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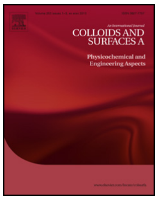

Size and elemental analyses of nano colloids in deep granitic groundwater: Implications for transport of trace elements

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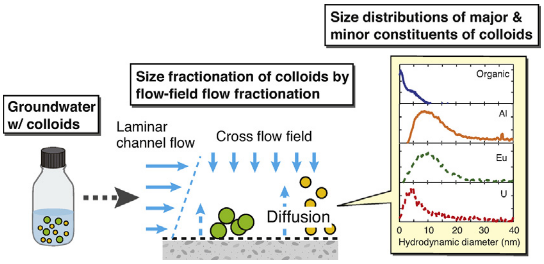
HIGHLIGHTS

- Groundwater colloids were size-fractionated by flow-field flow fractionation.
- Three-step enrichment was performed to measure the size distribution of colloids.
- Trace elements were found to be associated with certain host colloids.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano colloids in granitic groundwater obtained from a borehole located at the −300-m access/research gallery of the Mizunami Underground Research Laboratory in Japan were studied in terms of their size distributions by flow-field flow fractionation (Fl-FFF). Colloids were enriched first by ultrafiltration, and then by *in-situ* enrichment using the focusing technique with a large injection loop and the slot flow technique because of the relatively low concentrations of colloids in the groundwater. The slot flow technique is a colloid enrichment technique inherent to Fl-FFF, where colloids are concentrated inside the channel of Fl-FFF by removing supernatant. Underestimation of colloid sizes by this technique was addressed and corrected, based on empirical linear relationship between the sizes of protein standards with and without the slot flow. The size distributions of organic constituents of colloids were measured by UV/vis and fluorescence detectors and those of inorganic constituents by inductively coupled plasma mass spectrometry (ICP-MS). By comparing the size distributions, possible association of trace elements with host colloidal phases consisting of major elements and organic materials was discussed. Trace elements, namely, Sr, lanthanides (La, Ce, Eu, Lu), actinides (U, Th) and heavy metals (Cu, Zn and W), exhibited distinct size distributions, reflecting their preferential association with certain host colloidal phases.

1. Introduction

Colloids are particulates and macromolecules, having at least one of their dimensions within a range of 1 nm to 1 μm [1], and are ubiquitous in many natural water systems [2]. Mineral particles produced by dissolution and precipitation of rocks' constitute inorganic colloids; biopolymers such as polysaccharides and proteins, bacteria and poorly-defined natural organic matters (NOM) such as humic substances are examples of organic colloids. Owing to reactive functional groups on the surfaces of inorganic colloids and inside the macromolecular bodies of organic colloids, colloids are charged and stable in dilute aqueous media and sorb nutrients and contaminants. We particularly focus on relatively small colloids (called nano colloids hereafter) in this study, which may include various reactive colloids such as humic substances and very fine clay minerals or metal (hydr)oxides like ferrihydrite. Special

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attention has been made to nano colloids in the field of geoscience as they can mediate various processes in natural environments [3].

There are an increasing number of evidences that natural colloids act as carriers for toxic substances in subsurface environments [4–6]. This is called colloid facilitated transport [4] and is of great concern in geological disposal of nuclear wastes, as a part of its safety functions relies on retardation of released radionuclides in subsurface environments. It was reported that plutonium was transported by the colloidal fraction of groundwater at the Nevada Test Site in the United States [5]. Plutonium and uranium were found with poorly crystalline iron oxide colloids at 3 km away from a former reprocessing plant site in Mayak, Russia [6]. Laboratory experiments and field tests at underground research laboratories (URLs) with synthesized or purified model colloids have also confirmed the impacts of colloids on the migration of radionuclides and toxic elements [7–10].

Analyzing colloids in natural water systems in terms of their sizes, compositions, and interaction with trace elements is not a simple task especially for groundwater colloids, partly because of difficulties in sampling [4]. Colloids can be collected from a range of groundwater, using boreholes from surface [11]. Some countries operate URLs for studies of geological disposal of nuclear wastes, where one can obtain large amounts of groundwater samples with less contamination or transformation, compared with the surface borehole sampling [8,12]. Low colloid concentration, the presence of a spectrum of colloids with different sizes and compositions and possible aggregation among them hinder analyses further [13]. Therefore, the first step of groundwater colloid analyses is often concentration and fractionation of colloids in a given sample. This is most frequently achieved on the basis of their sizes; membrane (ultra)filtration or ultracentrifugation is a popular size fractionation and/or concentration technique, though it only gives a discrete size distribution and may suffer from clogging of the pores or an increase of the effective pore size [2]. Cross-flow filtration can mitigate a part of the difficulties and be effectively used for large-scale preparative size fractionation [2,14]. For analytical fractionation, continuous size fractionation by size-exclusion chromatography (SEC) or flow-field flow fractionation (Fl-FFF) is more appropriate [15–17]. Fl-FFF is a chromatographic fractionation technique and can be easily coupled with various on-line detectors. In Fl-FFF the retention time of a colloid is directly related to its diffusion coefficient and thus to its hydrodynamic size [16,17]. The advantages of Fl-FFF over SEC are easily adjustable fractionation range and resolution and relatively weak interaction of colloids with the fractionation medium.

