Characteristics of the chemical composition of groundwater on Tanegashima, Yakushima, and Nakanoshima islands, Kagoshima Prefecture, Japan

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Abstract

Twenty-six groundwater samples were collected from Tanegashima, Yakushima, and Nakanoshima islands between July 27 and August 2, 2003. The interpretation of chemical analyses suggested that the groundwater on the islands have been affected by sea salt (ss). Chlorine (Cl\(^-\)) concentrations on Yakushima, which were inversely related to elevation, were considerably lower than those on Nakanoshima and Tanegashima, reflecting higher annual rainfall on Yakushima. However, groundwater samples from Yakushima had a higher ratio of ss components—more than 50% (except one sample). Non-sea salt (nss) components of the groundwater on Tanegashima, Yakushima, and Nakanoshima were found to be affected mostly by the chemical weathering of plagioclase feldspars. The groundwater on Tanegashima was also thought to be affected by ion exchange between clay minerals and Ca\(^2+\). The effects of sulfuric acid and carbonic acid on chemical weathering were nearly equivalent on Nakanoshima. Therefore, the average concentrations of nssSO\(_4^{2-}\) and dissolved SiO\(_2\) were remarkably higher than those for Yakushima and Tanegashima. The arithmetic mean concentration of nssK\(^+\) on Yakushima was high even though the total concentration of all nss components was low. The nssK\(^+\) probably originates from chemical weathering of K-feldspar in granite. The total concentration of nss components on Yakushima was remarkably lower than that on Tanegashima or Nakanoshima. Low NO\(_3^-\)-N concentrations in these mountainous and forested islands reflect a low load from anthropogenic activities.

Key Words: groundwater chemistry, chemical composition, chemical weathering, nitrate, Tanegashima, Yakushima, Nakanoshima

1. Introduction

Tanegashima, Yakushima, and Nakanoshima islands, with population sizes of 35695, 13875, and 183 in 2000, respectively, are located between Kyushu and Amamioshima islands in southwestern Japan.

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Japan, as shown in Figure 1 (Kagoshima Prefecture, 2001; Toshima Village, 2001). These islands are in a subtropical climate region. Tanegashima Island has an area of 454 km² and a maximum elevation of 282 m. Mt. Miyanouradake (1935 m a.s.l.) on Yakushima Island is the highest mountain in Kyushu, but many mountains on this small island (503 km²) are higher than 1500 m. Therefore, Yakushima Island has both temperate and subtropical climate zones. Nakanoshima Island, a volcanic island, has an area of 34.5 km². Mt. Otake (979 m a.s.l.) is its highest mountain. The annual average temperatures on these islands are 19.6 °C, 19.2 °C, and 18.9 °C, and the annual amounts of rainfall are 2322 mm, 4359 mm, and 3082 mm (JMA, 1971–2000, 2003–2006), respectively. An warm current (Kuroshio) in the East China Sea flows northward west of Nakanoshima and passes eastward south of Yakushima and Tanegashima to the Pacific Ocean. Rainfall on Yakushima is much greater than that on Tanegashima. Differences in temperature between the surface seawater and the atmosphere and of water vapor pressure between the surface seawater and the air mass on Yakushima, which is located on the axis of the Kuroshio Current, are greater than those for the other Nansei Islands. Therefore, climate disturbance (i.e., rainfall) is strongly affected by low-pressure systems passing through the area south of Yakushima (Ishijima and Itokazu, 1980; Eguchi, 1984).

Nagafuchi et al. (2001) studied the composition of rime ice on Yakushima. The geochemical characteristics of acidic stream water and the effects of acid deposition on the water quality of mountainous streams were studied on Yakushima by Nakano (2001) and Nagafuchi et al. (2003), respectively. Yamanaka et al. (2005) described river and spring water chemistry on Yakushima. These studies, with respect to the effect of acid deposition on the stream water of Yakushima Island, revealed that the acid species are transported from the Asian continent. The results show that the pollutants that acidify stream water on Yakushima Island accelerate chemical weathering, mainly of plagioclase.

Many chemical studies on meteoric water have been conducted on Yakushima Island, mainly because the island was registered as a UNESCO World Natural Heritage Site in 1993. However, the meteoric waters of Tanegashima and Nakanoshima islands have yet to be studied. In this study, contributions from sea salt and chemical weathering of silicate rocks inferred from chemical data of groundwater will be presented and discussed to clarify the geochemical characteristics of groundwater on Tanegashima, Yakushima, and Nakanoshima, each of which has different geographical and geological environments—sedimentary rocks, granites, and volcanic rocks, respectively.

