



HAL
open science

Iron-organic matter colloid control rare earth element environmental mobility

Yasaman Tadayon, Mélanie Davranche, Delphine Vantelon, Aline Dia, Julien Gigault

► **To cite this version:**

Yasaman Tadayon, Mélanie Davranche, Delphine Vantelon, Aline Dia, Julien Gigault. Iron-organic matter colloid control rare earth element environmental mobility. *Current Opinion in Colloid & Interface Science*, 2024, 74, pp.101859. 10.1016/j.cocis.2024.101859 . insu-04719776

HAL Id: insu-04719776

<https://insu.hal.science/insu-04719776v1>

Submitted on 3 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



Iron-organic matter colloid control rare earth element environmental mobility

Yasaman Tadayon¹, Mélanie Davranche¹, Delphine Vantelon²,
Aline Dia¹ and Julien Gigault^{1,3}

Rare earth elements (REE) have raised significant environmental concerns due to their increasing use in human activities and subsequent release into the environment. Hence, in the context of growing demand for “green” technologies and potential mismanagement of their life cycle, understanding their potential mobility within and between environmental compartments becomes crucial for evaluating their environmental risks. Colloids emerge as primary carriers/vectors facilitating REE mobility and transfer in the environment. This work addresses major topics related to the control exerted by colloids on the REE speciation and subsequent patterns. Among colloids, iron-organic matter colloids have been identified as the major REE carrier in surface water under various pedoclimatic conditions. Compelling evidences were provided that the mixing of iron-, organic- and iron-organic colloids could explain both REE concentration and pattern under environmental conditions. However, there is currently a lack of data on the specific distribution of REE between the iron and organic matter phases within Fe-OM colloids. It remains unclear whether REE distribution is primarily controlled by colloid mixing since structural rearrangements of Fe-OM colloids under varying hydrological and physicochemical conditions exert also a significant role.

Addresses

¹ Univ. Rennes, CNRS, Géosciences Rennes - UMR 6118, F-35000 Rennes, France

² Synchrotron SOLEIL, L'orme des merisiers, Saint Aubin BP48, 91192 Gif sur Yvette Cedex, France

³ TAKUVIK Laboratory, UMI3376 CNRS/Université Laval, Québec, Canada

Corresponding author: Davranche, Mélanie (melanie.davranche@univ-rennes.fr)

Current Opinion in Colloid & Interface Science 2024, 74:101859

This review comes from a themed issue on **Environmental Technologies (2023)**

Edited by **Julien Gigault**

For a complete overview see the [Issue](#) and the [Editorial](#)

<https://doi.org/10.1016/j.cocis.2024.101859>

1359-0294/© 2024 The Authors. Published by Elsevier Ltd. This is an

Given the role as Guest Editor, Julien Gigault had no involvement in the peer review of the article and has no access to information regarding its peer-review. Full responsibility for the editorial process of this article was delegated to Marie Pierre Krafft.

open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Keywords

Rare earth element, Iron, Organic matter, Colloids, Mobility/transfer.

Introduction

As classified by the International Union of Pure and Applied Chemistry (IUPAC), rare-earth elements (REE) are a group of seventeen chemical elements in the periodic table, including fifteen lanthanides, yttrium (Y), and scandium (Sc). In coherence with their chemical properties, REE are separated into three groups, the light REE (LREE; La–Nd), the middle REE (MREE; Sm–Dy), and the heavy REE (HREE; Ho–Lu) [1]. These elements are becoming critical for modern technologies, from cell phones and televisions to LED light bulbs and wind turbines. New expressive naming such as “Vitamins of Modern Industry” defines their importance in high-tech products [2]. They became so essential that their mining is even expected on the moon [3]. REE are also used in agriculture, and an increase was already noted in concentration for some REE in native plants [4–7]. Gadolinium (Gd), is also employed in magnetic resonance imaging (MRI) to enhance contrast [8–10]. Some studies also indicate that REE can enter the bodies of biological species such as humans and animals [11,12] through food consumption [13] or even breathing dust [14], which is raising some concerns about their effect on main (bio) geochemical cycles [9,15–17].

More generally, in contrast to their socio-economic benefits, their environmental dissemination and associated threats are still poorly investigated [18]. REE are thus classified as emerging pollutants and yet, more ecological impacts are expected since the growing development of “green” technologies will be undeniably accompanied by increased discharges due to mismanagement of their life cycle. The REE recycling is still being underdeveloped at present, since it is less profitable than extraction [19–23].

