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Characterization of rare earth elements (REEs) associated with suspended particles in deep granitic groundwater and their post-closure behavior from a simulated underground facility

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ABSTRACT

Understanding radionuclide transport processes deep underground is indispensable for safety assessments of the geological disposal of radioactive wastes. This study investigated the behavior of rare earth elements (REEs) associated with suspended particles in deep granitic groundwater and in a sealed drift at a depth of 500 m in the Mizunami Underground Research Laboratory (URL) in Japan, as an analogue study of radionuclide behavior around an underground waste disposal facility.

Particles suspended in natural groundwater consist of silicate minerals including clays, and iron hydroxide, calcite, sulfide, and organic substances. Approximately 10%–60% of REEs in groundwater are associated with suspended particles. Furthermore, sequential chemical extraction analyses of the suspended materials trapped on membrane filters suggests that REEs are primarily sorbed onto carbonate particles in deep granitic groundwater. Carbonate particles in groundwater are most likely derived from *in situ* precipitation of supersaturated carbonate minerals such as calcite. The concentration of Lanthanum associated with suspended particles, as an example, is highest when the calcite saturation index shows equilibrium ($SI = 0$) and decreases as the calcite saturation index increase. Because deep granitic groundwater is generally in equilibrium with the saturated condition for calcite, the results of this study suggest that calcite particles inevitably exist in groundwater and preferentially sorb REEs.

The REE concentrations in the water and suspended particles from the closed drift are significantly lower compared with concentrations in the surrounding groundwater. Thermodynamic calculations show that the dissolved REE carbonate complexes in the closed drift decreased in the drift closure period. These complexes may have been absorbed or co-precipitated within the shotcrete on the drift wall. In the closed drift, ZnS particles and large amounts of organic suspensions, as artificial suspended particles, were observed in addition to the particles observed in natural groundwater. A sequential chemical extraction analysis indicates that REEs are primarily sorbed onto the carbonate particles and not on the large quantity of organic particles. There may be little REE adsorption onto organic suspensions, or REEs may have preferentially adsorbed onto calcite particles or shotcrete rather than organic matter. The occurrence of calcite particles under the cementitious conditions of the closed drift changes from the large suspended particles to aggregates of relatively small particles with time. Precipitation of carbonate particle–borne REEs is probably one of reasons for the decrease in the suspended REEs concentrations. The usage of cement–based materials would generate environmental conditions in which REEs are fundamentally immobile in and around the underground facilities.

1. Introduction

Safety assessments of the geological disposal of radioactive wastes consider the long-term migration of contaminants to the biosphere from facilities isolated deep underground (JNC, 2000;

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Murray, 2001; Nagra, 2002; IAEA, 2009). The mobility of radionuclides in the geosphere strongly depends on both sorption/desorption processes occurring on mineral surfaces along groundwater flow paths (Maskenskaya et al., 2015; McKinley and Alexander, 1993; Vandergraaf et al., 1996). In addition, radionuclides may be adsorbed onto colloidal particles being transported in the groundwater (Novikov et al., 2009). Thus, a range of radionuclides could be transported by groundwater flow either as solutes or via mobile colloid particles that may be present in the groundwater. Colloidal material transport is a well-recognized phenomenon and is important because some types of colloidal particles may facilitate or retard radionuclide migration along groundwater flow paths (Grindrod, 1993; Ryan and Elimelech, 1996; Sen and Khilar, 2009). The significance of colloidal transport of radionuclides to geological disposal safety assessments is highly dependent on the reversibility of the sorption process because, if radionuclides readily desorb when chemical changes occur along the flow path, colloids would have little effect on radionuclide migration (Alexander et al., 2011). It is a challenge to estimate theoretically the potential magnitude of colloidal radionuclide transport due to the variability in the range of colloidal types likely to be present in groundwaters, e.g., minerals, organics, and microbes (Degueldre et al., 2000; Laaksoharju, 2005), and is further complicated by uncertainty in their interactions with radionuclides and rock surfaces in the natural subsurface. Therefore, actual observations of colloids and their interactions with various disposal facility construction elements underground are essential to evaluate and understand the importance of colloidal radionuclide transport.

To understand the role of colloid particles in the transport of contaminants, previous studies have included laboratory work, *in situ* field experiments, observations of colloid types and their interactions on rock surfaces, and theoretical modeling (e.g. Ding and Wen, 2005; Erel and Stolper, 1993; Loveland et al., 2003). Alexander et al. (2011) and Swanton et al. (2010) reviewed mobile colloids present in the subsurface and assessed their potential for transporting radionuclides. Colloids in deep groundwaters were studied at crystalline rock sites in Canada (Vilks and Bachinski, 1996), Germany (Degueldre et al., 1996), Spain (Ivanovich and Gardiner, 2001), Sweden (Laaksoharju, 2005; Nilsson et al., 2008), Switzerland (Degueldre, 1994; 1997; Hauser et al., 2002) and at sedimentary rock sites in Germany (Dearlove et al., 1990), UK (Gardiner et al., 2000). Colloid particles in deep groundwaters consist of minerals such as quartz, clay, iron (oxy)hydroxides, calcite and humic substances, etc. with concentrations of between 0.3 μg $L^{-1}$and 20 mg L^{-1}. The inorganic colloids reflect the mineralogy of the host rock and can be comprised of mineral fragments of the rock matrix or secondary minerals from the groundwater flow paths.

Natural analogue studies using analogue elements of the trivalent actinides also provide an insight on the mobilization of radionuclides by colloidal particles. Because the light rare earth elements (REEs) have ionic radii close to those of Am and Cm, and solubilities are correspondingly similar, the analogy using such REEs is significant to infer the mobilization process of radionuclides (Krauskopf, 1986). Interactions between colloids and radionuclides have been studied by focusing on natural radioelements (e.g., U and Th) and REEs (Vilks et al., 1993; Ivanovich et al., 1992; Missana et al., 2004). Besides, studies of analogue element interactions with organic colloids and microbial cells (Ozaki et al., 2006; Takahashi et al., 2005), humic substances (Seida et al., 2010), and clay colloids (Degueldre et al., 1996; Missana et al., 2004; Möri et al., 2003; Ohlander et al., 1996; Geckeis et al., 2004) have been done. These previous studies suggest that colloidal particles of clay, iron (oxy) hydroxide, and organics could potentially transport radioelements in natural groundwater.

In addition, the construction, operation and closure of underground geological waste repositories will introduce extrinsic materials, including cement, steel, and sealing materials, into the underground environment. As these materials age, they will likely degrade and release colloids into deep groundwaters (e.g. Swanton et al., 2010). Thus the emplacement of extrinsic materials likely will bring in substances that could be the source of artificial colloids. The nature of the extrinsic materials will depend on the facility design and concept chosen. Cement–based materials are widely used in the construction of underground facilities according to the design (e.g. shotcrete on gallery, grouting for water–conducting features in host rock) and are expected to produce alkaline conditions during the post–closure period, which will suppress the solubility of the radionuclides and enhance their sorption onto the cement (e.g. Hodgkinson and Robinson, 1987; Tits et al., 2004). Then, if radionuclides are associated with cement–derived colloids and the colloids are mobile, the effective solubility and flux of radionuclides from the repository into the surrounding host rock are potentially increased (e.g. Chambers et al., 1995; Wieland, 2001; Wieland et al., 2004). Cementitious colloids are not expected to be chemically stable (Swanton et al., 2010), but further experimental data would assist in building confidence in the understanding of colloidal processes in cementitious near–field conditions.

This study examines the interaction between suspended particles including colloids and REEs in the groundwater and estimates the geochemical processes, including the behavior of REEs and suspended particles, in a sealed drift, simulating a post–closure environment containing cement–based materials, at a depth of 500 m in granitic rock.

2. Study area

2.1. Geology and groundwater chemistry

This study was conducted at the Mizunami Underground Research Laboratory (Mizunami URL: MIU) in Japan (Fig. 1). At this site, Miocene sedimentary rocks of the Mizunami Group (±170-m thick) unconformably overlie a basement of Cretaceous granitic rocks (Toki granite). The Toki granite consists of medium– to coarse–grained biotite granite and medium-grained hornblende-biotite porphyry and is partly intruded by quartz porphyry and

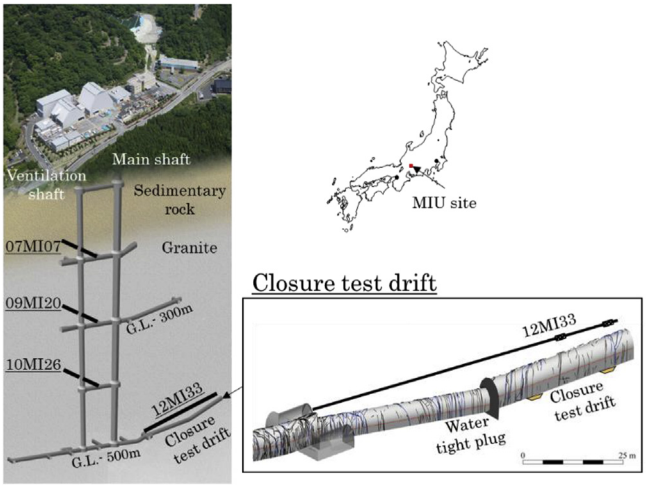


Fig. 1. Outline of the study area and sampling points. An *in situ* mock–up drift (Closure Test Drift) at a depth of 500 m was excavated and closed for a simulation experiment of environmental change following a deep underground facility closure.

aplite dykes. Previous borehole investigations from ground surface show that the groundwater chemistry in the granite is dominantly Na–Ca–Cl type, and that the salinity of the groundwater generally increases with depth, reaching 2500 mg L^{-1} at 1000 m below ground level (mbgl). In addition, the concentration of major solutes such as Na, Ca, K, and F correlates well with that of Cl (Iwatsuki et al., 2005).