2. Geological Features

Tanegashima is elevated from the main submarine bedrock, which consists of Kumage Group formations including the Sumiyoshi, Fukago, Hamatsuwaki, and Nijyuuban formations (Figure
The formations consist of sandstone, shale, and tuff-silt rocks that represent neritic marine deposits. These rocks are widely distributed around hills at about 200 m (a.s.l.) in the northern, central, and southwestern parts of this island. Eroded surfaces of Kumage Group formations are partially covered unconformably by Kukinaga Group formations. Unconformity surfaces of Kumage and Kukinaga Group formations are covered by Masuda Formation sandstone, which is distributed below 120 m (a.s.l.) in the southern part of the island. Additionally, unconformity surfaces of Kumage and Kukinaga Group formations and the Masuda Formation are overlaid by the Hase Formation, which consists of gravels distributed in the southern part of the island (Hayasaka, 1985). A camptonite dike about 20 km long exists in the northern part of this island, as presented in Figure 2. Minerals in the intrusive rock include biotite, alkali amphibole, and plagioclase (albite to oligoclase), which is associated with calcite (Hayasaka, 1985). Yagi et al. (1975) reported that this intrusive rock is older than the Kukinaga Group, which includes pebbles and boulders of the camptonite dike. Tanegashima is covered with andesitic two-pyroxene volcanic ash (Hamazaki, 1972). The volcanic ash soils consist mainly of hypersthene, augite, basic plagioclase, and an unidentified iron mineral. Clay minerals in the soils include mostly allophane, chlorite, vermiculite, illite, and kaolinite, among others.

Figure 3 shows granite in the central part of Yakushima Island that is surrounded by sedimentary rocks, including siltstones, sandstones, and gravels (Hayasaka, 1985). Major minerals in the granite are biotite, quartz, K-feldspar, and plagioclase feldspar. Argillaceous rock contains biotite, muscovite, chlorite, and others (Hayasaka, 1985).

On Nakanoshima Island, Otake and Shizaki volcanic rocks, consisting of either lavas or tuff breccias, are distributed in the northern and the southern halves of the island, respectively (Figure 4). Both volcanic rocks consist mostly of two-pyroxene andesites (Daishi, 1985). Yokoyama and Tiba (1990) reported that andesitic to dacitic volcanic rocks on Nakanoshima contain plagioclase, orthopyroxene, clinoptyroxene, and amphibole. The island has hot springs in Satomura (Nishiku and Amadomari hot springs) and Funagura (Higashiku Hot Spring) (Daishi, 1985).

3. Experimental Methods

Thirteen, eight, and five groundwater samples from Tanegashima, Yakushima, and Nakanoshima islands, respectively, were collected into 0.5-L polyethylene bottles between July 27 and August 2, 2003. Water temperature, pH, and EC were measured at each sampling point using a glass electrode pH meter (HM-10P; Toa Corp.) and an electrical conductivity meter (CM-10P; Toa Corp.). After filtration with a 0.45-µm membrane filter, Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4^{2-}\), and NO\(_3^-\) concentrations were determined in the laboratory using an ion chromatograph (L-7000; Hitachi Ltd.). The HCO\(_3^-\) concentrations were determined by alkalinity titration (JISC, 1992) and dissolved silica by the molybdate yellow method using a spectrophotometer (AE-300; Erma Inc.; JISC, 1992).

4. Results and Discussion

Table 1 presents the chemical composition of groundwater from Tanegashima, Yakushima, and Nakanoshima islands. Ion charge balances \((\Sigma \text{cation} - \Sigma \text{anion})/(\Sigma \text{cation} + \Sigma \text{anion})\) for 23 of 26 samples were in the \(\pm 5\%\) range. The other three samples (Nos. 2, 3, and 4) on Tanegashima had balances ranging from \(-5.1\%\) to \(-6.3\%\). The non-sea salt (nss) component concentrations shown in Table 1 were calculated using the following equation (Ishiki et al., 2009):

\[
nss X = \frac{X_{\text{groundwater}} - \left(\frac{X_{\text{sea}}}{Cl_{\text{sea}}}\right) \times Cl_{\text{groundwater}}}{1}
\]

where \(X\) is the concentration of the dissolved species and \(Cl\) is the chloride concentration. Arithmetic mean concentrations for the respective islands
Fig. 2 Locations of groundwater sampling points on a geological map of Tanegashima Island and hexadiagrams for groundwater samples. Hexadiagrams for non-sea salt (nss) components are also shown by dotted lines. Numbers showing sampling points are the same as in Table 1.
are also shown in Table 1. Here, nssHCO$_3^-$, nss NO$_3^-$-N, and dissolved nssSiO$_2$ concentrations are excluded from Table 1 because those concentrations derived from seawater are generally extremely low (Berner and Berner, 1987). Hexadiagrams for groundwater on these islands are shown in Figures 2, 3, and 4, respectively, and those for nss components are shown in the same figures by dotted lines.

