Title	Size and composition analyses of colloids in deep granitic groundwater using microfiltration/ultrafiltration while maintaining in situ hydrochemical conditions
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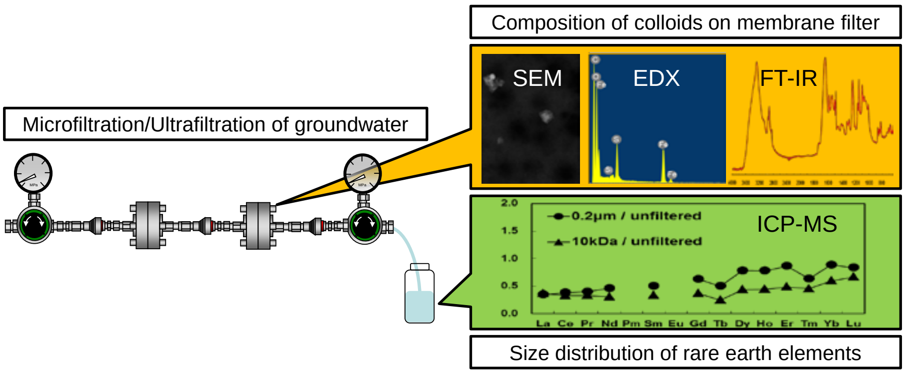
Highlights

- Filtration technique while maintaining hydrochemical conditions was developed.
- Applicability of the filtration technique for analyzing colloids was demonstrated.
- Complex formation of colloids with rare earth elements was suggested.



Graphical abstract

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Size and composition analyses of colloids in deep granitic groundwater using microfiltration/ultrafiltration while maintaining in situ hydrochemical conditions

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Abstract

In studies of colloids in deep groundwater, a serious problem exists because the properties of the colloids are influenced by changes in the chemistry of groundwater upon exposure to the atmosphere and pressure release during sampling. To collect and analyze colloids in deep groundwater without significantly changing the groundwater chemistry, a microfiltration/ultrafiltration technique, while maintaining in situ hydrochemical conditions (mainly hydraulic pressure and anaerobic condition), was developed. The size distributions and compositions of colloids in granitic groundwater obtained at a depth of 300 m at the Mizunami Underground Research Laboratory (MIU) in Japan were studied using the microfiltration/ultrafiltration technique. The shapes and compositions of the fractionated colloids collected on the membrane filter were determined by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and attenuated total reflection infrared spectroscopy. Additionally, partitioning of rare earth elements (REEs) based on colloid size was compared with REE concentrations in the filtered and unfiltered groundwater samples using inductively coupled plasma mass spectrometry. Different types of colloids consisting of inorganic and organic substances were observed and complex formation between the colloids and REEs was suggested. Furthermore, characteristic partitioning of REEs depending on colloids size was observed in complex natural environments without chemical disturbance. The current findings are useful for understanding migration of radionuclides.

Keywords

Ultrafiltration, Microfiltration, Groundwater, Colloids, Rare earth elements

1. Introduction

Understanding the behavior of elements in underground environments is important for geological disposal of high-level radioactive waste (HLW), carbon dioxide capture and storage, and groundwater pollution. In particular, the migration of radionuclides is of great concern in the geological disposal of HLW. The behavior of elements in underground environments is mainly controlled by groundwater flow, precipitation, diffusion, and interaction with rocks (e.g., adsorption and filtration). Additionally, it has been clearly shown that the migration velocity of elements either increases or decreases in the presence of colloids (particles and macromolecules in the size range from 1 to 1000 nm) [1–4]. Therefore, studying the physicochemical properties (e.g., concentration, size, shape, and chemical composition) of colloids is important for understanding the behavior of elements in underground environments.

