Abstract: The Korean bottled water market has continuously expanded during the last 25 years. However, in-depth studies of its geochemistry have not been conducted. Four types of bottled water manufactured in South Korea (i.e., natural mineral water, NMW; functional water, FW; carbonated water, CW; and desalinated seawater, DSW) were investigated to classify the water type, verify the accuracy of the ion contents detailed on the bottle labels, and decipher the origin of the water sources using major and trace elements and their isotopes. The waters was classified into three types: Ca-HCO$_3$, Ca(Mg)-Cl, and Na-HCO$_3$. NMW and FW are mainly of the Ca-HCO$_3$ type. Our findings indicate that Korean bottled water chemistry is associated with lithological features and manufacturing processes; NMW is closely related to lithology while FW and DSW are strongly affected by manufacturing processes. Unlike major ions, trace elements cannot be used to decipher Korean bottled water chemistry because they show little apparent relationship with lithology. Regardless of the water chemistry, typical isotopic signals corresponding to intrinsic water were observed in all of the samples, indicating that groundwater and seawater were the sources of Korean bottled water.

Keywords: Korean bottled water; trace element; water isotope; manufacturing processes; lithology

1. Introduction

Since the law for the management of drinking water was enacted in South Korea in 1995, the sale of drinking water to the public has been permitted and the Korean drinking water market has been continuously growing. The sales volume of bottled water in South Korea increased from 471 kilotons (kt) in 1995 to 2110 kt in 2005, and since 2005, the annual growth rate of sales has increased by 10% every year, reaching 3543 kt in 2013 [1]. This trend applies to South Korea as well as the entire world, and consumption keeps increasing for several reasons. For example, health-conscious people are uncertain whether tap water is safe to drink due to water pollution, and people tend to believe that the quality of bottled water is beneficial to their health and well-being.

European residents living in certain geological regions (e.g., areas with carbonate rocks) prefer to drink water with guaranteed quality; approximately 20% of the surficial lithology in Europe is occupied by carbonate rocks [2]. Consequently, the study of bottled water has been highly active in Europe during the last decade. A wide variety of bottled water brands are commercially available in Europe. Various components (i.e., pH, electrical conductivity [EC], and ionic concentrations) of bottled
waters are provided to consumers, and additional information is available from the FineWaters website (http://www.finewaters.com/). Substantial research has been conducted on bottled water chemistry and even groundwater used as a source of bottled water (e.g., [3–7]); the research has been reviewed by Reimann and Birke [8]. In Greece, Demetriades [9] explored groundwater recharge processes and suggested that the geochemistry of source aquifers has been constant for at least 10 years. In Italy, bottled mineral waters drained from plutonic rocks contained relatively high contents of rare earth elements (e.g., Ce, Dy, Gd, Er, Ho, Lu, Pr, Tb, Tm, and Yb) compared to those drained from other rock types, and a large concentration spread of many elements reflected the effects of particular lithologies on water chemistry [10]. In addition, Lourenço et al. [11] classified Portuguese bottled waters into three hydrochemical groups using multivariate analyses.

However, only a few studies on South Korean bottled waters have been conducted to date. The origins of bottled water sold in South Korea were initially identified by their major elements and isotopes [12]. According to Kim et al. [13,14], Korean bottled water (i.e., still water) sourced from groundwater clearly reflects the lithological distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, suggesting that bottled water chemistry is closely related to water–rock interactions. According to the Korean Drinking Water Quality Standard, the quality of drinking water, including desalinated seawater (DSW), must be characterized by about 50 elements/parameters (e.g., pH, microbes, organic compounds, trace elements). However, manufacturers’ labels for most Korean bottled waters provide concentrations of only five elements, i.e., Ca, Mg, Na, K, and F. Although government-certified laboratories analyze their concentrations, the values need to be verified. Trace-element concentrations of Korean bottled waters are unavailable.

The objectives of this study were to verify the accuracy of the ion contents indicated on bottle labels and to identify the factors controlling the geochemistry of bottled water using major and trace elements. In addition, isotopic compositions of various types of bottled water were analyzed to ascertain whether intrinsic features of water were preserved throughout different manufacturing steps.

2. Materials and Methods

2.1. Samples

Korean bottled water samples (60) were purchased from Korean markets in 2016; the samples were packed in PET bottles with the capacity of approximately 200 mL~2 L. The samples were divided into four different types based on the label information: natural mineral water (NMW), functional water (FW), carbonated water (CW), and desalinated seawater (DSW). The FW included hydrogen-rich water, alkaline water, and oxygen-rich water. In South Korea, NMW is groundwater sourced from aquifers. The FW is artificially manufactured by adding various additives (e.g., vitamins, oxygen, and hydrogen) or by electrolysis, regardless of the source water. According to the label information, CW is produced by adding artificial CO$_2$. Groundwater-derived bottled water mainly originates from areas underlying granitic and metamorphic rocks (Figure 1).
2.2. Physicochemical Analyses

The pH and EC were measured using an Orion 5-Star portable meter equipped with an Orion combination epoxy pH electrode and DuraProbe four-electrode conductivity cell. For chemical and isotopic measurements, two aliquots of the samples were separately transferred into prewashed containers, of which one was acidified using ultrapure HNO$_3$ to pH < 2 for the cations measurement. Then all samples were stored in a refrigerator until analysis, and all analyses described below were carried out as soon as possible after the samples were separated into aliquots.

Alkalinity was determined with 0.01 N HCl using a Mettler Toledo T50A titrator. Cation and anion concentrations were analyzed with a PerkinElmer Optima 4300DU ICP-AES and a Dionex ICS-1500 IC, respectively, at the Korean Institute of Geoscience and Mineral Resources. Trace elements were measured using a Thermo Fisher Scientific iCAPTM Q ICP-MS at the Korean Basic Science Institute. Repeated analyses of certified reference materials (i.e., river-water reference material and trace metals in drinking water) yielded analytical uncertainties within the range of ±5%. Isotopic compositions of water ($\delta^{18}$O and $\delta^2$H) were analyzed using a L2120-i Picarro cavity ring-down spectroscopy analyzer (Santa Clara, CA, USA) equipped with a vaporizer maintained at 110 °C. Nitrogen gas of >99.999% purity was used as the carrier gas. The analytical reproducibility obtained from laboratory standards were ±0.1‰ for $\delta^{18}$O and ±0.5‰ for $\delta^2$H, respectively.

