Geochemical monitoring of deionized seawater injected underground during construction of an LPG rock cavern in Namikata, Japan, for the safety water curtain system

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Abstract

An underground liquified petroleum gas (LPG) storage facility was constructed between 1998 and 2006 in Namikata, Imabari City, Ehime Prefecture, Japan, to increase domestic LPG stockpiles. The most important issue during construction and operation of this facility is gas leakage prevention. To thwart water leakage, the water curtain system was constructed according to design standards, and a large amount of deionized seawater (seal water) was continuously injected into the rock mass around the cavern to keep the water level constant during both construction and operation. It is possible to distinguish three end member waters (existing groundwater, seawater or fossil seawater, and seal water) using the salinity and isotope ($\delta^{18}O$) difference because seal water injected underground has almost the same $\delta^{18}O$ value as seawater. In this study, continuous observation is carried out using the geochemical techniques for flow analysis with a mixing ratio of three end members in the initial construction period (April 2005 to March 2006) of the LPG underground storage facility. It is determined that existing groundwater and seawater originally distributed in this region are partly replaced by seal water in the cavern.

1. Introduction

Liquified petroleum gas (LPG) is a gaseous fuel that is mainly composed of butane and propane extracted from by-product gases in oil fields, natural gas fields, and oil refineries. It can be easily liquefied at room temperature by simple compressors and cooling. It is transported, stored, and delivered in liquid form. LPG is among the most important energy resources for social and economic prosperity that is widely used as a power source for homes and automobiles (Agency for Natural Resources and Energy, 2017). In addition to storage in aboveground tanks, many methods of storing LPG in underground facilities have been implemented in countries other than Japan. To store LPG safely, the groundwater level and the chemical and isotopic composition must be monitored (Nenoen and Blindheim, 1989; Hamberger, 1991; Kim et al., 2000; Appelo, J. et al., 2003, 2007, 2011; Lee, J.Y., Yamamoto and Pruess, 2004; Eric et al., 2005; Park et al., 2005; Raghavan et al., 2007; Li et al., 2009; Lim et al., 2013; Saikat, Kannan, 2015; Lin et al., 2016). J. Lee et al. (2007) calculated the mixing ratio of seawater and groundwater based on the chlorine (Cl) concentration and oxygen isotopic composition ($\delta^{18}O$) of tunnel spring water. Using tritium and helium isotopes, they analyzed groundwater around an LPG stockpiling location in a coastal area of Korea. Lim et al. (2013) analyzed the flow of groundwater in oil storage depots for which seawater is injected as seal water into the ground. The main components and hydrogen and oxygen isotopic compositions were analyzed to determine the mixing ratio of injected seawater to existing groundwater.

To increase domestic LPG stockpiles, the Japanese government started construction of two underground LPG stockpiling locations in Namikata, Imabari City, Ehime Prefecture, and Kurashiki City, Okayama Prefecture, in 2003 (Fig. 1a). Namikata base construction was started by the National LPG Stockpiling Company, which was established in December 1998 to promote the construction. In 2004, the Japan Oil, Gas and Metals National Corporation (JOGMEC) took over the construction operations through a

transition of the national stockpiling system. JOGMEC continued construction work on behalf of the national government and completed the project in March 2013. The Namikata base, like the Kurashiki base, is Japan's first underground LPG storage facility that uses a water-sealed rock mass tank. Approximately 450,000 tons of LPG are stored at the base, making it the world's largest LPG storage facility (Otake, 2000; Okazaki et al., 2014; Kurose et al., 2014; JOGMEC, 2000, 2020). Among the important safety measures in the construction of underground LPG storage facilities is preventing LPG leakage into the ground. Because the annual precipitation (1219 mm; Japan Meteorological Agency, 2020) in Ehime Prefecture is less than that in other areas in Japan, a large amount of seawater (approx. 1500 L/min) is deionized and continuously injected as seal water into the rock mass around the cavern from the water gallery; this is intended to keep the groundwater level constant during the period of tunnel construction for the storage facility (Fig. 1b). It is important to maintain a safe water-sealing system with injected seal water, and methods such as water-level observation using observation pits that continuously monitor the groundwater table are implemented before and during construction. Monitoring of the injected seal water's underground flow and changes in water quality because of mixing with existing groundwater and seawater is necessary to understand the flow of water around the cavern. The chemical composition of groundwater originally distributed in the Namikata area is similar to that of seal water, with a low salt concentration, and existing groundwater and seal water cannot be distinguished from each other by chemical composition. On the tank's north side, seawater gushes into the tunnel.

The purposes of this study were to identify the contribution ratio of seal water, existing groundwater, and seawater in the tunnel and observation wells and to examine the environmental change in groundwater, which is altered as construction progresses from distribution of these three end-member waters, by paying attention to when the hydrogen and oxygen isotopic compositions of seal water show almost the same deuterium (δD) and δ^{18}O values as those of seawater. In this study, the hydrogen and oxygen isotopic compositions and Cl concentration values of water samples were measured monthly during the initial construction period (April 2005 to March 2006), and the main chemical components were analyzed to examine the groundwater behavior geochemically.

2. Geological Overview Of The Namikata Area

The Namikata area is located on a peninsula in Imabari City, Ehime Prefecture, facing the Seto Inland Sea (Fig. 1a). The Namikata LPG terminal had already been operating as a ground facility. For underground storage of LPG, three caverns (maximum width of 26 m, height of 30 m, and length of 500 m) at elevations from − 180 to − 150 meters above sea level (mASL), water galleries (− 120 mASL), and working tunnels were constructed. The area was largely separated into a Propane cavern area and a Butane/Propane cavern (Fig. 1b). A geological map of the study area is shown in Fig. 2 (modified from Otake, 2000). The study area belongs to the Inner Zone of Southwest Japan, and granite formed in the Mesozoic's Cretaceous period is widely distributed. The main rock is Namikata granite, and Takanawa granodiorite is distributed near the northern coast. Takanawa granodiorite is inferred to be widely distributed under sea surface in northern areas, although its distribution over land areas is small. In the

northwestern part of the land area, quartz porphyry dikes penetrate the granite, and it is estimated that they are continuously distributed in the northern sea area. Quaternary sediments cover these plutons. Namikata and Takanawa granodiorite exhibit a course, semi-granular structure. The constituent minerals are mainly composed of plagioclase, quartz, and biotite; trace amounts of K-feldspar and amphibole are included; and zircon was observed in Takanawa granodiorite (this study). Plagioclase, which constitutes Namikata granite and Takanawa granodiorite are relatively homogeneous feldspar rich in andesine (Na; this study). Namikata granite is classified as a weathered part, a weathered−fresh transition part, and a fresh part, according to the degree of weathering. Fresh top elevations range from about + 20 mASL (ridge part) to about − 30 to − 40 mASL (coastal area) and tend to be deeper toward the coast. The fresh rock mass below this depth is composed of an almost-homogeneous rock mass with low permeability, except for some sections. Takanawa granodiorite is distributed from the cavern's northern part to the adjacent site, and it is seen as bedrock similar to Namikata granite. According to outcrop observation, the quartz porphyry has more cracks than both granitic rocks and is estimated to be highly permeable. Crack systems in the Namikata area tend to be relatively steep and run predominately in north−northwest to north−northeast and northwest to east−northeast directions (Otake, 2000).

3. Sampling And Analytical Procedures

The sampling points for water samples were spring water points in the working tunnel, the water gallery, the cavern, and the tunnel connecting them (Fig. 3). Water samples from the water-gallery facilities on the ground, the surrounding streams, and observation wells were also collected (Table 1). In this study period, analysis was advanced for the sample water for 1 year, from April 2005 to March 2006. In this period, excavation was completed for the working tunnel and the water gallery. In the cavern, the 30-m height was excavated in five stages, and excavation of the arch section (7.5 m from the top) was in progress.

Spring water in the tunnel was collected monthly in 100-mL polyethylene bottles for isotope analysis (Fig. 3). For major chemical component analysis, samples were collected monthly from April to October 2005, for 7 months, and once every 2 months from November to March 2006 in polyethylene bottles (indicated in red in Fig. 3). Seawater was sampled on May 25 and August 10, 2005. Groundwater from well 15 near the study area was sampled five times between May 2005 and January 2006. At these sampling times, water was pumped upward using an electric pump and sampled from a faucet. Stream water in the study area was sampled on July 12, 2005. Measurements at the time of sampling were water temperature, flow rate, pH, electric conductivity (EC), and oxidation−reduction potential (ORP). The pH, EC, ORP, and water temperature were measured using a portable pH/EC meter (WM-32EP; DKK-TOA) and an ORP meter (RM-12P; DKK-TOA). The flow rate was measured using a measuring cylinder or beaker. For areas from which water could not be sampled by measuring cylinders or beakers because of flow down the wall, the approximate flow rate was determined by measuring part of the flow rate.

Hydrogen and oxygen isotopic compositions and main chemical components were analyzed at the Analysis Center of Mitsubishi Materials Techno Co. The oxygen isotopic composition ($\delta^{18}O$) of the water samples was measured by the $H_2O−CO_2$ isotope exchange reaction method (Epstein and Mayeda, 1953).

The Optima Micromass mass spectrometer was used. The analytical precision was ± 0.1‰. The hydrogen isotopic composition (δD) was determined by reacting a water sample of about 3 μL with about 1 g of metallic zinc in a vacuum at 410°C for 2 to 5 hours to generate H_2 gas (Coleman et al., 1982) and then introducing the hydrogen gas into the mass spectrometer. The analytical precision was ± 1‰

Na and K were determined by flame atomic absorption spectrometry (Hitachi Z-8200). Calcium (Ca), magnesium (Mg), aluminum, silicon, boron, iron, and manganese were determined by inductively coupled plasma (ICP) emission spectrometry (7700cx ICP mass spectrometry; Agilent Technologies). Cl and sulfate (SO_4) were determined by ion chromatography (Metrohm 761 Compact IC). Total carbonate concentration was determined by the acid consumption (pH 4.8) titration method. The charge balance (Err % = [(Scat − San)/(Scat + San)] × 100, where Scat and San show total cation and total anion equivalents; Appelo and Postma, 1993) of the main components was within ± 5 % in all samples.

4. Results And Discussion

The major chemical components and the hydrogen and oxygen isotopic compositions of water samples in the Namikata area are shown in Table 1. The samples in which only the oxygen isotopic compositions and the Cl concentration values of spring water in the tunnel were analyzed are shown in the supplement data.

4.1. Hydrogen and oxygen isotopic compositions

The hydrogen and oxygen isotopic compositions of water samples in this study are shown in Fig. 4. The solid line in the figure shows a global meteoric water line (δD = $δ^{18}O$ + 10; Craig, 1961; Dansgaard, 1964). The water samples showed the composition near the straight-line connecting groundwater in the observation well and seawater. The δD and $δ^{18}O$ values of the collected seawater were − 7‰ and − 0.5‰, respectively, which were slightly lower than those of Vienna Standard Mean Ocean Water (δD = $δ^{18}O$ = 0‰). Because this seawater came from the Seto Inland Sea, seawater in the bay was slightly diluted by surrounding river water or precipitation. Seal water was obtained by desalting the surrounding seawater using the osmotic membrane method, and the EC value was as low as 8.0 to 27.6 mS/m. The δD and $δ^{18}O$ values were − 7‰ to − 8‰ and − 0.8‰, respectively, which were slightly lower than those values for seawater (Table 1). The reason for this is unknown, but some isotope fractionation may have occurred during the desalination process.

