         | 8.7       | 54         | −2.45                | 3.6  | 0.9 | 1.7 | 3.6 | 11.8  | 1.7   | 2.8       | 1.5   | 0.1 | 26     |
| Average of shallow GW | 17.6 | 6.50 | 379 | 139 | 6.5 | 109 | −2.00 | 17.8 | 0.9 | 1.3 | 7.3 | 15.3 | 11.2 | 13.3 | 3.0 | 1.0 | 38     |
| Standard deviation | 6.1 | 0.24 | 43 | 85 | 0.6 | 63 | 0.32 | 13.7 | 0.3 | 0.6 | 5.2 | 4.7 | 7.9 | 12.7 | 2.5 | 1.1 | 28     |
| Surface water |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| KW−5S      | Jul−01−98     | 14.5       | 6.75 | 366    | 94         | 9.4       | 56         | −2.35                | 6.9  | 1.7 | 1.4 | 3.7 | 7.5   | 3.7   | 3.4       | 2.4   | 0.5 | 24     |
| KW−8S      | Oct−30−98     | 13.4       | 7.77 | 354    | 53         | 9.4       | 52         | −3.36                | 2.1  | 0.5 | 0.9 | 6.8 | 9.9   | 1.0   | 4.1       | 1.4   | 0.0 | 25     |
| KW−9S      | Oct−30−98     | 13.0       | 7.46 | 384    | 47         | 9.1       | 46         | −3.16                | 3.3  | 0.6 | 0.7 | 5.1 | 10.1  | 1.2   | 4.3       | 1.4   | 0.1 | 19     |
| KW−10S     | Oct−30−98     | 10.2       | 6.86 | 389    | 60         | 9.6       | 50         | −2.46                | 1.9  | 0.5 | 0.1 | 8.1 | 8.4   | 0.9   | 4.5       | 1.0   | 0.1 | 24     |
| KW−13S     | Aug−01−98     | 15.2       | 6.87 | 366    | 29         | 6.4       | 29         | −2.89                | 1.8  | 0.4 | 0.6 | 3.3 | 6.4   | 0.7   | 2.2       | 4.2   | 0.1 | 9      |
| KW−14S     | Jul−01−99     | 17.2       | 6.89 | 358    | 46         | 8.7       | 54         | −2.45                | 3.6  | 0.9 | 1.7 | 3.6 | 11.8  | 1.7   | 2.8       | 1.5   | 0.1 | 26     |
| Average of surface water | 13.9 | 7.10 | 370 | 55 | 8.8 | 48 | −2.78 | 3.3 | 0.8 | 0.9 | 5.1 | 9.0   | 1.5   | 3.5       | 2.0   | 0.1 | 21     |
| Standard deviation | 2.1 | 0.38 | 13 | 20 | 1.1 | 9 | 0.38 | 1.8 | 0.5 | 0.5 | 1.8 | 1.8   | 1.0  | 0.8       | 1.1   | 0.1 | 6      |

(1) Data sources in parenthesis: “a” from Choi et al. [27], “b” from Choi et al. [26], and “c” from Choi et al. [25]. (2) Calculated from measured alkalinity and pH data using PHREEQC [36]. (3) Alkalinity as HCO_3^−.
Table 2. The concentrations of minor and trace elements in water samples in the Gangwon Province of South Korea. CO₂–rich water is grouped based on the Piper diagram (see Figure 3).