All $\delta^{18}$O and $\delta^2$H values are reported in the delta (δ) notation relative to the Vienna Standard Mean Ocean Water (VSMOW), where $\delta$ (‰) = ($R_{\text{sample}}/R_{\text{standard}} - 1$) × 1000 and R represents $^{18}$O/$^{16}$O or $^2$H/$^1$H, respectively. The $\delta^{18}$O and $\delta^2$H values were calibrated using three international standards, i.e., VSMOW2 (0‰ for $\delta^{18}$O and 0‰ for $\delta^2$H), Greenland ice sheet precipitation (~24.76‰ for $\delta^{18}$O and ~189.5‰ for $\delta^2$H), and standard light Antarctic precipitation (~55.5‰ for $\delta^{18}$O and ~427.5‰ for $\delta^2$H) as well as three laboratory standards (~5.21‰, ~8.57‰, and ~12.23‰ for $\delta^{18}$O and ~46.08‰, ~56.86‰, and ~87.56‰ for $\delta^2$H).

3. Results and Discussion

The physiochemical parameters and chemical and isotopic compositions of the bottled water samples are listed in Table 1. Some of the major cation concentrations (e.g., Ca, Mg, Na, and K) identified on the labels of the bottled waters are provided in Table 2 for comparison with those measured in this study.
Table 1. Statistics for major and trace element contents and water isotopes in four types of Korean bottled water. pH and EC measured in laboratory are listed as well.

| Type                       | pH  | EC   | Ca   | Mg   | Na   | K    | Cl   | NO₃  | SO₄  | Alk  | TDS  | Li   | B    | V    | Cr   | Sr   | Rb   | Ba   | δ¹⁸O | δ²H  | d-Excess ¹ |
|----------------------------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|                            | µS/cm | mg/L | µg/L | µg/L | µg/L | %    | %    | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L |
| Natural mineral water (NMW, n = 22) |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| min                        | 6.8 | 91.0 | 10.9 | 1.20 | 2.04 | 0.65 | 2.16 | 0.11 | 3.02 | 38.4 | 80.6 | 0.78 | 1.42 | 0.01 | 0.02 | 57.6 | 0.02 | 0.06 | −9.7 | −64  | 10.6 |
| max                        | 8.6 | 361  | 51.1 | 15.3 | 14.7 | 1.93 | 11.6 | 10.2 | 29.3 | 204  | 312  | 27.9 | 378  | 2.26 | 0.67 | 1016 | 6.27 | 75.5 | −8.1 | −53  | 13.4 |
| avg.                       | 7.8 | 157  | 20.2 | 3.34 | 6.86 | 1.05 | 5.34 | 4.99 | 8.58 | 75.9 | 132  | 8.06 | 25.6 | 0.67 | 0.26 | 170  | 1.58 | 10.0 | −8.8 | −59  | 11.9 |
| std.                       | 0.5 | 77.0 | 10.2 | 3.65 | 3.24 | 0.32 | 3.32 | 3.26 | 6.28 | 44.1 | 65.1 | 7.03 | 91.0 | 0.67 | 0.23 | 198  | 1.62 | 19.3 | 0.4  | 4    | 0.8  |
| Functional water (FW, n = 23) |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| min                        | 6.5 | 9.00 | n.d. | n.d. | 0.68 | 0.32 | 0.16 | n.d. | n.d. | 3.78 | 5.26 | 0.06 | 0.95 | 0.01 | 0.01 | 1.40 | 0.04 | 0.04 | −9.6 | −66  | 7.6  |
| max                        | 8.4 | 668  | 76.5 | 27.2 | 61.3 | 17.3 | 54.0 | 39.9 | 103  | 287  | 519  | 238  | 150  | 3.19 | 1.27 | 1018 | 4.93 | 177  | −7.3 | −50  | 12.5 |
| avg.                       | 7.9 | 247  | 25.6 | 9.70 | 16.4 | 2.41 | 9.04 | 5.13 | 17.1 | 128  | 219  | 22.3 | 32.9 | 0.67 | 0.23 | 1720 | 1.35 | 37.4 | −8.8 | −60  | 10.1 |
| std.                       | 0.5 | 166  | 16.8 | 8.59 | 15.2 | 4.01 | 11.5 | 9.48 | 20.8 | 86.6 | 144  | 48.2 | 44.0 | 0.86 | 0.36 | 3120 | 1.34 | 47.1 | 0.6  | 4    | 1.6  |
| Desalinated seawater (DSW, n = 8) |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| min                        | 5.9 | 274  | 5.5  | 17.3 | 8.28 | 5.07 | 6.74 | n.d. | 2.99 | 2.20 | 72.5 | 3.13 | 302  | 0.01 | 0.01 | 7.29 | 1.76 | 0.02 | −0.4 | −1   | 0.6  |
| max                        | 6.5 | 668  | 14.7 | 50.4 | 16.4 | 10.3 | 155  | 10.0 | 60.2 | 4.52 | 308  | 9.68 | 513  | 0.05 | 0.07 | 275  | 5.10 | 16.0 | 0.0  | 1    | 2.0  |
| avg.                       | 6.2 | 474  | 10.5 | 33.3 | 13.0 | 7.83 | 91.7 | 0.02 | 42.2 | 3.02 | 202  | 6.28 | 388  | 0.02 | 0.04 | 119  | 3.40 | 0.07 | −0.1 | 0    | 1.1  |
| std.                       | 0.2 | 114  | 2.95 | 9.33 | 2.85 | 1.60 | 44.8 | 0.03 | 19.2 | 0.85 | 75.0 | 1.85 | 74.6 | 0.02 | 0.02 | 106  | 0.96 | 0.04 | 0.1  | 1    | 0.5  |
| Carbonated water (CW, n = 7) |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| min                        | 4.0 | 109  | 5.72 | 0.95 | 5.11 | 1.13 | 7.57 | 1.78 | 1.69 | n.a. | 33.2 | 0.58 | 2.11 | 0.04 | 0.01 | 53.7 | 0.13 | 1.73 | −9.6 | −64  | 7.1  |
| max                        | 5.2 | 338  | 38.8 | 6.99 | 28.3 | 2.61 | 27.5 | 20.4 | 31.7 | 108  | 241  | 20.6 | 18.4 | 2.59 | 0.57 | 264  | 1.64 | 17.7 | −6.9 | −46  | 13.0 |
| avg.                       | 4.5 | 214  | 21.6 | 3.52 | 14.3 | 1.73 | 15.4 | 8.04 | 14.7 | 36.7 | 122  | 8.34 | 7.51 | 0.55 | 0.19 | 159  | 0.92 | 8.56 | −8.3 | −57  | 9.4  |
| std.                       | 0.4 | 86.6 | 11.8 | 2.18 | 9.17 | 0.61 | 7.77 | 6.33 | 11.3 | 44.7 | 81.0 | 7.20 | 7.69 | 0.91 | 0.19 | 80.5 | 0.55 | 5.19 | 1.0  | 7    | 2.1  |

n.d.: not detected; n.a.: not analyzed; ¹ d-Excess = δ²H − 8¹⁸O.
Table 2. Major cation contents measured for natural mineral water and deep-sea drinking water collected in this study and described on bottle labels.