Water samples, except those from observation well 39, showed lower EC values of 20 to 58 mS/m, δD values of − 54‰ to − 47‰, and $δ^{18}O$ values of − 8.4‰ to − 7.4‰ than those of seal water or seawater (Table 1). River water and groundwater in Ehime Prefecture had δD values of − 60‰ and − 42‰ and $δ^{18}O$ values of − 8.9‰ and − 7.1‰, respectively (Mizota and Kusakabe, 1994). Groundwater in the study area showed similar values, so it was judged to reflect the average precipitation in this area. The δD and $δ^{18}O$ values of precipitation are known to vary widely from month to month, but groundwater in this area

showed almost constant values, suggesting that precipitation infiltrated underground for more than 1 year. The δD value of groundwater in well 39 was – 30‰ and the $\delta^{18}O$ value was – 4.4‰; these are intermediate values between those of seawater and existing groundwater (Fig. 4). However, because the EC value was 103 mS/m and the pH value was extremely high (pH 11.6), it is highly likely that half of the seal water was mixed into existing groundwater and reacted with the cement injected around the tunnel to increase both the EC value and the pH value. Seal water was used in borehole drilling, and it is possible that it was not replaced by groundwater and instead remained in the mix; however, seal water may have infiltrated to this point. The proportion of seal water was estimated to be around 40 %, with the remainder as existing groundwater. The δD value of groundwater in well 15 was – 50.6‰, which was the δD value of existing groundwater in this area.

4.2. Three end-members in water samples in the tunnel

The $\delta^{18}O$ value and Cl concentration values of the water samples in the tunnel and observation wells are shown in Fig. 5a. Most of these samples were plotted in the area surrounded by three points of seawater, seal water, and existing groundwater. Because there were significant differences in isotopic composition between seal water and groundwater in the study area, and because seawater and seal water have a similar isotopic composition but different salt concentrations (Cl concentration and EC value), these three end-members can be distinguished (Fig. 5a). Assuming that the water samples in the study area were mixed with seal water, existing groundwater, and seawater (water of high salinity north or south) at an arbitrary ratio, the mixing ratio of these three end-members was determined from the $\delta^{18}O$ value and Cl concentration value using the following formula. Only $\delta^{18}O$ was used for the mixing ratio calculation, because as shown in Fig. 4, there was a 1:1 correlation between $\delta^{18}O$ and δD values; thus, $\delta^{18}O$ values, which are relatively easy to apply to isotopic composition analysis, were used:

$$Cl = Cl_D \times X_D + Cl_S \times X_S + Cl_G \times X_G \ (1)$$

$$\delta^{18}O = \delta^{18}O_D \times X_D + \delta^{18}O_S \times X_S + \delta^{18}O_G \times X_G \ (2)$$

$$X_D + X_S + X_G = 1 \ (3)$$

where D, S, and G denote seal water, seawater, and existing groundwater and X denotes the proportion of each end-member. The settings for the three end-members are shown in Table 2. Considering the analytical error of $\delta^{18}O$ and Cl concentration value, the error of the obtained mixing ratio is about ± 5 %.

As an example of the time variation of the mixing ratio, the results at sample point B-6 of water gallery No. 1 in the Butane/Propane are shown in Fig. 5b. The horizontal axis shows the monthly values for the survey period from March 2005 to February 2006, and the vertical axis shows the percentage of each source water contained in the water sample. At this point, seawater was about 90 %, and the remaining water was existing groundwater. However, from July 2005, as construction progressed, the impact of seal water began to appear, and it can be seen that the proportion of three end-members fluctuated by about 10 % monthly. It can also be seen that although the contribution of seawater decreased relatively, the

groundwater portion increased slightly. In the Namikata area, oxygen isotope and Cl concentration analysis for working tunnel, water gallery, carven, and surrounding groundwater and seal water was determined for about 400 samples at 103 sites (Table 1 and supplement data).

4.2.1. Working tunnel (0 to – 125 mASL)

At the working-tunnel level (Fig. 5c), several springs were found. Water at sample points T-6 (TD (tunnel distance) 62 m), T-7 (TD 270 m) in water supply tunnel and T-2 (TD 400 m), T-3 (TD 600 m), and T-9 (TD 507 m) in working tunnel were considered fresh seawater based on their chemical composition (Table 1). These sample points are located in the northeastern part of the water supply tunnel, where fresh seawater gushes out. At sample point T-4 (TD 717 m) and T-8 (TD 710 m), the contribution of groundwater was large, but seawater is mixed in, accounting for around 10 %. These springs are transformed into Ca-rich seawater (Table 1), which distinguishes them from the northeastern regions where fresh seawater gushes out. At sample point T-5 (TD 948 m), which sample point up on the west side of the working tunnel, seal water replaced 90 % in March and 100 % in April. At point T-1 (TD 250 m), seawater accounts for 20 %, groundwater for 70%, and seal water seal for 10 %. From the chemical composition, fresh seawater contributes to this seawater component, and it is judged that it is spring water near the seawater/freshwater interface.

4.2.2. Water gallery (– 125 mASL)

At the water-gallery level (Fig. 5d), the source water mixing ratio greatly changed with time, depending on the gushing point. A major feature was the large contribution of seawater to the tunnel's north side. In the southern part, the water from sample points P-16 (TD 917 m) and P-15 (TD 937 m) from the investigation hole was judged to be a Ca-rich fossil seawater type (Table 1). Existing groundwater with 100 % of the water sample in the tunnel could be identified only at the following four locations: sample point B-1 (TD 63 m) in the Butane/Propane water gallery No. 1, sample point B-45 (TD 467 m) in Butane/Propane water gallery No. 2, sample point P-97 (TD 68 m) in Propane water gallery No. 2, and sample point P-20 (TD 97 m) in Propane water gallery No. 3 (Fig. 5d). In addition, a range of mixed water was found in the horizontal tunnel (sample point P-58). Such water was distributed to the south and was considered to correspond to areas with high groundwater potential. As for seal water, it made up 100 % of the contribution in the central zone in the water gallery, but in other places, it was mixed with water of another origin.

The mixing ratio of each end-member in water gallery as of February 2006 is shown in Fig. 6a. The black circles in the figure represent measurement points, and the other sections are interpolated data. This figure also shows that seawater (or fossil seawater) was distributed to the north and south, as mentioned previously, and that more water gushed out on the Butane/Propane side. A considerable amount of groundwater flowed out not only to the south but also to the north.

4.2.3. Cavern (– 150 mASL)

At the cavern level, it was difficult to track long-term changes because many sites were unable to collect spring water due to the progress of excavation work, and also because the source site was changed. The inflow of water into Carven, compared to the water gallery tunnel, indicates that the seal water is flowing out predominantly, replacing existing groundwater and seawater (Fig. 5e). The mixing ratio of each end-member in carven as of February 2006 is shown in Fig. 6b. Seawater springs in the northeastern region account for less than 20 % of spring water, but they still spring out. Similarly, the proportion of groundwater has not fluctuated significantly during the study period but has emerged in the southeast and northwest regions.

4.2.4 Change in proportion of three end-members in water samples from April to December 2005

Figure 7 compares the results of change of the proportion of end-members in water samples at the water-gallery level between April and December 2005. In Fig. 7, the red and blue areas indicate an increase and a decrease in the end-members' contribution to the water samples in December compared with April 2005. The line in the figure also shows the difference between April and December in the observation well's water level. If this value is negative, it means that the water level was slightly lower than in April. The results show that seawater increased in the south and north during the eight months. This was considered the effect of increasing the pressure of seal water at the south side during this period. The amount of spring water originating from seawater decreased in the north, which is in harmony with the ratio of seal water. Therefore, the amount of seawater decreased because of the increase of seal water.

4.3. Chemical composition

The Stiff diagram (Stiff, 1951) in Fig. 8 shows water samples in the study area indicating that the water samples are mixture of seawater, seal water and groundwater. The relationship between each chemical component and the Cl concentration are shown in Fig. 9. The broken line in Fig. 9 shows a simple mixing of seawater and seal water or groundwater. There was no significant chemical difference in water sample from the Butane/Propane and Propane areas. Na, Mg and SO_4 ions are plotted near this simple mixing line or show slightly lower values (Fig. 9). K ion for most samples except for those in working tunnel were clearly lower than the line. In contrast, Ca and HCO_3 ions were quite higher than the mixing line. These results suggested that the saline spring waters in the tunnel are of current sea water in some places and the fossil sea water rich in Ca components in other places.

p>The Piper diagram (Piper, 1944) of the water samples is shown in Fig. 10. In the northern part of a working tunnel, the water was characterized by its high salt concentration, and two water samples (T-7 and T-9) in working tunnel had a Cl concentration value almost equal that of current seawater (Fig. 10a). At sample point T-1, the spring water consisted of 10 % seal water, nearly 70 % groundwater, and the remainder was sea water (Fig. 5c), which was judged to be current sea water (Fig. 10a). On the other hand, T-4 and T-7 are spring waters in which more than 90 % of the ground water is mixed with about 10 % of the sea water, but because of their Ca-rich composition, this sea water is highly likely to be fossil sea

water. That is, sea water was altered to the Na·Ca – Cl type. Lee, J. et al. (2007) reported that a major chemical composition analysis and hydrogen and oxygen isotopic compositions of groundwater at an LPG stockpiling base constructed in the coastal area of South Korea resulted in mixing of seawater and existing groundwater. Most spring waters in the tunnels were plotted far away from the 1:1 line of sea water and groundwater mixing line except bromide. They discussed using a principal component analysis and showed that cations in the ground water such as Ca, Na, Mg, and K are irregularly enriched or depleted by various hydrogeochemical reactions between host rock and the ground water along the flow path. In general, seawater that changes its water quality by reacting with rocks is called fossil seawater and has been reported worldwide (e.g., Meyers, 1968; Capuano, 1990, 1992). Fossil seawater has also been reported in many places in Japan (e.g., Sakai and Matsubaya, 1974; Mizukami et al., 1977; Ueda et al., 2010; Okano et al., 2020).

In water gallery, there are many types of spring waters were gushing out. As same as the working tunnel, there are saline spring waters in the northeastern part (Fig. 10b). Water sample at B-15, 100 % current sea water gushes out from the chemical composition, and at P-59, sea water was diluted with seal water (Fig. 5d). Other spring waters with high salt concentration are considered to be formed by the dilution of fossil seawater into groundwater or sea water at various rates. In the water gallery, 100 % of the groundwater is gushed out at B-1 and P-20 and its water quality is Ca-HCO$_3$ type. Other spring waters (< 10 meq/L) are mixture of the seal water and groundwater and show Na-Cl type (Fig. 10b). At sites P-15 and P-16 of the south investigation tunnel in the water gallery, a mixture of groundwater and fossil sea water.

The chemical composition of spring waters in carven were analyzed for 1 and 5 samples in the Propane No. 1 and No. 2 carven, respectively, and other two spring waters (P-69, B-43) from connecting tunnels nearby the Propane No. 2 and Buran/Propane carven were also analyzed (Fig. 10c). Spring waters (P-42, P-53, P-81) in the central part of the carven are dominant in the seal water with small amount of groundwater, and in the northern part (B-43, P-114, P-49) and point P-95 of the No. 1 Propane carven are judged that fossil sea water is diluted with seal water and groundwater. In the northwest part of the No. 2 Propane carven, water samples (P-114, P-115) are adjacent springs, and the former is a dilution of fossil seawater, while the latter is mostly seal water. Thus, it can be seen that the quality of spring water is different even in areas that are only a few meters away.