Colloids in deep groundwater have been studied in several papers. Degueldre et al. [5] discussed the properties of colloids from various geological formations, ranging from crystalline to sedimentary, from organic-rich to organic-poor systems, and from subsurface to very deep groundwater. The authors summarized the influence of geochemical conditions, such as pH, redox potential, and concentration of primary ions, on colloid properties. Geckeis et al. [6] reported the size distribution of smectitic colloids and the interaction between humic colloids in groundwater and trace metal ions, such as U, Th, and rare earth elements (REEs), using flow-field flow fractionation (Fl-FFF) combined with online inductively coupled plasma mass spectrometry (ICP–MS). However, there are difficulties in collecting and analyzing colloids in terms of their size, composition, and interaction with trace elements in groundwater because of the low concentrations of colloids in groundwater [7, 8]. To address this issue, enrichment and fractionation techniques based on colloid size have been developed. Saito et al. [9] reported a colloid enrichment technique, first using ultrafiltration, and then using the focusing technique with a large injection loop and the slot flow technique inherent to Fl-FFF. However, the most serious problem is that the physicochemical properties of colloids are likely to change owing to variations in the physicochemical parameters of groundwater, such as pH, redox potential, and hydraulic pressure, and exposure to the atmosphere during sampling [10]. For example, CO_2 degassing of groundwater resulting from a decrease in the hydraulic pressure may cause an increase in the pH. Precipitation of metal (hydr)oxides can occur upon oxidation of groundwater. These changes influence the properties of the colloids in groundwater. Thus, a method for collecting and analyzing colloids while maintaining in situ hydrochemical conditions (mainly hydraulic pressure and anaerobic condition) without chemical disturbance is required. Moreover, understanding the interaction between colloids and REEs in natural environments is important; REEs can be regarded as analogues of trivalent actinides [11]. The hydrogeochemistry of REEs in groundwater has been studied in terms of their usefulness as tracers for various geochemical processes such as water–rock interactions and hydrothermal activity. REEs are known to have high affinities for colloids owing to their large ionic potential (ionic charge/ionic radius) [12–21]. However, the interaction between colloids and REEs is not well understood. Interactions evaluated on a laboratory scale do not necessarily correspond to that measured in in situ experiments possibly because of chemical disturbance. For example, preferential adsorption of heavy REEs (HREEs) onto iron (hydr)oxide colloids has been determined from laboratory experiments [22], whereas preferential adsorption of light REEs (LREEs) onto colloids has been reported in in situ experiments [23–25].

The objectives of this study are to develop a microfiltration/ultrafiltration technique while maintaining in situ hydraulic pressure and anaerobic condition and to understand the partitioning of REEs in the presence of colloids in complex natural environment without chemical disturbance. Using the technique developed herein, we sampled colloids and filtered groundwater in granite at a depth of 300 m that corresponds to the depth of geological disposal sites for HLW according to the Designated Radioactive Waste Final Disposal Act [26]. Moreover, to understand the influence of hydrochemical conditions (mainly hydraulic pressure and anaerobic condition) on colloid properties, the groundwater at a depth of 200 m was exposed to the atmosphere for different periods of time and fractionated by microfiltration/ultrafiltration. This study provides useful information on the size distribution and composition of colloids, and the interaction between colloids and REEs in complex natural environments.

2. Development of the microfiltration/ultrafiltration apparatus

The microfiltration/ultrafiltration apparatus developed in this study consisted of two filter holders: an inlet pressure regulator and an outlet pressure regulator (Fig. 1). The filter holders were made of stainless used steel (SUS) and designed to maintain anaerobic conditions under high hydraulic pressures (10 MPa). To prevent contamination from SUS, a part of the apparatus that had contact with groundwater was passivated. The concentration of Fe in ultrapure water flowing through the apparatus was less than 0.01 μg/L and that of REEs was less than 0.1 ng/L. The results confirmed that colloid characterization was not influenced by contamination from SUS. Microfiltration/ultrafiltration membranes with different pore sizes were packed into the filter holders. For example, when membranes with pore sizes of 0.45 and 0.01 μm were set into the pre- and post-filter holders, respectively, colloids in the size range of 0.01–0.45 μm were collected. The inlet and outlet pressure regulator valves connected to the filter holders were used to adjust the differential pressure to prevent excess resistance pressure (~0.4 MPa) of the microfiltration/ultrafiltration membrane filter in the filter holder. Thus, though the pressure of groundwater is higher than the resistance pressure of the membrane filter, microfiltration/ultrafiltration can be performed without failure of the membrane filter. The inlet pressure regulator, outlet pressure regulator, and two filter holders were connected using quick-connects (Swagelok, Solon, OH, USA) with double-end shut-off stems to prevent exposure to the atmosphere. Though the filter holders are separated from the inlet and outlet pressure regulators after microfiltration/ultrafiltration, hydraulic pressure and anaerobic condition in the filter holder can be maintained. Following discharge of residual groundwater in the filter holder using inert gas (e.g., Ar), the membrane filters were collected from the filter holder in an anaerobic chamber purged with an inert gas. The relatively small package size (180 mm × 500 mm × 120 mm; 3.2 kg) of the microfiltration/ultrafiltration apparatus affords easy transport and assembly in underground facilities. Moreover, the present microfiltration/ultrafiltration technique can be conducted under artesian pressure as the driving force without pumping that may cause artificial alteration.