| Sample No. (1) | Sampling Date | Concentrations (µg/L) |
|---------------|---------------|-----------------------|
|               |               | Fe  | Sr  | Mn  | Al  | Li  | B   | Cr  | Zn  | Rb  | Cs  | Ba  | U   |
| CO₂–rich water (Na–HCO₃ type) |               |     |     |     |     |     |     |     |     |     |     |     |     |
| KW–1(a)       | Sep–01–98     | 1465.0 | 284.1 | 294.0 | 961.0 | 254.0 | 104.0 | 24.0 | 15.7 | 666.0 | 18.1 | 218.0 | 2.6 |
| KW–1'(a, c)   | Jul–07–99     | 5220.0 | 412.0 | 103.0 | 270.0 | 50.9  | 16.4  | 5.7  | 8.4  | 121.0 | 22.4 | 214.0 | 3.9 |
| KW–1''(b)     | Apr–08–02     | 1215.0 | 337.5 | 133.0 | 457.5 | 107.2 | 69.6  | 2.1  | 26.6 | 178.4 | 17.4 | 188.4 | 3.9 |
| KW–2(a)       | Sep–01–98     | 2543.0 | 453.6 | 341.0 | 1270.0 | 345.0 | 123.0 | 24.8 | 44.2 | 932.0 | 25.1 | 282.0 | 25.1 |
| KW–2'(a, c)   | Jul–07–99     | 2123.0 | 524.0 | 113.0 | 117.0 | 61.9  | 22.9  | 10.7 | 8.3  | 150.0 | 24.9 | 170.0 | 25.0 |
| KW–2'''(b)    | Apr–08–02     | 6752.0 | 420.0 | 154.2 | 196.0 | 141.6 | 107.0 | 14.6 | 29.7 | 189.9 | 21.8 | 118.3 | 16.9 |
| KW–2''''(a)   | Nov–19–10     | 6617.4 | 464.5 | 358.7 | 1517.4 | 607.1 | 146.6 | n.d. | 38.3 | n.a. | n.a. | n.a. | n.a. |
| KW–3          | Sep–01–98     | 3752.0 | 62.4  | 469.0 | 308.0 | 340.0 | 62.0  | 16.0 | 51.1 | 334.0 | 21.5 | 105.0 | 10.0 |
| KW–3'         | Jul–07–99     | 4123.0 | 53.0  | 127.0 | 53.5  | 93.1  | 12.7  | 4.9  | 23.2 | 54.0  | 21.0 | 53.4  | 6.9  |
| KW–3'''(b, c) | Apr–08–02     | 3275.0 | 59.4  | 173.8 | 114.6 | 196.3 | 61.4  | 0.8  | 57.3 | 117.6 | 20.4 | 9.2   | 7.9  |
| KW–4          | Sep–01–98     | 1342.0 | 480.3 | 221.0 | 14.4  | 475.0 | 133.0 | 23.8 | 15.6 | 439.0 | 30.9 | 137.0 | 81.0 |
| KW–4'         | Jul–07–99     | 1794.0 | 495.0 | 95.4  | 3.1   | 220.0 | 37.4  | 8.0  | 12.9 | 80.8  | 30.0 | 105.0 | 56.5 |
| KW–4''''(b, c)| Apr–08–02     | 1235.0 | 519.4 | 105.7 | 8.4   | 317.8 | 123.0 | 2.9  | 23.3 | 137.7 | 28.4 | 44.3  | 60.4 |
| KW–4''''      | Nov–19–10     | 1824.8 | 476.1 | 260.4 | n.d.  | 1336.2 | 138.1 | n.d. | 285.2 | n.a. | n.a. | n.a. |
| Average       |               | 3091.7 | 360.1 | 210.7 | 377.9 | 324.7 | 82.6  | 10.6 | 45.7 | 283.4 | 23.5 | 137.1 | 25.0 |
| Std. Dev.     |               | 1872.7 | 169.9 | 112.8 | 484.4 | 320.4 | 46.3  | 8.8  | 68.1 | 258.2 | 4.2  | 77.2  | 25.3 |
| CO₂–rich water (Ca–Na–HCO₃ type) |               |     |     |     |     |     |     |     |     |     |     |     |     |
| KW–5          | Jul–01–98     | 6267.0 | 1032.2 | 635.0 | 167.0 | 105.0 | 167.0 | 18.0 | 16.5 | 19.0 | 2.1  | 106.7 | 0.7  |
| KW–5'         | Jul–07–99     | 6702.0 | 1263.0 | 329.0 | 95.2  | 41.7  | 35.5  | 8.4  | 8.1  | 12.8 | 2.6  | 106.0 | 0.8  |
| KW–5''''(b)   | Apr–08–02     | 5738.0 | 1031.0 | 254.7 | 101.4 | 125.5 | 80.4  | 2.0  | 13.6 | 17.6 | 2.0  | 90.1  | 1.1   |
| KW–5''''      | Nov–18–10     | 8987.0 | 1554.0 | 968.0 | 386.0 | 296.0 | 175.0 | n.d. | n.d. | n.a. | n.a. | n.a. |
| KW–7(b, c)    | Apr–08–02     | 5653.0 | 1848.0 | 261.7 | 24.3  | 114.5 | 95.9  | 0.9  | 5.9  | 7.7  | 0.5  | 810.2 | 8.2   |
| Average       |               | 6673.4 | 1345.6 | 497.9 | 154.8 | 136.5 | 110.8 | 5.9  | 8.8  | 14.3 | 1.8  | 278.2 | 2.7   |
| Std. Dev.     |               | 1216.4 | 316.2 | 276.7 | 124.1 | 84.9  | 53.1  | 6.7  | 5.8  | 4.4  | 0.8  | 307.2 | 3.2   |
| CO₂–rich water (Ca–HCO₃ type) |               |     |     |     |     |     |     |     |     |     |     |     |     |
| KW–8(b, c)    | Oct–30–98     | 16309.0 | 1733.0 | 857.0 | 25.1  | 60.8  | 4.7   | 56.7 | 5.9  | 8.1  | 0.8  | 112.5 | n.d.  |
| KW–8'(a)      | Nov–19–10     | 15620.2 | 1704.5 | 1335.6 | n.d.  | 91.4  | 97.5  | n.d. | 55.8 | n.a. | n.a. | n.a. |
| KW–9(a, b, c) | Oct–30–98     | 6641.0 | 364.2 | 656.0 | 524.7 | 58.3  | 2.8   | 42.5 | 59.6 | 2.1  | 0.6  | 75.8  | 0.7   |
| KW–10(a, b, c)| Oct–30–98     | 14335.0 | 492.6 | 676.0 | 480.5 | 82.2  | 2.2   | 47.3 | 10.6 | 13.1 | 3.7  | 96.9  | n.d.  |
| KW–10''(a)    | Nov–19–10     | 29981.7 | 867.5 | 1235.5 | 723.7 | 123.5 | 153.6 | n.d. | 43.2 | n.a. | n.a. | n.a. | n.a. |
| Sample No. (1) | Sampling Date | Fe     | Sr     | Mn     | Al     | Li     | B      | Cr     | Zn     | Rb     | Cs     | Ba     | U     |
|---------------|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
| KW–11(c)      | Apr–08–02     | 16256.0|1859.0  |795.7   |83.4    |85.5    |13.4    |9.8     |2.3     |31.5    |7.7     |80.7    |n.d.  |
| KW–12         | Jul–01–99     | 9225.0 |1954.0  |404.0   |3.8     |29.2    |7.3     |9.9     |12.5    |3.3     |0.5     |218.0   |1.1   |
| KW–12′(b, c)  | Apr–08–02     | 8757.0 |1848.0  |293.1   |13.9    |117.8   |12.7    |1.9     |20.3    |4.1     |0.4     |243.2   |1.2   |
| KW–13         | Aug–01–98     | 15231.0|1580.3  |391.0   |2.9     |12.2    |8.0     |12.5    |3.3     |0.5     |218.0   |1.1   |
| KW–13′        | Jul–07–99     | 13812.0|1583.0  |280.0   |10.0    |16.2    |2.6     |0.3     |219.0   |1.2     |0.0     |217.0   |0.3   |
| KW–14(c)      | Jul–07–99     | 25516.0|752.0   |259.0   |5.6     |12.2    |3.9     |8.0     |62.3    |11.5    |1.0     |273.0   |n.d.  |
| KW–14′(b)     | Apr–08–02     | 24830.0|734.3   |237.4   |2.5     |111.3   |2.5     |0.7     |101.2   |0.7     |0.2     |85.3    |0.2   |