Groundwater in 13 observation wells was sampled in May 2005 (blue) and November 2005 (green) (Fig. 10d). In wells 7, 10, 25, and 40, groundwater was analyzed at different depths. Most chemical components for groundwaters in the wells remained almost constant at different depth. Groundwater in the observation wells except for well No. 29 was weakly acidic to weakly alkaline, with a pH of 6.0 to 8.8, and the EC value was 60 mS/m or less (most samples contained approx. 30 mS/m). This is similar to the EC value of the water sample from sample point B-1 in the Butane/Propane water gallery (TD 63 m), which was considered to contain 100 % existing groundwater (31 to 43 mS/m) (Figs. 5d and 10b). From the δD and δ^{18}O values of water samples in the observation wells, groundwater in this area showed almost constant values, suggesting that precipitation infiltrated underground for more than 1 year

(Fig. 4). The chemical composition of the water samples shows the Ca-HCO$_3$ type and the EC value is high in a part, but the relation with the geology has not been found. These results indicated that seal water did not infiltrate into these wells. In well 39, water sample showed the intermediate values between seawater and groundwater and the proportion of seal water was estimated to be around 40 % (Fig. 4). The pH value was extremely high (pH 11.6). Seal water was used in the borehole drilling and mixed with existing groundwater and reacted with the cement.

4.4. Behavior of seal water injected into the LPG carven

In the Namikata LPG carven, a large amount (1500 L/min) of seal water (deionized sea water) had been continuously injected into ground. From the isotopic composition and main chemical composition of water samples gushing in the tunnels, three types of source water gushed out in the water gallery and cavern. The source water was sea water or Ca-rich seawater (fossil seawater), existing groundwater, and seal water. In the center part of the tunnel, only seal water gushed but in other areas, spring waters in the tunnels are mixture of three end-members. Saline groundwater spouted in the north and south portions of the water gallery. Groundwater mainly distributes in the southwestern part in the tunnels because water potential is high due to high altitude on the surface (Fig. 8a). Seal water is infiltrating into the main part of the water galleys (Fig. 5b). The groundwater and sea water initially distributed in this area cannot be completely replaced by seal water. Also, sea water-groundwater interface has not been largely changed.

5. Conclusions

In the underground LPG storage base constructed in Namikata, a large amount of seal water (deionized seawater) is continuously charged around the cavern to keep the water level constant. The δ^{18}O value of seal water is almost the same as that of seawater, but the salinity is different. The proportion of three end-members (seal water, sea water, and groundwater) can be estimated using the δ^{18}O value and Cl concentration of the water samples. To monitor the distribution of seal water, water samples in the tunnels and observation wells are collected monthly. The main chemical components and hydrogen and oxygen isotopic compositions are measured for 1 year from April 2005, and the secular change of the three end-members in water samples at each site are examined. These results show that existing groundwater and seawater before the construction were not completely replaced by seal water. With increasing injected water pressure, the fraction of seal water increases and will be expected to be almost 100 % when the water pressure is 1.3MPa as the designed value. This study is a one-year observation of spring water, and it is expected that the proportion of seal water into each spring will increase but it is estimated that the position of the boundary between sea water/groundwater or seal water will not change much.

Declarations

Acknowledgments

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Tables

Table 1 Isotopic and chemical compositions of water samples in tunnels and observation wells.

Sample No.	Sample locality (TD m)	Date	Water temperature (C)	pH	EC (S/m)	ORP (mV)	δD	δ^{18}O (‰)	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	SiO$_2$	B	Al	Fe	Mn (mg/L)
Butan area																				
No.2 Butan/Propane water gallery																				
B-9	310	2006/01/19	14.7	7.81	0.040	328	-35	-5.0	47	2	34	0	85	12	31	14	0.38	<0.1	<0.001	<0.001
		2005/04/18	19.1	8.17	0.051	216	-22	-3.1	70	3	26	1	120	14	29	8	0.78	<0.1	0.03	<0.001
		2005/05/24	19.3	8.45	0.061	102	-25	-3.6	68	3	23	1	110	17	34	9	0.77	<0.1		0.020
		2005/06/15	19.7	8.34	0.049	196	-27	-4.1	67	3	25	1	110	19	33	12	0.72	<0.1	0.22	<0.001
		2005/07/12	20.0	8.26	0.053	232	-28	-4.5	58	3	25	2	94	20	31	10	0.61	0.12	0.06	0.002
B-10	278	2005/08/10	21.0	8.49	0.048	291	-29	-4.4	62	3	27	2	120	22	29	10	0.68	0.14	0.00	<0.001
		2005/09/13	20.5	8.44	0.053	260	-28	-4.1	71	3	26	1	120	19	33	9	0.75	<0.1	0.00	<0.001
		2005/10/14	20.2	8.40	0.052	251	-28	-4.3	75	3	29	2	120	18	31	11	0.75	<0.1	0.00	<0.001
		2005/11/14	19.5	8.23	0.048	278	-31	-4.7	64	3	26	1	90	22	34	11	0.55	<0.1	0.00	<0.001
		2006/01/18	18.1	8.59	0.058	142	-31	-4.4	63	3	30	2	95	21	33	12	0.56	<0.1	0.00	<0.001
		2006/03/06	17.3	8.31	0.039	209	-31	-5.0	49	3	25	1	79	20	34	10	0.40	<0.1	0.01	<0.001
B-21	116	2005/11/14	20.0	7.43	1.402	150	-39	-5.9	1200	11	1700	86	4600	420	25	11	0.03	<0.1	0.16	0.44
		2006/01/18	18.3	7.62	1.307	89	-42	-6.0	1100	21	1800	85	4400	440	26	13	0.04	<0.1	0.12	0.38
		2006/03/06	17.6	7.51	1.210	128	-40	-6.5	1100	13	1600	82	4000	390	26	18	0.04	<0.1	0.06	0.34
B-23	84	2005/11/14	19.9	7.28	2.340	140	-33	-4.7	2100	23	3000	210	8000	760	32	13	0.14	<0.1	0.00	0.85
		2006/01/18	18.6	7.37	2.500	98	-35	-4.9	2200	45	3500	250	8900	830	32	13	0.12	<0.1	<0.001	0.89
		2006/03/06	18.2	7.36	2.390	94	-33	-5.1	2100	35	3200	230	8500	750	29	15	0.13	<0.1	0.05	0.84
B-24	66	2005/11/14	20.5	7.22	0.326	220	-9	-1.3	250	7	350	15	940	43	15	9	0.74	<0.1	0.10	0.037
No.1 Butan/Propane water gallery																				
B-2	276	2005/04/18	18.5	7.83	0.060	226	-5	-0.7	100	5	8	2	170	5	16	8	1.40	<0.1	0.04	<0.001
		2005/05/24	18.9	8.66	0.062	152	-4	-0.5	110	5	7	2	170	4	14	1	1.40	<0.1		<0.001
B-4	160	2005/08/10	22.5	8.05	0.065	338	-6	-0.7	110	5	6	2	190	5	17	1	1.50		0.00	<0.001
		2005/06/15	20.8	7.56	0.240	103	-9	-1.3	210	6	210	13	700	45	11	2	1.30	<0.1	0.02	0.032
		2006/03/06	18.1	7.22	0.156	214	-12	-1.9	150	5	130	8	470	31	17	2	0.66	<0.1	0.01	0.003
		2005/06/15	20.0	7.46	1.686	23	-36	-5.5	2400	34	1000	230	5400	850	75	14	0.84	<0.1	0.19	0.110
		2005/07/12	20.6	7.03	1.665	14	-39	-5.6	2400	31	930	200	5300	880	74	13	0.76	<0.1	0.06	0.84
		2005/08/10	21.4	7.40	1.645	189	-38	-5.7	2300	31	850	210	5300	860	77	14	0.84		0.00	0.78
B-7	102	2005/10/14	21.1	7.67	1.443	235	-40	-5.9	2200	23	850	200	4600	740	71	14	0.58	<0.1	0.08	0.74
		2005/11/14	19.8	7.74	1.470	182	-39	-6.0	2000	23	920	200	4400	720	68	20	0.51		0.03	0.81
		2006/01/18	17.6	7.74	1.586	197	-40	-5.9	2100	38	1200	270	5200	800	72	14	0.49		0.02	0.90
		2006/03/06	17.6	7.61	1.651	175	-38	-5.8	2000	40	1300	290	5400	790	68	16	0.43	<0.1	0.01	1.10
B-44	42	2006/01/18	15.4	7.55	3.940	293	-8	-0.8	7000	200	2700	780	15000	2400	58	13	0.78	<0.1	0.16	0.078
B-6	4	2006/01/18	16.5	7.43	2.680	198	-14	-1.9	2500	60	3700	270	9500	820	22	13	0.42	<0.1	0.03	0.800
		2006/03/06	17.0	7.44	2.530	165	-14	-2.0	2200	65	3300	250	8800	720	22	10	0.41	<0.1	0.02	0.690
Branch tunnel (Butan/Propane area)																				
B-1	63	2005/4/18*	18.8	7.60	0.032	240	-53	-8.0	24	3	36	2	31	32	57	18	<0.1	<0.1	0.04	<0.001
		2005/10/14*	21.8	7.85	0.030	289	-53	-8.0	25	2	37	3	30	30	56	19	<0.02	<0.1	<0.001	<0.001
		2005/11/14*	20.4	7.63	0.031	321	-52	-7.9	24	2	34	2	28	32	49	20	<0.02		0.00	<0.001
		2006/1/19*	18.2	8.13	0.034	184	-52	-8.1	25	3	37	2	31	31	55	19	<0.02	<0.1	<0.001	<0.001
		2006/03/06	17.2	7.70	0.031	531	-54	-8.1	24	3	35	2	36	32	54	18	<0.02	<0.1	0.00	<0.001
B-16	76	2006/01/19	17.5	6.84	3.840	180	-32	-4.2	2800	28	6800	350	15000	1100	12	11	0.03	<0.1	0.08	1.1
B-49	60	2006/03/06	17.4	7.10	3.860	136	-31	-4.2	2900	41	6400	340	15000	1100	14	17	0.04	<0.1	0.07	1.1
		2006/03/06	17.7	7.54	4.880	95	-6	-0.7	9000	64	2100	1100	19000	2500	79	14	1.60	<0.1	<0.001	0.34
		2005/05/24	19.1	7.08	4.790	93	-8	-0.6	9000	58	1700	1200	19000	2500	104	14	2.60	<0.1		4.3
		2005/06/15	20.0	7.14	4.910	53	-6	-0.6	9000	59	1700	1100	19000	2600	89	13	2.80	<0.1	0.10	0.086
		2005/07/12	20.8	6.53	4.860	50	-7	-0.7	9200	59	1500	1100	18000	2600	45	13	2.70	<0.1	0.07	3.6
		2005/08/10	21.0	6.90	4.900	115	-7	-0.6	9000	59	1300	1100	18000	2600	95	13	3.20		0.02	4.0
B-15	37	2005/09/13	21.1	7.02	4.900	75	-6	-0.7	9100	58	1400	1100	18000	2600	89	12	3.40		0.07	2.9
		2005/10/14	20.3	7.03	4.860	180	-8	-0.8	9500	44	1500	1100	18000	2600	88	14	3.10		0.12	3.2
		2005/11/14	19.3	7.12	4.870	182	-7	-0.5	9400	45	1600	1200	17000	2600	92	14	1.90		0.04	4.3
		2006/01/18	18.1	7.17	4.880	224	-6	-0.5	9600	61	1600	1200	18000	2700	96	14	2.80		0.03	3.4
		2006/03/06	17.7	7.21	4.860	157	-8	-0.6	9500	58	1400	1200	18000	2600	91	20	2.60	<0.1	0.01	3.0
B-43	65	2006/03/07	17.2	8.68	0.667	267	-11	-1.4	560	10	850	26	2000	410	14	10	0.62	<0.1	0.02	0.011
Propane section																				
No.2 Propane water gallery																				
P-97	68	2006/1/19*	17.1	10.25	0.032	123	-54	-8.0	28	6	26	0	29	36	16	17	0.02	0.61	0.02	<0.001
P-93	436	2005/11/15	19.5	7.44	2.000	105	-19	-2.6	1800	34	2500	170	6700	1000	18	12	0.41	<0.1	0.08	0.390
		2006/01/18	18.7	7.46	1.961	7	-19	-2.8	1700	58	2800	180	6600	990	20	10	0.48	<0.1	0.11	0.350
P-111	450	2006/03/06	18.5	7.45	1.846	149	-17	-2.5	1600	46	2400	170	6300	870	21	10	0.50	<0.1	0.04	0.310
P-60	468	2006/03/06	12.8	7.78	4.610	223	-8	-1.0	8500	70	1400	1200	18000	2300	65	25	2.50	<0.1	0.00	4.300
		2005/11/15	19.5	7.31	1.636	215	-11	-1.4	2200	24	970	190	5100	920	38	11	0.93	<0.1	0.07	0.400
P-14	479	2006/03/06	18.2	7.47	2.680	155	-12	-1.1	3800	58	1900	520	9300	1400	47	17	1.40	<0.1	0.00	0.500
		2006/03/06	17.3	7.38	2.180	247	-10	-1.3	2800	39	1400	400	7500	970	37	6	1.40	<0.1	0.00	0.001
P-17	508	2006/01/19	18.1	7.42	3.160	258	-8	-0.7	5300	160	1600	650	11000	1700	63	11	2.00	<0.1	0.00	0.083
		2006/03/06	18.0	7.45	3.560	228	-8	-1.1	5900	96	1600	780	13000	1900	68	17	2.20	<0.1	0.00	0.200