4.1 Chemical Features of Groundwater on Tanegashima

Hexadiagrams using data from 13 groundwater samples taken from Tanegashima Island are shown in Figure 2. According to a grouping method (Nagai, 1968; Horiuchi, 1992), the groundwater was found to be the Na-Ca-HCO$_3$-Cl type at Nos. 1 and 3; the Na-HCO$_3$ type at Nos. 2, 4, and 5; the Ca-HCO$_3$ type at Nos. 6, 7, and 9; the Na-Cl type at Nos. 8, 10, 12, and 13; and the Ca-Na-HCO$_3$-SO$_4$-Cl type at No. 11. However, compositions of nss com-
Components on Tanegashima were found to be the \( \text{Ca-HCO}_3 \) type, except for Nos. 5, 8, 10, and 11, which belong to either the \( \text{Na-HCO}_3 \), \( \text{Mg-SO}_4 \), \( \text{Na-HCO}_3\text{-SO}_4 \), or \( \text{Ca-Na-HCO}_3\text{-SO}_4 \) types (Figure 2).

Chloride (\( \text{Cl}^- \)) concentrations were in a range from 17.3 to 50.7 mg L\(^{-1}\) with an average of 25.8 mg L\(^{-1}\), as shown in Table 1. These values are remarkably higher than the average \( \text{Cl}^- \) concentration of river waters throughout Japan, 5.8 mg L\(^{-1}\) (Kobayashi, 1971). Judging from hexadiagram results, sea salt is thought to be included in the water.

Figure 5 presents a key diagram (Nagai, 1991) based on relative percentages in milliequivalents for groundwater on Tanegashima, Yakushima, and Nakanoshima islands. The mixing line of seawater with groundwater at No. 7 was shown as a straight line (■ - 7) because No. 7 on Tanegashima had
the highest HCO$_3^-$ and Ca$^{2+}$ concentrations. The groundwaters in the carbonate hardness area were shown to be the farthest from seawater. The groundwaters on Tanegashima were plotted along this line, which suggests that sea salt affects more or less the groundwater components.

The hexadiagram for No. 3 (Tanowaki 1, a bored well used as a source of tap water) shows that it is the Na-Ca-HCO$_3$-Cl type (Figure 2). The Cl$^-$, sea salt (ss) Na$^+$, ssMg$^{2+}$, and ssSO$_4^{2-}$ concentrations at this location were the highest on Tanegashima at 50.7, 28.2, 3.4, and 7.1 mg L$^{-1}$, respectively. The well has a depth of 100 m below ground level and is only 100 m from the coastline. Judging from the high concentrations of seawater components, the groundwater is probably affected by seawater intrusion. The hexadiagram for No. 13 (Arasaki Spring) shows that the groundwater groups into the Na-Cl type (Figure 2). The Cl$^-$, ssNa$^+$, ssMg$^{2+}$, and ssSO$_4^{2-}$ concentrations were second highest on Tanegashima at 39.5, 22.0, 2.6, and 5.5 mg L$^{-1}$, respectively. This spring is only 20 m from the coastline.

Correlations of the concentration of dissolved SiO$_2$ with those of nssNa$^+$, nssCa$^{2+}$, nssK$^+$, and nssMg$^{2+}$ were not positive for the groundwater samples from Tanegashima. Figure 6 shows correlations of HCO$_3^-$ with nssCa$^{2+}$ (A), nss(Ca$^{2+}$ + Na$^+$) (B), and nss(Ca$^{2+}$ + Na$^+$ + K$^+$ + Mg$^{2+}$) (C).

Correlations of HCO$_3^-$ with nss(Ca$^{2+}$ + Na$^+$) concentrations appeared to be positive in the groundwater (Figure 6B). This indicates that nssCa$^{2+}$ and nssNa$^+$ are probably enriched by the reaction of plagioclase feldspars in the volcanic ash soils and sedimentary rocks with groundwater containing CO$_2$, as shown by the following equation (Stumm and Morgan, 1981; Tamari et al., 1988).

$$4 \text{Na}_0.5\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8 + 6 \text{CO}_2 + 17 \text{H}_2\text{O} \rightarrow 2 \text{Na}^+ + 2 \text{Ca}^{2+} + 4 \text{H}_2\text{SiO}_4 + 6 \text{HCO}_3^- + 3 \text{Al}_4\text{Si}_2\text{O}_9(\text{OH})_4$$