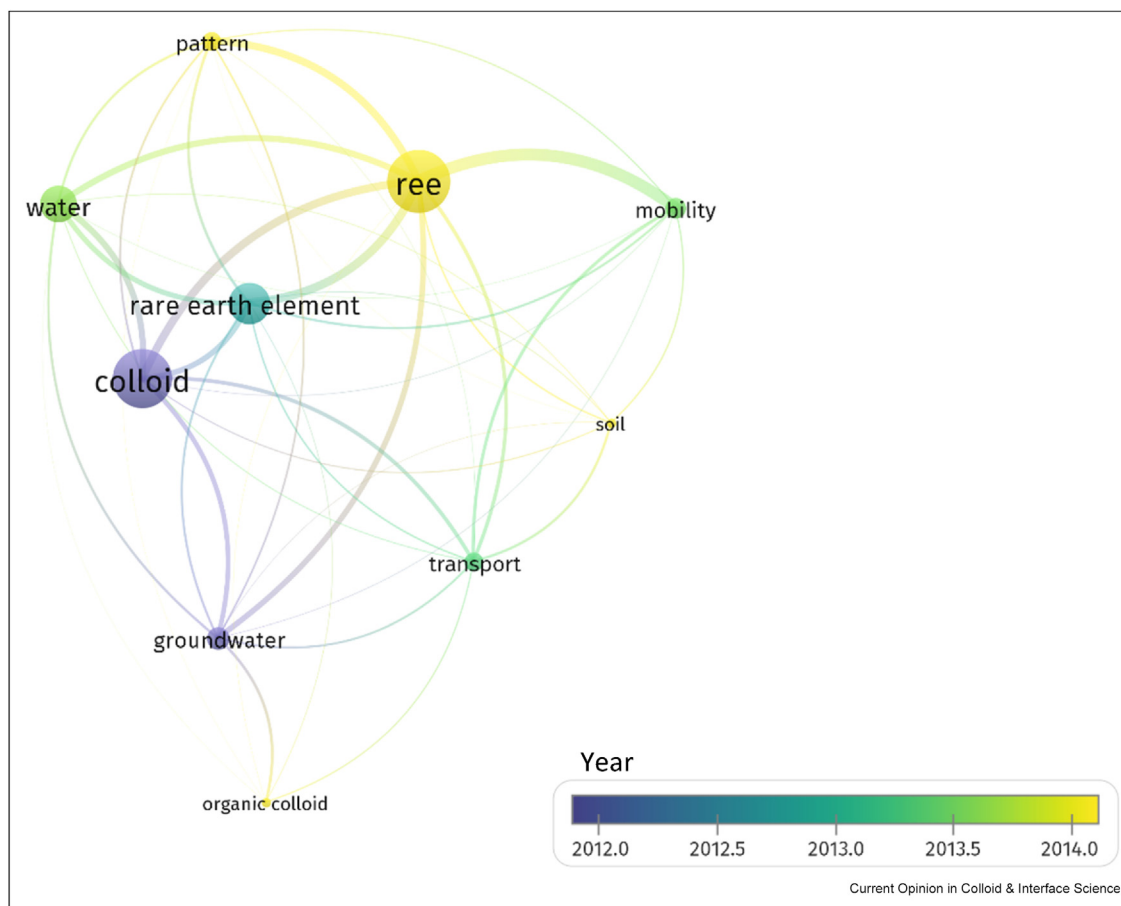
As a crucial first step in evaluating the environmental risks associated with REE, their mobility pathways

under environmental conditions have to be deciphered. Among all studies conducted on REE, their speciation appears to be the key parameter influencing their mobility and further transfers in the environment. This speciation is controlled by physicochemical parameters of the medium such as pH, temperature, ionic strength and the presence of organic or inorganic, soluble, or solid ligands. One of the great peculiarities of REE as metals is their strong affinity for hydrated organic and inorganic surfaces [24–28]. They can bind to chemical functions developed onto solid surfaces through hydration or during their forming process. If these solids are in particulate state, REE can be immobilized for more or less long periods [28]. However, when these solids are of nanometric size ($<1\ \mu\text{m}$) and exhibit colloidal behaviour, dissemination of REE is no longer controlled by their own properties but rather by those of the colloidal nanoparticles (NPs) themselves. Generally, colloids are smaller in size than pores for water drainage allowing them to migrate with their metal loading over large distances [29]. They can however become immobilized

along with their elemental loading through aggregation and deposition processes [29]. Although their impact on the biogeochemical cycle of metals is well-known, the scientific community has struggled to incorporate them into geochemical models due to the difficulties and challenges in characterizing and describing their heterogeneous and dynamic behaviour in response to variations of geochemical conditions. As a consequence, many studies dedicated to the geochemical behaviour of REE did not systematically consider and determine colloidal compartment [30–32].