Table 1 (Continued)

Sample No.	Sample locality (TD m)	Date	Water temperature (C)	pH	EC (S/m)	ORP (mV)	δD	δ^{18}O (‰)	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	SiO$_2$	B	Al	Fe	Mn
No.1 Propane water gallery												(mg/L)								
P-4	20	2005/05/24	20.0	7.00	0.320	231	-43	-6.5	28	2	31	1	53	21	47	15	0.20	<0.1		<0.001
		2005/06/14	20.1	8.05	0.040	137	-42	-6.3	32	2	32	1	56	20	41	15	0.24	<0.1	0.01	0.001
		2005/07/11	19.9	8.39	0.061	152	-21	-3.1	63	3	28	2	130	12	26	7	0.81	<0.1	0.00	0.001
		2005/08/09	22.4	8.41	0.055	310	-22	-3.2	72	3	24	4	120	13	29	7	0.94		0.00	<0.001
		2005/09/12	22.0	8.47	0.060	210	-21	-3.3	84	3	24	1	150	12	31	7	1.00		0.01	<0.001
		2005/10/13	21.2	8.39	0.055	239	-21	-2.9	89	3	23	1	150	11	28	7	1.00		0.01	<0.001
		2005/11/15	19.3	8.48	0.055	233	-22	-3.2	81	3	24	1	120	13	32	9	0.89	<0.1	0.00	<0.001
		2006/01/19	18.9	8.83	0.054	161	-20	-3.1	77	4	25	1	120	13	30	7	0.06		0.00	<0.001
		2006/03/06	19.5	7.62	0.047	318	-12	-1.8	77	5	14	2	120	7	25	3	0.85	<0.1	0.00	0.003
P-5	1.57	2005/04/18	19.6	8.14	0.062	177	-13	-1.8	80	4	22	1	140	7	20	6	1.10	<0.1	0.04	<0.001
		2005/05/24	19.3	7.04	0.059	224	-7	-1.4	86	4	19	1	160	6	25	5	1.20	<0.1		<0.001
P-7	3.52	2005/04/18	19.2	7.86	0.044	192	-31	-4.4	52	2	28	1	97	11	31	11	0.59	<0.1	0.05	<0.001
		2005/05/24	19.0	8.01	0.048	203	-25	-3.4	60	2	25	1	110	10	36	9	0.79	<0.1		<0.001
P-8	420	2006/03/06	18.9	7.01	0.432	261	-12	-1.8	460	7	330	52	1300	140	26	5	0.78	<0.1	0.01	0.008
No.3 Propane water gallery																				
P-105	93	2006/1/18*	18.7	7.89	0.028	234	-52	-8.1	22	3	36	1	20	30	60	17	<0.02	<0.1	0.01	<0.001
P-20	97	2005/09/12	21.6	7.76	0.027	241	-49	-7.9	19	2	28	2	20	29	63	14	<0.02	<0.1	<0.001	<0.001
P-19	134	2005/05/24	19.4	8.19	0.048	203	-25	-3.6	64	3	24	1	110	11	46	9	0.80	<0.1		<0.001
		2005/06/14	20.1	8.16	0.049	198	-29	-3.9	67	3	24	1	100	11	36	10	0.76	0.16	0.22	0.003
		2005/07/11	20.4	8.24	0.042	228	-32	-4.9	53	3	21	1	83	14	40	10	0.56	<0.1	0.01	<0.001
		2005/08/09	20.6	8.12	0.053	252	-29	-4.4	62	3	30	3	120	16	35	10	0.71	0.13	0.01	0.002
		2005/09/12	20.6	8.05	0.045	232	-33	-4.9	61	3	22	1	96	15	39	9	0.63	<0.1	<0.001	<0.001
		2005/10/13	20.4	8.16	0.052	257	-29	-4.3	71	3	32	2	120	14	42	10	0.74	<0.1	0.00	<0.001
		2005/11/15	19.5	8.05	0.048	252	-30	-4.5	65	3	26	1	100	15	42	11	0.66		0.01	<0.001
		2006/1/18*	18.8	8.19	0.045	198	-30	-4.7	59	3	29	1	85	16	43	11	0.55	<0.1	<0.001	<0.001
		2006/03/06	18.5	8.24	0.041	359	-26	-4.1	54	3	24	1	91	14	40	9	0.52	<0.1	0.00	<0.001
P-74	238	2005/09/12	22.8	8.46	0.090	222	-4	-0.7	150	7	13	2	240	5	30	2	1.60	0.1	<0.001	<0.001
P-75	245	2005/09/12	23.6	7.24	0.086	249	-5	-0.8	140	7	7	2	240	5	20	1	1.60	<0.1	<0.001	0.002
P-104	248	2006/01/18	17.3	7.30	0.062	132	-4	-0.6	110	6	4	2	170	5	18	1	1.30	<0.1	0.20	0.011
P-32	457	2006/01/18	18.2	7.64	0.568	260	-49	-7.4	540	9	640	34	1700	240	66	16	0.42	<0.1	<0.001	0.130
		2006/03/06	18.7	7.95	0.133	342	-21	-3.1	170	4	80	5	360	45	40	8	0.74	<0.1	0.01	0.002
P-110	489	2006/03/06	17.7	7.86	0.450	257	-46	-6.9	650	9	270	33	1300	180	91	15	0.58	<0.1	0.00	0.089
P-109	508	2006/03/06	18.8	7.67	4.200	229	-13	-1.9	7900	94	1300	960	15000	2100	130	13	2.50	<0.1	0.01	1.9
Branch tunnel (Propane area)																				
P-15	-	2005/04/18	19.3	7.37	2.390	74	-35	-5.1	1800	18	2800	500	8800	890	80	16	0.26	<0.1	0.03	5.6
P-69	245	2006/01/19	18.3	7.48	1.224	173	-9	-1.2	1800	23	850	88	3700	890	14	1	0.88	<0.1	0.49	0.400
P-16	917	2005/05/24	21.3	6.95	2.210	16	-36	-5.0	1900	18	2400	470	7800	850	92	16	0.30	<0.1		5.2
		2005/07/11	20.3	7.23	2.290	158	-34	-5.0	2000	18	2200	450	8200	920	81	15	0.31	<0.1	0.02	5.7
		2005/08/09	21.0	7.24	2.360	226	-33	-5.0	2100	20	2400	510	8400	970	86	15	0.36		0.00	6.4
		2005/10/13	20.5	7.27	2.400	220	-32	-4.7	2500	13	2500	560	8800	1000	83	16	0.40		0.06	5.8
		2005/11/15	19.9	7.27	2.520	208	-32	-4.6	2600	14	2500	540	8400	1000	89	16	0.32		0.07	7.8
		2006/01/19	19.0	7.37	2.650	132	-31	-4.5	2800	50	2700	570	9500	1100	91	17	0.45		<0.001	7.2
		2006/03/06	19.1	7.06	2.730	138	-31	-4.5	2900	38	2600	600	9700	1200	92	20	0.52	<0.1	0.00	8.5
P-50	19	2006/01/18	18.5	7.63	0.359	179	-4	-0.5	520	10	110	54	1000	110	22	2	1.30	<0.1	0.01	0.003
P-59	11	2006/01/18	18.5	7.39	4.680	215	-7	-0.5	8700	160	1500	1100	17000	2500	90	11	2.80	<0.1	<0.001	0.015
P-92	19	2005/11/15	20.0	7.52	3.440	114	-21	-2.9	5800	45	720	660	11000	970	100	15	1.80	<0.1	0.03	1.5
		2006/01/18	17.1	7.61	3.370	171	-20	-3.1	5900	69	1600	700	12000	2000	100	21	2.10	<0.1	<0.001	1.4
		2006/03/06	18.0	7.40	3.150	130	-14	-2.2	5500	57	1200	650	11000	1800	87	13	2.00	<0.1	0.01	1.2
P-33	60	2005/04/18	19.1	7.47	1.218	40	-46	-6.6	1400	15	980	140	3900	510	49	16	0.39	<0.1	0.04	0.530
		2005/10/13	19.7	7.18	2.260	126	-36	-5.3	3100	26	1500	350	7200	1100	72	15	0.94	<0.1	0.31	1.2
		2005/11/15	18.9	7.24	2.330	109	-36	-5.0	3200	28	1500	370	7500	1100	75	15	0.76		0.00	1.3
		2006/01/18	17.9	7.13	2.280	83	-34	-5.0	3500	60	1700	420	8300	1100	81	17	0.99		0.77	1.3
		2006/03/06	18.7	7.18	2.410	113	-34	-5.1	3400	40	1700	390	8100	1100	77	15	1.00	<0.1	0.00	1.3
No. 2 Propane cavern																				
P-62	180	2005/06/14	22.5	9.70	0.072	94	-7	-0.9	110	5	19	1	170	9	18	9	1.30	0.50	0.03	<0.001
P-53	208	2005/06/14	20.4	9.07	0.068	120	-5	-0.8	110	5	12	2	170	4	18	2	1.40	0.12	0.10	<0.01
P-81	421	2006/03/07	17.4	7.99	0.246	278	-9	-1.4	360	5	92	12	700	86	23	9	0.75	<0.1	0.03	0.004
P-114	483	2006/03/07	19.3	10.68	1.870	-87	-53	-7.7	1000	11	3100	3	6600	410	11	13	0.04	<0.1	0.00	0.001
P-115	485	2006/03/07	19.6	8.90	0.447	125	-9	-1.4	630	6	140	46	1200	180	24	3	0.92	<0.1	0.00	0.003
No. 1 Propane cavern																				
P-95	425	2005/11/15	20.0	7.58	0.536	228	-26	-4.0	580	7	430	48	1600	200	30	12	0.64	<0.1	0.02	0.060