2.2. Details of research site

The MIU has been excavated to 500 mbgl. Fig. 1 shows the layout of the shafts and galleries of the MIU and several monitoring boreholes drilled from the galleries. The design of the underground facility consists of a main shaft and a ventilation shaft, two access/research galleries at 300 m and 500 m below ground level, and sub-stages at depths of 100 m between the two shafts. The construction of the shafts commenced in July 2003 and the construction of the 500 m gallery including an *in situ* mock–up drift (the Closure Test Drift; CTD) at one end of the gallery had been completed by the end of February 2014.

Horizontal boreholes (07MI07, 09MI20, 10MI26, and 12MI33) with lengths of approximately 100 m have been drilled from the galleries at depths of 200 m, 300 m, 400 m, and 500 m, respectively (Fig. 1). Groundwater contamination due to introduction of drilling fluids and drilling related materials into the boreholes was completely purged during borehole development and long–term monitoring over several years of study (Iwatsuki et al., 2015).

The CTD, 45 m long × 5 m × 4.5 m (approximately 900 m^3), was isolated from the rest of the URL tunnel system by an arch-shaped concrete plug (1.5–2.5 m thick) with an access manhole. The tunnel walls of the galleries including the CTD, are covered by a 5–10 cm thick shotcrete lining for safety. Ordinary Portland Cement (OPC) and low-heat Portland Cement were used for shotcrete and the concrete plug, respectively. The CTD is used for an experiment to study environmental changes following a simulated facility closure in fractured crystalline rock. The experiment has been planned to observe any environmental changes following water-filling without backfill in the closed tunnel, and subsequently emplacing backfill and repeating the experiment in the tunnel and again observing any environmental changes in a backfilled condition. By conducting experiments in two stages, it is possible to understand the environmental changes due to first, the sprayed cement (shotcrete) separately from the changes with backfill added (Onoe et al., 2014). Such fundamental findings will be reflected in future URL facility backfilling plans.

Currently, the monitoring of environmental changes related to the cement shotcrete materials alone are being conducted in the CTD filled with groundwater. The manhole in the concrete plug was closed in January 2016, then the groundwater at the 500 m gallery was pumped into the CTD. Teflon tubes from the inside of the CTD were used to penetrate the concrete plug and connect the chemical monitoring electrodes for pH, redox potential of groundwater without introducing air. This enables the collection of groundwater from the CTD and monitoring of the chemical parameters under anaerobic conditions.

The borehole 12MI33 had been drilled parallel to the CTD at a distance of 5 m from the drift before the CTD was excavated. Water pressure response during the CTD excavation was detected at one of the water sampling points (12MI33–2) in the borehole. After the CTD excavation, the fractures with water inflow were observed only on the tunnel wall in the vicinity of the 12MI33–2. Consequently, water sampling at the 12MI33–2 location was used to supply reference groundwater data for the experiment site.

3. Methods

The IUPAC definition of the term colloid is “state of sub–division in which molecules dispersed in a medium have dimensions roughly between 1 nm and 1000 nm in size” (Everett, 1972). In this study, 0.1–100 μm (100–100,000 nm) filters, exceeding the maximum size of a true colloid, by definition, are used. Therefore, the term “suspended particle” has been adopted for this study, and includes true “colloids”.

3.1. Sampling methods

The stepwise characterization of geological environments is conducted by geophysical surveying, borehole investigations and investigations from underground galleries, such as in the MIU project (Saegusa et al., 2009; Semba et al., 2009; Kunimaru et al., 2010). This study was carried out in the sub stages and galleries at depths of 200–500 m where groundwater, with and without *in situ* filtration, can be easily collected from the boreholes and the CTD. In addition, a sequential chemical extraction of the suspended materials on the filter was performed to identify the REEs associated with the suspended particles. In the CTD, the pH and redox potential of groundwater were measured by a flow-through type electrode (HORIBA–9615, 9300) every week for more than half a year in order to monitor the environmental change. The electrodes were calibrated with pH and ORP standard solutions before and after measuring the water sample, and it was confirmed that there was no measurement drift. The groundwater and suspended particles were collected every two months to estimate the variation of REEs distribution.

The boreholes have been divided into discrete sampling intervals using hydraulic packers. The groundwater and suspended materials were simultaneously collected from each packer interval and from the CTD. A schematic illustration of the sampling system is shown in Fig. 2. The groundwaters from 07MI07, 09MI20 and 10MI26 were directly filtered through a 0.2 μm membrane (Regenerated cellulose filter, Durapore, Millipore). Because there are many particle size fractions in the CTD, 0.1 μm, 1 μm, 10 μm and 100 μm membranes (Regenerated cellulose filter, ADVANTEC) were used for the sampling and its reference point 12MI33–2.

The set of constant–pressure valves on both sides of the filter holder connecting to the sampling point in the borehole was used to maintain the *in situ* groundwater pressure, and the pressure difference between the front and back of the membrane filter was maintained at less than 0.5 MPa to avoid rupturing the filter. This method was applied anaerobically to reduce degassing from groundwater and change of pH, ORP, and prevent contamination from the atmosphere (Aosai et al., 2014).

The ultrafiltration was simultaneously conducted by using two set of filter holders, one for gravimetric measurement and observing the morphologies and chemical composition of the collected particles by secondary electron microscopy with energy dispersive X–ray (SEM–EDS) analysis, and the other for sequential chemical extraction (see Section 3.2). After filtration, the residual water in the air–tight filter holder of former membrane was removed by a vacuum pump and dried in the laboratory. The concentration of the suspended particles was gravimetrically estimated based on the difference in weight of the membrane before and after the sample collection.

In order to conduct sequential chemical extractions, adequate amounts of the suspended particles should be collected from the groundwater. Consequently, a large quantity of groundwater from each borehole and the CTD was filtered for the sequential extraction analyses. Approximately 180, 373, 688, 118 and 22 L of groundwater was filtered for 14, 35, 22, 15 and 1 days for boreholes

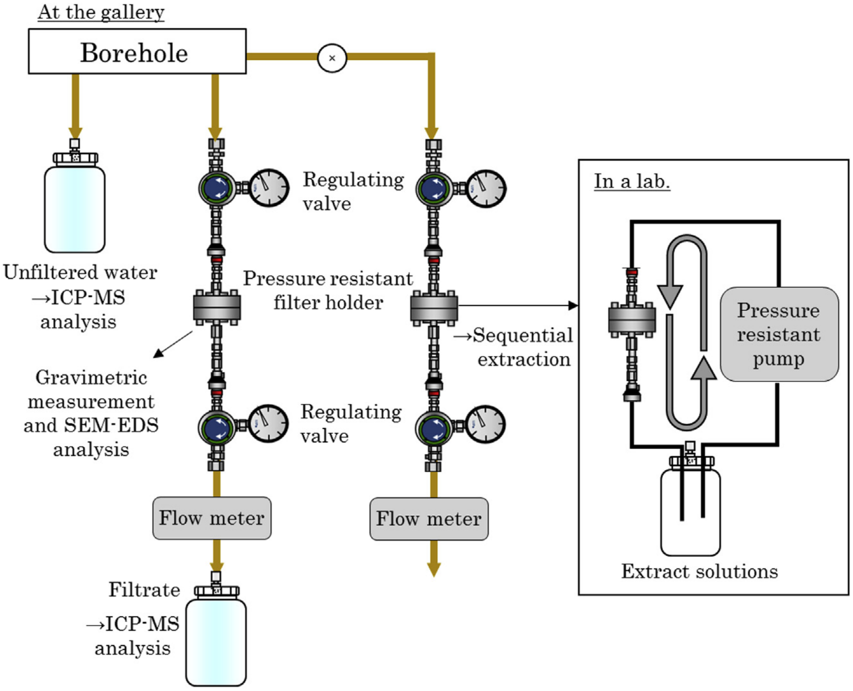


Fig. 2. Schematic of groundwater sampling system for boreholes and the CTD.

07MI07, 09MI20, 10MI26, 12MI33 and the CTD, respectively. Since the filter gradually clogged, it was not possible to accurately measure the filtration flow rate with the flow meter. Therefore, these filtered water volumes are rough estimates.

3.2. Sequential chemical extraction of REEs from suspended particles

The suspended particles were collected via long–term and large–volume filtration onto membrane filters. The groundwaters from 07MI07, 09MI20 and 10MI26 were passed through 0.2 μm membranes and those from 12MI33 and the CTD through 0.1 μm membranes. The pressure–resistant filter holder including the filter was brought to the laboratory in a sealed vessel to avoid contact with the atmosphere and was connected to the chemical solution circulation line using a pressure–resistant pump (Fig. 2). The sequential extraction procedures of Tessier et al. (1979) and Novikov et al. (2009) were applied in the present study. Fifty (50) ml of the following chemical solutions were circulated for various lengths of time in the laboratory to extract the REEs, which are sorbed onto various suspended materials. The ultra–pure water was used to prepare the chemical solutions.