| Sample       | Ca   | Mg   | Na   | K    | Ca   | Mg   | Na   | K    |
|--------------|------|------|------|------|------|------|------|------|
| **Measured concentration (mg/L)** | | | | | | | | |
| **Concentration on the bottle label (mg/L)** | | | | | | | | |
| Natural mineral water (NMW) | | | | | | | | |
| NMW-1 | 39.3  | 15.3  | 14.7  | 1.60  | 36.0–41.0 (38.5) | 15.0–17.0 (16.0) | 11.0–13.0 (12.0) | 1.00–1.20 (1.10) |
| NMW-2 | 12.9  | 1.21  | 5.86  | 0.65  | 7.60–12.2 (9.90) | 1.20–1.30 (1.25) | 5.10–6.70 (5.90) | 0.40–0.70 (0.55) |
| NMW-3 | 13.4  | 1.23  | 5.97  | 0.68  | 8.10–13.5 (10.8) | 1.10–1.30 (1.20) | 4.70–6.70 (5.70) | 0.40–0.70 (0.55) |
| NMW-4 | 24.3  | 3.26  | 12.8  | 0.91  | 8.40–25.6 (17.0) | 2.20–3.90 (3.05) | 7.10–14.6 (10.9) | 0.60–1.10 (0.85) |
| NMW-5 | 17.5  | 2.07  | 4.97  | 1.27  | 13.5–19.9 (16.7) | 1.56–2.18 (1.87) | 4.14–5.40 (4.77) | 0.98–1.18 (1.08) |
| NMW-6 | 10.9  | 1.23  | 4.73  | 1.14  | 8.70–8.90 (8.80) | 1.10–1.20 (1.15) | 4.70–4.80 (4.75) | 0.70–0.80 (0.75) |
| NMW-7 | 19.5  | 1.64  | 10.7  | 0.84  | 19.8–21.6 (20.7) | 1.50–1.70 (1.60) | 7.10–8.40 (7.75) | 0.60–0.70 (0.65) |
| NMW-8 | 16.6  | 6.39  | 2.04  | 0.96  | 13.9–14.7 (14.3) | 5.30–5.80 (5.55) | 1.60–3.00 (2.30) | 0.70–0.80 (0.75) |
| NMW-9 | 17.4  | 2.03  | 4.88  | 1.25  | 13.0–20.0 (16.5) | 1.40–2.30 (1.85) | 3.90–5.50 (4.70) | 0.90–1.20 (1.05) |
| NMW-10 | 25.4  | 3.31  | 4.48  | 1.39  | 27.4–30.5 (29.0) | 3.50–3.80 (3.65) | 4.70–5.20 (4.95) | 1.30–2.00 (1.65) |
| NMW-11 | 51.1  | 9.96  | 14.0  | 1.93  | 8.50–44.8 (26.7) | 4.10–14.1 (9.10) | 1.80–12.6 (7.20) | 1.20–3.50 (2.35) |
| NMW-12 | 12.7  | 1.21  | 5.80  | 0.65  | 8.10–13.5 (10.8) | 1.10–1.30 (1.20) | 4.70–6.70 (5.70) | 0.40–0.70 (0.55) |
| NMW-13 | 12.7  | 1.20  | 5.90  | 0.65  | 8.10–13.5 (10.8) | 1.10–1.30 (1.20) | 4.70–6.70 (5.70) | 0.40–0.70 (0.55) |
| NMW-14 | 17.1  | 2.05  | 4.94  | 1.30  | 13.5–19.9 (16.7) | 1.56–2.18 (1.87) | 4.14–5.40 (4.77) | 0.98–1.18 (1.08) |
| NMW-15 | 21.1  | 1.69  | 6.55  | 0.88  | 22.6–23.2 (22.9) | 1.52–1.55 (1.54) | 6.05–6.09 (6.07) | 0.65–0.73 (0.69) |
| NMW-16 | 19.4  | 1.70  | 6.18  | 0.91  | 22.6–23.2 (22.9) | 1.52–1.55 (1.54) | 6.05–6.09 (6.07) | 0.65–0.73 (0.69) |
| NMW-17 | 14.4  | 1.41  | 5.18  | 1.12  | 9.00–16.0 (12.5) | 0.70–1.50 (1.10) | 4.00–7.00 (5.50) | 0.80–1.50 (1.15) |
| NMW-18 | 14.0  | 1.37  | 5.13  | 1.12  | 9.00–16.0 (12.5) | 0.70–1.50 (1.10) | 4.00–7.00 (5.50) | 0.80–1.50 (1.15) |
| NMW-19 | 14.8  | 2.06  | 7.64  | 0.73  | 11.0–16.6 (13.8) | 1.40–2.20 (1.80) | 5.30–8.10 (6.70) | 0.30–0.60 (0.45) |
| NMW-20 | 20.5  | 2.78  | 6.56  | 0.90  | 16.8–20.1 (18.5) | 2.38–2.54 (2.46) | 6.47–8.96 (7.72) | 0.66–0.99 (0.83) |
| NMW-21 | 11.7  | 1.33  | 5.44  | 1.10  | 8.70–8.90 (8.80) | 1.10–1.20 (1.15) | 4.70–4.80 (4.75) | 0.70–0.80 (0.75) |
| NMW-22 | 38.0  | 9.15  | 6.51  | 1.02  | 30.4–38.7 (34.6) | 7.20–9.20 (8.20) | 6.10–7.20 (6.65) | 0.80–0.90 (0.85) |
| Desalinated seawater (DSW) | | | | | | | | |
| DSW-1 | 10.5  | 31.5  | 12.0  | 7.60  | 10.0  | 30.0  | 8.00  | 10.0  |
| DSW-2 | 5.46  | 17.3  | 8.28  | 5.07  | 5.50  | 16.4  | 12.0  | 5.50  |
| DSW-3 | 9.20  | 31.3  | 16.4  | 7.47  | 9.00  | 27.5  | 10.0  | 9.00  |
| DSW-4 | 11.1  | 34.2  | 15.5  | 8.20  | 11.0  | 32.8  | 19.0  | 11.0  |
| DSW-5 | 9.45  | 28.9  | 11.8  | 7.10  | 10.0  | 30.0  | 10.5  | 10.0  |
| DSW-6 | 14.2  | 39.1  | 15.3  | 9.53  | 14.0  | 40.5  | 14.5  | 14.0  |
| DSW-7 | 9.41  | 33.2  | 10.5  | 7.31  | 9.00  | 27.5  | 10.0  | 9.00  |
| DSW-8 | 14.7  | 50.4  | 14.6  | 10.3  | 16.5  | 48.0  | 10.0  | 15.0  |
3.1. Physiochemical Parameters