Table 1 (Continued)

| Sample No.	Sample locality (TD m)	Date	Water temperature (C)	pH	EC (S/m)	ORP (mV)	δD (‰)	$\delta^{18}O$ (‰)	Na	K	Ca	Mg	Cl	SO₄	HCO₃	SiO₂	B	Al	Fe	Mn
Working tunnel									(mg/L)											
T-1	250	2006/01/19	16.0	7.55	1.404	246	-35	-5.5	2500	97	140	320	4500	670	110	31	0.93	<0.1	0.01	0.003
T-9	51	2006/01/19	16.7	7.14	4.930	251	-5	-0.4	10000	400	520	1300	18000	2600	98	14	3.80	<0.1	<0.001	0.73
T-8	710	2005/06/15	19.7	7.80	0.462	143	-47	-7.1	290	4	510	98	1400	140	83	20	<0.02	<0.1	0.04	0.002
		2006/01/19	16.2	7.50	0.406	260	-46	-7.0	260	6	580	120	1500	170	95	21	0.03	<0.1	0.00	0.012
T-4	717	2005/04/18	17.8	7.85	0.435	242	-49	-7.4	320	4	460	99	1400	120	75	20	<0.1	<0.1	0.06	<0.01
T-7	270	2005/04/18	18.2	7.48	4.810	252	-7	-0.4	9700	380	390	1100	18000	2500	76	15	3.80	<0.1	0.02	1.4
		2005/05/24	19.5	7.52	4.830	130	-6	-0.3	9900	400	400	1200	18000	2500	90	15	3.40	<0.1		1.3
		2005/07/12	21.1	7.18	4.840	130	-6	-0.3	9500	370	420	1100	18000	2500	69	17	3.00	<0.1	0.02	0.9
		2005/08/10	21.9	7.51	4.850	230	-7	-0.5	9700	400	430	1200	18000	2600	72	13	3.50		0.05	0.5
		2005/11/15	19.1	7.58	4.920	240	-6	-0.4	10000	360	410	1200	18000	2500	86	15	3.50		0.02	0.2
		2006/01/19	15.9	7.51	5.010	261	-4	-0.4	10000	520	440	1200	18000	2600	85	15	4.00		0.01	0.005
		2006/03/07	20.8	7.64	5.020	318	-5	-0.2	10000	400	410	1300	19000	2600	80	19	4.10	<0.1	0.00	0.030
Observation well	Depth (Elevation; mASL)																			
No.1	-27.27	2005/05/25	19.5	8.04	0.037	107	-49	-7.5	28	1	39	2	31	26	109	44	<0.02	<0.1	0.01	<0.001
		2005/11/14	16.8	7.44	0.044	-96	-50	-7.6	28	3	46	5	29	25	94	82	<0.02	<0.1	0.01	<0.001
No.5	-13.68	2005/06/15	19.0	7.78	0.020	-57	-54	-8.0	12	3	24	1	16	14	53	23	<0.02	<0.1	0.18	0.052
		2005/11/15	16.3	8.05	0.024	-82	-54	-8.0	12	3	34	2	18	11	77	24	<0.02	<0.1	0.04	0.075
No.7-1	-10.3	2005/05/25	18.2	7.47	0.031	1	-51	-7.6	27	2	21	4	27	24	92	30	<0.02	<0.1	0.04	0.030
		2005/05/25	18.9	7.41	0.031	64	-50	-7.7	28	2	19	4	28	26	86	30	<0.02	<0.1	0.04	0.004
		2005/11/15	15.8	7.51	0.028	134	-51	-7.7	29	2	20	5	26	28	56	59	<0.02	<0.1	0.08	<0.001
No.9	26.85	2005/05/25	18.1	7.95	0.032	47	-51	-7.9	18	4	39	1	21	16	133	29	<0.02	<0.1	0.04	0.002
		2005/11/15	16.3	7.54	0.033	1	-52	-8.0	19	4	48	2	20	16	110	32	<0.02	<0.1	0.00	0.005
No.10-1	24.49	2005/05/25	18.9	9.03	0.039	100	-50	-7.6	35	4	28	1	45	45	64	25	<0.02	<0.1	0.01	<0.001
		2005/11/15	16.2	8.80	0.034	-82	-50	-7.7	34	3	28	2	32	41	61	26	<0.02	<0.1	0.01	<0.001
No.10-2	-19.41	2005/11/15	16.5	9.20	0.034	-131	-50	-7.7	34	3	33	2	33	41	58	29	<0.02	<0.1	0.01	<0.001
No.11	11.71	2005/05/25	17.5	7.62	0.058	134	-48	-7.5	44	6	56	7	81	44	144	26	<0.02	<0.1	0.05	0.002
		2005/11/15	15.9	8.03	0.047	107	-50	-7.6	44	8	46	6	58	42	90	36	<0.02	<0.1	0.00	0.002
No.12	-40.18	2005/06/15	18.8	7.54	0.033	257	-51	-7.8	21	2	25	4	17	33	73	25	<0.02	<0.1	0.00	0.004
		2005/11/15	16.4	7.94	0.027	147	-51	-7.8	22	2	25	5	16	31	67	26	<0.02	<0.1	0.00	<0.001
No.15	Private well	2005/05/25	23.6	6.80	0.046		-50	-7.5	46	0	23	6	40	49	90	43	<0.02	<0.1	0.01	<0.001
		2005/08/10	26.1	6.65	0.041	290	-49	-7.5	43	1	24	7	61	46	76	40	0.01		0.01	<0.001
		2005/09/13	21.9	6.11	0.041		-50	-7.5	41	0	27	9	48	55	69	36	<0.02	<0.1	<0.001	<0.001
		2005/11/15	18.4	6.56	0.041	233	-49	-7.6	46	0	24	6	46	42	60	42	<0.02	<0.1	0.11	0.009
		2006/01/19	15.7	6.82	0.042	251	-51	-7.7	47	0	29	6	49	46	89	42	<0.02		0.02	<0.001
No.17	-23.77	2005/06/15	19.4	7.43	0.028	197	-49	-7.6	24	2	24	5	24	26	58	24	<0.02	<0.1	0.04	0.001
		2005/11/15	15.8	7.80	0.029	91	-47	-7.6	25	3	24	5	21	29	62	28	<0.02	<0.1	0.00	<0.001
No.25-1	-61.29 ~ -100.29	2005/06/15	19.0	7.80	0.026	179	-49	-7.6	19	2	24	4	18	25	52	22	<0.02	<0.1	0.12	0.004
		2005/11/14*	16.3	8.07	0.037	87	-50	-7.6	20	2	27	4	18	27	47	26	<0.02	<0.1	0.03	<0.001
No.25-2	-101.79 ~ -139.79	2005/11/14*	16.3	8.20	0.029	-140	-51	-7.9	20	2	23	2	21	16	46	21	<0.02	0.13	0.30	0.002
No.25-3	-141.29 ~ -170.29	2005/11/14	16.4	8.21	0.020	-177	-52	-7.9	25	2	13	1	22	12	38	19	<0.02	<0.1	0.04	0.011
No.29	-25.62	2005/05/25	17.2	6.14	0.030	58	-52	-7.9	21	1	22	5	29	24	66	30	<0.02	<0.1	0.03	0.040
		2005/11/15	16.3	6.00	0.029	-45	-55	-8.4	20	6	18	5	28	22	63	39	<0.02	<0.1	0.01	0.72
No.39	-41.18	2005/5/25*	16.9	11.55	0.103	53	-30	-4.4	60	7	69	0	69	16	2	12	0.49	0.70	0.01	<0.001
No.40-2	-1.97	2005/11/15	15.8	8.34	0.030	21	-49	-7.5	21	2	36	5	18	36	76	69	<0.02	<0.1	0.00	0.001
No.40-3	80 ~ -8.5	2005/05/23	17.0	7.55	0.031	230	-49	-7.4	20	3	28	5	20	40	52	26	<0.02	0.21	0.74	0.014
No.40-4	-51.97	2005/11/15	16.1	8.31	0.028	-114	-51	-7.7	20	2	30	3	19	30	63	21	<0.02	<0.1	0.09	0.005
No.40-6	-111.97	2005/11/15	15.7	8.44	0.027	-55	-51	-7.9	21	1	27	1	17	23	57	18	<0.02	<0.1	0.09	0.005
Others (Out of tunnel)																				
Seal water		2005/04/18	15.0	8.43	0.046	174	-22	-3.2	75	4	6	3	120	7	14	6.9	0.88	<0.1	0.06	<0.001
		2005/05/24	19.6	7.84	0.072	120	-4	-0.6	110	5	1	2	170	4	8	0.2	1.40	<0.1		<0.001
		2005/06/15	22.4	7.44	0.062	93	-9	-1.5	100	5	3	2	160	5	11	2.1	1.30	<0.1	0.01	<0.001
		2005/07/12	24.5	8.32	0.064	173	-5	-0.5	98	5	3	4	150	4	7	0.4	1.30	<0.1	0.03	<0.001
		2005/08/10	27.0	7.69	0.078	238	-7	-1.0	110	5	2	5	180	5	12	2.0	1.40		0.01	<0.001
		2005/09/13	27.6	7.35	0.077	N.D.	-4	-0.5	130	6	1	2	220	4	8	0.1	1.70	<0.1	0.00	<0.001
		2005/11/15	21.6	7.70	0.067	263	-4	-0.6	120	5	1	2	160	5	7	4.6	1.10	<0.1	0.01	<0.001
		2006/01/19	12.5	6.46	0.064	379	-5	-0.4	120	6	1	2	180	4	14	0.4	1.30	<0.1	0.01	<0.001
		2006/03/07	16.1	6.96	0.038	513	-7	-1.4	67	4	1	2	110	4	7	1.0	0.67	<0.1	0.01	<0.001
		2005/10/14	26.1	7.05	0.073	288	-5	-0.7	130	5	3	4	210	3	6	0.1	1.60		0.01	<0.001
		2006/01/19	8.0	7.71	0.008	344	-13	-1.8	12	1	1	0	19	1	9	0.0	0.23	<0.1	0.01	<0.001
New seal water		2006/02/07	19.7	7.90	0.013	410	-13	-2.0	20	1	2	1	30	2	9	0.1	0.12	<0.1	0.01	0.002
		2006/03/07	19.0	7.08	0.006	488	-11	-1.9	9	0	0	0	14	1	10	0.2	0.15	<0.1	0.00	<0.001
Sea water		2005/08/10	25.2	7.97	4.950	242	-4	-0.3	10000	430	380	1200	18000	2600	91	0.5	4.40	<0.1	0.01	<0.001
Precipitation		2006/03/06	9.4	6.62	0.004	520	-20	-5.4	1	0	2	0	3	7	9	0.8	<0.02	<0.1	0.01	0.008

Table 2 $\delta^{18}O$ and Cl concentration values for the three end-members.

| End member	δD ‰	$\delta^{18}O$ ‰	Cl mg/L
Sea water	-6.4	-0.5	18,300
Seal water	-7.1	-0.6	110
Groundwater	-49.8	-8.0	15