**Average** | 3091.7 | 360.1 | 210.7 | 377.9 | 324.7 | 82.6 | 10.6 | 45.7 | 283.4 | 23.5 | 137.1 | 25.0 |

**Std. Dev.** | 1872.7 | 169.9 | 112.8 | 484.4 | 320.4 | 46.3 | 8.8 | 68.1 | 258.2 | 4.2 | 77.2 | 25.3 |

**Shallow groundwater**

| Sample No. | Sampling Date | Fe     | Sr     | Mn     | Al     | Li     | B      | Cr     | Zn     | Rb     | Cs     | Ba     | U     |
|------------|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
| KW–16      | Jul–01–98     | 6.3    |31.1    |0.9     |6.7     |5.7     |5.5     |0.3     |22.0    |1.7     |n.d.   |46.1    |0.3   |
| KW–16′     | Feb–17–00     | 5.2    |25.3    |1.5     |15.4    |1.1     |3.8     |n.d.   |42.1    |1.1     |n.d.   |76.8    |n.d.  |
| KW–16″     | Oct–16–00     | 25.3   |63.4    |1.3     |71.9    |130.9   |21.1    |0.7     |3.3     |1.1     |0.2    |1.8     |6.4   |
| KW–17      | Sep–05–00     | 15.2   |98.6    |1.3     |7.0     |27.6    |16.4    |0.3     |217.7   |0.8     |n.d.   |2.4     |3.4   |
| KW–18(a)   | Jul–01–98     | 6.7    |63.0    |3.4     |4.0     |0.9     |1.9     |2.7     |7.1     |n.d.   |44.2    |n.d.  |
| KW–20(a)   | Jul–07–99     | 23.0   |24.0    |1.2     |17.0    |4.6     |0.6     |12.9    |1.9     |n.d.   |38.4    |0.3   |

**Average** | 13.6 | 50.9 | 1.6 | 20.3 | 27.7 | 8.9 | 0.8 | 50.8 | 1.1 | 0.1 | 34.9 | 1.7 |

**Std. Dev.** | 8.2 | 26.9 | 0.8 | 23.5 | 47.1 | 7.2 | 0.9 | 75.7 | 0.6 | 0.0 | 26.2 | 2.4 |

**Surface water**

| Sample No. | Sampling Date | Fe     | Sr     | Mn     | Al     | Li     | B      | Cr     | Zn     | Rb     | Cs     | Ba     | U     |
|------------|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
| KW–5S      | Jul–01–98     | 67.3   |38.7    |16.9    |53.6    |0.9     |19.5    |2.1     |5.9     |3.0     |n.d.   |36.4    |n.d.  |
| KW–8S      | Oct–30–98     | 34.3   |35.6    |1.8     |1.3     |3.0     |n.d.   |4.3     |0.8     |0.8     |n.d.   |44.1    |n.a.  |
| KW–9S      | Oct–30–98     | 33.5   |36.4    |10.9    |2.6     |3.0     |n.d.   |4.1     |1.3     |0.9     |n.d.   |63.7    |0.7   |
| KW–10S     | Oct–30–98     | 61.2   |36.2    |3.7     |6.0     |1.4     |n.d.   |6.9     |1.1     |1.1     |n.d.   |38.3    |n.d.  |
| KW–13S     | Aug–01–98     | 35.2   |20.8    |1.5     |14.4    |0.2     |33.8    |3.1     |2.6     |0.9     |n.d.   |31.6    |n.a.  |
| KW–14S     | Jul–01–99     | 91.0   |32.0    |2.2     |4.7     |n.d.   |2.6     |0.9     |1.4     |2.0     |n.d.   |106.0   |n.d.  |

**Average** | 53.8 | 33.3 | 6.2 | 13.8 | 9.3 | 3.6 | 2.2 | 1.4 | 53.4 |

**Std. Dev.** | 21.4 | 5.9 | 5.8 | 18.3 | 1.0 | 13.0 | 1.9 | 1.8 | 25.7 |

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Guidelines for Drinking–Water Quality in Chemical Aspects (WHO)

- Fe: 2400 µg/L
- Mn, Sr, Al: 1300 µg/L
- Zn, Rb: 4000 µg/L

Guidelines for Drinking–Water Quality in Acceptability Aspects (WHO)