The pH values of NMW and FW were similar, at 6.8–8.6 (average 7.8 ± 0.5, n = 22) and from 6.5–8.7 (average 7.9 ± 0.5, n = 23), respectively. Compared to NMW and FW, DSW and CW had relatively lower pH, at 5.9–6.5 (average 6.2 ± 0.2, n = 8) and 4.0–5.2 (average 4.5 ± 0.4, n = 7), respectively. Interestingly, the pH of DSW was more acidic than seawater (7.40 to 8.35 [15]); this resulted from H₂SO₄ addition during the desalination process [16]. The low pH of CW may be due to dissolution of either naturally derived CO₂ or artificially injected CO₂ [13]; based on the label information, CO₂ was more likely to be artificially injected during manufacturing processes.

The EC of samples showed a wide variability in the range of 91.0–361 µS/cm (average 157 ± 77.0 µS/cm) for NMW, 9.00–668 µS/cm (average 247 ± 166 µS/cm) for FW, 274–668 µS/cm (average 474 ± 114 µS/cm) for DSW, and 109–338 µS/cm (average 214 ± 86.6 µS/cm) for CW. Some FW samples had extremely low ECs (<10 µS/cm), which may be attributable to manufacturing processes that reduce the ion concentrations of the source water. For example, a company manufacturing hydrogen-rich FWs insisted that pure water with no dissolved ions would be beneficial to health. Thus, the manufacturer may control source-water chemistry by removing dissolved ions or adding hydrogen to the pure water.

3.2. Major Ion Geochemistry

Total dissolved solids (TDS) as a sum of major ions ranged from 5.26 to 519 mg/L (average 173 ± 111 mg/L). The NMWs had a wide range of TDS from 80.6 to 312 mg/L (average 132 ± 65.1 mg/L). On average, Ca accounted for 64.3% of the total cations on a molar basis, followed by Na (22.9%), Mg (9.1%), and K (3.7%). Alkalinity (78.5%) dominated the total anions, followed by SO₄ (9.0%), NO₃ (7.0%), and Cl (5.6%). The FWs also showed a wide range of TDS from 5.26 to 519 mg/L (average 219 ± 144 mg/L) and had the highest deviation between the samples compared to the other types of water. Although Ca in FWs dominated (44.3%), followed by Na (35.9%), Mg (17.5%), and K (7.5%), Ca and Mg concentrations for a few samples were below the detection limit. For the anions, alkalinity accounted for 82.7%, followed by SO₄ (9.3%), Cl (5.3%), and NO₃ (2.7%). The DSWs had TDS ranging from 72.5 to 308 mg/L (average 202 ± 75.0 mg/L). The DSWs contained a distinctly higher proportion of Mg (51.1%) than other types of water, followed by Na, Ca, and K accounting for 20.5%, 16.1%, and 12.3%, respectively. For anions, both Cl and SO₄ accounted for approximately 96% (65.3% and 30.3%, respectively), followed by alkalinity (4.3%) and NO₃ (0.01%). For all major ions, the concentration deviations between DSWs were relatively constant compared to other water types. For the CW samples, TDS ranged from 33.2 to 241 mg/L (average 122 ± 81.0 mg/L). Calcium accounted for 51.7%, followed by Na (34.7%), Mg (8.6%), and K (5.0%). Of anions, Cl accounted for 34.3%, followed by alkalinity (32.6%), SO₄ (21.4%), and NO₃ (11.7%). The percent charge balance error (CBE [%] = [TZ⁺ − TZ⁻]/[TZ⁺ + TZ⁻] × 100) for most samples was within the range of ±5%, where TZ⁺ = Na⁺ + K⁺ + 2Ca²⁺ + 2Mg²⁺ and TZ⁻ = Cl⁻ + 2SO₄²⁻ + NO₃⁻ + HCO₃⁻, respectively, except for CWs, whose alkalinity could not be measured due to low pH (~4.5).

3.3. Comparison of Labeled and Measured Ion Concentrations

For the NMW and DSW samples, the major ion concentrations (Ca, Mg, Na, K, and F) were provided on the bottle label. However, such information was not given for the majority of FWs or for all CWs. For most of the samples, information concerning pH, EC, and major anions was unavailable, while both pH and oxygen–reduction potential (ORP) were frequently given on the bottle label of hydrogen-rich water. The major cation concentrations were averaged to facilitate comparison with the measured values (Table 2). Regarding analytical errors related to the production date and analytical conditions, different agencies analyzed the drinking water chemistry (a total of 75 agencies [17]); the concentrations of the major cations analyzed for NMWs and DSWs in this study were similar to those reported on the bottle labels. Because the calculated p-values for Ca and Mg were less than 0.0001
at the 95% confidence interval, there was a statistically significant relationship between the two data sets (Figure 2).

Figure 2. Comparison of major cation concentrations measured in this study and those on bottle label: (a) Ca, (b) Mg, (c) Na, and (d) K. The regression lines for NMW and DMW are superimposed within the range of 95% confidence interval.

In the same manner, the differences in Na and K concentrations between the two data sets for the NMWs were statistically significant ($p < 0.0001$) although a relatively low correlation coefficient ($R^2 = 0.703$) was estimated for K (Figure 2). For the DSWs, the label K concentrations were approximately twice as high as the measured values. The differences between Na concentrations of the DSWs were non-significant ($R^2 = 0.122$, $p = 0.396$). Nonetheless, the poor linear correlation for Na and the slope of approximately two for K may be due to the label values being the average of wide concentration ranges. In practice, the measured Na and K concentrations were entirely within the ranges indicated on the bottle labels.

3.4. Classification of Water Types

The chemistry of four kinds of Korean bottled water was evaluated using a piper diagram (Figure 3). The samples were classified into three major groups (Ca-HCO$_3$, Ca(Mg)-Cl, and Na-HCO$_3$). Due to the poor CBE for the CWs, the mixed Ca-Mg-Cl type was not considered a main group.
Figure 3. Piper diagram including four types of Korean bottled waters along with previous studies [12,13].