3. Materials and methods

3.1. Sampling point

Groundwater samples were collected from boreholes 07MI07 and 09MI20. 07MI07 and 09MI20 boreholes are both horizontal boreholes with the lengths of 55 and 102 m, respectively, located on the -200 and -300 m access/research galleries of MIU, respectively. The geological site at MIU consists of Cretaceous granitic rocks (Toki granite; ~60–70 Ma) and Miocene sedimentary rocks (Mizunami Group; ~15–20 Ma). The Mizunami Group unconformably overlies the Toki granite at a depth of ~160 m at the MIU site. The 07MI07 and 09MI20 boreholes are designed for investigations of any hydrochemical changes related to facility construction. The 07MI07 and 09MI20 boreholes are divided into six sections by impermeable packers. The sections are numbered from 1 to 6 according to the distance from the base of the 07MI07 and 09MI20 boreholes. Groundwater samples were collected from each section through nylon tubing without exposure to the atmosphere. The outlet of the nylon tubing was directly connected to the microfiltration/ultrafiltration apparatus developed in this study using quick-connects with a double-end shut-off stem, i.e., a valve was used to simplify connection and disconnection of the microfiltration/ultrafiltration apparatus from the nylon tubing.

3.2. Air exposure experiment

Microfiltration of groundwater samples collected from section 4 of borehole 07MI07 at a depth of 200 m was performed under different exposure times to the atmosphere (0, 180, and 43,200 min) following pressure release. The sample exposed to the atmosphere for 0 min was filtered using the apparatus mentioned above under artesian pressure (~1 MPa). A microfiltration membrane with a pore size of 0.2 μm (H020A047A, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) was used. The samples exposed to the atmosphere for 180 and 43,200 min were filtered using a filter holder (SAKE-142, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) in the laboratory under gas pressure (~0.3 MPa) after exposure to atmosphere and pressure release in a Teflon bottle. A microfiltration membrane with a pore size of 0.2 μm (H020A142C, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) was used.

3.3. Microfiltration/ultrafiltration under maintained in situ conditions

Microfiltration/ultrafiltration of groundwater samples collected from sections 1–6 of borehole

09MI20 at a depth of 300 m was performed using the apparatus mentioned above under artesian pressure. To remove large particles, membrane filters with a pore size of 0.45 μm (A045A047A, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) were fitted into pre-filter holders. A microfiltration membrane with a pore size of 0.2 μm (H020A047A, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) or an ultrafiltration membrane with a molecular weight cut-off (MWCO) of 10 kDa (13622, Merck, Darmstadt, Germany) was used for the post-filter. The filtered volume was 1 L for both types of filtration. The duration of the micro- and ultrafiltration was ~0.5 and 10 h, respectively. The in situ groundwater pressure as displayed on the inlet pressure gauge remained mostly constant and was comparable with the in situ pressure (~2 MPa) during filtration. The differential pressure between the inlet and outlet pressures was adjusted to ~0.3 MPa at the start of filtration, and remained mostly constant during filtration. The dissolved oxygen (DO) was measured by colorimetric method. The DO concentration in the unfiltered groundwater was less than 0.02 mg/L, however, rapidly increased upon exposure to the atmosphere. The DO concentration of groundwater filtered using the microfiltration/ultrafiltration apparatus was less than 0.02 mg/L even after sample collection and differed slightly from that of unfiltered groundwater. This indicates that the hydraulic pressure and anaerobic condition of groundwater are maintained during the filtration process.

3.4. Characterization of colloids

3.4.1. ICP–MS measurements

The concentrations of Fe and REE in the filtered and unfiltered groundwater were determined by ICP–MS (ELAN DRC-II, PerkinElmer Inc., Waltham, MA, USA). The REE concentrations were determined after preconcentration using chelate resin (Chelate Disc Empore, Sumitomo 3M

Ltd., Tokyo, Japan). The calibration curves were constructed from 0.01, 0.05, 0.1, 0.5, 1, 5, and 10 μg/L REE solutions prepared from 10 mg/L REE standard solution (SPEX CertiPrep Ltd. London, UK). Sample preparation and ICP–MS measurements were conducted in a clean room (Class 10,000). The detection limit values of Fe and REEs were 0.01 μg/L and 0.1 ng/L, respectively.

3.4.2. Scanning electron microscopy–energy-dispersive X-ray spectroscopy

After filtration, the 10 kDa MWCO membrane filters were dried in an anaerobic chamber under Ar atmosphere. The dry membrane filters were coated with Os. The filters were imaged using a field-emission scanning electron microscope (FE–SEM, Quanta 200, FEI Co., Hillsboro, OR, USA) equipped with an energy-dispersive X-ray analyzer (EDX, INCA Energy version 4.05, Oxford Instruments plc., Abingdon, UK) under high vacuum conditions. Sample preparation was performed in a clean room (Class 10,000). The accelerating voltage was 15 kV. The magnification was in the range of 100–40,000×. The equivalent circle diameters of the colloids were calculated by image processing of the obtained backscattered electron images.

