

Chemical and isotopic characteristics of stagnant water isolated in a coastal area

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Abstract Groundwater was investigated at the Kushiro Coal Mine after the mining area was extended by up to 8.5 km off the Pacific shore and 700 m below m.s.l. Three different types of water were found in the mine. The first is freshwater, which flows from the land and is present in the shallow mining area down to 150 m depth. The second is saline water with chloride ranging 5 000–22 000 mg/L, which was found in water drops from the tunnel ceilings throughout the entire undersea mining area and has the chemical properties of altered present-day seawater. The third is estimated to be fossil seawater; it is very saline water from boreholes, and has homogeneous chemical and isotopic properties. Based on the ratio of ³⁶Cl/Cl, the altered seawater had been in the Cretaceous formations and isolated from groundwater–seawater mixing for more than 2 million years, despite being located in a coastal area.

Key words groundwater–seawater interaction; fossil seawater; groundwater residence time; radiogenic chlorine-36; secular equilibrium ratio

INTRODUCTION

The Kushiro Coal Mine (formerly called the Taiheiyou Coal Mine) has been mining from the land, offshore, under the sea for approximately 86 years since 1920. The mining area under the Pacific Ocean has been extended to a maximum of 8.5 km offshore and 700 m depth below mean sea level (b.m.s.l). According to mining records, mining tunnels were excavated along the Harutori coal-bearing layers formed in the Palaeogene period. Also, the inside tunnel has stayed very dry, and there is little seepage of water from the tunnel walls and floor except for water-drops from the ceilings. But as the underlying Cretaceous beds, which are rich in natural gas and pressurized very saline water, is below the coal formation, some boreholes were drilled from the tunnel floor towards the formation to prevent gas explosions and flooding. Water flow from these boreholes stops within a few months or years after drilling, and dries up. In this study, we investigated the chemical and isotopic characteristics in flowing saline water compared with other water collected in the mining area and the present seawater overlying the undersea coal mine. Furthermore, we estimated the isolated duration from the growth of the radiogenic ³⁶Cl/Cl ratio under the *in situ* weak neutron activation.

MATERIALS AND METHODS

Geological setting of study area and chloride ion concentration contour map

The geological setting around the Kushiro Coal Mine has the upper Cretaceous Nemuro formation (Mesozoic era) composed of sandstone and mudstone, as the basement rock. Palaeogene, Neogene and Quaternary formations widely overlay the basement rock from the bottom towards the top, sequentially (Sato & Sato, 1980). The mining tunnels were excavated along the coal-bearing formation, located just above the Cretaceous (Fig. 1).

The chloride-ion concentration varies horizontally from low (0–1000 mg/L) to high (>17 000 mg/L), increasing in the offshore direction (Fig. 2). However, vertically it increases up to 22 000 mg/L in the Palaeogene formation and decreases to 13 300 mg/L in the Cretaceous, increasing with depth below sea level (Fig. 1).

Groundwater sampling method

We collected nine seepage water samples from tunnel walls and floors, 45 water-drop samples from the ceiling of the tunnel, and 10 flowing water samples from boreholes drilled toward the Cretaceous. The flowing groundwater from the boreholes were characterized by chloride-ion concentrations of 13 000–15 000 mg/L, shown by the grey-interior circles in Fig. 2. We paid great attention to using the closed sampling system in order to prevent evaporation from the small water-drop samples. We only collected groundwater samples for measurement of $^{36}\text{Cl}/\text{Cl}$ ratio from relatively large flowing or seepage volumes to avoid air-borne ^{36}Cl contamination.

Analytical methods

Tritium The concentration of tritium was measured by counting beta rays after electrolytic enrichment. One litre of groundwater was reduced to about 40 mL by electrolysis using Ni/Fe electrodes. Forty millilitres of distillate and 60 mL of scintillation cocktail were mixed in a 100-mL Teflon vial. This mixture was analysed over 1000 min using a low-background liquid-scintillation counter. The detection limit for this method is 0.3 TU.

Cations and anions The concentrations of dissolved cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and anions (Cl^- , SO_4^{2-} and HCO_3^-) were measured using ICP and liquid chromatography, respectively. The analytical procedures followed the standard methods for the examination of water (Clesceri *et al.*, 1989).