- Fe, Sr, Mn, Al: 300 µg/L

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Abbreviations: n.a. = not analyzed, n.d. = not detected, Std. Dev. = Standard deviation. (1) Data sources in parenthesis: “a” for Fe by Choi et al. [27]; “d” for data of Fe, Sr, Mn and Al by Choi et al. [26]; and “c” for data of Fe and Al by Choi et al. [25].
Table 3. Isotopic compositions of water samples in the Gangwon Province of South Korea. CO₂-rich water is grouped based on the Piper diagram (see Figure 3).

| Sample no. (1) | Sampling Date | δ¹⁸O (%) | δD (%) | δ¹³C (%) | Tritium (T.U.) |
|----------------|---------------|----------|--------|----------|----------------|
| **CO₂-rich water (Na–HCO₃ type)** |               |          |        |          |                |
| KW–1 (a)       | Sep–01–98     | −10.9    | −76.8  | −8.1     | 5.0            |
| KW–1’ (a)      | Jul–07–99     | −11.3    | −81.6  | −4.0     | n.a.           |
| KW–2 (a)       | Sep–01–98     | −11.7    | −83.3  | −8.3     | 1.7            |
| KW–2’ (a)      | Jul–07–99     | −12.1    | −89.3  | −0.3     | n.a.           |
| KW–2” (a)      | Nov–19–10     | −11.8    | −82.5  | −3.7     | n.a.           |
| KW–3           | Sep–01–98     | −11.3    | −78.3  | −7.8     | 0.0            |
| KW–3’          | Jul–07–99     | −11.3    | −83.3  | −2.8     | n.a.           |
| KW–4           | Sep–01–98     | −11.5    | −80.0  | −3.0     | 0.0            |
| KW–4’          | Jul–07–99     | −11.4    | −84.0  | −7.4     | n.a.           |
| KW–4”          | Nov–19–10     | −11.3    | −80.1  | −4.5     | n.a.           |
| **CO₂-rich water (Ca–Na–HCO₃ type)** |               |          |        |          |                |
| KW–5           | Jul–01–98     | −10.4    | −72.7  | −8.8     | 7.6            |
| KW–5’          | Jul–07–99     | −10.5    | −75.3  | −5.3     | n.a.           |
| KW–5”          | Nov–18–10     | −10.6    | −72.7  | −4.6     | n.a.           |
| **CO₂-rich water (Ca–HCO₃ type)** |               |          |        |          |                |
| KW–8 (a)       | Oct–30–98     | −10.7    | −74.4  | 0.8      | 2.5            |
| KW–8’ (a)      | Nov–19–10     | −10.7    | −73.6  | −4.3     | n.a.           |
| KW–9           | Oct–30–98     | −10.1    | −72.3  | −6.1     | 7.6            |
| KW–10          | Oct–30–98     | −10.8    | −75.2  | −5.1     | 5.2            |
| KW–10’ (a)     | Nov–19–10     | −10.7    | −74.7  | −4.7     | n.a.           |
| KW–12          | Aug–01–98     | −10.6    | −77.7  | −5.4     | 7.0            |
| KW–13          | Aug–01–98     | −10.7    | −69.5  | n.a.     | 7.0            |
| KW–13’         | Jul–07–99     | −10.7    | −77.3  | n.a.     | n.a.           |
| KW–14          | Jul–07–99     | −9.9     | −70.3  | −6.6     | n.a.           |
| KW–15          | Sep–30–99     | n.a.     | n.a.   | −4.7     | n.a.           |
| **Shallow groundwater** |               |          |        |          |                |
| KW–16          | Jul–01–98     | −8.6     | −54.8  | −16.8    | 4.1            |
| KW–16’         | Feb–17–00     | −8.7     | −62.3  | −15.7    | 6.7            |
| KW–18 (a)      | Jul–01–98     | −8.9     | −58.3  | −19.0    | 6.1            |
| KW–20 (a)      | Jul–07–99     | −11.0    | −81.3  | −17.2    | n.a.           |
| **Surface water** |               |          |        |          |                |
| KW–5S          | Oct–30–98     | −10.2    | −72.4  | n.a.     | 7.9            |
| KW–8S          | Jul–01–98     | −8.7     | −65.2  | n.a.     | 12.5           |

n.a.: not analyzed. (1) Data of the samples with “a” in parenthesis are from Choi et al. [27].
Table 4. Chemical compositions of rock samples collected from the vicinity of CO$_2$–rich water in the Gangwon Province of South Korea.