The NMW and FW samples were mainly characterized by the Ca-HCO$_3$ water type, in agreement with previous studies [12,13]. Groundwater as a source for bottled water predominantly represented the Ca-HCO$_3$ water type [18]. These results strongly indicate that lithology with relatively prominent Ca concentration characterize the groundwater aquifers in South Korea, and that the groundwater chemistry is preserved in the bottled water. The Ca-rich water chemistry may have resulted from disseminated calcite in silicate rocks because areas underlying carbonate rocks are mostly concentrated in northeastern Korea and occupy approximately 5% of the country’s area. Compared to the NMWs, many FWs had relatively high proportions of Mg and/or Na (Figure 3). Bottled water collected from a basaltic basin can include a high proportion of Na + K because basalts have high contents of Na and K (e.g., [13]). However, the FWs with high levels of Na + K in this study were not related to specific lithology because they were collected from various basins consisting of granitic, metamorphic, and clastic sedimentary and volcanic rocks. Therefore, the water chemistry of the FWs could have changed during the manufacturing process.

Korean DSWs in previous studies were subdivided into Ca(Mg)-Cl and Na-Cl-SO$_4$ types [13]. The water samples representing Na-Cl-SO$_4$ types were not analyzed in this study, and all DSW samples representing the Ca(Mg)-Cl type were precisely distinguished from other waters. Divalent ions (e.g., Ca, Mg, and SO$_4$) are more readily removed by desalination processes than monovalent ions (e.g., Na, K, Cl) [19,20]. For example, nanofiltration membranes remove divalent ions more efficiently than monovalent ions [21]. Thus, Kim et al. [13] inferred that DSWs with high Ca + Mg concentrations were post-treated after desalination processes (e.g., reverse osmosis [RO]). As we previously suggested, our results indicate that the DSWs characterized in this study were subjected to post-treatment processes after desalination processes.

3.5. Source of Bottled Water

3.5.1. Groundwater-Derived Bottled Water

Source-water chemistry is primarily controlled by the lithological properties of an aquifer system resulting from strong water–rock interactions over a prolonged period. Bottled water reflects the chemical properties of source water as long as there is no change in water chemistry during the manufacturing processes. Typically, the molar Na/K and (Ca + Mg)/(Na + K) ratios of bottled water have been used to identify the source water (e.g., rainwater, sea water, or groundwater recharge) and
to infer whether groundwater recharge occurs continuously [9]; Na/K ratios of 15–25 and <10 are indicative of groundwater recharge and rainwater, respectively. A (Ca + Mg)/(Na + K) ratio > 1.0 represents continuous groundwater recharge [9].

Based on the (Ca + Mg)/(Na + K) ratio, most bottled water samples in this study were likely to be derived from continuous groundwater recharge; one CW sample had a ratio of 0.76. Furthermore, the Na/K ratios for nine NMWs and two CWs were <10, indicating that the source water was affected by rainwater. Interestingly, the water samples originated from only two areas, suggesting that the water chemistry was site-specific. The rest of the NMWs showed a wide range of Na/K ratios, between 10 and 25, indicating that their source water was derived from groundwater recharge. These observations suggest that their source water originated from a shallow aquifer and was continuously replenished because their Na/K ratios were <50 and their (Ca + Mg)/(Na + K) ratios were >1.0.

3.5.2. Desalinated Seawater

The average boron (B) concentration in seawater (~4.6 mg/L [22]) is typically higher than that of freshwater. Thus, B concentration can be used to identify DSW. The B concentration for the DSWs ranged from 302 to 513 µg/L (388 ± 74.6 µg/L, n = 8). As expected, the B concentration was much higher than that of others derived from freshwater: with an exception for one sample (NMW-14, 378 µg/L), 1.42–9.29 µg/L (3.52 ± 2.47 µg/L, n = 16) for NMWs, 2.11–18.4 µg/L (7.51 ± 7.69 µg/L, n = 4) for CWs, and 0.95–150 µg/L (average 32.9 ± 44.0 µg/L, n = 21) for FWs. On average, groundwater in Korea had a B concentration less than approximately 10 ± 5.85 µg/L (n = 320 [23]), 8.21 ± 7.27 µg/L (n = 54 [24]), and 1.56 ± 1.49 µg/L (n = 17 [25]). Therefore, the much higher B concentration in DSWs probably indicates that seawater was the source water for DSWs. In addition, the average molar B/Cl ratio of 0.0363 ± 0.0664 (n = 8) of the DSWs was much higher than that of seawater (0.0008). Compared to the Cl concentration, the B concentration can be relatively elevated during RO processes because undissociated boric acid can penetrate RO membranes while Cl cannot [19,26]. These results verify that the DSWs were derived from seawater and post-treated after desalination processes.

3.6. Trace-Element Geochemistry of Groundwater-Derived Bottled Waters

Significant variation in trace elements reported for Estonian bottled water was attributed to mineral dissolution and ion exchange processes within the aquifers [27]. In addition, waters containing high concentrations of Fe and Mn have higher dissolved CO₂ content, and trace element concentrations may change during manufacturing processes, such as aeration and degassing [4], or during precipitation with Fe and Mn oxides and adsorption onto colloids. In addition, some trace element concentrations of bottled water can be affected by storage materials and storage conditions [28,29]. In the following sections, we report several trace elements (i.e., Li, V, Ba, Rb, Cr, and Ga) concentrations of Korean bottled waters and discuss their concentration ranges and whether they were affected by manufacturing processes. Other trace elements (i.e., Be, Ni, Cu, Zn, Se, Zr, Ag, and Cd) that were not detected in some bottled waters are not discussed below.

3.6.1. Lithium (Li) and Vanadium (V)

Lithium is typically more enriched in felsic rocks (e.g., granite) and sedimentary rocks than in mafic (or ultramafic) rocks (e.g., basalt), whereas V concentrations are higher in mafic rocks than in felsic and carbonate rocks [8]. The lithological distribution in South Korea is complex (Figure 1), and it is difficult to identify whether source water chemistry predominantly reflects mono-lithological properties. Nonetheless, Li and V concentrations for bottled water originating from granitic rocks, which are the most extensively distributed in South Korea, were compared to those from metamorphic rocks; the contribution of clastic sedimentary/volcanic rocks to bottle water chemistry was not compared to the others because only one sample originated from them.

The Li concentration in the bottled waters from granitic and metamorphic rocks ranged from 0.58 to 27.9 µg/L (average 7.52 ± 7.18 µg/L, n = 22) and 11.6 to 14.8 µg/L (average 13.6 ± 1.31 µg/L,
n = 5), respectively (Table 3, Figure 4). The water samples from metamorphic rocks had higher Li concentrations, similar to that of groundwater in Jeju Island, Korea, which is mostly composed of basaltic rocks (12.0 ± 20.0 µg/L, n = 11) [30]. By contrast, Hyun et al. [31] reported significantly lower Li concentrations (0.6 µg/L) in Jeju groundwater (n = 258). By comparison, the Li concentration ranges in European bottled water range widely: 2.59 µg/L for the 25th percentile and 54.4 µg/L for the 75th percentile (median 10.0 µg/L). A high Li concentration was reported in areas enriched in alkalic volcanic rocks (e.g., central-southern Italy) [10].