Stable isotopes The ratio of deuterium to hydrogen (D/H) was measured by mass spectrometry after reducing water to hydrogen gas using metallic uranium heated to 600°C. The $^{18}\text{O}/^{16}\text{O}$ ratio was measured by mass spectrometry after reaching isotopic exchange equilibrium between water and gaseous CO_2 . Both D/H and $^{18}\text{O}/^{16}\text{O}$ ratios were expressed as deviations per thousand (‰) from standard mean ocean water (SMOW), following the conventional method defined by Craig (1961). The measurement uncertainties were $\pm 1\%$ for D/H and $\pm 0.1\%$ for $^{18}\text{O}/^{16}\text{O}$.

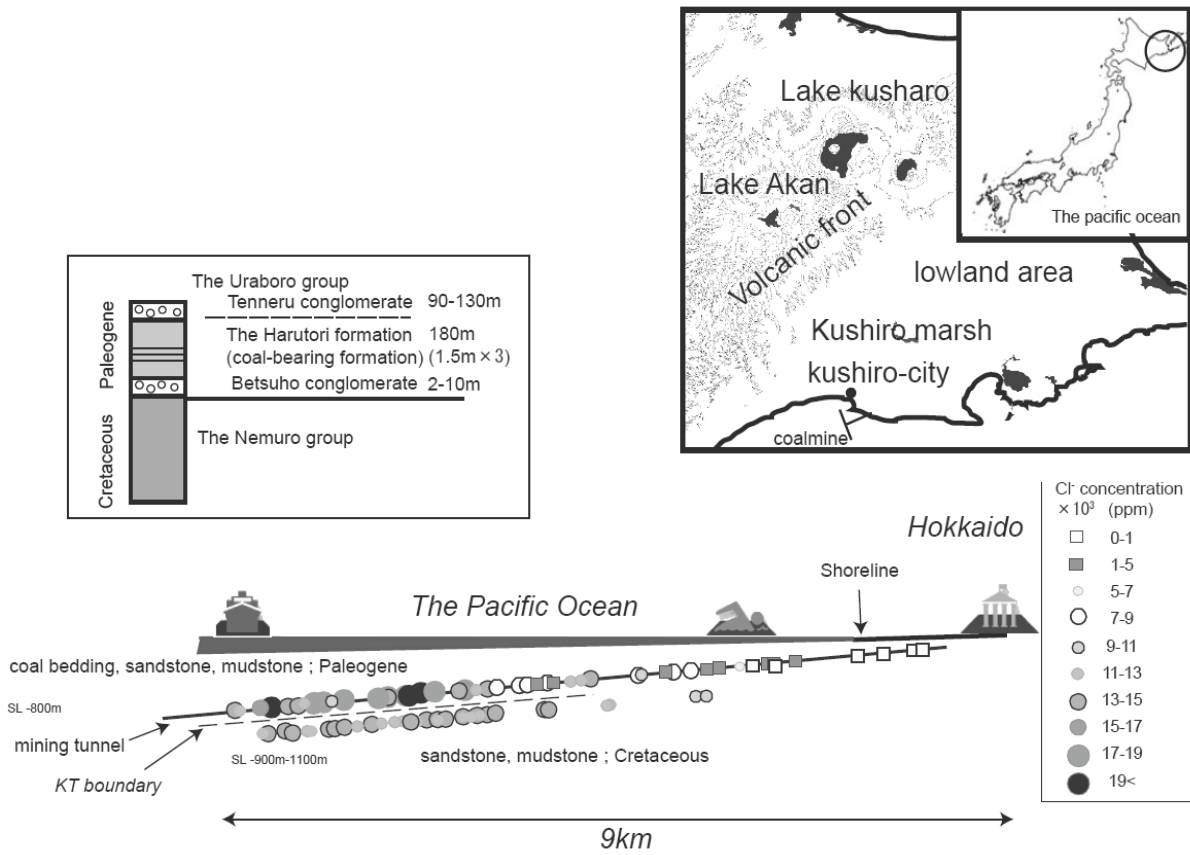


Fig. 1 Location of the study area in Hokkaido in Japan and geological setting of study area (vertical section of the Kushi Coal Mine) and vertical distribution of chloride ion concentration in the mining area.