3.4.3. Fourier transform infrared spectroscopy

After filtration, the 10 kDa MWCO membrane filters were dried in an anaerobic chamber under Ar atmosphere. Each filter was examined by attenuated total reflection infrared spectroscopy (ATR-FTIR). The ATR-IR spectra (650-4000 cm^{-1}) were recorded on a Fourier transform infrared spectrophotometer (Spectrum Spotlight400, PerkinElmer Inc.).

4. Results and discussion

4.1. Air exposure experiment

To understand the influence of the hydrochemical conditions (mainly hydraulic pressure and anaerobic condition) on the colloid properties, filtrations were performed under different exposure times to the atmosphere (0,180, and 43,200 min) following pressure release.

Table 1 shows the concentration of Fe in the filtered groundwater for different exposure times to the atmosphere. The Fe concentration in the filtered groundwater sample at 180 min was lower than that at 0 min. This indicates that Fe colloids larger than 0.2 μm formed by oxidation within 180 min after sample collection. The Fe concentrations at 180 and 43,200 min were not markedly different, suggesting that the formation of Fe colloids may be a rapid process reaching equilibrium quickly. The results of the Fe concentration indicate that exposure to the atmosphere during filtration impedes on the concentration determination of redox-sensitive elements in the filtered groundwater sample. For instance, Fe colloid formation as a result of oxidation may lead to an overestimation of the colloid size.

Fig. 2 shows the relative REE concentrations in the filtered groundwater samples for different exposure times to the atmosphere (180 and 43,200 min) after pressure release. Each concentration was normalized to filtered groundwater at 0 min. The data at 180 and 0 min were not markedly different, suggesting that REEs remained in the <0.2 μm fraction despite formation of Fe colloids. In contrast to the data at 180 min, the REE concentrations in the filtered groundwater sample at 43,200 min were less than those at 0 min, especially for LREEs (La, Ce, Pr, and Nd). This indicates that REE adsorption onto the Fe colloids occurred within 180–43,200 min; however, Fe colloids were formed within 180 min. This discrepancy may be due to the degassing of carbon dioxide from groundwater after pressure release. Carbonate ions can form stable complexes with REEs in groundwater, especially with heavier REEs [27] under both pressurized and anaerobic conditions. Most HREEs–carbonate complexes (<0.2 µm) were stable after 43,200 min. On the other hand, a part of LREE-carbonate complexes (<0.2 µm) might have dissociated within 180–43,200 min upon degassing of carbon dioxide owing to exposure to the atmosphere and pressure release because the stability of LREE-carbonate complexes are weaker than that of HREEs–carbonate complexes. Then, the free ion of LREEs may be adsorbed onto Fe colloids (>0.2 µm). However, this hypothesis was not verified because the concentration of inorganic carbon and pH were not measured. Based on these results, the oxidation of groundwater influenced the size distribution of the REEs though the REEs (except for Ce and Eu) were insensitive to the redox conditions.

4.2. Size distribution of colloids and REE partitioning

The REE concentrations in the unfiltered groundwater of the 09MI20 borehole are shown in Fig. 3. The groundwater samples collected from all sections contained 0–25 ng/L REEs. The rock–water interaction is the main source of REEs because granitic rocks contain relatively large amounts of REE [28]. The difference in the REE concentrations between the sections suggests spatial variation of REEs. Mizuno et al. [29] reported that the salinity of groundwater changes according to variations in the flow conditions of groundwater owing to the shaft construction at MIU. Therefore, the spatial variation of REEs may result from the shaft construction as well as the salinity. Moreover, a short sampling time is required to understand the size distribution of colloids and REEs in groundwater during construction of the facilities.

Fig. 4 shows the relative REE concentrations in the filtered groundwater samples collected from the six sections of 09MI20 borehole. The groundwater samples were filtered using membranes with different pore sizes (10 kDa MWCO and 0.2 µm). Each concentration was normalized to the unfiltered groundwater. All samples were collected on July 21, 2011 and July 26, 2011. For samples collected from section 2, the REE concentrations in the filtered groundwater samples were higher than those of the unfiltered groundwater. This was believed to be due to an analytical error during ICP–MS measurements because the REE concentrations of samples from section 2 were the lowest among samples collected from all sections of 09MI20 borehole and comparable with the detection limit of the ICP–MS instrument. Thus, results relating to samples from section 2 are not discussed. The REE concentrations in the filtered groundwater decreased with decreasing membrane pore sizes (except for sample collected from section 2). The results indicate REE association with colloids present with size ranges of 10 kDa–0.2 μm and 0.2–0.45 μm. About 50% of the REEs present in all sections (except for section 2) associated with colloids with sizes larger than 10 kDa. Preferential association of LREEs with colloids with sizes ranging from 10 kDa to 0.2 μm and from 0.2 to 0.45 μm was observed in samples collected from sections 5 and 6, whereas that of LREEs with colloids with sizes ranging from 0.2 to 0.45 μm was observed in samples collected from section 1. Preferential association of LREEs with colloids, as observed in groundwater, has also been observed in river water [30].