| Rock Type $^{(1)}$ | Sample No. | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MnO | CaO | MgO | K$_2$O | Na$_2$O | P$_2$O$_5$ | TiO$_2$ | Loss on Ignition | Sum |
|--------------------|------------|---------|------------|------------|-----|-----|-----|-------|-------|----------|--------|----------------|------|
| **Na$\rightarrow$HCO$_3$ type** | | wt. % | | | | | | | | | | | |
| Biotite granite     | KW–1       | 74.68   | 13.85      | 1.33       | 0.11 | 0.52 | 0.12 | 4.20  | 3.14  | 0.03     | 0.03   | 0.55         | 98.56 |
| Biotite granite (a)| "          | 73.83   | 13.99      | 1.67       | 0.05 | 0.96 | 0.40 | 4.99  | 2.83  | 0.04     | 0.17   | 0.54         | 99.47 |
| Biotite granite gneiss| "        | 73.43   | 13.99      | 2.04       | 0.05 | 0.83 | 0.19 | 5.48  | 3.21  | 0.03     | 0.19   | 0.27         | 99.71 |
| Porphyroblastic gneiss| "      | 71.16   | 15.16      | 2.15       | 0.04 | 1.23 | 0.24 | 5.55  | 3.50  | 0.04     | 0.22   | 0.29         | 99.58 |
| Biotite granite (a) |KW–2       | 73.17   | 14.30      | 1.94       | 0.08 | 1.75 | 0.30 | 4.04  | 3.14  | 0.06     | 0.23   | 0.34         | 99.35 |
| Granite gneiss     |KW–3       | 74.91   | 14.21      | 1.55       | 0.06 | 1.25 | 0.15 | 4.24  | 3.06  | 0.02     | 0.06   | 0.39         | 99.90 |
| Biotite granite gneiss| KW–4    | 68.93   | 15.47      | 3.40       | 0.06 | 3.19 | 1.33 | 2.66  | 3.19  | 0.12     | 0.33   | 0.47         | 99.15 |
| Biotite granite (a)| "          | 76.65   | 12.45      | 1.33       | 0.03 | 0.43 | 0.02 | 4.53  | 3.53  | –        | 0.04   | 0.29         | 99.30 |
| Porphyroblastic gneiss| "        | 63.39   | 17.16      | 5.11       | 0.10 | 3.91 | 2.35 | 3.15  | 3.23  | 0.15     | 0.63   | 1.29         | 100.47|
| Average             |            | 72.24   | 14.51      | 2.28       | 0.06 | 1.56 | 0.57 | 4.32  | 3.20  | 0.06     | 0.21   | 0.49         | 99.50 |

| **Ca$\rightarrow$HCO$_3$ type** | | wt. % | | | | | | | | | | | |
| Biotite granite gneiss| KW–8       | 73.90   | 14.81      | 1.43       | 0.02 | 0.97 | 0.29 | 4.69  | 3.02  | 0.05     | 0.19   | 0.69         | 100.06|
| Biotite granite (a)| "          | 69.47   | 15.64      | 3.45       | 0.06 | 2.90 | 1.13 | 4.06  | 2.76  | 0.11     | 0.47   | 0.42         | 100.47|
| Biotite granite (a)| "          | 72.40   | 14.70      | 2.33       | 0.04 | 2.08 | 0.63 | 4.03  | 2.89  | 0.09     | 0.32   | 0.48         | 99.99 |
| Biotite granite (a)| "          | 67.96   | 15.93      | 4.15       | 0.06 | 3.28 | 1.38 | 3.43  | 2.88  | 0.13     | 0.56   | 0.35         | 100.11|
| Biotite granite (a)| KW–9       | 67.48   | 15.95      | 3.52       | 0.06 | 3.42 | 1.09 | 3.89  | 2.88  | 0.11     | 0.44   | 0.60         | 99.44 |
| Banded gneiss       |KW–11       | 70.59   | 16.76      | 3.01       | 0.04 | 1.97 | 0.98 | 4.02  | 2.76  | 0.10     | 0.40   | 1.05         | 100.59|
| Banded gneiss       |KW–12       | 75.20   | 12.44      | 4.06       | 0.08 | 1.26 | 1.31 | 2.24  | 2.35  | 0.04     | 0.31   | 0.83         | 100.12|
| Average             |            | 71.00   | 15.02      | 3.14       | 0.05 | 2.27 | 0.97 | 3.77  | 2.79  | 0.09     | 0.38   | 0.63         | 100.11|

$^{(1)}$ Data of the samples denoted with “a” in parenthesis are from Choi et al. [27].
4. Results and Discussion

4.1. Hydrochemical and Isotopic Data

Data on field measurements and major constituents of water samples are summarized in Table 1. The concentrations of minor to trace elements are shown in Table 2. It is notable that the CO₂-rich water samples show relatively low pH values (5.5 to 6.7) and high EC values (454 to 2220 µS/cm), while the shallow groundwater and surface water have higher pH values (averages of 6.5 and 7.1, respectively) and lower EC values (averages of 138.7 and 54.8 µS/cm, respectively) than the CO₂-rich water (see Table 1). The P_{CO2} values of the CO₂-rich water range from 10⁻⁰.⁶₆ to 10⁺⁰.₄₁ atm, and are clearly distinguished from those of shallow groundwater (average of 10⁻² atm) and surface water (average of 10⁻².₈ atm) (Table 1).

4.1.1. Origin of the CO₂

The relation between P_{CO2} and δ¹³C of water samples in Figure 2 shows a clear difference between CO₂-rich water and the others. The CO₂-rich water has heavy δ¹³C values (average = −⁴.⁹‰; Table 3) as well as elevated P_{CO2} (average = 10⁻⁰.¹³ atm), whereas the shallow groundwater and surface water show considerably lighter δ¹³C values as well as lower P_{CO2}. Considering the high δ¹³C values and the few carbonate minerals in the study area, external CO₂ seems a likely major source for the high P_{CO2} rather than in-situ reactions such as the decomposition of organic matter or the dissolution of carbonate minerals.