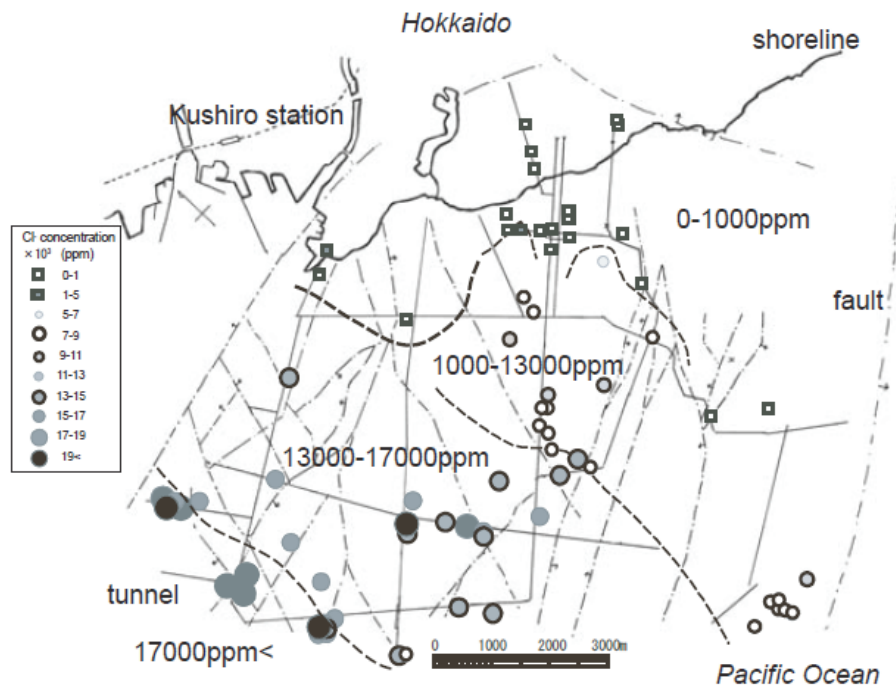


Fig. 2 The horizontal distribution of chloride ion concentration in the mining area.

$^{36}\text{Cl}/\text{Cl}$ ratio Chloride was precipitated as AgCl in a clean room. The precipitate was purified by repeated re-dissolution in NH_4OH and re-precipitation (after the removal of sulfur as BaSO_4). All AgCl precipitation samples for acceleration mass spectrometry (AMS) measurement were made following the standard procedures used at the Australian National University (ANU) (Creswell, 2001). The $^{36}\text{Cl}/\text{Cl}$ ratio for the groundwater samples was measured using AMS facilities at ANU and ETH, Zurich.

U and Th in the rock A sample of 0.5 g of pulverized rock powder was placed in a Teflon beaker and completely dissolved by heating on a hot plate after adding concentrated HNO_3 and HF. The dissolved material was heated again until HClO_4 fuming after adding concentrated HNO_3 and HClO_4 . The residual dried material was re-dissolved with a small amount of weak HCl, and diluted further to 100 ml using super-pure distilled water. The U and Th concentrations were measured using inductively coupled plasma-mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Vertical distribution of chloride ion concentration

Figure 3 shows the vertical relationship between changes in chloride ion concentration and sampling depth. We can estimate the location of the interface of freshwater and seawater from the changing chloride ion concentration. The location of the boundary between the freshwater flow region and seawater can be deduced from a drastic change in the chloride concentration at around 450 m b.m.s.l. The chloride concentration increases to 22 000 mg/L, which is greater than that of the present seawater, down to a depth of 600–700 m b.m.s.l. Although different mechanisms of concentrating chloride are possible, e.g. strong evaporation in the very dry mining tunnel, long-term water rock interaction (Frape *et al.*, 1984), re-dissolution of residual sea salt by pore water,