4.3. Size distribution and composition of colloids on the ultrafiltration membrane

Fig. 5 shows representative SEM images of the inorganic colloids in the groundwater samples collected from all six sections of 09MI20 borehole. The equivalent circle diameters of the inorganic colloids were estimated by image processing of backscattered electron images. For all sections, the equivalent circle diameters of most of the inorganic colloids were in the range of 0.05–0.45 μm. These results were consistent with the size distribution of the colloids estimated from the size distribution of REEs, as mentioned in section 4.2. In this study, it was difficult to measure the equivalent circle diameters of colloids smaller than 0.05 μm. High-resolution analysis techniques, such as transmission electron microscopy and atomic force microscopy, are required for such measurements.

Fig. 6 (a) shows representative SEM images of the inorganic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole and Fig. 6 (b) shows EDX spectra of the inorganic colloids shown in Fig. 6 (a). The spectra show the presence of C, O, and S that are from the polysulfone membrane filter. Inorganic particles containing Fe believed to be iron sulfide and iron (hydr)oxide were found in samples collected from sections 1 and 3. Inorganic particles containing Al, Si, alkaline earths, and alkaline earth metals were found in samples collected from sections 2, 5, and 6. Inorganic particles containing Al and Mg were found in samples collected from section 4. These particles are believed to be fragments of either granite or clay minerals. Because Fe (hydr)oxide and clay minerals have high affinities for REEs [14–18], inorganic colloids seem to form complexes with the REEs.

Vilks et al. [31] reported that organic colloids with a range of sizes were present together with inorganic colloids. Thus, the effect of organic colloids on partitioning of REEs was considered. Identification of organic matter by SEM was difficult because the membrane filter was made of an organic substance. To confirm the presence of organic matter, IR analysis was performed. The FTIR spectra of all six sections and the Suwannee River humic acid standard (2S101H, International Humic Substances Society) are shown in Fig. 7. All FTIR spectra were characterized by a number of absorption bands, exhibiting varying relative intensities. The strong broad band at 2400–3700 cm^{-1} is generally attributed to O–H stretching of hydroxyl groups involved in hydrogen links, carboxyl groups, and phenol groups. The band at 3292 cm^{-1}, which was weak in the humic acid spectrum, was attributed to the N–H stretch absorption band of amines and amides [32,33]. There were also a few absorption bands at 2923 and 2853 cm^{-1}. These bands were assigned to C–H stretching of methyl (CH_3) and methylene (CH_2) groups of aliphatic chains [34–36]. The bands at 1730 and 1701 cm^{-1} are generally attributed to C=O stretching vibrations, mainly of carboxyl groups and, to a lesser extent, of ketones and aldehydes [34–36]. The band at 1644 cm^{-1}, which was absent from the humic acid spectrum, was ascribed to C=C stretching of aromatic rings [37] and C=O stretching vibration in amides (amide I band) [38]. The band at 1605 cm^{-1}, which was absent from the spectra in all groundwater samples, was ascribed to stretching of the C=C group conjugated with another C=C group (aromatic ring), C=O and/or COO^{-} in unsaturated ketones, carboxylic acids, and amides [39]. The band at 1545 cm^{-1}, which was absent from the humic acid spectrum, was ascribed to NH bending in secondary amides (amide II band) [38]. All samples exhibit broad bands in the region 1000–1300 cm^{-1}, which are probably because of the C–O stretching vibration in alcohols, ethers, phenols, carboxylic acids, and esters [38, 40]. For the groundwater samples collected from all sections of the borehole, it was difficult to detect absorption bands in the region of 650–1400 cm^{-1} because of the strong absorption bands of the blank.

The FTIR spectra of organic matter present in samples collected from all sections showed similar shapes and intensities, suggesting that all sections of the 09MI20 borehole were similar structures. Some differences were observed between the FTIR spectra of organic matter and humic acid. Although the organic matter showed some absorption bands relating to nitrogen, such as absorption bands at 1545, 1644, and 3292 cm^{-1}, these absorption bands were weak or different from those of humic acid. These differences indicated that the nitrogen content of the organic matter in the groundwater samples collected from all sections of the borehole was greater than that of humic acid. Previous studies reported that most of the REEs in groundwater bound to humic substances by forming stable complexes [41]. Organic matter present in 09MI20 borehole may associate with REEs as well as inorganic colloids.