1st extraction for ion–exchangeable elements: $CaCl_2$ solution [1 M], (5 h)
2nd extraction for carbonate elements: NH_4 acetate [1 M] + acetic acid pH = 4.8 (6 h)
3rd extraction for iron and manganese oxide elements: $NH_2OH \cdot HCl$ [0.04 M] + acetic acid [25%], (6 h)
4th extraction for the elements with organic matter: NaOH [2 M], (6 h)
5th extraction for residue: HNO_3 [60%], (1 day)

Although Tessier et al. (1979) used a $HF–HClO_4$ solution to digest the residue, an HNO_3 solution was used in the 5th step in this study since the filter may not be resistant to hydrofluoric acid. During the extraction, the extracting solutions continuously circulated through the membrane filter. The extractable REEs passed through the membrane but insoluble particles remained on the membrane. After each chemical solution had circulated, ultra–pure water was circulated in the system to flush the chemical solution. The ultra–pure water probably contains slightly dissolved oxygen. Therefore, if reducing materials such as organic substances, sulfides are contained in collected particles, there is a possibility that some of them are oxidized and eluted during extraction. If they contain REEs, they are counted as REEs eluted in each extraction step. The residue contains mainly primary and secondary minerals, which may hold trace metals within their crystal structure (Tessier et al., 1979). Due to the rough estimate of the filtered water volume, the results of the REE analyses in the extracted solutions were used only to infer the dominant chemical form of the suspended materials carrying the REEs.

3.3. Analyses of the colloid particles and solutions

Microscopic observations and analyses using SEM–EDS (HITACHI TD–1000, HORIBA E–Max Energy–250) were performed to identify the types of colloid particles on the filter.

The chemical composition and the REE concentration of the unfiltered groundwater, filtrate, and extracted solutions were analyzed to estimate the quantity of REEs with the colloid particles. The concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO_3^-, NO_2^-, NH_4^+, and SO_4^{2-} were measured via ion chromatography (Dionex ICS–1000). The total Fe, Si, and Al were determined via ICP (Rigaku CIROS–MarkII). The dissolved inorganic and organic carbon (DIC, DOC) was estimated via a TOC meter (Analytikjena, multi N/C 2100S). As for the REE analysis, the pH–controlled water samples were pretreated using a chelate disk (3M, 10 mm/6 mL: P/N4371). Then, the REE concentrations of the acidified sample (pH 2) were quantified via ICP–MS (Thermo Fisher Scientific Element 2). The analytical detection limits for REEs are 0.1 ng L^{-1} for groundwater, 2 μg L^{-1} for $CaCl_2$ solutions, 0.2 μg L^{-1} for NH_4 acetate–acetic acid solutions, 0.2 μg L^{-1} for $NH_2OH \cdot HCl$—acetic acid solution, 2 μg L^{-1} for NaOH solutions, and 0.02 μg L^{-1} for HNO_3 solution. The analytical value of each extracted solution was divided by the volume of filtered groundwater to estimate the concentration of REEs associated with each type of particle.

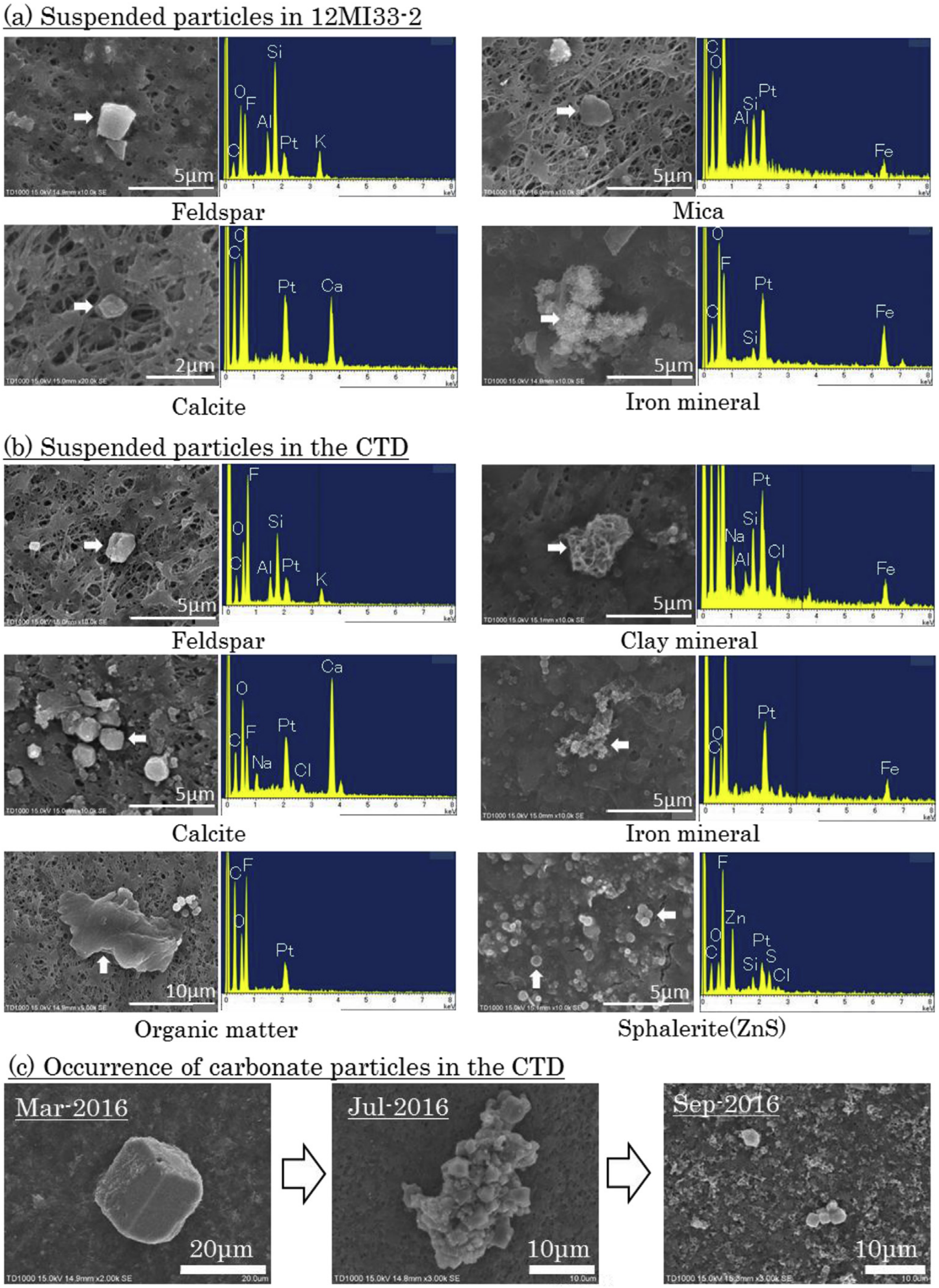
3.4. *Thermodynamic analysis*

Thermodynamic calculations using PHREEQC Ver. 3 [LLNL.dat] (Parkhurst and Appelo, 2013) were performed to evaluate theoretically the saturation index of minerals, ion strength of water and chemical speciation of the REEs. The Geochemist's Workbench [Thermo.dat] (GWB ver. 8.0.8) was used to present data in phase diagrams.

4. Results

4.1. *Suspended particles and REEs in the granitic groundwater*

The chemical compositions and ionic strength of the groundwater at depths between 200 and 500 m are shown in Table 1S (Supporting Material), and the REE concentrations in unfiltered and filtered water are presented in Table 2S. Suspended particles such as sulfides, iron minerals, carbonate minerals, silicate minerals


(a) Suspended particles in 12MI33-2

Feldspar

Mica

Calcite

Iron mineral

(b) Suspended particles in the CTD

Feldspar

Clay mineral

Calcite

Iron mineral

Organic matter

Sphalerite(ZnS)

(c) Occurrence of carbonate particles in the CTD

Mar-2016

Jul-2016

Sep-2016

Fig. 3. Observation of suspended particles. (a) Suspended particles in 12MI33–2, (b) Suspended particles in the CTD, (c) Time variation of the occurrence of carbonate particles in the CTD groundwater.

(clay minerals), and organic matter (Fig. 3) were identified in the groundwater having concentrations of 14.5, 4.1, 3.3 and 1.1 μg L^{-1} at 07MI07, 09MI20, 10MI26 and 12MI33, respectively. These types of particles are similar to those observed in previous studies at various granitic sites in the countries mentioned in the Introduction (Alexander et al., 2011; Swanton et al., 2010). Although the amount of particles in groundwater at a depth of 200 m is large, the amount of particles at a depth of 300–500 m is about the same as previous studies. The type of suspended particles at each depth was similar.

Alexander et al. (2011) reviewed the data of colloid concentration and synthetic NaCl–solution versus ionic strength in various granitic groundwater at German and Swedish research sites (Degueldre et al., 1996; Hauser et al., 2007). Colloidal particles of several tens of μg L^{-1} have been observed in those groundwater with an ionic strength around 10 mmol L^{-1} similar to that at the MIU (Table 1S), and so the suspended particle concentrations at MIU are not unique.