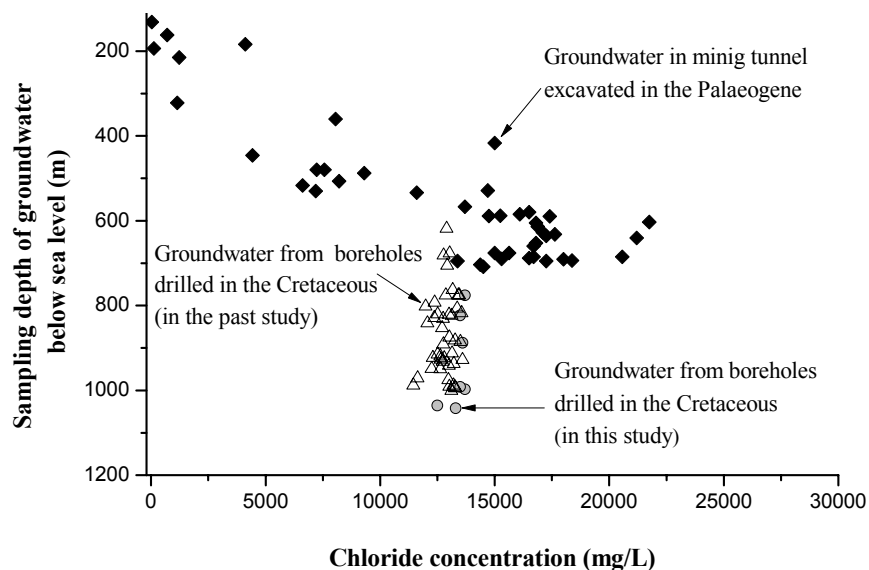


Fig. 3 Vertical chloride ion concentration with groundwater sampling depth.

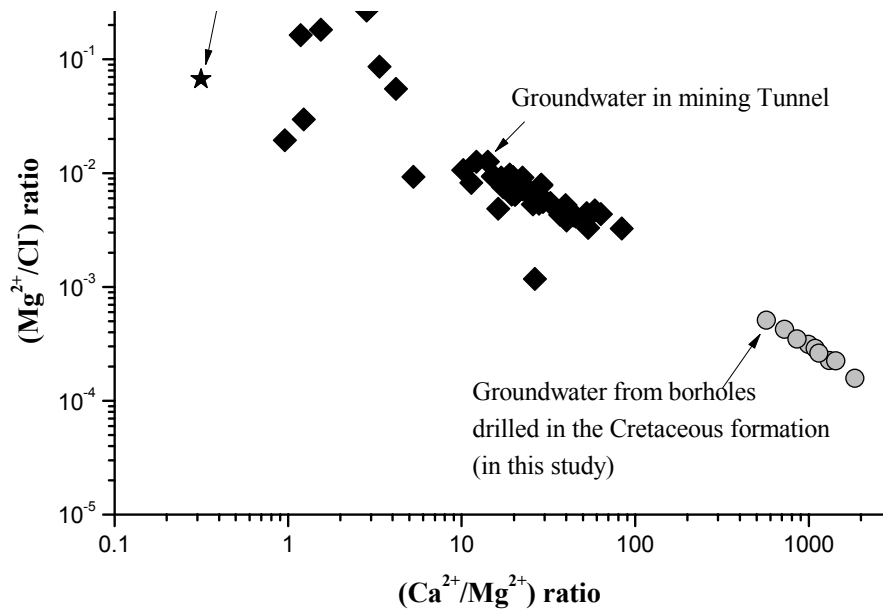


Fig. 4 Correlation between ratio of Mg^{2+} and Cl^- and ratio of Ca^{2+} and Mg^{2+} in the modern seawater and groundwater collected in the Kushiro Coal Mine.

or squeezing of pore water from the formation under a high geo-pressure, more detailed investigations and additional studies are required to adequately explain the formation of the excess chloride concentration.

In contrast, chloride concentration in the Cretaceous formation suddenly drops to 12 000–14 000 mg/L at depths of 800–1000 m b.m.s.l. The chloride concentration is very stable and nearly constant (an average of 13 300 mg/L) in groundwater flowing from boreholes. Its chemical properties are drastically different from the freshwater, shallow brackish water, and very saline water in the Palaeogene formation. The cation exchange between Mg^{2+} and Ca^{2+} is especially marked (Fig. 4), owing to water–rock interaction.

A certain boundary appears to exist between the Cretaceous and Palaeogene. The groundwater appears to not exchange or mix between the two different geological formations, as evidenced by the sudden change in chloride concentration, change in other chemical properties, and the fact that water flow from boreholes stops within a few years after drilling without recharging, and dries up.

Origin of waters

All the stable isotopes (δD and $\delta^{18}\text{O}$) data are displayed in Fig. 5. Most data from fresh and brackish groundwater, collected at shallower than 450 m b.m.s.l., are aligned with the global meteoric water line (GMWL). This indicates that the shallow groundwater originates from rainwater.