Vilks et al. [31] reported that inorganic colloids consisting of clay minerals, ferrioxide, and carbonate minerals were present in a wide size range with organic matter in groundwater. Saito et al. [9] reported that Al-, Mg-, and Fe-bearing colloids associated with organic matter at a depth of 300 m at the MIU site. Additionally, in this study, we reveal that organic matter in groundwater associated with inorganic colloids and clarified the structures of organic matter. Although the results obtained from this study are qualitatively similar to those of previous studies [9, 31], our results may give more useful information owing to the newly developed sampling technique that can be operated under in situ hydrochemical conditions.

5. Conclusions

In this study, we developed a microfiltration/ultrafiltration technique that can maintain in situ physicochemical parameters and afford collection of colloids without chemical disturbance. The microfiltration/ultrafiltration technique can solve some of the uncertainties regarding colloid properties such as size distribution and interaction with REEs.

Using the microfiltration/ultrafiltration technique developed in this study, we obtained useful information on the presence of inorganic (e.g., Fe, Al, Mg, and Si) and organic colloids with a wide size range, and REEs characteristic partitioning in granite groundwater at a depth of 300 m. The latter depth corresponds to that of geological disposal sites for high-level radioactive waste. The inorganic colloids are primary minerals (i.e. fragments of granites) or secondary minerals such as clay minerals resulting from dissolution and precipitation of the host rock. Moreover, the findings indicated the co-existence of inorganic and organic colloids, and colloids bound metal ions. REEs characteristic partitioning, such as preferential association of LREEs with colloids with sizes ranging from 10 kDa to 0.2 μm and from 0.2 to 0.45 μm in a specific section of borehole, may be due to the influence of the wide variety of colloids. In future studies, we will investigate the effect of these colloids on radioactive behaviors using combined microfiltration/ultrafiltration technique and bulk analyses.

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Figure captions

Fig. 1. Schematic illustration of the microfiltration/ultrafiltration apparatus operating under pressurized/anaerobic conditions.

Fig. 2. Relative REE concentrations in the filtered groundwater samples at different exposure times to the atmosphere (180 and 43,200 min). Each concentration was normalized to filtered groundwater sample at 0 min.

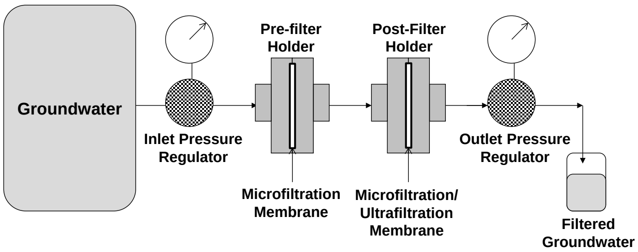
Fig. 3. Concentrations of REEs in the groundwater samples collected from all six sections of the 09MI20 borehole.

Fig. 4. Relative REE concentrations in the filtered groundwater samples collected from all six sections of the 09MI20 borehole. The groundwater samples were filtered using membranes with different pore sizes (10 kDa MWCO and 0.2 μm). Each concentration was normalized to the unfiltered groundwater sample.

Fig. 5. Representative SEM images of inorganic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole. The equivalent circle diameters of several colloids are shown.

Fig. 6. Representative SEM images and EDX spectra of inorganic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole: (a) SEM images and (b) EDX spectra of the inorganic colloids shown in Fig. 6 (a).

Fig. 7. FTIR spectra of the reference humic acid and organic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole.



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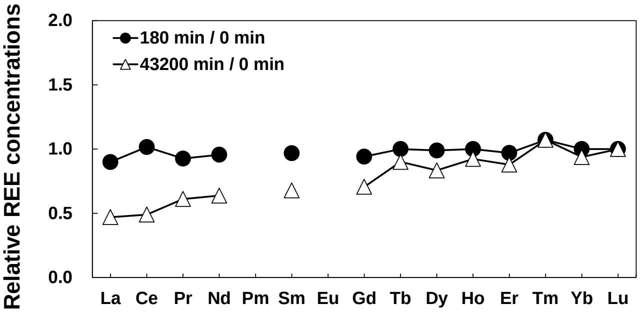

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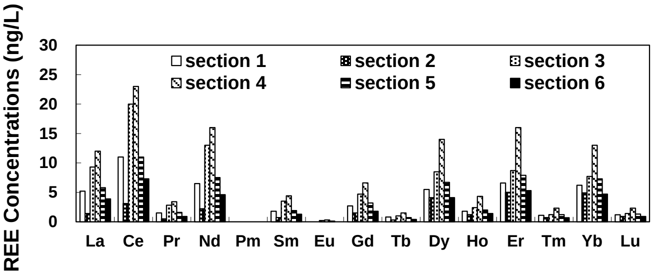