Previous studies (Aosai et al., 2014; Saito et al., 2013) have identified the suspended particles of sulfide, iron hydroxide, carbonates, silicate minerals including clay, and organics in the groundwater from 300 m depth (09MI20 borehole). In this study, similar kinds of suspended particles were also observed in the groundwater at other depths. Aosai et al. (2014) indicated that about 50% of the REEs present with the concentrations in the range from 0 to 25 ng L^{-1} are associated with suspended particles in the groundwater at 300 m depth. Fig. 4 illustrates the distribution of REEs to water and suspended particles in groundwater at depths 200–500 m. The quantities of REEs sorbed onto the suspended particles were calculated by deducting the concentration in the filtrate from that in the unfiltered water. The concentrations of REEs are less than 20 ng L^{-1}. Up to 60% of each REE in groundwater is associated with suspended particles. Although the distribution ratio of REEs is not clearly different depending on the depth, light REEs tend to have a high proportion associated with suspended particles. Aosai et al. (2014) suggested the preferential association of light REEs onto suspended particles with sizes of 10 kDa–0.2 μm and 0.2–0.45 μm in the groundwater at 300 m depth. This study shows the preferential association of light REEs onto suspended particles larger than 0.2 μm in the groundwater at depths 200–500 m. Although the concentration of light REEs in 12MI33 was slightly higher than those at other depths, the difference in REE concentrations depending on the depth is not clear.

To identify which suspended particles have the ability to transport the REEs, a sequential chemical extraction of the suspended particles trapped on the membrane filter was conducted. The filtered water volume and REE concentrations with each chemical form of suspended particle are shown in Table 3S and Fig. 5. The REEs are primarily detected in the extracted solution of carbonate and partially iron– and manganese–oxide, residues, whereas they are not detected in the extracted solutions for the ion–exchangeable and organic matter. The proportion of the ion–exchangeable REE and REE–organic complex is probably low in the suspended particles. Alternatively, the ion–exchangeable REEs and organic REEs may have not been detected because the detection limit of REEs for those extracts is 10 times higher than that of the carbonate and iron– and manganese–oxide extracts.

The SEM observation of the residual particles on the filter after doing the 1st–4th extraction procedures shows that silicate minerals such as feldspar, plagioclase remain on the filter. It is likely that the REEs in the residual substance were a part of the silicate minerals. Because the filtered water volume for the sequential chemical extraction is a rough estimation, quantitative consideration is difficult. The analytical data should only be used to infer the main suspended particle species bearing REEs. The suspended materials carrying the REEs are primarily carbonate particles at any depth. However, it is necessary to further confirm the REEs associated with clay particles, presumably contained in the ion–exchangeable extract.

4.2. Suspended particles and REEs in the drift closure environment

The chemical composition of the groundwater in the CTD are shown in Tables 1S and 2S In the CTD groundwater the concentrations of potassium, calcium, aluminum, sulfate and iron increased compared with the groundwater around the CTD (12MI33–2). As a result, the ionic strength and pH of the groundwater rose in the groundwater of CTD. Fig. 6 summarizes the changes of the pH and redox potential in the groundwater in the CTD. The pH gradually increased to approximately 10 after closure of the drift. The redox potential changed from oxidizing (~+300 mV) to reducing conditions (~–200 mV) within four months of closure and finally reached a value similar to the

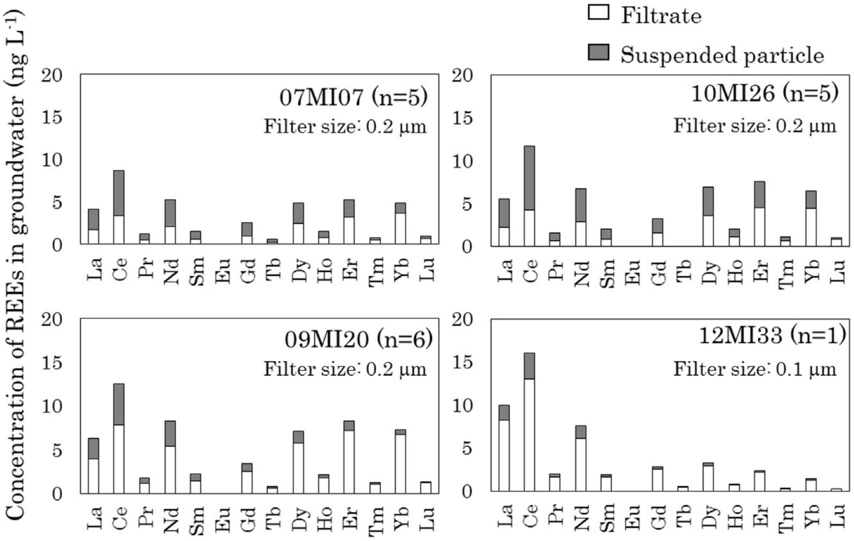


Fig. 4. Distribution of REEs to water and suspended particles in the groundwater at depths between 200 and 500 m (200 m: borehole 07MI07, 300 m: borehole 09MI20, 400 m: borehole 10MI26, and 500 m: borehole 12MI33).

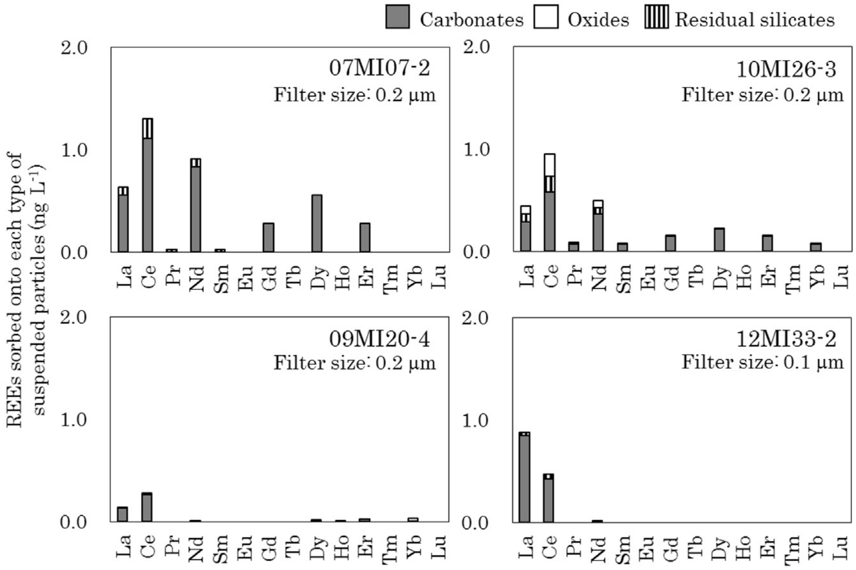


Fig. 5. REEs associated with each type of suspended particles in the groundwater at depths between 200 and 500 m.

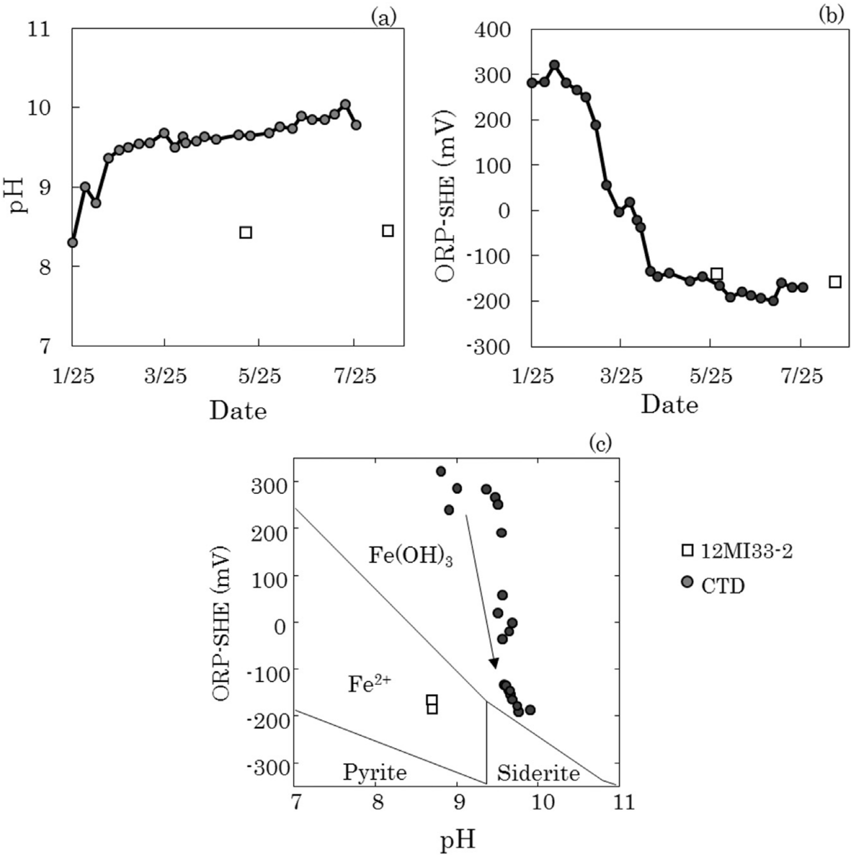


Fig. 6. The chemical change of groundwater in the CTD and 12MI33 borehole. (a) pH, (b) redox condition, (c) pH, ORP values on phase diagram of iron species (activity [Fe]:$10^{-6.084}$). The arrow in diagram shows the time variation.

groundwater in the vicinity of the test drift. This roughly corresponds to the value of the redox boundary between water–$Fe(OH)_3$ and siderite (Fig. 6c).