Saline water having chloride concentrations in excess of 5000 mg/L is lined up on a correlation straight line with a slope of 4.7. The magnitude of this slope is expected in evaporation, ion filtration (Coplen & Hanshaw, 1973) or mixing with seawater.

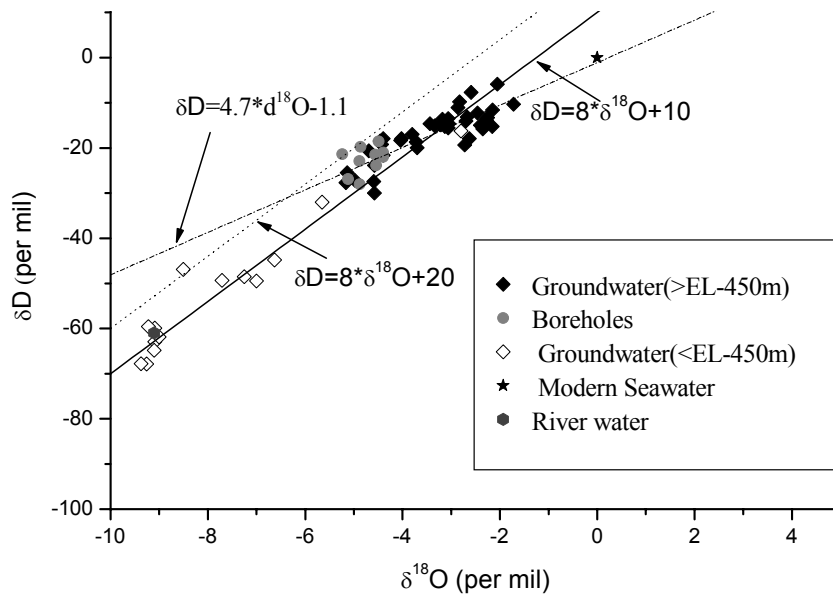


Fig. 5 Correlation between δD and $\delta^{18}O$ for estimation of origin of groundwater (the global meteoric water line: $\delta D = 8 \times \delta^{18}O + 10$, the meteoric water line in northeast Japan: $\delta D = 8 \times \delta^{18}O + 20$, the estimated mixing line in groundwater collected from 400 to 700 m b.m.s.l.: $\delta D = 4.7 \times \delta^{18}O - 1.1$).

Thus, we cannot conclude which mechanism was responsible solely from the data collected in this study.

All the data from flowing groundwater collected from boreholes drilled in the Cretaceous are plotted in a narrow zone on the aforementioned straight line. This suggests groundwater in the Cretaceous rock has a homogeneous original water quality, and is not created by mixing among different end-members. Consequently, this groundwater has one origin, when we consider the mixing of other groundwaters found in the surrounding region.

Residence time

We estimated groundwater residence time based on ^{36}Cl concentrations in groundwater. Usually, we estimate residence time using cosmogenic ^{36}Cl atoms. But, if the origin of groundwater collected in the Cretaceous is seawater or very saline water, we can ignore input of cosmogenic ^{36}Cl atoms due to an overabundance of stable chlorine atoms.

Furthermore, groundwater has been stored sufficiently deep in the Cretaceous rock to be free from the affects of cosmic ray interactions (Lehmann, *et al.*, 1993). We can expect a growing number of radiogenic ^{36}Cl atoms produced by neutrons, released in (α, n) reactions, caused by α -particles scattered from uranium and thorium radionuclides contained in the deep rock. The number of ^{36}Cl atoms in groundwater may be estimated by the following equation (Feige *et al.*, 1968; Andrews *et al.*, 1986; Lehmann & Loosli, 1991):