The HCO$_3^-$ and nssCa$^{2+}$ concentrations were in a range from 0.16 to 3.03 meq L$^{-1}$ and from 0.25 to 1.75 meq L$^{-1}$, respectively, with averages of 1.37 and 0.73 meq L$^{-1}$ (Table 1). Concentrations of HCO$_3^-$ and nssCa$^{2+}$ at No. 7 were the second highest overall and the highest on Tanegashima, 2.85 and 1.75 meq L$^{-1}$, respectively.
respectively. This sampling point is located at the southernmost extent of the camptonite dike. Therefore, the high HCO$_3^-$ and nssCa$^{2+}$ concentrations in the groundwater are thought to be related to the reaction between calcium carbonate in the camptonite dike and CO$_2$ in groundwater, as shown by the following equation (Stumm and Morgan, 1981):

$$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^- \tag{3}$$

The nssCa$^{2+}$ and HCO$_3^-$ concentrations and the pH of groundwater in Kumage Group formations in the northern part of Tanegashima were higher than those in the Masuda Formation at the southern part of the island. The relationship between nssCa$^{2+}$ and HCO$_3^-$ is shown in Figure 6A. As this figure shows, equivalent concentrations of nssCa$^{2+}$ were deficient compared to those of HCO$_3^-$. However, equivalent concentrations of nss(Ca$^{2+}$ + Na$^+$) were only slightly deficient against HCO$_3^-$ concentrations (Figure 6B).

These results suggest that the chemical composition of the groundwater has been affected by ion exchange. Ion exchange between clay minerals and Ca$^{2+}$ can be illustrated by the following reaction (Stumm and Morgan, 1970):

$$2\text{NaY} + \text{Ca}^{2+} \rightarrow \text{CaY}_2 + 2\text{Na}^+ \tag{4}$$

where Y is the monovalent cation exchanger. The direction of ion exchange is shown in Figure 5. The key diagram illustrates that the chemical composition of No. 5 formed as a result of ion exchange (Agata, 1993). Figure 6C shows that concentrations of HCO$_3^-$ are mostly equivalent to those of nss(Ca$^{2+}$ + Na$^+$ + K$^+$ + Mg$^{2+}$). Judging from the nss components, the groundwater at No. 11 (a well in Noma) was found to be the Ca + Na-HCO$_3$ + SO$_4$ type, which plots far from the equivalent line in Figure 6C. Hamazaki (1972) reported that the volcanic ash soils of the island contained an unidentified iron mineral, which could be a kind of pyrite. Studies have suggested that nssSO$_4^{2-}$ in the groundwater might originate from the oxidation of sulfur in the volcanic ash soils (Stumm and Morgan, 1970; Agata et al., 2001).

The nssK$^+$ concentrations positively correlate with nssMg$^{2+}$ ($r=0.88$), except at Nos. 12 and 13. These non-sea salts are probably attributable to the chemical weathering of hypersthene, augite, and illite in the volcanic ash soils and sedimentary rocks.

Figure 7 shows a histogram of total nss concentrations. The amounts of nss components at Nos. 2–7 and 13 (northern part of island) taken from Kumage Group formations were larger than those at Nos. 8–12 (southern part of island) in the Masuda Formation area, which suggests that chemical weathering reactions differ considerably
between the Kumage Group and the Masuda Formation in Tanegashima; i.e., the nss components in the northern region might originate from mudstone and tuff-silt of the Kumage Group (Tamari et al., 1988).

It is therefore concluded that the chemical characteristics of groundwater on Tanegashima are affected mostly by sea salt, chemical weathering of plagioclase feldspars, and ion exchange.

4.2 Chemical Features of Groundwater on Yakushima

Figure 3 shows data from eight samples (Nos. 14–21) taken from Yakushima. All of the samples were found to be the Na-Cl type, as shown by the hexadiagrams, and the proportion of sea salt components was greater than 50%, except in No. 18 (38.8% for a well in Myanoura). These results suggested that the amounts of nss components were relatively small and that dissolved chemical species were mainly from sea salt.

The total concentrations of dissolved chemical species at No. 16 (Oko Spring), including the Cl$^-$ concentration (24.0 mg L$^{-1}$), were the highest of any on Yakushima Island. This result suggests that the groundwater at No. 16 is strongly affected by sea salt as a result of it being only 100 m from the coastline.