Table 3. Some trace element contents for Korean bottled water originating from groundwater underlying granitic rocks and metamorphic rocks, respectively. Functional water (FW) and desalinated seawater (DW) were not shown because the samples were not closely related to lithological property.

| Sample | Li  | B   | V   | Cr  | Rb  | Ba  | Ga  |
|--------|-----|-----|-----|-----|-----|-----|-----|
|        | (µg/L) |     |     |     |     |     |     |
| Granitic rocks |     |     |     |     |     |     |     |
| NMW-1  | 8.52| 9.01| 0.27| 0.02| 2.77| 75.5| 0.01|
| NMW-4  | 27.9| 5.76| 0.25| 0.07| 1.13| 1.99| 0.15|
| NMW-5  | 2.39| 2.61| 2.26| 0.39| 0.41| 1.19| 0.03|
| NMW-6  | 1.99| n.d.| 1.13| 0.36| 0.48| 0.47| 0.06|
| NMW-8  | 1.62| 1.52| 0.34| 0.67| 1.42| 55.2| 0.00|
| NMW-9  | 2.27| n.d.| 2.17| 0.39| 0.24| 1.10| 0.10|
| NMW-10 | 0.78| 3.06| 0.67| 0.40| 0.75| 4.32| 0.02|
| NMW-11 | 19.2| 2.61| 0.62| 0.05| 4.37| 5.78| 0.42|
| NMW-14 | 5.33| 378 | 0.01| 0.04| 3.11| 0.06| n.d.|
| NMW-15 | 7.98| 4.47| 0.61| 0.13| 1.22| 10.7| 0.80|
| NMW-16 | 7.29| 1.87| 0.57| 0.14| 1.20| 9.84| 0.76|
| NMW-17 | 2.37| n.d.| 1.53| 0.30| 0.93| 1.01| 0.12|
| NMW-18 | 2.38| 3.33| 1.64| 0.32| 0.85| 0.87| 0.04|
| NMW-19 | 8.19| 3.07| 0.42| 0.59| 0.27| 0.97| 0.02|
| NMW-20 | 7.86| 9.29| 0.84| 0.63| 0.71| 28.7| 2.18|
| NMW-21 | 1.70| 1.95| 0.76| 0.21| 0.24| 1.00| 0.11|
| CW-1   | 20.6| 18.4| 2.59| 0.27| 1.28| 10.8| 0.41|
| CW-2   | 6.67| 2.11| 0.07| 0.02| 0.30| 1.73| 0.01|
| CW-4   | 11.5| 2.17| 0.43| 0.20| 0.13| 3.49| n.d.|
| CW-5   | 13.0| n.d. | 0.26| 0.15| 0.86| 7.98| n.d.|
| CW-6   | 5.30| n.d. | 0.30| 0.10| 0.90| 8.80| 0.01|
| CW-7   | 0.58| n.d. | 0.04| 0.01| 1.34| 17.7| 0.01|
| min    | 0.58| 1.52| 0.01| 0.01| 0.13| 0.06| 0.00|
| max    | 27.9 | 378 | 2.59| 0.67| 4.37| 75.5| 2.18|
| avg.   | 7.52 | 28.1| 0.81| 0.25| 1.13| 11.3| 0.27|
| std.   | 7.18 | 93.5| 0.76| 0.20| 1.04| 19.1| 0.52|
| Metamorphic rocks |     |     |     |     |     |     |     |
| NMW-2  | 13.0| 2.40| 0.12| 0.02| 0.42| 0.55| 0.01|
| NMW-3  | 14.3| n.d. | 0.03| 0.03| 0.51| 0.60| 0.06|
| NMW-7  | 11.6| 1.75| 0.15| 0.11| 3.39| 7.02| 0.61|
| NMW-12 | 14.4| n.d. | 0.17| 0.05| 0.46| 0.55| 0.06|
| NMW-13 | 14.8| 2.33| 0.16| 0.02| 0.46| 0.77| 0.02|
| min    | 11.6| 1.75| 0.03| 0.02| 0.42| 0.55| 0.01|
| max    | 14.8 | 2.40| 0.17| 0.11| 3.39| 7.02| 0.61|
| avg.   | 13.6 | 2.16| 0.13| 0.05| 1.05| 1.90| 0.15|
| std.   | 1.31 | 0.36| 0.06| 0.04| 1.31| 2.87| 0.26|

n.d.: not detected.
The V concentration in the Korean bottled waters was highest in samples derived from granitic rocks: 0.01–2.59 µg/L (average 0.81 ± 0.76 µg/L, n = 22) compared to 0.03–0.17 µg/L (average 0.13 ± 0.06 µg/L, n = 5) for metamorphic rock (Table 3, Figure 4). The V concentration in European bottled waters ranged from <0.1 µg/L for the 25th percentile to 0.41 µg/L for the 75th percentile (median 0.17 µg/L). A relatively high V concentration (>10 µg/L) was reported in water samples from volcanic areas [29]. Similarly, the V concentration for groundwater in Jeju Island was relatively higher (12.0 µg/L, n = 2595) [31].

Lithium and V concentrations in bottled water samples thus provide site-specific information. In addition, according to the Korean drinking water legislation, major cation concentrations in bottled water following after-treatment processes (e.g., filtration, precipitation, and aeration) must be within 20% of the values of the source water [32]. Trace element concentrations can change during a treatment process. For example, removal of arsenite and chromate in simulated drinking water has been reported when using a filter column consisting of a mixture of powdered carbon black and powdered carbon steel [33]. Thus, we infer that the concentration of trace elements can be altered by manufacturing processes, and conclude that Korean bottled water chemistry is determined by water–rock interactions and affected by manufacturing processes.

3.6.2. Barium (Ba)

The concentration of dissolved Ba is typically low because it is either adsorbed in clay minerals or precipitated in the form of sulfate and carbonate in nature [8]. The solubility of Ba compounds increases with decreasing pH, and the highest Ba concentrations in bottled water are expected in low-pH water derived from igneous (e.g., granite), alkaline igneous, volcanic, and Mn-rich sedimentary rocks [34]. In addition, the Ba concentration can increase under anaerobic conditions whereby sulfate reduction occurs [8]. In South Korea, groundwater underlying metamorphic and granitic rocks has Ba concentrations averaging 20.8 µg/L and 9.47 µg/L, respectively [35]. Metamorphic rock-derived groundwater has a higher Ba concentration than rather than granitic rock-derived groundwater. Sung et al. [36] suggested complex lithological distributions could account for substantial differences in water chemistry.