The results of the filtration showed that suspended particles such as silicate minerals including clay, biofilms, calcite, iron minerals and sulfur are present in the groundwater around the CTD (Fig. 3, Table 1). Conversely, materials identified in the groundwater of CTD were primarily suspended particles larger than 10 µm such as biofilms, silicate minerals and particles of sphalerite (ZnS), iron minerals, calcite, and amorphous silica. Approximately 800 times

Table 1
Observed suspended particles in 12MI33–2 and the CTD (Apr. 2016).

		Observed particles	
		Borehole (12MI33-2)	Closure test drift (CTD)
Conc. of suspended particles (particle size)		1.1 μg L^{-1} (>0.1 μm)	844 μg L^{-1} (>10 μm) 44 μg L^{-1} (0.1–10 μm)
Suspended particle size	>100 μm	Feldspar, plagioclases, clay minerals	Biofilms
	10 - 100 μm	Feldspar, plagioclases, amorphous silica, biofilms, calcite, iron-minerals	Feldspar, plagioclases, biofilms, calcite, ZnS
	1 - 10 μm	Feldspar, plagioclases, mica, amorphous silica, biofilms, clay, calcite, iron-minerals	Feldspar, plagioclases, amorphous silica, biofilms, clay, calcite, iron-minerals, ZnS
	0.1–1 μm	Feldspar, plagioclases, amorphous silica, biofilms, clay, calcite, iron-minerals, sulfur	Calcite, amorphous silica, ZnS

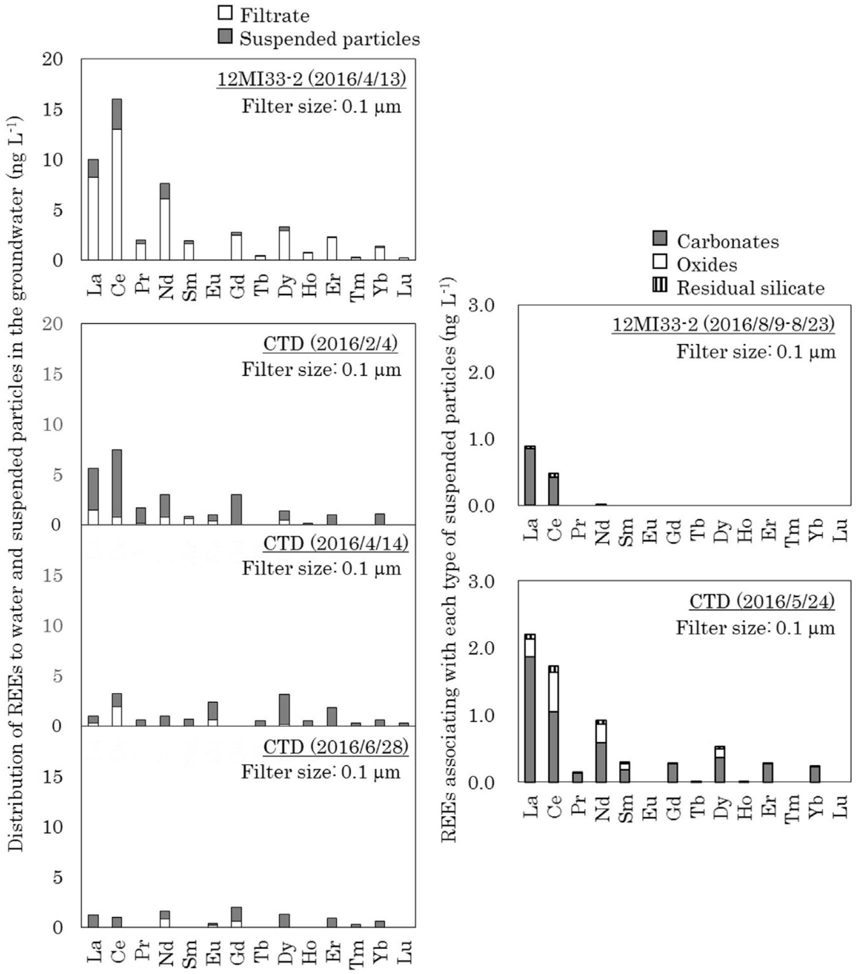


Fig. 7. Occurrence of REEs in the groundwater and the suspended particles in the borehole 12MI33–2 and the CTD.

more suspended particles formed in the CTD groundwater than in the surrounding natural groundwater. The difference between the groundwater sampled from 12MI33–2 and the groundwater in the CTD, is that much of the suspended organic matter and zinc particles were found in the closed tunnel, and particles of iron minerals and amorphous silica larger than 10 μm were not observed.

Fig. 7 shows the REE concentrations of these groundwaters and the results of the sequential extraction analyses of the suspended materials trapped on the membrane filter. The decrease in the dissolved REEs during the several months following closure of the CTD is remarkable, and the quantity of suspended particles loaded with light REEs also declined to approximately half of those in the groundwater of 12MI33–2.

The result of the sequential chemical extraction of the REEs sorbed onto suspended matter in the CTD suggests that the REEs occur primarily with carbonate and partially with oxide particles as well as suspended particles in the groundwater at 200–500 m depths (Fig. 5). Despite the large amount of organic particles found in the CTD, REEs were not be detected in the extracted solution of organics. Therefore, it is inferred that REEs do not associate with organics under the chemical conditions in the CTD (a cementitious alkaline groundwater environment).

5. Discussion

5.1. Interaction between REEs and suspended particles in the granitic groundwater

Ryan and Elimelech (1996) suggested that colloids in groundwater originate because of two processes: (1) the mobilization of existing colloid–sized minerals in the aquifer sediments (as an analogy to a repository host rock) and (2) *in situ* precipitation of supersaturated mineral phases. The observed suspended particles of silicate minerals such as clay and the particles of non–silicate secondary minerals such as sulfide, iron, and carbonate minerals likely originate from sources (1) and (2), respectively.

The REEs in the suspended materials are primarily associated with the carbonate, and partially iron– and manganese–oxides, silicate mineral particles (Fig. 5). Aosai et al. (2014) and Munemoto et al. (2014) suggested that REEs are adsorbed onto carbonate and iron particles based on their concentrations in filtered and unfiltered groundwater samples at 300 m depth. The results of this study are consistent with the previous research. Although further confirmation is required for adsorption of REEs onto clay particles (probably in ion–exchangeable extract solution), the studies using the sequential extraction method allowed us to directly confirm the suspended particles with sorbed REEs. The analogue study of colloids regarding the geological disposal of radioactive waste focuses on two types of radionuclide–bearing colloids; intrinsic colloids consist predominantly of radionuclide–containing phases and carrier colloids consist of non–radioactive mineral phases (e.g. metal hydrous oxides, and clays) or organic macromolecules to which radionuclides may be bound (Swanton et al., 2010). Therefore, REEs originally contained in the suspended silicate crystal particles are not targeted in this study.

The REEs are primarily associated with the carbonate particles in groundwater. It is difficult to quantify the relative content of carbonate particles by comparing the concentration of inorganic carbon in the filtrate with those in the unfiltered water, due to large variations and thus uncertainty in analysis values. In this area, secondary calcite precipitate is clearly observed on fracture surfaces in granite (Iwatsuki et al., 2002). Carbonate particles in groundwater are most likely derived from *in situ* precipitation of supersaturated carbonate minerals. The saturation index of calcite in the groundwater was estimated using PHREEQC (Table 1S) to examine and assess the interaction between the groundwater, calcite, and carbonate particles carrying REEs (Fig. 8). Groundwaters at depths of 200–500 m are nearly in equilibrium with calcite. The REE patterns of the fracture–filling calcite in this area are enriched in light REE (LREE) (Munemoto et al., 2015). The extracted carbonate solutions are also enriched in LREE (Fig. 5). Fig. 8a shows the relationship between the concentrations of Lanthanum (La) associated with suspended particles and the saturation indices of calcite. Fig. 8b presents the theoretical concentration of calcite related to the equilibrium reaction with calcium and bicarbonate ions in the groundwater as estimated by PHREEQC. The groundwater at depths of 200–500 m is in equilibrium with a slightly supersaturated condition for calcite. The concentration of La associated with suspended particles is highest when the calcite saturation index is zero and decreases as the calcite saturation index and theoretical calcite concentration increase. This suggests that the carbonate particles with associated REEs precipitate in the groundwater under a supersaturated condition for calcite. The calcite–groundwater reaction is generally in an equilibrium state in deep groundwater. There would usually be some quantity of