The Cl$^-$ concentrations on Yakushima were in the range of 4.2–14.4 mg L$^{-1}$ except for one sampling point with its highest 24.0 mg L$^{-1}$ and the average 12.7 mg L$^{-1}$ (Table 1). Yamanaka et al. (2005) reported that Cl$^-$ concentrations in river waters of Yakushima were mostly lower than 10 mg L$^{-1}$ (1.50–10.1 mg L$^{-1}$, and 23.9 mg L$^{-1}$) and were about one-half of those on Tanegashima Island (avg. 25.8 mg L$^{-1}$). The annual rainfall on Tanegashima is 2322 mm (JMA, 1971–2000). The annual weighted mean Cl$^-$ concentrations in rainwater at Yaku Town (3685 mm of annual rainfall) and Mt. Dichu-dake (1497 m high and 5721 mm of annual rainfall) on Yakushima were 5.7 and 3.5 mg L$^{-1}$, respectively (Hara, 1992). These Cl$^-$ concentrations are remarkably lower than those on Ishigaki Island (avg. 24.9 mg L$^{-1}$ in ground and river waters [Agata, 1994]; annual weighted mean of 10.4 mg L$^{-1}$ in rainwater; 2429 mm of annual rainfall [Agata et al., 2006]). The low Cl$^-$ concentrations reflect the climatic characteristics of Yakushima Island, which has high rainfall-Cl$^-$ concentrations in meteoric water decrease concomitantly with increasing rainfall (Agata et al., 2006).

The lowest Cl$^-$ concentrations of 4.2 and 7.2 mg L$^{-1}$ were from No. 14 (Kigenmeisui) and No. 20 (Yakuunsui) at elevations of 1250 m and 600 m, respectively, which suggests that the Cl$^-$ concentrations decrease concomitantly with increasing elevation. The Cl$^-$ concentrations are probably determined both by elevation and distance from the coast (Tokuyama and Shimoji, 1978).
As shown in Figure 5, the chemical composition of groundwater on Yakushima grouped into the non-carbonate alkali type and distributed along a line at about 25% HCO$_3^-$ The nss components are the Na-HCO$_3$ type, except for No. 18 which belongs to the Ca·Na-HCO$_3$·SO$_4$ type, as shown in Figure 3. The results suggest that the chemical composition of groundwater on Yakushima is affected mostly by chemical weathering reactions.

The percentages (meq L$^{-1}$) of nssNa$^+$ in the total nss cation concentrations on Yakushima and Tanegashima were 36.8% and 27.9%, respectively. Correlations of HCO$_3^-$ with nssNa$^+$ and nss(Ca$^{2+}$ + Na$^+$) in the groundwater were positive (Figure 8), which indicates that the nssNa$^+$ and nssCa$^{2+}$ components are probably attributable to the chemical weathering of sodium-enriched plagioclase feldspars in the granites (Tamari et al., 1988). Table 1 shows the nssK$^+$ concentrations in groundwater samples from Yakushima, Tanegashima, and Nakano-shima. The arithmetic mean of nssK$^+$ concentrations was high despite low concentrations of total nss components on Yakushima. The nssK$^+$ percentages (meq L$^{-1}$) in the total nss cation concentrations on Yakushima and Tanegashima were 28.3% and 7.0%, respectively.

Correlations of HCO$_3^-$ with both nssK$^+$ and nss(K$^+$+Mg$^{2+}$) concentrations were positive in the groundwater samples (Figure 9). The nssMg$^{2+}$ concentrations were very low and the average was 0.043 meq L$^{-1}$. Those in four samples were lower than 1.0 mg L$^{-1}$ (Table 1). These indicate that the nssK$^+$ and the nssMg$^{2+}$ components are probably attributable to chemical weathering of K-feldspar and biotite in the granites (Tamari et al., 1988). The nssK$^+$ is probably liberated by a reaction between K-feldspar and CO$_2$ in groundwater, as shown by the following equation (Drever, 1982).

$$\begin{align*}
2\text{KAlSi}_3\text{O}_8 + 2\text{CO}_2 + 11\text{H}_2\text{O} &
\rightarrow 2\text{K}^+ + 4\text{H}_2\text{SiO}_4 \\
&+ 2\text{HCO}_3^- + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4
\end{align*}$$

(5) kaolinite

Correlations of HCO$_3^-$ with nss(Na$^+$ +K$^+$+Ca$^{2+}$ +Mg$^{2+}$) concentrations were also positive (Figure

![Correlation of HCO$_3^-$ with nssNa$^+$ (A) and nss(Ca$^{2+}$+Na$^+$) (B) concentrations in groundwater samples from Yakushima Island.](image1)

![Correlation of HCO$_3^-$ with nssK$^+$ (A) and nss(K$^+$+Mg$^{2+}$) (B) concentrations in groundwater samples from Yakushima Island.](image2)
This chemical characteristic of the groundwater on Yakushima reflects the chemical weathering of granite.