In our study, the Ba concentration for Korean bottled water ranged from 0.06 to 75.5 µg/L (average 11.3 ± 19.1 µg/L, n = 22) from a granitic rock environment, mainly lying between 0.5 µg/L and 11 µg/L (in this case, average 4.21 ± 3.91 µg/L, n = 17) (Table 3, Figure 4). For the samples from a metamorphic rock environment, it ranged from 0.55 to 0.77 µg/L (average 0.62 ± 0.10 µg/L, n = 4), except for one
sample with a particularly high value (7.02 µg/L; Table 3, Figure 4). The Ba concentrations were not in agreement with lithology-related groundwater chemistry in South Korea, which could be due to manufacturing processes as noted above for Li and V. However, the Ba concentration in European bottled water ranged from 10.1 µg/L for the 25th percentile to 77.9 µg/L for the 75th percentile, with a median value of 29.2 µg/L. No clear regional features and no geographical gradients were mapped for the European bottled water. Hence, the main factor controlling Ba concentration is likely to be site-specific, e.g., redox conditions [8]. In addition, groundwater derived from volcanic rocks in Korea (e.g., Jeju Island [31]) had higher Ba concentration than that from metamorphic rocks (Figure 4), which reflects the lithological features.

3.6.3. Rubidium (Rb)

Rubidium observed in the pedosphere and hydrosphere is mostly derived from silicate weathering. Typically, Rb is more enriched in felsic rock, such as granitic rock, than in mafic rock (e.g., basalt) [8]. The Rb concentrations for the bottled water samples in this study ranged from 0.13 to 4.37 µg/L (average 1.13 ± 1.04 µg/L, n = 22) for granitic and from 0.42 to 0.51 µg/L (average 0.46 ± 0.04 µg/L, n = 4) for metamorphic rocks, excluding one sample with the relatively high value of 3.39 µg/L (Table 3, Figure 4). In comparison, the Rb concentration in European bottled water ranges from 0.61 for the 25th percentile to 7.69 µg/L for the 75th percentile (median value 2.12 µg/L). Although the K in mica and K-feldspar can be substituted by Rb [8], the Rb/K ratio in water would be less than that in the host rocks due to incongruent mineral dissolution. In this study, the Rb/K ratio for bottled waters from granitic and metamorphic rocks spanned a wide range from 8.7 × 10⁻⁴ to 1.1 × 10⁻³ (average 4.9 × 10⁻⁴) and from 2.9 × 10⁻⁴ to 1.8 × 10⁻³ (average 6.3 × 10⁻⁴), respectively. No correlation was observed between Rb and K, unlike in a previous study that reported a linear dependency of the Rb concentration on the K concentration, i.e., [Rb] = 2.2 × 10⁻⁴ [K] + 8.7 × 10⁻⁹ (R² = 0.637) [37]. As noted above, these results suggest that Korean bottled water chemistry is altered by the manufacturing process. In a previous study, the Rb concentration in groundwater sourced from a basaltic aquifer in Jeju Island (9.98 µg/L, n = 258 [31]) was several times higher than that in groundwater sourced from granitic and metamorphic rocks, which supports this interpretation.

3.6.4. Chromium (Cr)

Chromium is commonly enriched in mafic and ultramafic rocks [8]. The Cr concentration in the bottled water samples ranged from 0.01 to 0.67 µg/L (0.25 ± 0.20 µg/L, n = 22) for granitic and from 0.02 to 0.11 (0.05 ± 0.04 µg/L, n = 4) for metamorphic rock waters, respectively (Table 3, Figure 4). The Cr concentrations were below the Korean Drinking Water Quality Standard and European Union limit (<0.05 mg/L). Most of the Korean bottled water had Cr concentrations below 0.5 µg/L, as found in European bottled water [8]. European bottled waters with the highest Cr concentrations (up to 27.2 µg/L) are linked to the occurrence of ultramafic rocks [8]. Similarly, groundwater from the volcanic island of Jeju in Korea have a higher Cr concentration (average 1.5 ± 1.41 µg/L, n = 258 [31]) than those in the Korean bottled waters. Likewise, the lower Cr concentration in the Korean bottled waters derived from felsic rocks water likely reflects lithological features. Nonetheless, it is possible that the Cr concentration for bottled water was altered by manufacturing processes.

3.6.5. Gallium (Ga)

Most rocks contain about 0.5–20 mg/kg Ga, and the highest level is typically observed in sedimentary rocks, particularly fine-grained ones such as shales and schists [8]. The Ga concentration in the bottled water samples ranged from 0.001 to 2.18 µg/L (0.27 ± 0.52 µg/L, n = 22) for granitic and from 0.01 to 0.06 (0.04 ± 0.03 µg/L, n = 4) for metamorphic rock waters, respectively, with the exception of one sample with a relatively high concentration (0.611 µg/L; Table 3, Figure 4). In Europe, more than 69% of all analyzed bottled water samples (n = 1785) contain Ga below the detection limit of 0.005 µg/L [8]. According to the literature, water purification process, such as aeration, may precipitate
ferric hydroxides and cause removal of Ga together with Fe. Most of the NMWs and CWs in this study had Fe concentrations below the detection limit. Interestingly, for some samples \((n = 8)\) Ga was positively and strongly correlated with Ba \((R^2 = 0.960)\). The eight samples were derived from an area underlain by granitic rocks, and they were characterized by Na/K ratios > 10, indicating that groundwater recharge occurred continuously. To account for this phenomenon, the occurrence of Ga and Ba may be constant in certain lithologies and the chemical behaviors of Ga and Ba may counterbalance until the water is bottled. Meanwhile, Ga anomalies may be related to the occurrence of alkaline thermal waters originating from granites, metamorphic silicic rocks, and andesites in Bulgaria, and in areas underlying felsic gneisses with pegmatite dykes containing various unusual minerals in Norway [8]. In addition, Ga is frequently retained in clay minerals (e.g., kaolinite, smectite, and aluminum hydroxide minerals) [38]. Further study is needed to better understand the relationship between Ga and Ba.