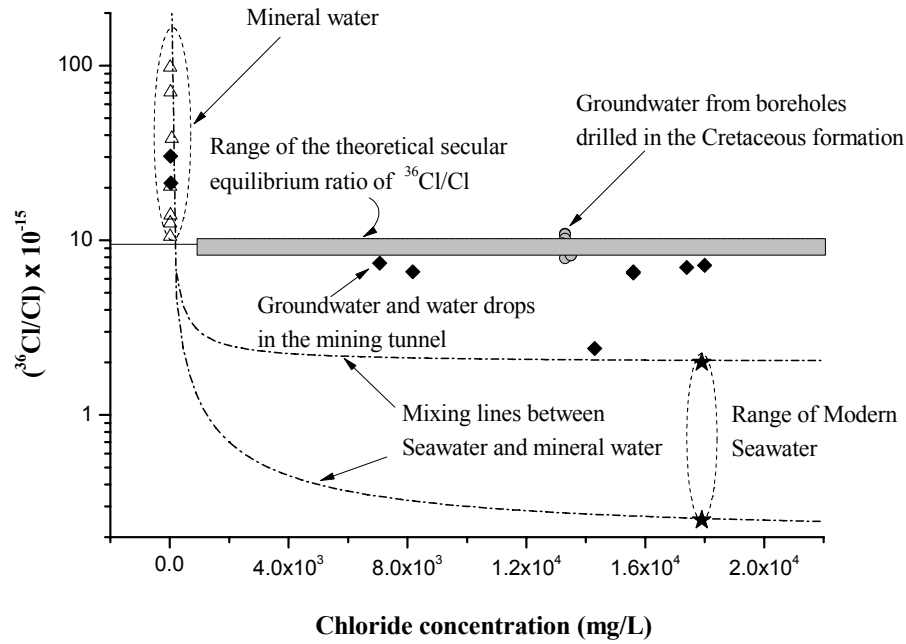


Fig. 6 The correlation between the chloride ion concentration and the $^{36}\text{Cl}/\text{Cl}$ ratio in groundwater from boreholes drilled in the Cretaceous, groundwater in the coal mining tunnel excavated in the Palaeogene formation, and the commercial mineral waters, showing the mixing water line between modern seawater and commercial mineral waters.

$$^{36}\text{Cl} = 4.55 \times 10^{-10} \times \Phi \times (1 - e^{-\tau}) \times \text{Cl} \quad (1)$$

where, Φ is the neutron flux determined by the content of U, Th and other light elements, and the density of the surrounding rock, τ is the radioactive decay constant ($7.3 \times 10^{-14} \text{ s}^{-1}$) for ^{36}Cl , and Cl is the chloride ion concentration in groundwater.

Furthermore, as equation (1) reaches secular equilibrium conditions after 2 million years, we can rewrite this equation to:

$$\frac{^{36}\text{Cl}}{\text{Cl}} = 4.55 \times 10^{-10} \times \Phi \quad (2)$$

We calculated the neutron flux to be $(2.09 \pm 0.16) \times 10^{-15} \text{ n/cm}^2 \text{ s}^{-1}$ following Lehmann & Loosli (1991), and using the U content of $1.97 \pm 0.15 \text{ mg/g}$ and the Th content of $6.17 \pm 0.85 \text{ mg/g}$ measured in rock samples drilled in the coal mine. Using equation (2) we estimated the theoretical secular equilibrium ratio of $^{36}\text{Cl}/\text{Cl}$ to be $(9.5 \pm 0.73) \times 10^{-15}$. We can roughly estimate the residence time by comparing the measured ratio with the theoretical value.

The correlation between the $^{36}\text{Cl}/\text{Cl}$ ratio and the chloride ion concentration is illustrated in Fig. 6 for three different water types in the mine. This figure indicates that most of groundwater collected in the coal mine has not been produced by mixing of present seawater and, e.g. commercial fresh-mineral water, which represents young groundwater (Mahara *et al.*, 2004). Groundwater in the Cretaceous is located further from the mixing zone in Fig. 6 than other groundwater collected in the Palaeogene formation. The measured $^{36}\text{Cl}/\text{Cl}$ ratios range from 8×10^{-15} to 1.08×10^{-14} , the average value being $(9.46 \pm 1.36) \times 10^{-15}$. The average measured $^{36}\text{Cl}/\text{Cl}$ ratio is in line with the estimated theoretical secular equilibrium ratio of $(9.5 \pm 0.73) \times 10^{-15}$.

We may conclude that groundwater in the Cretaceous rocks has a residence time of more than 2 million years. In other words, the groundwater has been isolated in the geological formation without exchanging and mixing with other groundwater circulating in the upper formations.

CONCLUSIONS

In this study, we have revealed that groundwater in the Cretaceous formations, which have no contact with the overlying present seawater, has remained in the undersea basement rocks of the study area for a geological time scale. Groundwater quality has altered by ion exchange owing to long-term water–rock interactions. The groundwater has been isolated for over 2 million years, as evidenced by *in situ* growth of ^{36}Cl activated by neutrons created naturally by α -decay of uranium and thorium contained in the deep rock.

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