Total concentrations of nss components on Yakushima were 0.15-1.28 meq L\(^{-1}\) with an average of 0.60 meq L\(^{-1}\). Those in seven samples of eight were distributed between 1.0 and 2.0 meq L\(^{-1}\) (Figure 7B). Thus, total nss components on Yakushima were remarkably lower than those on Tanegashima (avg. 3.49 meq L\(^{-1}\)).

### 4.3 Chemical Features of Groundwater on Nakanoshima

Three groundwater samples (Nos. 22, 23, and 26) among five from Nakanoshima Island were collected from the southern foot of Mt. Otake in the boundary area between Otake and Shizaki volcanic rocks. Hot springs are also located along the coastal site (Figure 4).

The groundwater of Nos. 22, 23, and 26 were found to be the Ca·Na·Mg·Cl-HCO\(_3\)·SO\(_4\) type and those of Nos. 24 and 25 were the Ca-Mg-Na-Cl-HCO\(_3\) type. The Cl\(^-\) concentrations were in a range from 19.9 to 31.7 mg L\(^{-1}\) and the average 26.4 mg L\(^{-1}\) (Table 1). These values were higher than those on Tanegashima (avg. 25.8 mg L\(^{-1}\)) or Yakushima (avg. 12.7 mg L\(^{-1}\)). The hexagrams show that sea salt contributed to the groundwater.
components on Nakanoshima (Figure 4).

Judging from the nss components, groundwater samples at Nos. 24 and 25 grouped into the Ca-HCO$_3$ type (Figure 4). However, No. 22 was found to be the Ca-Mg-HCO$_3$SO$_4$ type and Nos. 23 and 26 were the Ca-HCO$_3$SO$_4$ type. In Figure 5, these groundwater samples were plotted in the boundary area between the non-carbonate hardness and the non-carbonate alkali areas because of high SO$_4^{2-}$ concentrations that are in a range from 0.050 to 1.29 meq L$^{-1}$ and average 0.56 meq L$^{-1}$ (Table 1). The SO$_4^{2-}$ concentration at No. 22 (1.29 meq L$^{-1}$) was the highest on Nakanoshima.

Total nss on Nakanoshima (avg. 2.32 meq L$^{-1}$) was higher than that on Yakushima (avg. 0.60 meq L$^{-1}$) but lower than that on Tanegashima (avg. 3.47 meq L$^{-1}$).

Correlations of dissolved SiO$_2$ with nss(Ca$^{2+}$ + Mg$^{2+}$) concentrations were positive in the groundwater (Figure 11A). Correlations between concentrations of nssCa$^{2+}$ and nssMg$^{2+}$ also were positive ($r$=0.87), which suggests that the nssCa$^{2+}$ and nssMg$^{2+}$ components are derived from the reaction between pyroxenes in the two-pyroxene andesites and CO$_2$ in groundwater, as shown in the following equation (Berner and Berner, 1987):

$$\text{CaMgSi}_2\text{O}_6 + 4 \text{CO}_2 + 6 \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2 \text{H}_2\text{SiO}_4 + 4 \text{HCO}_3^- \quad (6)$$

The percentage (meq L$^{-1}$) of nssNa$^+$ in the total cation concentration is 14.3% on Nakanoshima, which was lower than that on Tanegashima (27.9%) and Yakushima (36.8%). The nssNa$^+$ and nssCa$^{2+}$ components are thought to come mainly from the reaction between plagioclase in the andesites and CO$_2$ in groundwater, as shown in equation 2, because the nssCa$^{2+}$ concentration was much greater than the nssMg$^{2+}$ concentration and the correlation of dissolved SiO$_2$ with nss(Ca$^{2+}$ + Na$^+$) was positive (Figure 11B).

Figure 11C shows that nssK$^+$ concentrations correlate positively with dissolved SiO$_2$ concentrations. However, nssK$^+$ and nssMg$^{2+}$ do not. Thus, nssK$^+$ is probably attributable to the reaction between K-feldspar in the volcanic rocks and CO$_2$ in groundwater (eq. 5).

Figure 12 shows that correlations of nssSO$_4^{2-}$ with nssK$^+$, nssNa$^+$, nss(Ca$^{2+}$ + Na$^+$), and nss(Ca$^{2+}$ + Na$^+$ + K$^+$ + Mg$^{2+}$) were positive ($r$=0.87, 0.90, 0.95, and 0.90, respectively). Chemical compositions of hot spring waters on Nakanoshima are shown in Table 2 (Toshima Village, 1999). The water chemistry of the hot springs is the sulfur type—the sample area smells of sulfur. It is thought that the nssK$^+$, nssNa$^+$, nssCa$^{2+}$, and nssMg$^{2+}$ are originated from the reaction between sulfuric acid and minerals in silicate rocks (e.g., K-feldspar, pyrox-