3.7. Trace Elements in Desalinated Water

In seawater, the Li concentration ranges between 140 and 200 \(\mu g/L\) [39] and V between 1.73 and 2.29 \(\mu g/L\) [40]; Li was higher than V, by up to 116-fold. The Li and V concentrations in the DSWs ranged from 3.13 to 9.68 \(\mu g/L\) (average 6.28 ± 1.85 \(\mu g/L\), \(n = 8\)) and from 0.01 to 0.05 \(\mu g/L\) (average 0.02 ± 0.02 \(\mu g/L\), \(n = 8\)), respectively (Table 1, Figure 4). Most Li and V in seawater (>95%) were removed in the desalination process. The average concentrations of Ba and Rb in seawater are 13 \(\mu g/L\) and 125 \(\mu g/L\), respectively [41]. Barium and Rb concentrations in our DSW samples ranged from 0.02 to 0.16 \(\mu g/L\) (average 0.07 ± 0.04 \(\mu g/L\), \(n = 8\)) and from 1.76 to 5.10 \(\mu g/L\) (average 3.40 ± 0.96 \(\mu g/L\), \(n = 8\)), respectively (Table 1, Figure 4). Most of the Ba and Rb in seawater (>99.9%) were removed during manufacturing processes. Chromium concentrations in seawater range from 0.04 to 0.5 \(\mu g/L\) [42]. Only four DSW samples had Cr concentrations ranging from 0.03 to 0.07 \(\mu g/L\) (average 0.04 ± 0.02 \(\mu g/L\), \(n = 4\)), i.e., within the Cr concentration in seawater. Thus, it is ambiguous whether Cr concentrations were changed during manufacturing processes. In the DSW samples, the Ga concentration was also below the detection limit, as was the case for Li and V. The B/Cl ratio and the concentrations of trace elements indicate that DSW chemistry was entirely regulated by the manufacturing processes, such as desalination (i.e., RO) and post-treatment steps.

3.8. Factors Controlling Geochemistry in Functional Water

Most chemical properties of FWs are dominated by water–rock interactions according to the bivariate relationships of TDS and Na/(Na + Ca), and Cl/(Cl + HCO\(_3\)) (i.e., Gibbs diagram, not shown). However, of the FWs, the extremely low TDS and Cl/(Cl + HCO\(_3\)) levels of three samples would not be have been determined by natural processes but closely affected by manufacturing processes. For example, hydrogen-rich water is produced by decreasing ion concentration as follows [43]: source water is purified by passing through primary and secondary filtering processes, and so mineral anions (e.g., Cl, NO\(_3\), HSO\(_4\), and HCO\(_3\)) and cations (e.g., Ca, Na, Mg, and K) in the filtered water accumulate at the anode and cathode compartments in the electrolyzed water generator, respectively, and hydrogen is released. Thus, the final hydrogen-rich water has very low mineral ion contents and low redox potential, depending on the characteristics of the source water.

There was a significant relationship between Ba and SO\(_4\) for the FWs derived from granitic rocks (except for alkali water) (Figure 5). Similar linear relationships are evident for the FWs derived from metamorphic and clastic sedimentary/volcanic rocks. Various Ba-bearing compounds form in water under alkaline conditions, and Ba in alkaline water in this study was not correlated with SO\(_4\). This result suggests that FW chemistry was not influenced by manufacturing processes (e.g., Gibbs diagram). These apparently conflicting results reveal the difficulty determining whether the water chemistry of the FWs was affected by manufacturing processes, water–rock interactions, or both.
Figure 5. Plot of Ba and SO$_4$ for FW samples corresponding to particular lithology. The water samples derived from granitic and metamorphic rocks are represented by regression lines with high correlations.

3.9. Oxygen and Hydrogen Isotopes

The relationships between $\delta^{18}$O and $\delta^2$H values for the Korean bottled water samples are shown in Figure 6. All of the samples were near the global meteoric water line ($\delta^2$H = 8 × $\delta^{18}$O + 10) and were expressed by the local meteoric water line (LMWL) of $\delta^2$H = 7.1 × $\delta^{18}$O + 3.20 ($R^2 = 0.945$), except for DSWs, which displayed the typical isotopic signal for seawater. Our results are similar to those of previous studies [12,13] that have reported $\delta^2$H = 7.2 × $\delta^{18}$O + 1.55 ($R^2 = 0.918$, $n = 36$). These results indicate that isotopic fractionation does not occur by water–rock interactions and during manufacturing processes, and that the isotopic signal of the source water is preserved at the national scale; isotopic fractionation caused by water–rock interactions can be ignored because groundwater in South Korea is typically <80 °C [44]. Lee and Kim [45] calculated that the deuterium excess (d-value; $d = \delta^2$H − 8 × $\delta^{18}$O) for precipitation in winter (>15‰) is higher than that for rainfall in summer (<10‰) in South Korea. Regardless of the sample type, the calculated d-values were below 15‰: 10.6–13.4‰ (average 11.9 ± 0.78‰) for NMW, 7.6–12.5‰ (average 10.1 ± 1.56‰) for FW, and 7.1–13.0‰ (average 9.4 ± 2.1‰) for CW. These results indicate that groundwater used to produce bottled water is mostly recharged in the summer season.

Figure 6. Plot of $\delta^{18}$O and $\delta^2$H values for four types of Korean bottled water samples along with previous studies [12,13].
4. Conclusions

Korean bottled water samples were purchased in 2016. The water chemistry of groundwater-derived bottled water and desalinated seawater was delineated using major ions, trace elements, and isotopes. The major cation contents were in agreement with those on the bottle labels. Of the bottled waters, the water chemistry of NMW was strongly influenced by the lithology, based on the major ions. In particular, the ratios of major cations are helpful to decipher the source-water origin. Groundwater was continuously recharged and the contribution of rainwater to forming groundwater was also considered. The FW showed abnormal ratios between cations and anions, indicating that the water chemistry was strongly determined by manufacturing processes rather than lithological properties. The DSW chemistry was dependent on manufacturing processes, such as desalination and post-treatment processes. Some of the trace elements in the bottled waters reflected lithological features but others were changed by manufacturing processes. Unlike major ions, trace elements are poor indicators of factors controlling bottled water geochemistry. Regardless of the contribution of natural and artificial processes to water chemistry, all of the water samples displayed the typical correlation between oxygen and hydrogen isotopes with isotopic signals corresponding to intrinsic water.

Author Contributions: Conceptualization, J.-S.R., K.-S.L., and W.-J.S.; methodology, J.-S.R., K.-S.L., and W.-J.S.; software, W.-J.S.; formal analysis, H.S.S. and Y.-Y.J.; writing—original draft preparation, W.-J.S.; writing—review and editing, J.-S.R. and K.-S.L.; visualization, W.-J.S.; funding acquisition, K.-S.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Research Council of Science and Technology (NST) grant by the Korea government (MSIP) (No. CAP-17-05-KIGAM) and partly by the KBSI grant (C050200).

Acknowledgments: We would like to thank S.H. Park and K.M. Kim for their help in analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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