Potential external CO₂ sources include diagenetic and metamorphic reactions [38–40] and deep-seated mantle and magmatic CO₂. However, the diagenetic and metamorphic reactions can be excluded, because burial and/or heating had not been observed to acquire a temperature above 450 °C in the study area based on its sedimentary sequence [39,41,42]. Moreover, the δ¹³C values of the CO₂-rich water (−⁸.₈ to 0.₈‰) are in good agreement with the general δ¹³C range of the magmatic CO₂ (−⁸ to −₁‰) and smaller than that of the metamorphic CO₂ (0 to +₁₀‰) [43,44]. Based on these facts, magmatic CO₂ gas seems a major source for the elevated P_{CO2} in the CO₂-rich water of this study. Similarly, previous studies suggested that the CO₂ gas comes from deep-seated sources such as magmatic CO₂ based on δ¹³C data in the study area [25,27].
4.1.2. Three Water Types of CO₂-Rich Water

The hydrochemical compositions of water samples were plotted on a Piper diagram to classify water types and to understand the hydrochemical characteristics of each water type (Figure 3). The CO₂-rich water in the study area is clearly grouped into three water types, similar to the previous studies [25–27]. The three types of Na-HCO₃, Ca-Na-HCO₃ and Ca-HCO₃ are distinct from each other based on the major cations, i.e., Ca and Na + K, while all have a high HCO₃ ratio compared to the surface water and shallow groundwater in the Piper diagram (Figure 3).

![Piper diagram showing the hydrochemical compositions of water samples in the study area. CO₂-rich water in the Gangwon area is clearly grouped into three water types, Na–HCO₃, Ca–Na–HCO₃ and Ca–HCO₃.](image)

The three types of CO₂-rich water differ in terms of trace element concentrations as well as major ions, and their correlations with total dissolved solids (TDS) (Figures 4 and 5). In particular, the Na-HCO₃ and Ca-HCO₃ types are distinct from each other by Na, Ca, K, Mg, F and SiO₂, while the Ca–Na–HCO₃ type has an intermediate characteristic between the other two water types (Figure 4). All the types of CO₂-rich water contain high concentrations of trace elements such as Fe, Mn, Sr, Li, Rb and Cs compared to the surface water and shallow groundwater (Table 2 and Figure 5). However, Fe concentrations are generally higher in the Ca–HCO₃ type (up to 26 mg/L) than those in the Na–HCO₃ type (Figure 5a). Mn and Sr concentrations are high in the Ca–HCO₃ type (Figure 5b,c), while Li, Rb and Cs, which are chemically compatible with Na and K, are enriched in the Na–HCO₃ type (Figure 5d–f).
4.1.3. Evolutionary Processes for Each Water Type of CO2−Rich Water

The different distribution patterns of major and minor elements depending on the water type in Figures 4 and 5 indicate that each type of CO2−rich water may follow a different geochemical process. Moreover, the chemical compositions of rock samples collected from the vicinity of the CO2−rich water show no remarkable differences (Table 4). The only noticeable difference is the Na2O content (p-value of the Mann−Whitney U−test = 0.002). Thus, the geology does not seem to be a major factor in differentiating the hydrochemistry in the CO2−rich water, and circulation depths and residence times are examined for each water type below.

Figure 4. Plots of TDS versus major elements for water samples: (a) Na, (b) Ca, (c) K, (d) Mg, (e) SiO2 and (f) F.
recharged at a relatively high altitude and circulated through a deep path for a relatively long residence time in the subsurface [25,27]. In the diagram of tritium concentrations versus $\delta^{18}O$ values (Figure 6b), the Na$^-$HCO$_3$ type CO$_2$−rich water also has lower tritium contents than the other types, indicating older age. Meanwhile, the Ca$^-$HCO$_3$ type CO$_2$−rich water has tritium concentrations similar to or higher than the shallow groundwater and surface water. This different tritium content suggests that the Na$^-$HCO$_3$ type has been little affected by the surface water and the shallow groundwater after the intensive water−rock interaction until discharge. On the other hand, the Ca$^-$HCO$_3$ type reflects a relatively low extent of water−rock reactions and mixing with recently recharged water [27].

Figure 5. Plots of TDS versus trace elements for water samples: (a) Fe, (b) Mn, (c) Sr, (d) Li, (e) Rb and (f) Cs.

4.1.3. Evolutionary Processes for Each Water Type of CO$_2$−Rich Water

The different distribution patterns of major and minor elements depending on the water type in Figures 4 and 5 indicate that each type of CO$_2$−rich water may follow a different geochemical process. Moreover, the chemical compositions of rock samples collected from the vicinity of the CO$_2$−rich water show no remarkable differences (Table 4). The only noticeable difference is the Na$_2$O content (p−value of the Mann−Whitney U−test = 0.002). Thus, the geology does not seem to be a major factor in differentiating the hydrochemistry in the CO$_2$−rich water, and circulation depths and residence times are examined for each water type below.

The circulation depth and residence time of water can be estimated using water isotope ratios ($\delta^{18}O$ and $\delta^D$) and tritium concentrations (e.g., [43]). All $\delta^{18}O$ and $\delta^D$ values of the water samples from the study area are plotted close to the global meteoric water line (GMWL), suggesting that all the water is of meteoric origin (Figure 6a and Table 3). However, the Ca−HCO$_3$ type CO$_2$−rich water has a heavier isotopic composition than the Na−HCO$_3$ type, whose $^{18}O$ and $\delta^D$ are relatively depleted compared to the other water types. This suggests that the Na−HCO$_3$ type CO$_2$−rich water was
recharged at a relatively high altitude and circulated through a deep path for a relatively long residence time in the subsurface [25,27]. In the diagram of tritium concentrations versus δ18O values (Figure 6b), the Na−HCO3 type CO2−rich water also has lower tritium contents than the other types, indicating older age. Meanwhile, the Ca−HCO3 type CO2−rich water has tritium concentrations similar to or higher than the shallow groundwater and surface water. This different tritium content suggests that the Na−HCO3 type has been little affected by the surface water and the shallow groundwater after the intensive water–rock interaction until discharge. On the other hand, the Ca−HCO3 type reflects a relatively low extent of water–rock reactions and mixing with recently recharged water [27].