![Fig. 11 Correlation of dissolved SiO$_2$ with nss(Ca$^{2+}$ + Mg$^{2+}$) (A), nss(Ca$^{2+}$ + Na$^+$) (B), and nssK$^+$ (C) concentrations in groundwater samples from Nakanoshima Island.](image-url)
enes, plagioclase). The sulfuric acid is probably attributable to oxidation of sulfur in the hot springs, as the following equation shows (Iwasaki, 1976):

$$3S + 3H_2O \rightarrow H_2SO_4 + 2H_2S$$

(7)

The nss$SO_4^{2-}$ concentrations, with an average of 0.560 meq L$^{-1}$, were remarkably higher than those of Yakushima (avg. 0.082 meq L$^{-1}$) and Tanegashima (avg. 0.257 meq L$^{-1}$) (Table 1). It is thought that both sulfuric acid and carbonic acid in the groundwater contribute to the chemical weathering of silicate rocks. Therefore, the dissolved $SiO_2$ concentration in the groundwater on Nakanoshima (0.980 m mol L$^{-1}$) was also remarkably higher than that on Yakushima (0.206 m mol L$^{-1}$) and Tanegashima (0.348 m mol L$^{-1}$). The effects on chemical weathering caused by sulfuric acid and carbonic acid on Nakanoshima were estimated to be nearly equal because the nss$SO_4^{2-}$ concentrations (avg. 0.560 meq L$^{-1}$) were nearly equal to the $HCO_3^-$ concentrations (avg. 0.595 meq L$^{-1}$).

### 4.4 Nitrate–nitrogen Concentration

The $NO_3^-$-N concentrations in groundwater on Tanegashima, Yakushima, and Nakanoshima were in ranges from 0.0 to 6.5 mg L$^{-1}$ (avg. 2.5 mg L$^{-1}$), 0.0 to 3.0 mg L$^{-1}$ (avg. 0.9 mg L$^{-1}$), and 0.0 to 0.4 mg L$^{-1}$ (avg. 0.1 mg L$^{-1}$), respectively. The $NO_3^-$-N concentrations of Nos. 11 and 12 (located in a residential and farm area, respectively) were high. The concentration of $NO_3^-$-N is a severe problem for Okinoerabu and Miyako islands of the Nansui Islands (Tashiro and Taniyama, 1995; Agata et al., 2003). Tashiro and Taniyama (1995) reported $NO_3^-$-N concentrations of 4.5–13.2 mg L$^{-1}$ (avg.

Table 2 Chemical compositions of hot spring waters on Nakanoshima Island.

<table>
<thead>
<tr>
<th>Site</th>
<th>$W_T^{1)}$</th>
<th>pH</th>
<th>$Na^+$ (mg kg$^{-1}$)</th>
<th>$K^+$ (mg kg$^{-1}$)</th>
<th>$Cl^-$ (mg kg$^{-1}$)</th>
<th>$HCO_3^-$ (mg kg$^{-1}$)</th>
<th>$Ca^{2+}$ (mg kg$^{-1}$)</th>
<th>$Mg^{2+}$ (mg kg$^{-1}$)</th>
<th>$SO_4^{2-}$ (mg kg$^{-1}$)</th>
<th>$H_2SiO_3$ (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higashiku hot spring</td>
<td>67.0</td>
<td>6.0</td>
<td>1266</td>
<td>57.9</td>
<td>2004</td>
<td>344.0</td>
<td>381.9</td>
<td>165.5</td>
<td>1216</td>
<td>73.1</td>
</tr>
<tr>
<td>Nishiku hot spring</td>
<td>71.2</td>
<td>6.1</td>
<td>678.7</td>
<td>92.1</td>
<td>940.5</td>
<td>152.9</td>
<td>111.9</td>
<td>51.6</td>
<td>631.7</td>
<td>89.3</td>
</tr>
</tbody>
</table>

Data were taken from Toshima Village (1999)

$1^{)}$ Water temperature
8.7 mg L$^{-1}$ in Kunigami area of Wadomari Town on Okinoerabu Island. The proportion of cultivated land in the area is very high (81%) mainly because of intensive floriculture. According to Agata et al. (2003), differences in NO$_3^-$-N concentrations among residential areas, farm villages, farms, and forest areas are distinct in groundwater on Miyako Island. The NO$_3^-$-N concentrations in tap water sources of farm and forest areas in Shirakawada area are 9.28 and 6.16 mg L$^{-1}$, respectively, and those in residential areas are also high. The difference in concentrations must be attributable to anthropogenic activities, such as overuse of fertilizers.