Colloids in deep groundwater from various geological settings have been studied, ranging from granitic groundwater with minute colloids to sedimentary groundwater rich in organic colloids [13,18,19]. Degueldre et al. [18] summarized the importance of geochemical conditions such as pH, redox potential and concentrations of major ions and organic carbon for the concentrations, attachment factors and size distributions of colloids. Plaschke et al. [13] characterized colloids obtained from the Gorleben aquifer in Germany by atomic force microscopy and reported the presence of different colloids and their aggregates. Studies on association of groundwater colloids with trace elements are rather scarce [19,20]. Vilks et al. [19] reported the size distribution and composition of colloids (mostly clays, organic materials and Fe oxides) in granitic groundwater, using size-fractionation and colloid enrichment by ultrafiltration. These authors investigated association of naturally present actinides or radionuclides, U, Th and Ra, with the colloids, though the effects of small colloids, especially those in the 1–10-nm size fraction, which may be more reactive and mobile than larger colloids, remains largely unknown.

The objective of this study is to analyze the size distributions and elemental compositions of nano colloids in the granitic groundwater collected at a depth of 300 m at the Mizunami Underground Research Laboratory (MIU) in Japan, using Fl-FFF coupled with on-line UV/vis, fluorescence detectors and inductively coupled plasma mass spectrometry (ICP-MS). It was assumed that organic materials in the groundwater probed by UV/vis and fluorescence as well as major elements that originally existed in the groundwater at relatively high concentrations consisted of host colloidal phases. Relatively low concentration of colloids in the MIU groundwater was tackled by three-step enrichment of colloids; colloids were first concentrated by ultrafiltration, and then by on-line enrichment using the focusing technique with a large injection loop and the slot flow technique [21]. Through this study, the size distribution of trace elements such as heavy metals and naturally occurring actinides were compared with those of the host colloidal phases to deduce their association with certain colloidal phases in the granitic groundwater. Note that this article focuses on comparing the size distributions of organic materials and major and minor elements in the size range of the Fl-FFF fractionation. Quantifying them and discussing the results with respect to the corresponding concentrations in the entire size range is the future work.

2. Principles of Fl-FFF

An overview of size fraction by trapezoidal asymmetric Fl-FFF is depicted in Fig. S1 in the Supplementary Data [17]. Sample liquid containing colloids is introduced to a channel created by a spacer with a stencil sandwiched by top and bottom blocks and an ultrafiltration membrane. Colloids are first forced into a narrow band (∼1 mm) by a channel flow and an opposing focus flow (the focusing step). Fractionation of colloids is achieved in the subsequent elution step, where colloids are transported by the longitudinal laminar channel flow along the channel under the external force field created by a flow perpendicular to the channel (cross flow). As the concentration of colloids decays exponentially as a function of the distance from the membrane, depending on the cross flow field and thermal motion of colloids against it, smaller colloids with larger diffusivity distribute further away from the membrane and thus elute faster than larger colloids.

The retention time, t_r, of colloids is determined with respect to the void time, t_0, which is elution time of a non-retained component, and converted to the hydrodynamic diameter, d_H, by the following relationship [17,22]:

$$R = 6\lambda \left[\coth\left(1/2\lambda\right) - 2\lambda\right], \tag{1}$$

where R is the so-called retention ratio, which can be calculated as the ratio of the void time, t_0, and t_r [17,23], and λ is defined as

$$\lambda = \frac{kTV^0}{3\pi\eta d_H V_c w^2}, \tag{2}$$

where k, T and η are the Boltzmann constant, the absolute temperature and the viscosity of water, V^0 is the void volume of the channel, V_c is the cross flow rate and w is the thickness of the channel, which is typically around 300 μm. The values of t_0 and V^0 are calculated according to the geometry of the channel [17,23].

The characteristic thickness, l, of a cloud of colloids near the accumulation wall depends on the diffusion coefficients of the colloids and given as $l = \lambda \cdot w$ [17,22]. For 1- and 10-nm colloids, l is calculated as 32 and 3 μm, respectively, using the cross flow rate and the channel geometry used in this study. Comparing these values with w, one can realize that colloids only exist in the close vicinity of the wall, that is, a major part of the channel contains only supernatant. A slot flow can be used to remove such supernatant and effectively concentrate colloids (Fig. S1(b)), though possible alternation of the flow profile in the channel could affect measured t_r [21].