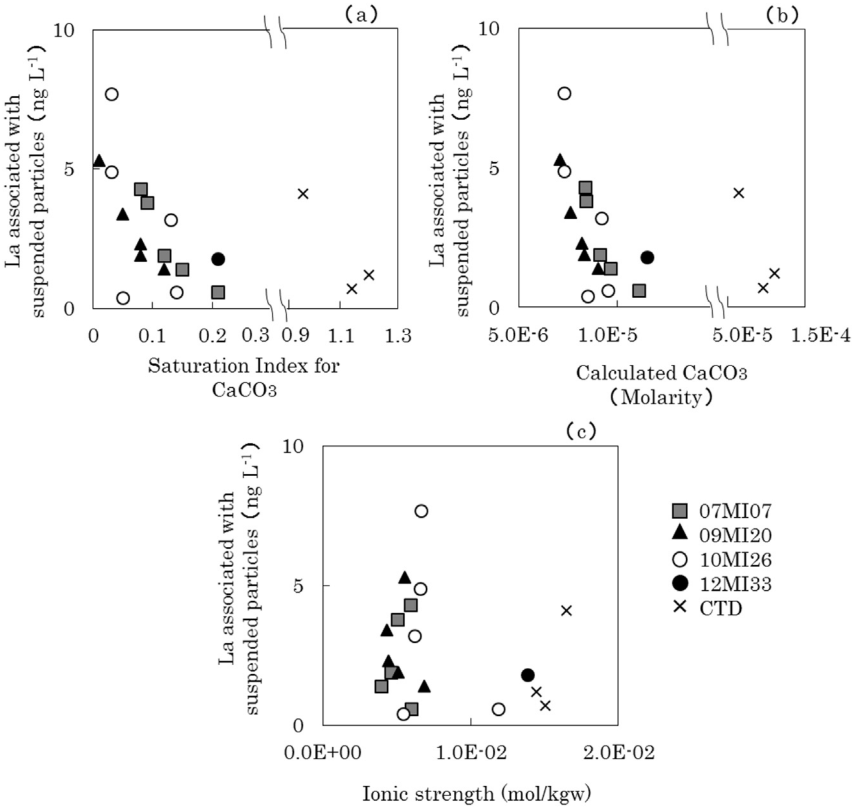


Fig. 8. Concentration of Lanthanum (La) associated with suspended particles vs. (a) saturation indices of calcite, (b) theoretical concentration of calcite, (c) ionic strength of groundwater.

carbonate particle–borne REEs in deep groundwater.

The colloid populations in groundwater with low organic concentrations are controlled by the ionic strength of the water, which controls the rate of particle aggregation (Swanton et al., 2010). As the ionic strength in the water is increased, a point is reached at which the net energy barrier is reduced to zero. At the critical coagulation concentration point, the system should coagulate rapidly with all colloid–colloid contact resulting in aggregation (Alexander et al., 2011). The relationship between the concentrations of La associated with suspended particles and the ionic strength of groundwater is not clear in the observed groundwater (Fig. 8c). The precipitation of carbonate particles due to aggregation in the groundwater is unknown.

5.2. *Behavior of REEs in the drift closure environment*

Portlandite alteration and calcite precipitation are observed on the surface of the shotcrete on the drift wall. A pH change can be caused by the following reactions in cement materials.

$$\mathrm{Ca\,(OH)_2(S) + 2H^+ \rightarrow Ca^{2+} + 2H_2O} \tag{1}$$

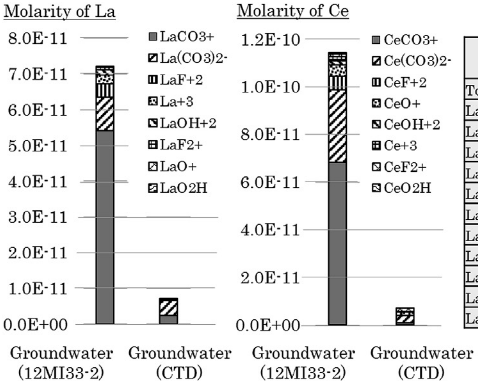
$$\mathrm{Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)} \tag{2}$$

The redox condition of the groundwater immediately after the drift closure was oxidizing due to contact with air. Then, the nitrate, nitrite, and sulfate ions decreased in the order shown after the drift closure (Table 1S). Because biofilms had formed on the wetted base and the drift wall in the drift pre–closure period, microbial activities oxidized organics on biofilms by using nitrate and sulfate ions and were likely responsible for the change to reducing condition of the groundwater. Metabolism of organics by fermenting microbes and microbial reducing processes such as bacterial sulfate reduction were identified in the granitic groundwater around the MIU facility (Suzuki et al., 2014;.Ino et al., 2016).

The decrease in the REE concentrations in CTD groundwater can be regarded as a phenomenon related to the mass transfer in the cementitious environment. The molarity of the dissolved chemical speciation of REEs was calculated using PHREEQC to determine the reason for the decrease in the dissolved REEs. As an example, Fig. 9 illustrates the chemical speciation of the dissolved La and Cerium (Ce) in the groundwater in and around the CTD. The concentration of the La– and Ce–carbonate complexes primarily decreased in the CTD. As described above, calcite formed during the alteration of the shotcrete on the drift wall. The La– and Ce–carbonate complexes were likely removed by adsorption and/or co–precipitation within the calcite. In addition, previous studies (e.g. Wieland and Loon, 2002; Tits et al., 2004; Felipe–Sotelo et al., 2012) show the uptake of lanthanides under alkaline conditions into the CSH phases (calcium aluminates and calcium silicate hydrates) by batch sorption experiments. Dissolved REEs are also expected to be associated with the CSH phase in the cement matrix. The adsorption of REEs onto biofilms is possible; however, this cannot be directly interpreted from the thermodynamic analysis.

Various suspended particles, such as biofilms and particles of sphalerite, iron–minerals, calcite, and amorphous silica, were observed in the CTD groundwater. Taking into account the result of the thermodynamic calculations (Fig. 6) and SEM–EDS observations, the iron particles in the groundwater should be iron hydroxides or siderite. Because there are few minerals containing zinc in the granite, the zinc particles may have originated from the galvanized steel access stairway fixed in the drift, a clear indication that a new, but clearly artificial suspended particle had formed from materials brought into the gallery.

Besides the Zn particles, cementitious particles and suspensions of organic matter are presumed to have been derived from shotcrete and biofilms on the drift wall, respectively. The quantity of suspended materials in the CTD groundwater increased to approximately 800 times than that in the natural groundwater, primarily due to biofilm suspensions (Table 1). However, REEs could not be detected in the sequential extract solution of organic particles in the CTD (Fig. 7, Table 3S). There may be little REE adsorption onto biofilm suspensions, or REEs may have preferentially adsorbed to calcite particles or shotcrete rather than organic matter under the cementitious conditions in the CTD. Because of the many organic suspensions present in the water, it is difficult to evaluate by the gravimetric measurement and SEM–EDS analysis whether cement–derived suspended particles increased after closing the tunnel. The light REEs associated with the suspended particles in the CTD groundwater immediately after the drift closure were more abundant than those in the groundwater sampled from 12MI33–2 (Fig. 7). It is possible that these REEs temporarily eluted from the shotcrete or that the dissolved REEs in the groundwater were adsorbed onto the cement–derived suspended particles. The saturation indices of calcite and portlandite for groundwater in the CTD increased with increasing alkalinity of the groundwater (Table 1S). The calcite is supersaturated in the CTD groundwater (Fig. 8a). Although the relationship between the concentrations of La associated with suspended particles and the ionic strength of groundwater is not clear in the CTD (Fig. 8c), occurrence of calcite particles in the CTD changes with time from large suspended particles to aggregates of relatively small particles (Fig. 3). The high calcium concentrations in a cementitious environment are expected to de–stabilise colloids leading to particle



Species	Molality		Species	Molality	
	12MI33-2	CTD		12MI33-2	CTD
Total	7.20E-11	7.20E-12	Total	1.14E-10	7.14E-12
LaCO3+	5.43E-11	2.51E-12	CeCO3+	6.81E-11	7.69E-13
La(CO3)2-	9.29E-12	4.20E-12	Ce(CO3)2-	3.05E-11	3.36E-12
LaF+2	3.77E-12	1.80E-14	CeF+2	5.72E-12	6.65E-15
La+3	2.39E-12	1.15E-14	CeO+	4.96E-12	1.44E-12
LaOH+2	1.56E-12	1.18E-13	CeOH+2	1.69E-12	3.13E-14
LaF2+	5.36E-13	2.53E-15	Ce+3	1.57E-12	1.84E-15
LaO+	1.38E-13	1.64E-13	CeF2+	1.28E-12	1.48E-15
LaO2H	9.54E-15	1.80E-13	CeO2H	3.33E-13	1.53E-12
LaCl+2	3.48E-14	1.74E-16	CeHCO3+2	2.29E-14	2.78E-15
LaF3	1.36E-14	6.42E-17	CeCl+2	2.28E-14	6.46E-17
LaHCO3+2	4.12E-14	1.21E-16	CeF4-	1.21E-15	2.78E-17

Fig. 9. Theoretical estimation of chemical speciation for the dissolved La and Ce in the groundwater at 12MI33–2 and CTD in April 2016.

aggregation and deposition (Degueldre, 1994). Precipitation of calcite particles with sorbed REEs is probably one of the reasons for decrease in suspended REE concentrations in CTD.