The amounts of cultivated land on Tanegashima and Yakushima islands are 19.5% and 1.9%, respectively (KAFS, 2006-2007). Almost all the land on Nakanoshima is covered with mountains and forests, so only a small area is available for farming. Therefore, the low NO$_3^-$-N concentrations are thought to be a result of low anthropogenic nitrogen load.

5. Conclusions

Chemical characteristics of groundwater on Tanegashima, Yakushima, and Nakanoshima islands, which are located between the East China Sea and Pacific Ocean, were investigated. Groundwater components reflect the geological and geographical environments and also anthropogenic activities, as summarized below.

All of the groundwater on Tanegashima, Yakushima, and Nakanoshima might be affected by sea salt. The averages of chloride (Cl$^-$) concentrations were 25.8, 11.7, and 26.4 mg L$^{-1}$, respectively. The Cl$^-$ concentrations for Tanegashima and Nakanoshima were remarkably higher than the average for river waters throughout Japan, 5.8 mg L$^{-1}$. Concentrations of Cl$^-$ were especially low on Yakushima, which reflects the high annual rainfall (3685 mm) of the island’s climate. The Cl$^-$ concentrations are also thought to be affected by elevation, decreasing with increasing elevation of the sampling location. All of the Yakushima groundwater samples were the Na-Cl type, which suggests that the chemical compositions have been strongly affected by sea salt. The proportion of sea salt components here was higher than 50%, except for sample No. 18 (a well in Miyanoura).

The nss components of the groundwater on Tanegashima and Nakanoshima, that are the Ca-HCO$_3^-$ type, are probably formed by chemical weathering of plagioclase feldspars in the volcanic ash soils, sedimentary rocks, and volcanic rocks. However, for No. 7, Ca-HCO$_3^-$ groundwater components are probably formed by reactions between calcite in the camptonite dike and CO$_2$ in groundwater. The Na-HCO$_3^-$ type of groundwater is probably caused by a contribution from ion exchange between clay minerals and Ca$^{2+}$.

The nss components of groundwater on Nakanoshima of the Ca-HCO$_3^-$SO$_4^2-$ type might be formed by reactions between plagioclase feldspars and sulfuric acid and carbonic acid in the groundwater. The nssSO$_4^{2-}$ concentrations (avg. 0.560 meq L$^{-1}$) were remarkably higher than those on Yakushima (avg. 0.082 meq L$^{-1}$) and Tanegashima (avg. 0.257 meq L$^{-1}$). Both sulfuric and carbonic acids in the groundwater were thought to contribute to the chemical weathering of silicate rocks. Therefore, the dissolved SiO$_2$ concentrations in groundwater on Nakanoshima (avg. 0.980 m mol L$^{-1}$) were also higher than those in groundwater on Yakushima (avg. 0.206 m mol L$^{-1}$) and Tanegashima (avg. 0.348 m mol L$^{-1}$). The effects of sulfuric acid and carbonic acid on chemical weathering on Nakanoshima were nearly equivalent because the concentration of nssSO$_4^{2-}$ (avg. 0.560 meq L$^{-1}$) was nearly equal to the concentration of HCO$_3^-$ (avg. 0.595 meq L$^{-1}$). The nss components of the groundwater on Nakanoshima of the Ca-Mg-HCO$_3^-$SO$_4^2-$ type might be formed by reactions of plagioclase and pyroxene with sulfuric and carbonic acids in the groundwater.

The nss components of groundwater on
Yakushima were the Na-HCO$_3$ type, except for one sampling point (No. 18). The nssNa$^+$ and nssCa$^{2+}$ might come from the chemical weathering of sodium-rich plagioclase in the granite. The nssK$^+$ and nssMg$^{2+}$ components probably also are originated from the chemical weathering of the granite. Although the total concentrations of all nss components were low, the arithmetic mean of nssK$^+$ was high. The total concentration of nss components on Yakushima (avg. 0.60 meq L$^{-1}$) was remarkably lower than that on Nakanoshima (avg. 2.32 meq L$^{-1}$) and Tanegashima (avg. 3.47 meq L$^{-1}$).

The low NO$_3^-$N concentrations on these islands reflect a low load of anthropogenic nitrogen.

Acknowledgements

We thank Mr. K. Sameshima, Mr. K. Ogata, Mr. K. Takesako, and Mr. E. Iwashita for collecting samples in Nishinoomote City; Mr. S. Nagata and Mr. T. Hamawaki for collecting samples in Nakatane Town on Tanegashima Island; and Mr. H. Terada and Mr. K. Hamasaki for collecting samples in Kamiyaku Town on Yakushima Island. Finally, we are grateful to three anonymous reviewers for valuable and critical comments to improve this paper.

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