Figures

(a)
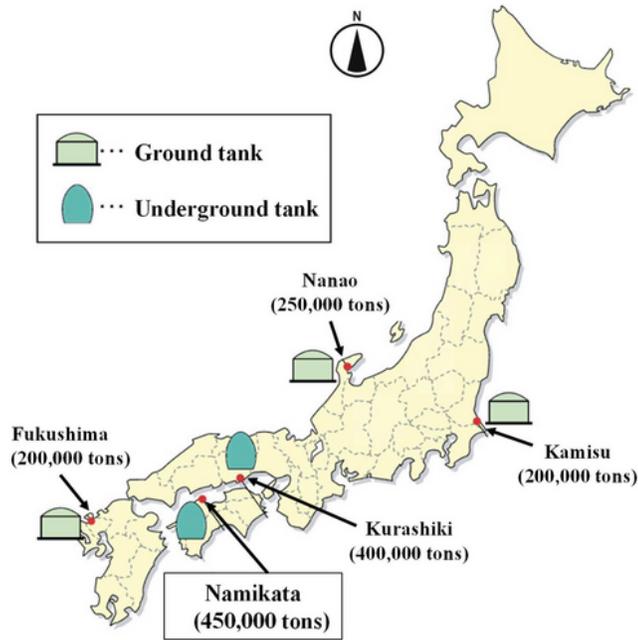
(b)
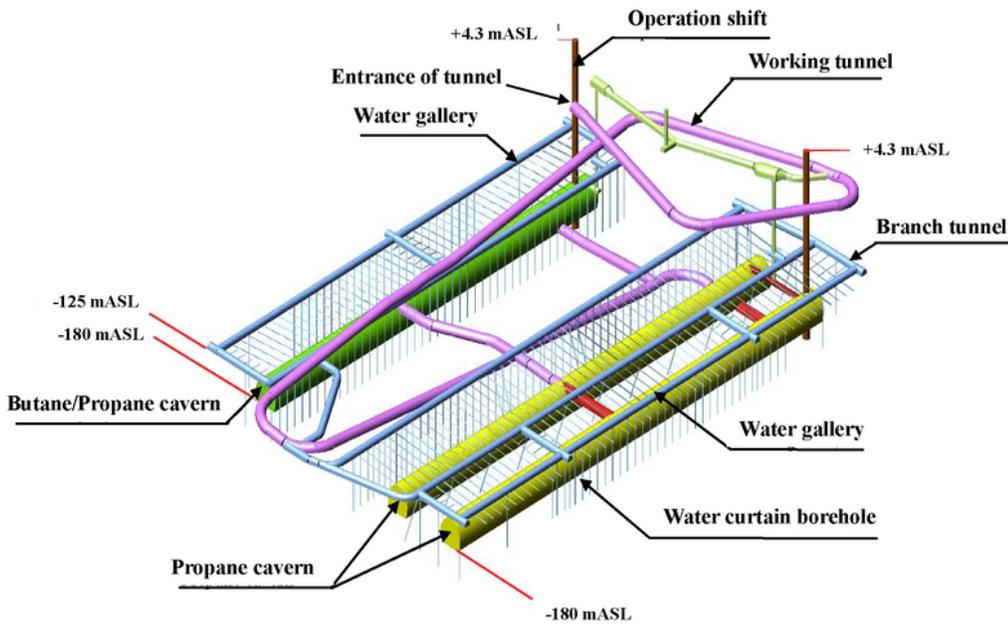
Figure 1

(a) Location and (b) tunnels of the underground storage base for LPG. (Modified from the location of LPG stockpiles in Japan; Ministry of Economy, Trade and Industry, https://www.meti.go.jp/press/2017/11/20171102002/20171102002.html.)
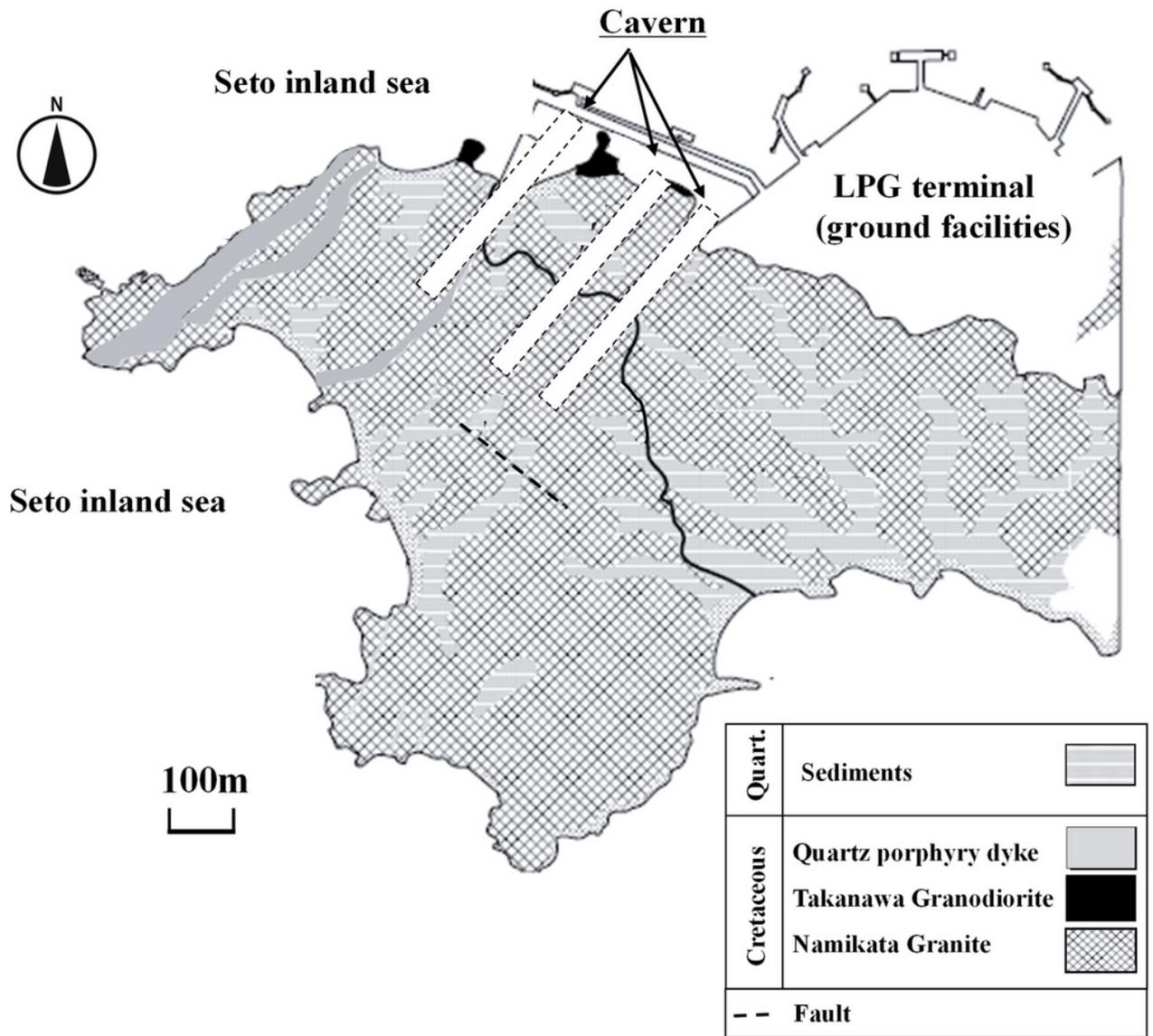
Figure 2

Geological map of the study area. (Modified from Otake, 2000.)
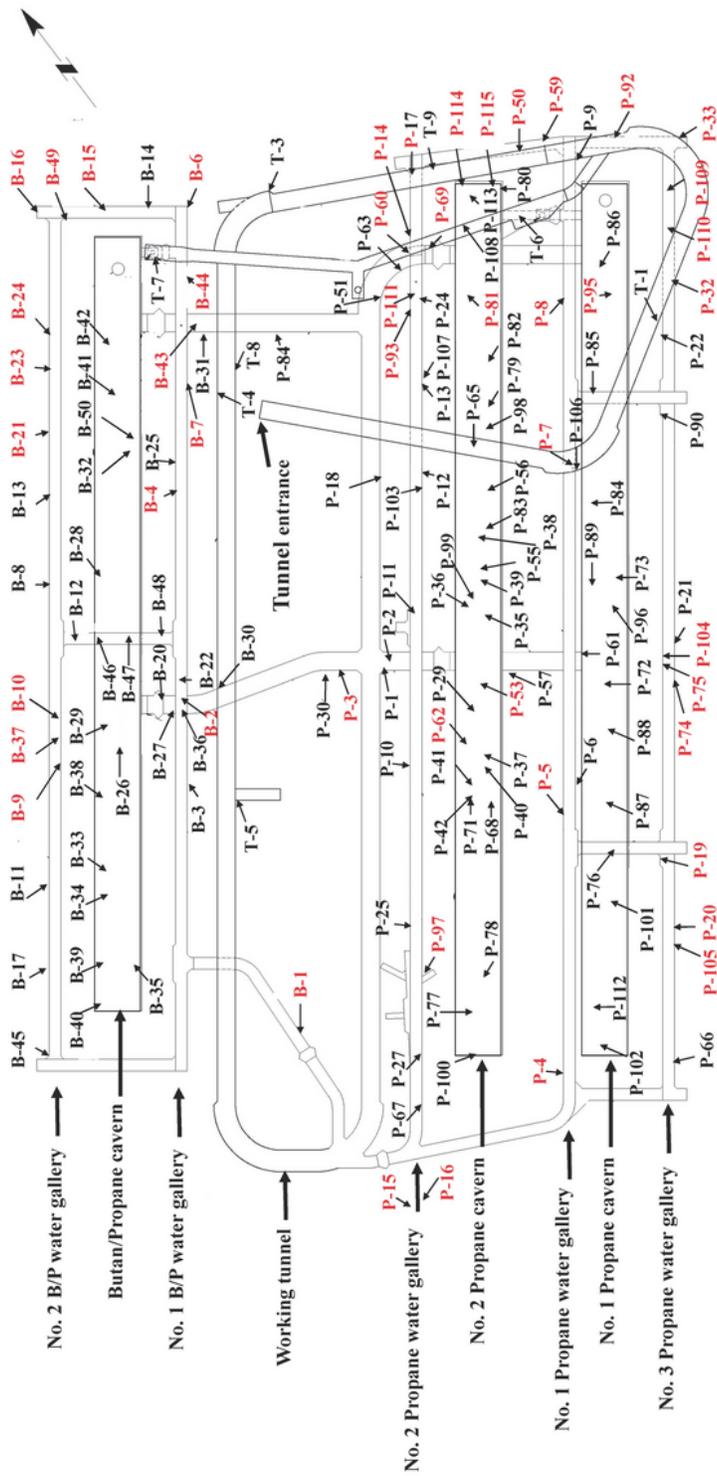
Figure 3