6. Concluding remarks

The occurrence of the REEs in deep granitic groundwater can be divided into dissolved REEs and REEs associated with suspended particles. Various types of suspended particles, e.g., silicate minerals, iron hydroxides, sulfur, calcites, and organic matter have been identified in the groundwater. Approximately 10%–60% of each REE in the groundwater is associated with suspended particles. Even though various suspended particles were recognized, the REEs were primarily sorbed onto carbonate particles. The quantity of REEs transportable by carbonate particles depends on the saturation index of calcite on the fracture surfaces in the granite, which is the possible source of the carbonate particles.

Observations such as presence/absence of REEs in and around the closed drift suggest that dissolved and carbonate particle–borne REEs have been removed from the groundwater under alkaline and calcite–saturated chemical conditions. The REEs (primarily light REEs) – carbonate complexes in the groundwater are possibly removed by adsorption and/or co–precipitation within the calcite. The cementitious environment in the closed drift leads to calcite particle aggregation and deposition.

The post–closure chemical environment in a disposal facility would evolve depending on hydrogeological structures in a host rock, groundwater flow and chemistry, geochemical buffer capacity and facility design (gallery layout, grouting, types and amount of buried material), etc. The usage of cement–based materials during the construction and closure of underground facilities could produce an environmental condition in which analogue elements hardly move depending on the facility design. The knowledge concerning the environment formed by the material used to close the tunnel and the behavior of the REE can be useful in the design of facilities to reduce the mobility of the elements adsorbed by the suspended particles and enhance safety.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2017.04.016.

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Table 1S. Chemical composition of the groundwaters at depths between 200–500 m and the isolated groundwater in the CTD.

Date	Depth (m)	Sampling location*	pH	Na^+	K^+	Ca^{2+}	Mg^{2+}	DIC	DOC	SO_4^{2-}	HS -	F^-	Cl^-	NO_3^-	NO_2^-	NH_4^+	Si	Al	T-Fe	Fe^{2+}	Saturation index		Ionic strength (mol kgw -1)
			—	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	Calcite	Portlandite	
2011/12/6	200	07MI07-1	8.7	73	0.3	8.3	<0.1	17.0	<0.5	16.0	0.70	8.2	47	<0.05	<0.05	0.1	6.8	0.01	<0.005	<0.2	0.15	-	3.95E-03
		07MI07-2	8.6	84	0.4	12.0	<0.1	14.0	<0.5	13.0	0.70	8.5	79	<0.05	<0.05	0.1	6.7	<0.01	<0.005	<0.2	0.12	-	4.63E-03
		07MI07-3	8.6	91	0.4	13.0	<0.1	12.0	<0.5	11.0	0.70	8.5	103	<0.05	<0.05	0.1	6.6	<0.01	<0.005	<0.2	0.09	-	5.04E-03
		07MI07-4	8.6	105	0.5	17.0	<0.1	9.3	<0.5	7.5	0.80	8.5	145	<0.05	<0.05	0.2	6.5	0.01	<0.005	<0.2	0.08	-	5.95E-03
		07MI07-5	8.7	105	0.5	18.0	<0.1	9.4	<0.5	7.4	0.80	8.5	145	<0.05	<0.05	0.2	6.4	0.01	<0.005	<0.2	0.21	-	6.01E-03
2011/7/26	300	09MI20-1	8.6	81	0.4	9.3	0.1	15.0	0.6	14.0	0.40	8.5	67	<0.05	<0.05	0.1	7.1	<0.01	0.017	<0.2	0.05	-	4.33E-03
		09MI20-2	8.6	79	0.4	8.8	0.1	16.0	0.6	15.0	0.60	8.5	60	<0.05	<0.05	0.1	7.0	<0.01	<0.005	<0.2	0.05	-	4.22E-03
		09MI20-3	8.6	81	0.4	10.0	0.3	15.0	0.7	14.0	0.30	8.9	70	<0.05	<0.05	0.1	7.0	<0.01	0.009	<0.2	0.08	-	4.42E-03
		09MI20-4	8.4	100	0.7	14.0	0.8	15.0	0.8	11.0	0.10	9.0	110	<0.05	<0.05	0.1	7.0	<0.01	0.041	<0.2	0.01	-	5.56E-03
		09MI20-5	8.5	91	0.6	13.0	0.6	15.0	0.8	14.0	0.20	9.1	91	<0.05	<0.05	0.1	7.1	<0.01	0.016	<0.2	0.08	-	5.10E-03
		09MI20-6	8.4	113	0.7	23.0	0.9	12.0	0.7	9.5	0.10	8.5	161	<0.05	<0.05	0.2	7.0	<0.01	0.031	<0.2	0.12	-	6.84E-03
2011/11/22	400	10MI26-1	8.4	118	0.8	17.0	0.7	13.0	<0.5	6.3	0.20	8.3	158	<0.05	<0.05	0.1	7.1	0.01	0.011	<0.2	0.03	-	6.58E-03
		10MI26-3	8.4	119	0.8	17.0	0.8	13.0	<0.5	6.7	0.20	8.5	159	<0.05	<0.05	0.1	7.1	<0.01	<0.005	<0.2	0.03	-	6.64E-03
		10MI26-4	8.5	98	0.6	14.0	0.6	13.0	<0.5	10.0	0.30	8.8	112	<0.05	<0.05	0.1	7.0	<0.01	<0.005	<0.2	0.05	-	5.43E-03
		10MI26-5	8.5	105	0.6	20.0	0.4	11.0	<0.5	10.0	0.40	8.3	143	<0.05	<0.05	0.1	6.9	<0.01	<0.005	<0.2	0.13	-	6.20E-03
		10MI26-6	8.3	158	0.9	64.0	0.6	6.4	<0.5	6.1	0.30	6.2	331	<0.05	<0.05	0.2	6.8	<0.01	0.018	<0.2	0.14	-	1.19E-02
2016/5/26	500	12MI33-2	8.5	181	0.8	79.0	0.12	3.7	<0.5	<0.1	<0.1	6.3	402	<0.05	<0.05	0.3	6.2	0.01	0.007	<0.2	0.21	-	1.39E-02
2016/1/25	500	CTD	8.3	194	3.0	108.0	0.16	5.0	0.8	0.8	<0.1	6.2	475	0.50	<0.05	0.1	6.5	0.11	0.038	<0.2	0.27	-8.51	1.67E-02
2016/2/2			9.0	193	6.0	106.0	0.16	5.1	1.3	0.9	<0.1	6.3	473	0.52	<0.05	0.2	6.4	0.11	0.038	<0.2	0.97	-6.92	1.65E-02
2016/2/17			9.4	195	4.3	104.0	0.16	5.1	<0.5	0.9	<0.1	6.1	464	<0.05	0.1	0.1	7.0	0.25	0.079	<0.2	1.18	-6.34	1.62E-02
2016/3/8			9.6	196	5.5	97.0	0.16	4.0	<0.5	0.9	<0.1	6.1	456	<0.05	<0.05	0.2	7.2	0.25	0.068	<0.2	1.17	-5.97	1.58E-02
2016/3/24			9.7	196	6.0	94.0	0.15	4.1	0.6	1.0	<0.1	6.1	452	<0.05	<0.05	0.2	7.3	0.31	0.055	<0.2	1.22	-5.78	1.56E-02
2016/4/14			9.6	193	6.3	88.0	0.14	4.0	<0.5	0.8	<0.1	6.1	438	<0.05	<0.05	0.2	7.3	0.22	0.049	<0.2	1.14	-6.00	1.51E-02
2016/5/31			9.7	189	6.2	83.0	0.13	4.2	<0.5	0.3	0.20	6.3	421	<0.05	<0.05	0.2	7.1	0.14	0.046	<0.2	1.20	-5.83	1.45E-02
2016/6/28			9.6	189	6.2	81.0	0.12	3.0	<0.5	0.7	<0.1	6.2	416	<0.05	<0.05	0.3	7.2	0.20	0.015	<0.2	1.00	-6.03	1.43E-02
2016/7/19			9.8	188	6.5	81.0	0.11	2.8	<0.5	0.6	<0.1	6.1	414	<0.05	<0.05	0.3	7.1	0.20	0.011	<0.2	1.07	-5.63	1.43E-02
2016/8/23			9.7	187	5.7	81.0	0.11	4.1	<0.5	0.6	<0.1	6.2	410	<0.05	<0.05	0.3	7.1	0.16	0.007	<0.2	1.19	-5.84	1.42E-02
2016/9/6			9.9	186	5.7	82.0	0.11	4.5	<0.5	0.5	<0.1	6.1	409	<0.05	<0.05	0.3	7.1	0.16	0.006	<0.2	1.32	-5.44	1.42E-02

* The sampling location in each borehole is numbered in turn from the bottom of the borehole.

Table 2S. REE concentrations in the groundwaters at depths between 200–500 m and the isolated groundwater in the CTD.