![Diagram](image-url)

**Figure 6.** (a) Diagram of δ18O versus δD values. The solid line is the global meteoric water line (δD = 8 × δ18O + 10). (b) Diagram of tritium versus δ18O.

The study results are consistent with the previous results on the genesis and evolution of CO2−rich water in the study area [25-27]. In the previous studies, the Na−HCO3 type CO2−rich water was explained by the water–rock interaction caused by the deep–seated CO2, which was enhanced by high reservoir temperatures around 140–160 °C [25]. The mixing of the Na−HCO3 type water with shallow groundwater would result in successive changes of groundwater chemistry from the Ca–Na–HCO3 type into the Ca–HCO3 type [26].

The Ca−HCO3 type and Na−HCO3 type have gone through different reaction times and circulation depths, while the Ca–Na–HCO3 type has intermediate characteristics between the other two types. It can be suggested that the supply of gaseous CO2 and the subsequent CO2–water–rock interaction for a long residence time at a deep depth causes the Na−HCO3 type CO2–rich water, while the vertical migration of CO2–rich fluid containing high concentrations of chemical species into shallow aquifers causes the Ca–HCO3 type CO2–rich water.

4.2. Behaviors of Trace Elements during Different Evolutional Processes

The hydrochemical characteristics of CO2–rich water were scrutinized by PCA using 21 chemical species (Na, K, Mg, Ca, SiO2, Cl, SO4, F, Fe, Sr, Mn, Al, Li, B, Cr, Zn, Rb, Cs, Ba, U and alkalinity), four measured variables (pH, Eh, EC, DO), and two calculated variables (P CO2 and TDS) to identify major evolutionary processes for each water type. As a result, the surface water and shallow groundwater and the three types of CO2–rich water are distinctly clustered by the first two components, as shown in Figure 7a.
which are discussed below in relation to the major geochemical process.

Figure 7. The first two components, 1 and 2, obtained by principal component analysis (PCA): (a) Scores of water samples, (b) Loadings of variables.

The CO$_2$–rich water is clearly distinguished from both the surface water and the shallow groundwater by component 1, while the three types of CO$_2$–rich water are made distinct by component 2. Component 1 has negative relations with DO, Eh, and pH, whose high values indicate recent recharge, while component 1 has positive correlations with $P_{\text{CO}_2}$, EC, alkalinity, SiO$_2$, and TDS. Thus, it can be concluded that component 1 represents that the CO$_2$–rich water is influenced by the CO$_2$ supply and the subsequent CO$_2$–water–rock interaction in the study area. In contrast, component 2 indicates that the three types of CO$_2$–rich water have different relationships with trace elements, which are discussed below in relation to the major geochemical process.

4.2.1. Extensive Water–Rock Interactions in the Na–HCO$_3$ Type

The Na–HCO$_3$ type CO$_2$–rich water shows a significant relation with alkali metals such as Li, Rb and Cs as well as Na and K, and also a strong relationship with Al, F, and U (Figure 7b), which suggests that the high concentrations of trace elements in the Na–HCO$_3$ type CO$_2$–rich water may be attributed to extensive water–rock interactions.

Specifically, fluoride is a well-known indicator of water–rock interactions in silicate bedrock [45], and the high F concentrations of the Na–HCO$_3$ type CO$_2$–rich water imply extensive water–rock interaction. The concentration of uranium also indicates that the Na–HCO$_3$ type CO$_2$–rich water has undergone more water–rock interactions than the Ca–HCO$_3$ type because the only source of U is the geology in the study area, but there is no difference in the rock compositions near the two types of CO$_2$–rich water (Figure 1 and Table 4). In general, U is dominantly present as uranyl (UO$_2^{2+}$) in oxic and suboxic conditions, and the uranyl forms uranyl carbonate (UO$_2$(CO$_3$)$_2^{2-}$ or UO$_2$(CO$_3$)$_3^{4-}$) when the bicarbonate concentration is high, as in the CO$_2$–rich water. In addition, it is known that U mobility is enhanced when the Ca concentration is high because the formation of calcium uranyl carbonate complexes (e.g., Ca$_2$UO$_2$(CO$_3$)$_3$) inhibits the sorption of U to the mineral surface [46–51]. For this reason, high uranium concentrations have often been observed in the Ca–HCO$_3$ type groundwater [48,50,51]. However, in this study, uranium shows a positive correlation with the Na–HCO$_3$ type CO$_2$–rich water (Figure 7), and U concentrations are higher in the Na–HCO$_3$ type than in the Ca–HCO$_3$ type (Table 2).

4.2.2. Mixing and Cation Exchange in the Ca–HCO$_3$ Type

The Ca–HCO$_3$ type CO$_2$–rich water is clearly differentiated from both the Na–HCO$_3$ type CO$_2$–rich water and the shallow groundwater by component 2 and is highly correlated with Ca, Mg, Sr, Fe, and Mn (Figure 7). This indicates that the Ca–HCO$_3$ type CO$_2$–rich water is formed by
the mixing of shallow groundwater and the Na–HCO₃ type CO₂–rich water, and then affected by other geochemical processes such as cation exchanges.