δD vs. δ18O of water samples in the study area. ●: Propane area, ●: Butane/Propane area, ●: working tunnel, ■: observation well, △: seal water, □: seawater.
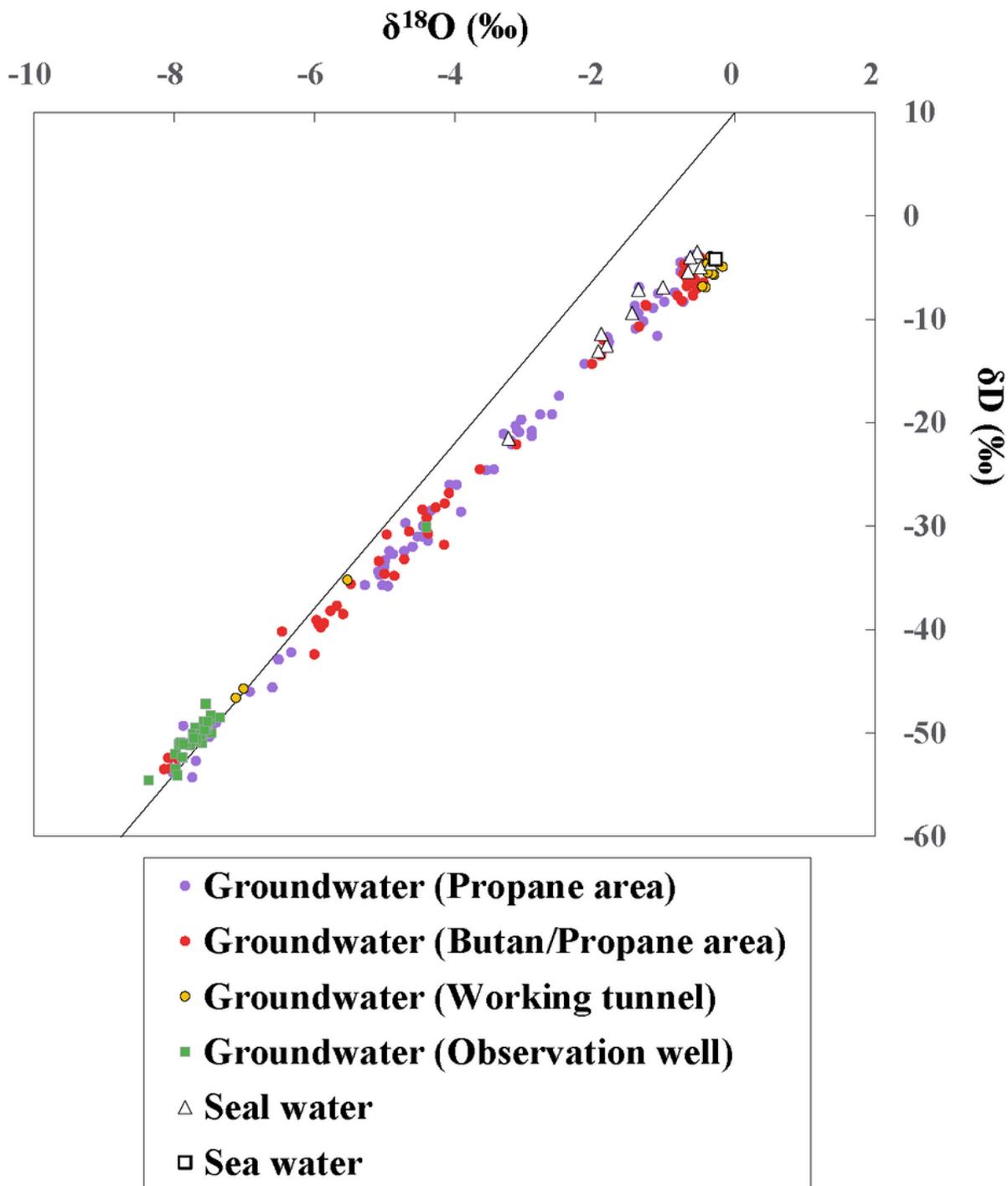
Figure 4

(a) δ18O vs. Cl. (b) change of the percentage of the three end-members at the water sampling site (March 2005 to February 2006). End-member diagrams for (c) working tunnel, (d) water gallery, and (e) cavern.
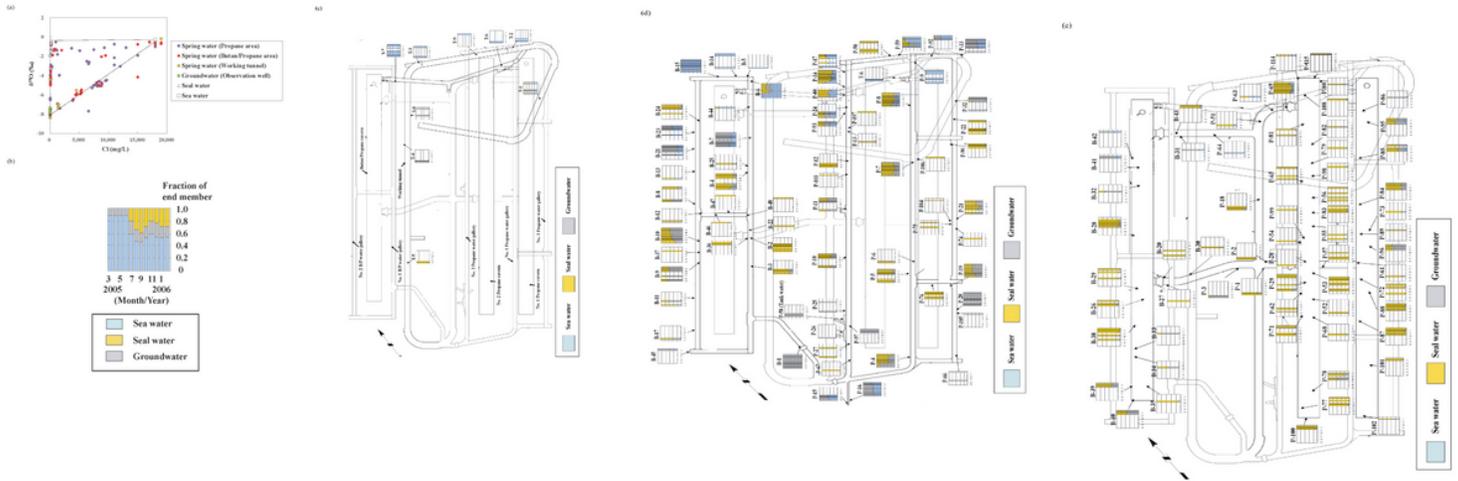
Figure 5

(a) δ18O vs. Cl. (b) change of the percentage of the three end-members at the water sampling site (March 2005 to February 2006). End-member diagrams for (c) working tunnel, (d) water gallery, and (e) cavern.
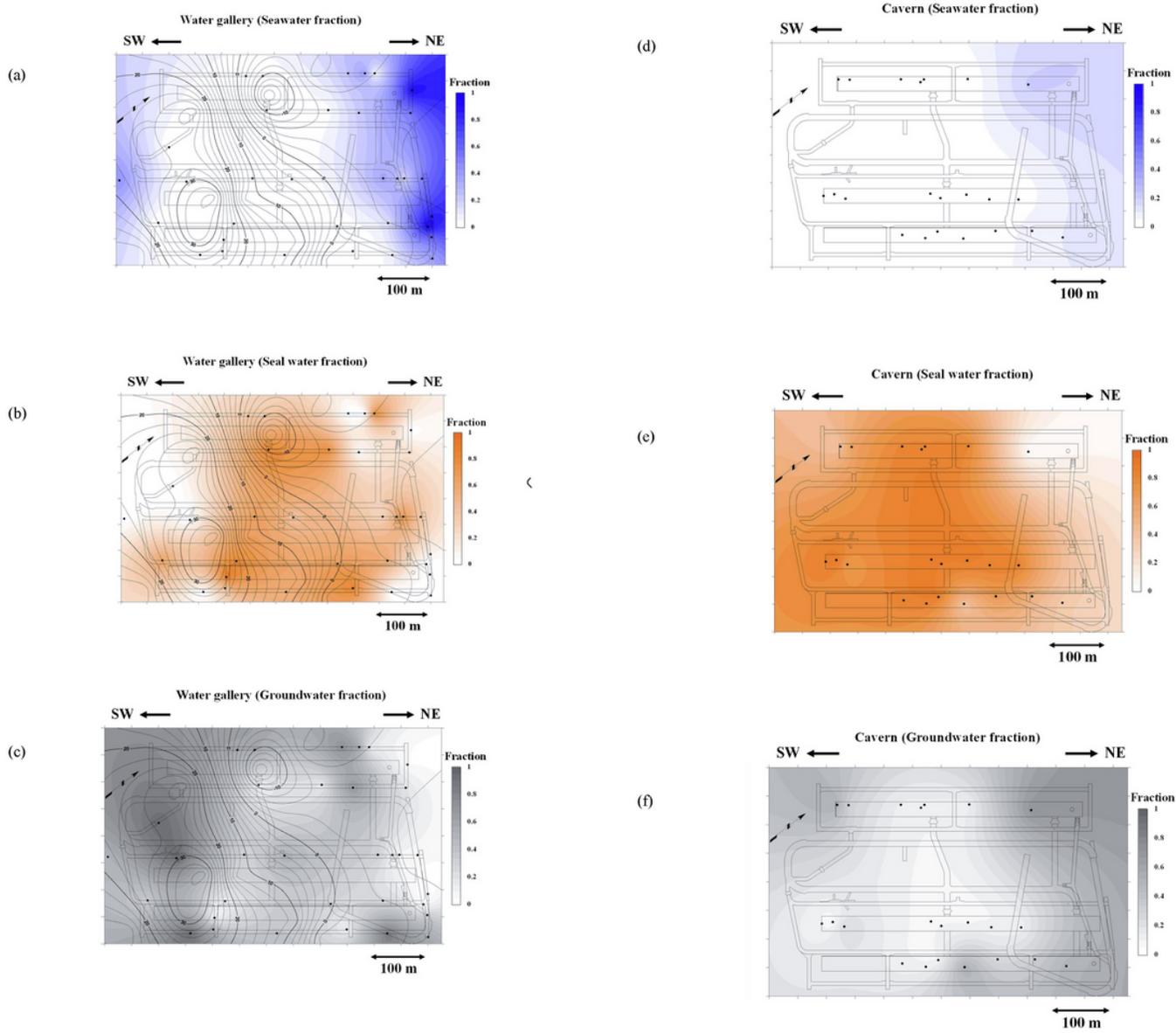
Figure 6

Distribution of three end-members, (a), (d) seawater, (b), (e) seal water, and (c), (f) groundwater, in the water gallery, (a)–(c) and the cavern, (d)–(f) in February 2006.
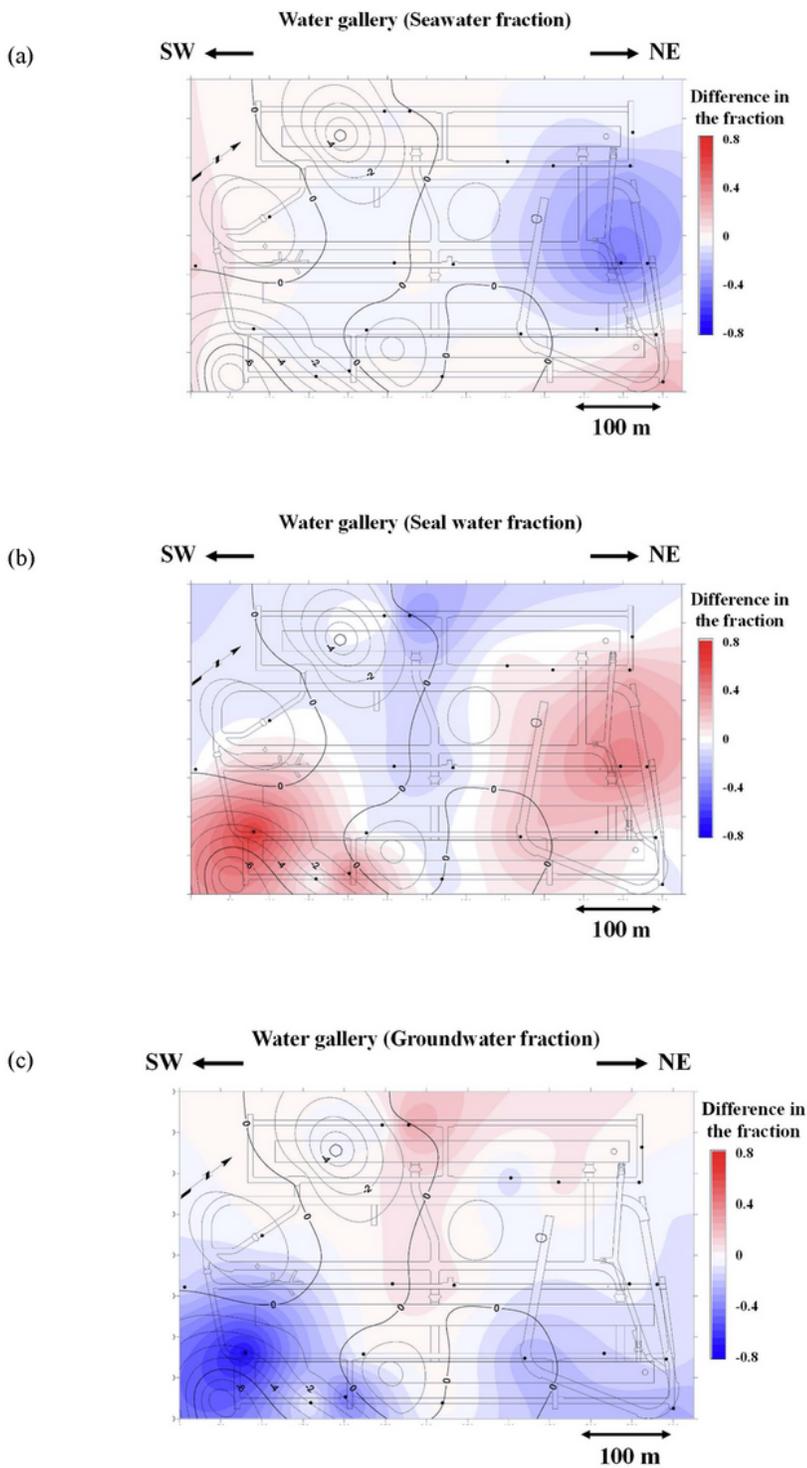
Figure 7