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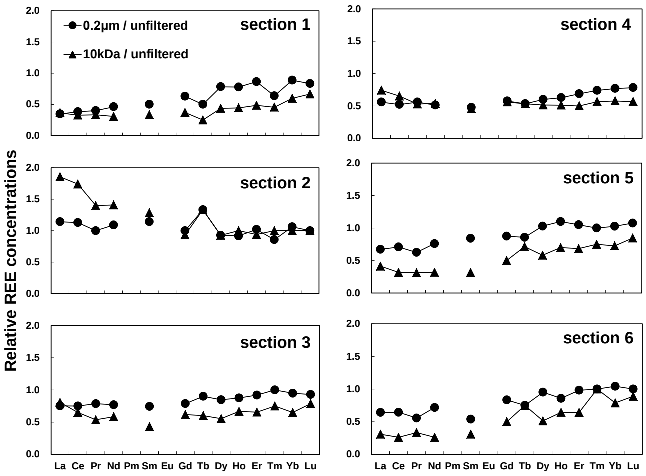

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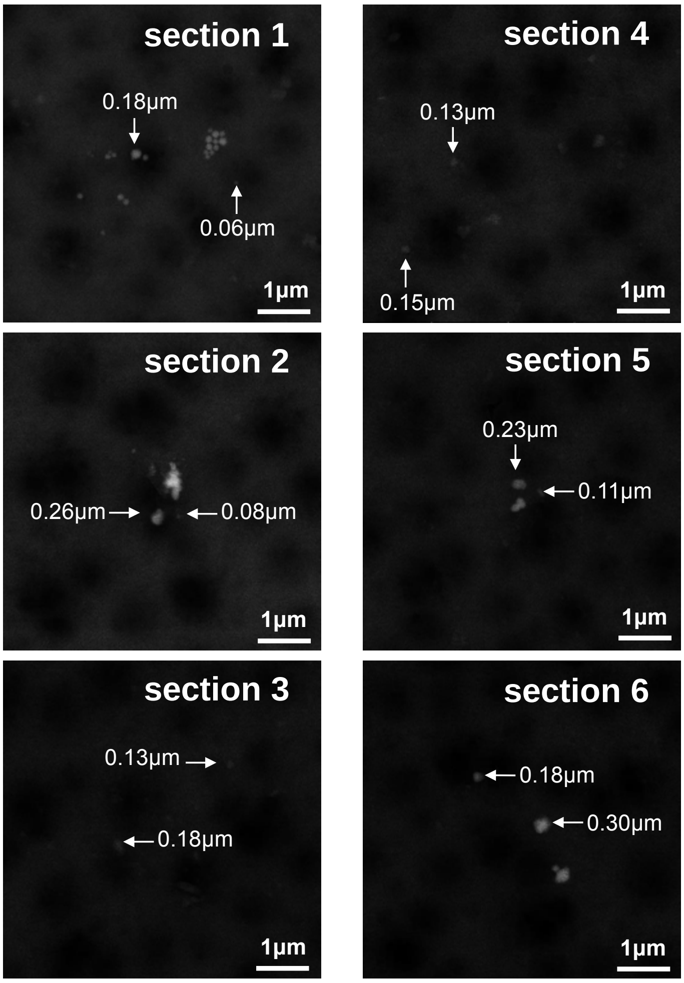

Fig. 5. Representative SEM images of inorganic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole. The equivalent circle diameters of several colloids are shown.