In particular, high Fe and Mn concentrations seem to be derived from the reverse cation exchange, similar to Ca and Mg as described by [27], for the following reasons. First, sulfide minerals such as pyrite (FeS₂) are not found in the bedrock of the study area (see Figure 1), and the average sulfate concentration of the Ca–HCO₃ type CO₂–rich water is low (11.2 mg/L). Thus, Fe and Mn concentrations did not increase due to the dissolution of sulfide minerals. Second, the Fe and Mn concentrations of the Na–HCO₃ type CO₂–rich water are lower than those of the Ca–HCO₃ type CO₂–rich water (Table 2 and Figure 5), and thus the concentrations of Fe and Mn in the Ca–HCO₃ type CO₂–rich water were not increased by the inflow of deep groundwater such as the Na–HCO₃ type CO₂–rich water. A previous study suggested that reverse cation exchange during the mixing of Na–HCO₃ type CO₂–rich water with shallow groundwater results in the Ca–HCO₃ type CO₂–rich water in the study area [27].

4.3. Comparison with WHO Guidelines for Drinking–Water Quality

The study results indicate that the dissolution of gaseous CO₂ and/or the inflow of CO₂–rich fluid into aquifers can degrade groundwater quality by increasing the concentrations of chemical species. To evaluate the impact of these CO₂–triggered geochemical processes (i.e., water–rock interactions and cation exchanges) on groundwater quality, the levels of trace elements were compared to those in the guidelines for drinking–water quality of the World Health Organization (WHO) (Table 2) [52]. The WHO suggests the guideline values of contaminants in drinking water as the guidelines for drinking–water quality. The guidelines were established for toxic contaminants that are harmful to human health, including B, Cr, Ba, and U in Table 2 (chemical aspects), and for contaminants regarding public acceptability in taste, odor and appearance (acceptability aspects), including Fe, Mn, Al, and Zn as in Table 2.

In all types of CO₂–rich water, the trace elements in chemical aspects (i.e., B, Cr, Ba, and U) do not exceed the guideline values. However, among the elements in acceptability aspects (i.e., Fe, Mn, Al and Zn), Fe and Mn significantly exceed the guideline levels: 10.9 and 2.1 times in the Na–HCO₃ type, 22.2 and 4.9 times in the Ca–Na–HCO₃ type, and 53.1 and 6.8 times in the Ca–HCO₃ type, respectively. In addition, Al is about four times as high as the guideline level in the Na–HCO₃ type, probably because of extensive water–rock interactions in deep and high–temperature conditions. Although uranium (U) does not exceed the guideline in all types of CO₂–rich water, the average concentration of U is close to the guideline (30 μg/L) in the Na–HCO₃ type CO₂–rich water (25.02 μg/L), and the three samples of the Na–HCO₃ type (KW–4 in Table 2) show U concentrations exceeding the guideline.

The high concentrations of Fe, Mn and Al can be harmful to human health when the water is taken for a long time [52]. In addition, when the groundwater is exposed to an oxic environment, they are rapidly oxidized to produce oxides/hydroxides, causing discoloration and increasing the turbidity of water [52,53]. Meanwhile, the long–term exposure to high concentrations of uranium is known to increase the incidence of cancer as well as kidney damage [52]. These results indicate that the long–term leakage of CO₂ in silicate bedrock areas such as granite and gneiss may significantly increase the risk to human health due to increased trace elements [30].

5. Summary and Conclusions

To evaluate the potential impact of CO₂ gas and CO₂–rich fluid leaked from GCS sites on groundwater quality, we investigated the hydrochemical and isotopic characteristics of naturally occurring CO₂–rich water and compared them with those of the adjacent shallow groundwater and surface water. The CO₂–rich water showed low pH, high P⁰CO₂, and high TDS including major and minor elements compared to the shallow groundwater and the surface water. The δ¹³C values of CO₂–rich water indicated that the deep–seated magmatic CO₂ caused the elevated P⁰CO₂ values in the CO₂–rich water.
The CO₂–rich water in the study area was divided into three types, Na−HCO₃, Ca−HCO₃ and Ca−Na−HCO₃, based on the hydrochemical compositions. Since the geochemical compositions of rock samples obtained in the vicinity of CO₂–rich water did not show any remarkable differences regardless of water type, the water types were ascribed to geochemical evolutionary processes. The water isotope ratios, tritium concentrations, and hydrochemical species suggested that the Na−HCO₃ type CO₂–rich water had been formed through extensive CO₂–water−rock interactions for a relatively long residence time at a deep depth, but was rarely affected by shallow aquifers until discharge, while the Ca−HCO₃ and Ca−Na−HCO₃ type CO₂–rich water reflected a relatively low extent of water−rock reactions and mixing with recently recharged water.

Specifically, the leakage of gaseous CO₂ into the groundwater aquifer at a deep depth seemed to enhance water−rock interactions, which consequently increased the concentrations of trace elements such as Li, Rb, Cs, Al and U in the Na−HCO₃ type CO₂–rich water. Then the migration of this high TDS CO₂−rich fluid into shallow aquifers and the following geochemical processes such as mixing and cation exchange increased metal concentrations such as Sr, Fe, and Mn. As a result, the concentrations of Fe, Mn, and Al in CO₂−rich water exceeded the guideline levels of the WHO. Although not exceeding the drinking water standard, elevated U concentrations in the Na−HCO₃ CO₂−rich water implied an increased risk to human health by the mobilization of U due to extensive CO₂−water−rock interactions.

The study results imply that the potential impact of CO₂ leakage on groundwater quality depends on the geochemical evolutionary processes of leaked CO₂ (e.g., reaction time and depth). In addition, changes in the hydrochemistry of groundwater due to the CO₂ leakage are related to groundwater contamination, especially increased trace elements such as iron, manganese, aluminum, and uranium in silicate basement areas.

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