Difference of three end-members, (a) seawater, (b) seal water, and (c) groundwater, in water samples from the water gallery taken in May and December 2005. The red and blue sections indicate the percentage of end-members that increased and decreased, respectively, during the December sampling period.
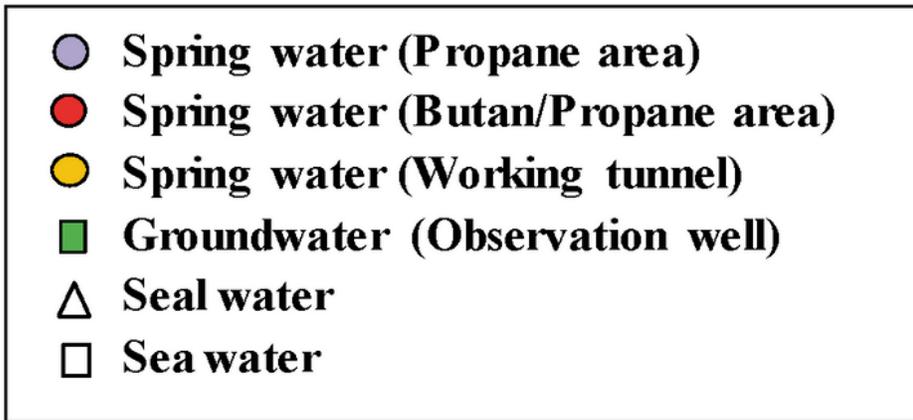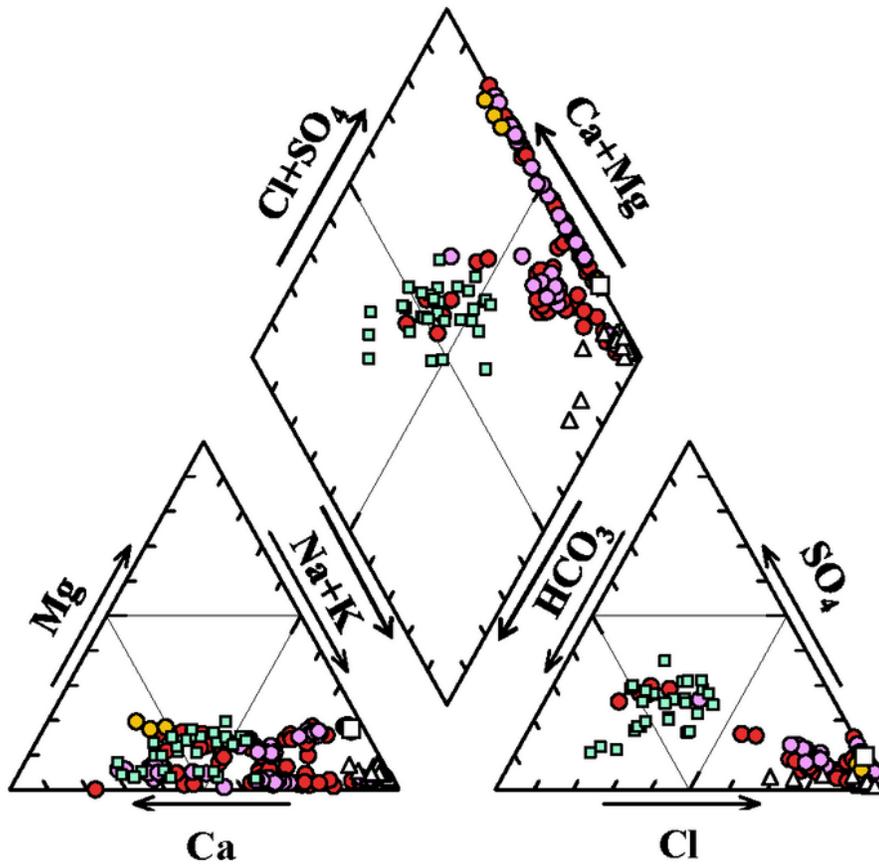
Figure 8

Stiff diagram of water samples in the study area.
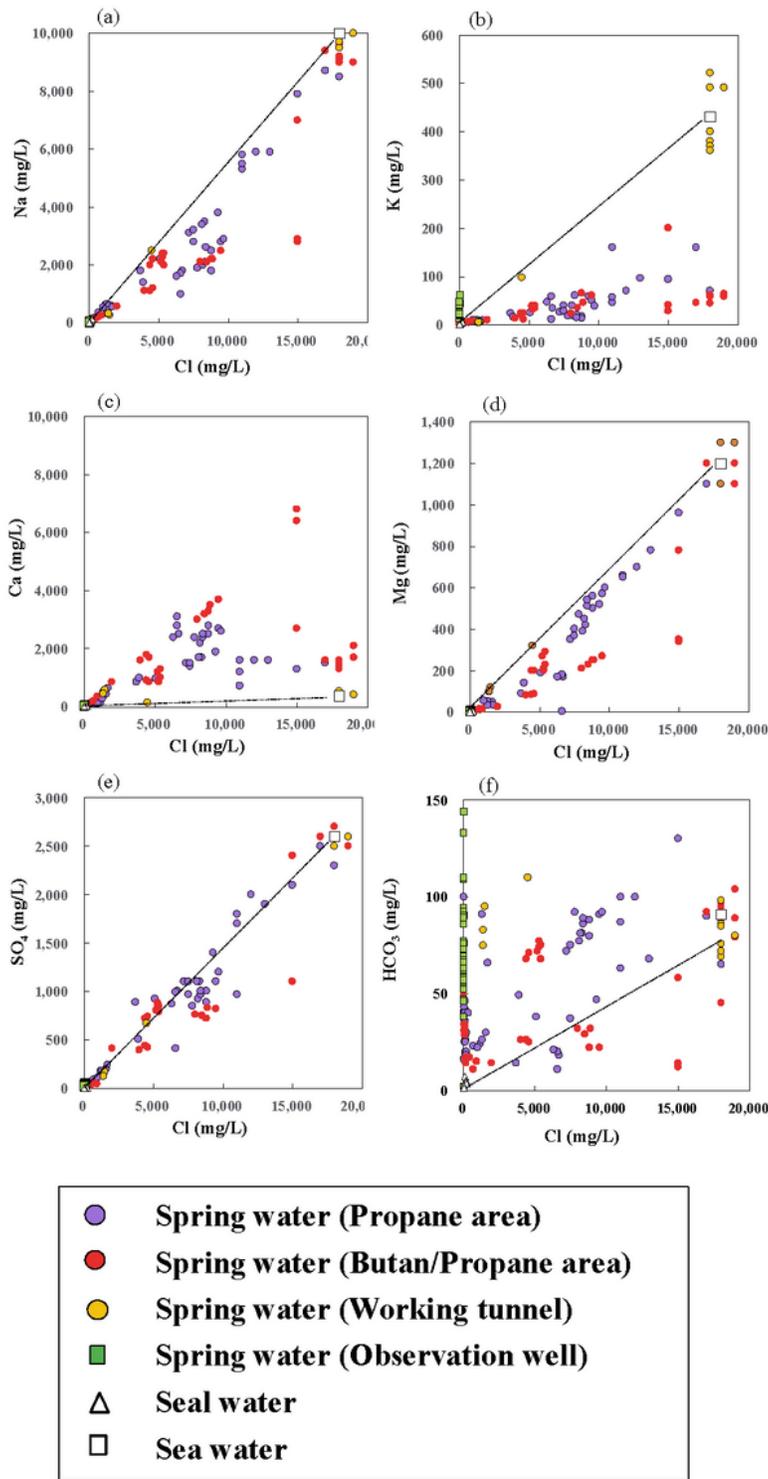
Figure 9

Relationship between Cl and major chemical constituents of water samples in the study area. The broken line in the figure shows the mixing line between seawater and existing groundwater or seal water.
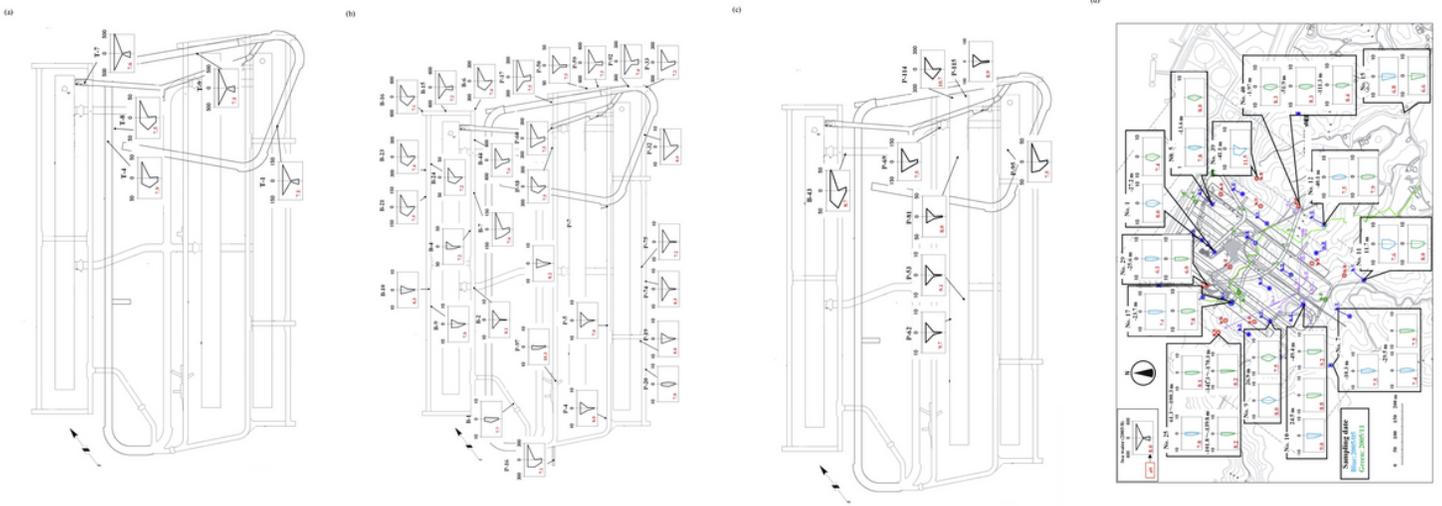
Figure 10

Piper diagram of water samples in (a) working tunnel, (b) water gallery, (c) cavern, and (d) observation well. Red in the figure indicates pH.

Supplementary Files

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