Figure 1 illustrates a bibliometric network of co-occurrence keywords (from entry keywords: Colloids, REE, Rare earth element, mobility) made with a publications database (522 publications from 2000 to 2023) collected from the Web of Science. Tree clusters were determined, cluster 1- REE, rare earth element, colloid, pattern and water; cluster 2- mobility, soil and transport; and cluster 3- groundwater and organic colloids. Even though the research was conducted from 2000 to 2023,

Figure 1



Bibliometric network visualization for the co-occurrence of the relevant keywords: organic matter, mobility, transfer, transport and rare earth element (REE), performed with VOSviewer. Interconnectedness (line) and frequency of keywords (balls size) illustrate the research trends and focus areas.

the highest co-occurrence corresponds to a short period between 2012 and 2014. In this period, REE interactions with colloids in water were the most studied. Interestingly, few co-occurrences exist between colloids, soil and transport. Finally, there was no direct co-occurrence between colloids and organic colloids although REE and rare earth elements co-occurred with organic colloids. REE speciation, and transfer controlled by particulate, and colloidal phases in surface water were studied by the scientific community interested in REE geochemistry through the work of Sholkovitch and Pokrovsky and their co-workers [33–40]. However, all these works are from pre-2010 years. The present bibliometric analysis displays that REE-colloid association was highlighted before 2010, and since then, they were only studied for a short time, focusing mainly on their occurrence in water rather than on their impact on REE mobility.

Among colloids, organo-mineral colloids have been identified as the main carriers of REE in freshwater and soil solution [33,35,40,41]. They have gained attention to understand geochemical processes occurring in groundwater, rivers, and oceans and to identify sources of both colloids and REE [42–48]. Field, analytical, and geochemical modelling approaches all provided evidence that organo-mineral colloids are a significant parameter of the control of REE speciation (high affinity) and subsequent mobility and transfer depending on the colloid's capacity to be mobile [25,29,40,48–54]. In such a context, this review aimed to take stock of the current knowledge of organo-mineral colloid-REE interactions in order to contextualize how organo-mineral colloids may control the REE mobility and transfer pathways in the environment and to highlight knowledge gaps and propose future research directions. We selected the most relevant research on the REE-colloids, namely that specifically address the interactions between REE and organo-mineral colloids. This work aims to provide current knowledge to guide future investigations concerning the REE exposome and to better develop a prediction model of their dispersion in the environment.

Organo-mineral colloids interaction with REE in natural waters

Advancements in ultra-filtration, experimental and speciation modelling studies of REE-colloid interactions suggested that REE speciation in natural waters is dominated by colloids [35,41,47,48,55–57]. More generally, organo-mineral colloids and more precisely for river waters, the Fe-organic colloids, are major carriers of REE [35,40,58]. For example, for large rivers, Lafrenière *et al.* [59] demonstrated along a 550 km transect of the St. Lawrence River (SLR) (Canada) and its tributaries, that REE speciation was dominated by their binding to OM-Fe-Al colloids even under alkaline and low DOC conditions. For river and coastal water, Hoyle *et al.* [60]

showed that REE were associated with the sub-micrometer particles (0.4–0.7 μm) mainly composed of Fe and OM. These Fe-OM colloids exhibited a REE pattern with a HREE enrichment. Andersson *et al.* [55] for boreal river demonstrated that REE are transported mainly in particulate and colloidal phases. The colloids concentration and size varied significantly with time. Before the spring flood, colloids were dominated by large Fe-colloids. During the spring flood, smaller carbon colloids dominated. Following the spring flood, colloidal concentrations decreased again, with smaller carbon colloids still dominating. During the spring flood, colloids were enriched in light REE. After the spring flood, the REE concentrations decreased and colloids exhibited a REE pattern similar to that of the local till. These changes are interpreted in terms of hydrological flow paths in soil and bedrock variation. For the Amazon rivers, organo-mineral colloids enriched in HREE in its major tributaries (Rios Negro and Solimoes) control REE patterns in the 0.2 μm fraction of the Amazon River after mixing [61].

In the mining area of Salsigne France, Heydon *et al.* [57] showed that REE patterns exhibited a MREE downward concavity (enrichment compared to the other REE) suggesting that colloidal OM control REE transport. The concomitant decrease in MREE enrichment and DOC concentration with cut-off size of membrane confirmed the association of REE with these colloids.