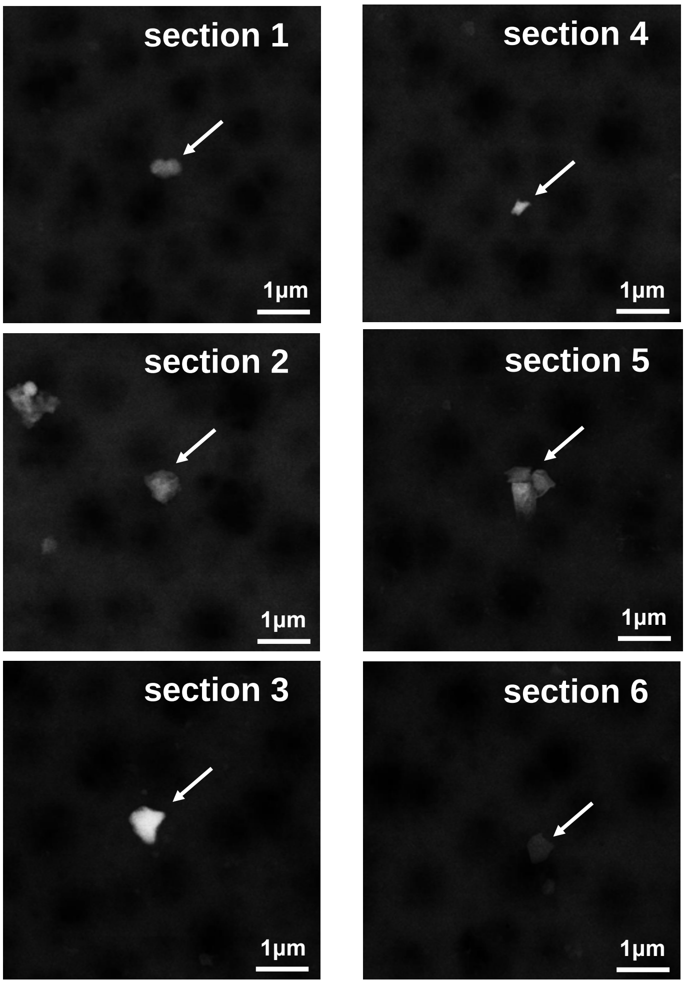

Fig. 6(a). Representative SEM images and EDX spectra of inorganic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole: (a) SEM images and (b) EDX spectra of the inorganic colloids shown in Fig. 6 (a).

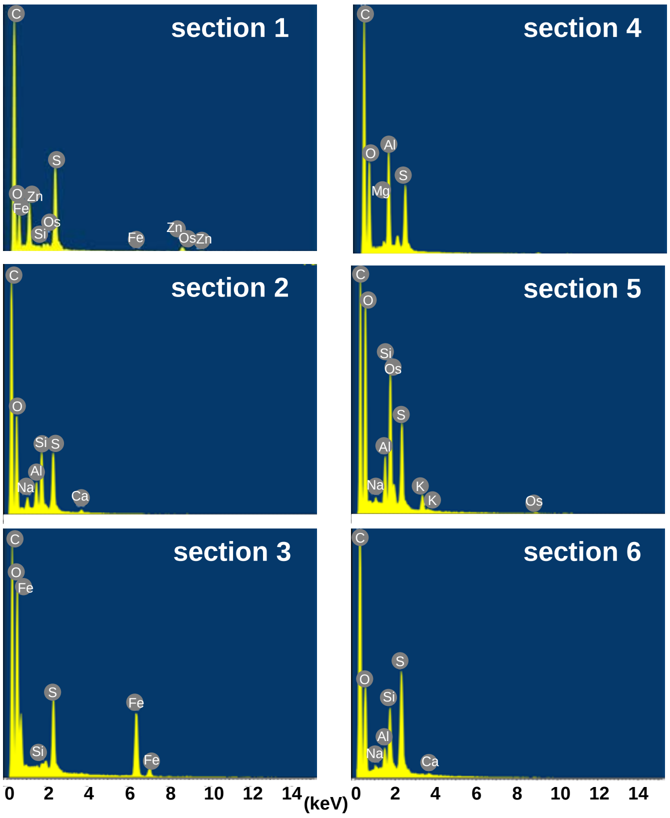

Fig. 6(b). Representative SEM images and EDX spectra of inorganic colloids in the groundwater samples collected from all six sections of the 09MI20 borehole: (a) SEM images and (b) EDX spectra of the inorganic colloids shown in Fig. 6 (a).

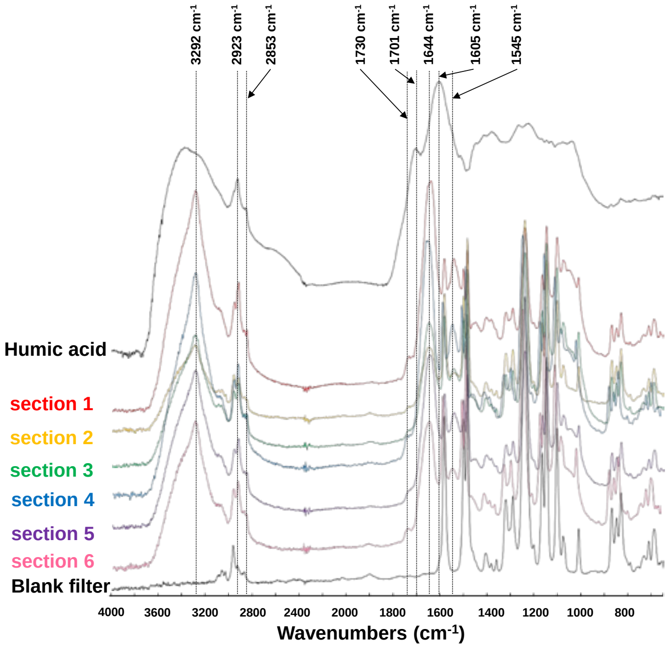

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Table 1
Average concentrations of total Fe in filtered groundwater.

	Exposure time					
	0 (min)		180 (min)		43200 (min)	
	Avg.	S.D[a]	Avg.	S.D[a]	Avg.	S.D[a]
Fe (μg/L)	5.5	0.52	3.2	0.42	2.7	0.28

[a] The standard deviation of three samples.