Date	sampling location	Preparation	La [ng L^{-1}]	Ce [ng L^{-1}]	Pr [ng L^{-1}]	Nd [ng L^{-1}]	Sm [ng L^{-1}]	Eu [ng L^{-1}]	Gd [ng L^{-1}]	Tb [ng L^{-1}]	Dy [ng L^{-1}]	Ho [ng L^{-1}]	Er [ng L^{-1}]	Tm [ng L^{-1}]	Yb [ng L^{-1}]	Lu [ng L^{-1}]
2011/12/6	07MI07-1	Unfiltered water	2.6	5.4	0.8	3.6	1.1	<0.1	1.8	0.5	4.2	1.3	5.2	0.8	5.5	1.1
		0.2 µm filtrate	1.2	2.5	0.3	1.5	0.5	<0.1	1.0	0.2	2.5	0.9	3.9	0.6	4.7	0.9
	07MI07-2	Unfiltered water	5.3	11	1.6	6.7	1.9	0.2	3.4	0.8	6.4	2.0	7.0	1.1	6.5	1.2
		0.2 µm filtrate	3.4	6.2	0.9	3.6	1.1	<0.1	1.6	0.3	3.6	1.1	4.3	0.6	4.4	0.8
	07MI07-3	Unfiltered water	5.6	12	1.7	7.2	2.2	0.1	3.2	0.8	6.1	1.8	6.1	0.9	5.4	1.0
		0.2 µm filtrate	1.8	3.2	0.5	2.2	0.6	<0.1	0.9	0.2	2.3	0.7	3.1	0.5	3.6	0.7
	07MI07-4	Unfiltered water	5.3	11	1.5	6.4	2.0	0.1	3.0	0.6	5.2	1.5	5.0	0.7	4.1	0.8
		0.2 µm filtrate	1.0	2.1	0.3	1.2	0.3	<0.1	0.7	0.2	1.5	0.5	2.0	0.3	2.3	0.5
	07MI07-5	Unfiltered water	1.9	4.2	0.6	2.4	0.7	<0.1	1.3	0.3	2.5	0.9	3.0	0.5	2.9	0.6
		0.2 µm filtrate	1.3	3.2	0.4	1.9	0.6	<0.1	0.9	0.2	2.3	0.8	2.9	0.5	3.4	0.7
2011/7/26	09MI20-1	Unfiltered water	5.2	11.0	1.5	6.5	1.8	<0.1	2.7	0.8	5.5	1.8	6.6	1.1	6.2	1.2
		0.2 µm filtrate	1.8	4.2	0.6	3.0	0.9	<0.1	1.7	0.4	4.3	1.4	5.7	0.7	5.5	1.0
	09MI20-2	Unfiltered water	1.4	3.1	0.5	2.2	0.7	<0.1	1.5	0.3	4.1	1.2	5.0	0.7	4.9	0.9
		0.2 µm filtrate	1.6	3.5	0.5	2.4	0.8	<0.1	1.5	0.4	3.8	1.1	5.1	0.6	5.2	0.9
	09MI20-3	Unfiltered water	9.3	20	2.8	13	3.5	0.2	4.7	1.0	8.5	2.4	8.7	1.2	7.7	1.4
		0.2 µm filtrate	7.0	15	2.2	10	2.6	0.1	3.7	0.9	7.2	2.1	8.0	1.2	7.3	1.3
	09MI20-4	Unfiltered water	12	23	3.4	16	4.4	0.3	6.6	1.5	14	4.3	16	2.3	13	2.3
		0.2 µm filtrate	6.7	12	1.9	8.2	2.1	0.2	3.8	0.8	8.4	2.7	11	1.7	10	1.8
	09MI20-5	Unfiltered water	5.8	11	1.6	7.5	1.9	0.1	3.2	0.7	6.7	2.0	7.9	1.2	7.3	1.3
		0.2 µm filtrate	3.9	7.8	1.0	5.7	1.6	<0.1	2.8	0.6	6.9	2.2	8.3	1.2	7.5	1.4
	09MI20-6	Unfiltered water	3.9	7.3	0.9	4.6	1.3	<0.1	1.8	0.4	4.1	1.4	5.3	0.7	4.7	0.9
		0.2 µm filtrate	2.5	4.7	0.5	3.3	0.7	<0.1	1.5	0.3	3.9	1.2	5.2	0.7	4.9	0.9
2011/11/22	10MI26-1	Unfiltered water	6.6	15	2.1	9.0	2.9	0.2	4.6	1.1	9.4	2.7	9.6	1.4	7.7	1.2
		0.2 µm filtrate	1.7	3.6	0.5	2.4	0.7	<0.1	1.5	0.3	3.8	1.3	4.7	0.7	4.4	0.8
	10MI26-3	Unfiltered water	10	21	2.8	11	3.3	0.3	4.6	1.1	9.3	2.6	9.3	1.3	7.8	1.2
		0.2 µm filtrate	2.3	4.7	0.7	3.2	1.0	<0.1	2.2	0.5	5.3	1.6	6.4	0.9	5.5	0.9
	10MI26-4	Unfiltered water	5.5	11	1.5	6.5	1.8	0.1	3.5	0.9	8.2	2.5	9.8	1.5	8.9	1.4
		0.2 µm filtrate	5.1	9.8	1.5	6.6	1.7	<0.1	2.8	0.6	5.9	1.8	6.8	1.1	6.9	1.3
	10MI26-5	Unfiltered water	4.3	8.6	1.3	5.6	1.6	0.1	2.8	0.7	5.9	1.7	6.7	0.9	5.4	1.0
		0.2 µm filtrate	1.1	1.6	0.3	1.2	0.3	<0.1	0.7	0.2	1.8	0.7	3.3	0.5	3.6	0.7
	10MI26-6	Unfiltered water	1.4	2.9	0.3	1.5	0.5	<0.1	0.7	0.2	1.8	0.5	2.1	0.3	2.2	0.4
		0.2 µm filtrate	0.8	1.3	0.2	0.8	0.2	<0.1	0.5	<0.1	1.0	0.3	1.5	0.2	1.8	0.4
2016/4/13	12MI33-2	Unfiltered water	10.0	16.0	2.0	7.6	1.9	<0.1	2.8	0.5	3.3	0.8	2.3	0.3	1.4	0.2
		0.1 µm filtrate	8.2	13.0	1.6	6.1	1.6	<0.1	2.5	0.4	2.9	0.7	2.2	0.2	1.2	0.2
2016/2/4	CTD	Unfiltered water	6	7.5	1.7	3.0	0.9	1.0	3.0	<0.1	1.4	0.2	1.0	<0.1	1.1	<0.1
		0.1 µm filtrate	2	0.8	0.2	0.8	0.6	0.4	<0.1	<0.1	0.5	<0.1	<0.1	<0.1	<0.1	<0.1
2016/4/14		Unfiltered water	1.0	3.2	0.6	1.0	0.7	2.4	<0.1	0.5	3.1	0.5	1.8	0.3	0.6	0.3
		0.1 µm filtrate	0.3	1.9	0.0	0.0	0.0	0.6	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
2016/6/28		Unfiltered water	1.2	1.0	< 0.1	1.6	< 0.1	0.4	2.0	< 0.1	1.3	< 0.1	0.9	0.3	0.6	< 0.1
		0.1 µm filtrate	< 0.1	< 0.1	< 0.1	0.8	< 0.1	0.2	0.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

Table 3S. Rough estimation of the REE concentrations associated with suspended particles in the groundwater

Sampling point	Date	Filtered water	Chemical form of REEs	La [ng L^{-1}]	Ce [ng L^{-1}]	Pr [ng L^{-1}]	Nd [ng L^{-1}]	Sm [ng L^{-1}]	Eu [ng L^{-1}]	Gd [ng L^{-1}]	Tb [ng L^{-1}]	Dy [ng L^{-1}]	Ho [ng L^{-1}]	Er [ng L^{-1}]	Tm [ng L^{-1}]	Yb [ng L^{-1}]	Lu [ng L^{-1}]
07MI07-2	2013/9/3 ~9/17	180	Ion exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Carbonates	0.56	1.11	n.d.	0.83	n.d.	n.d.	0.28	n.d.	0.56	n.d.	0.28	n.d.	n.d.	n.d.
			Oxides	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Organics	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Residual silicate mineral	0.08	0.19	0.02	0.08	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
09MI20-4	2013/7/23 ~8/27	373	Ion exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Carbonates	0.13	0.27	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Oxides	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Organics	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Residual silicate mineral	0.01	0.01	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.02	0.01	0.03	n.d.	0.03	n.d.
10MI26-3	2013/6/27 ~7/18	688	Ion exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Carbonates	0.29	0.58	0.07	0.36	0.07	n.d.	0.15	n.d.	0.22	n.d.	0.15	n.d.	0.07	n.d.
			Oxides	0.07	0.22	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Organics	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Residual silicate mineral	0.08	0.15	0.01	0.06	0.01	n.d.	0.01	n.d.	0.01	n.d.	0.00	n.d.	0.01	n.d.
12MI33-2	2016/8/9 ~8/23	118	Ion exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Carbonates	0.85	0.42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Oxides	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Organics	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Residual silicate mineral	0.03	0.05	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CTD	2016/5/24	22	Ion exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Carbonates	1.86	1.05	0.14	0.59	0.18	n.d.	0.27	n.d.	0.36	n.d.	0.27	n.d.	0.23	n.d.
			Oxides	0.27	0.59	n.d.	0.27	0.09	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.
			Organics	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			Residual silicate mineral	0.06	0.09	0.02	0.06	0.02	n.d.	0.01	0.00	0.03	0.00	0.01	n.d.	0.01	n.d.

n.d.: not detect. The size of filters used at each sampling point is same as in Table 2S.