In an agricultural watershed, Dia *et al.* [42] showed interesting REE pattern variations in the soil solution and shallow groundwater along a topographic transect. In the colloidal DOC-poor domain at the hillslope, they observed REE patterns with a significant negative Ce anomaly, while in the bottom-up (colloidal DOC-rich domain) shallow groundwater, REE patterns did not display any Ce anomaly. To explain such REE pattern variation, these authors suggested mixing of both poor and rich-colloidal DOC groundwaters. However, Pourret *et al.* [47] observed the same REE pattern systematically, namely topography-related REE signatures, challenged this hypothesis. They explained that the organic colloids produced by redox condition fluctuations in response to the water table rise in wetlands control the REE speciation and the subsequent REE patterns. Therefore the decrease in amplitude of the Ce anomaly from top to bottom is the result of the Ce(III) binding by the organic colloids, which prevents further Ce(III) oxidation to Ce(IV) [62–65]. In addition, Pédrot *et al.* [46] demonstrated that the soil organic carbon (OC)/Fe ratio played an important role in the topographic REE patterns. For a low OC/Fe ratio, negative Ce anomaly is large in the soil solution, compared to high OC/Fe ratio for which REE are bound to organic colloids and Ce anomaly development is prevented. Permafrost thawing is another environmental process known to be a rich colloid and metal source. Dissolved organic carbon, Fe,

and Al are present in extremely high concentrations in melted ice from permafrost cores and are systematically associated with trace elements [34,58,66]. From samples collected in lakes and small ponds (Siberia, Russia), Pokrovsky et al. [34,67] observed a DOC increase concomitant with a decrease OM of low molecular weight (fraction <1 kDa) suggesting that metals and REE were bound to OM and coprecipitated (Fe, Al) colloids. Lim et al. [68] in permafrost peatlands (Siberia, Russia) observed that DOC, Fe, and Al concentrations were connected in the porewaters of the active layer and in peat ice, indicating that organic and organo-mineral colloids are the primary carriers of REE in the interstitial fluids of permafrost.

In estuaries, several authors provided evidence that increased ionic strength and salinity induce the flocculation of Fe-OM colloids (i.e. electrical double-layer screening) carrying HREE into sediments [37,39,60,69,70]. They observed that the decrease in the colloidal fraction is related to the coagulation of Fe-OM colloids at the beginning of the estuary mixing zone, leading to the replacement of the colloidal fraction by the truly soluble fraction. However, Goldstein & Jacobsen [71] showed that profiles of Fe and REE vs. salinity are not consistent with simple coagulation of Fe and REE-bearing colloids. They observed a linear relationship between REE^{3+} activity and pH, suggesting a simple ion-exchange model for REE removal.

Davranche et al. [72] incubated organic-rich wetland soil under anaerobic and aerobic conditions at pH 3 and 7. They demonstrated that REE patterns of the soil solutions under anaerobic and aerobic conditions at pH 7 exhibited a Middle REE (MREE) downward concavity, indicating the REE binding to colloidal OM. By contrast, at pH 3, the REE pattern exhibited a positive Eu anomaly due to the dissolution of soil feldspar. Davranche et al. [50] completed this study by soil incubation under oxic conditions at pH 7 to promote OM colloid release and anoxic incubation at pH 5 to promote only Fe-oxyhydroxide reductive dissolution. Although REE patterns exhibited a MREE downward concavity under oxic conditions at pH 7, under anoxic conditions at pH 5, the REE pattern displayed a continuous REE enrichment from La to Lu. Compared to REE patterns observed in the field, they concluded that soil OM colloids were the main source of REE in the wetland solution and that oxido-reduction controls the REE release as REE-OM colloids in response to the pH increase [65]. However, such results were challenged by Guénet et al. [73], who studied the fate of the REE-OM colloids when oxidation reoccurred in the reduced wetland soil. They showed that REE were redistributed in several size fractions. In the highest colloidal fraction (0.2 μm -30 kDa), REE were bound to organic colloids associated with Fe nano-oxides. In the <30 kDa fraction, REE were bound to Fe nano-oxides embedded in small

molecules of terrestrial and bacterial OM. The resulting REE pattern displayed high enrichment of the last five HREE, indicating their binding to carboxy-phosphate sites of bacterial OM [43,74,75]. The bacterial source of OM was confirmed by fluorescence and Py-GCMS analysis.

All these studies demonstrate that when organo-mineral colloids occur in natural water, the REE speciation is controlled by colloidal OM associated with Fe and Al species (adsorbed ions or colloids). They highlight that Fe-OM colloids, by controlling the REE speciation in natural water, also control REE transfer. This transfer depends on the Fe-OM colloids' ability to be transported relative to prevailing physicochemical conditions.

REE interactions with Fe-OM colloids

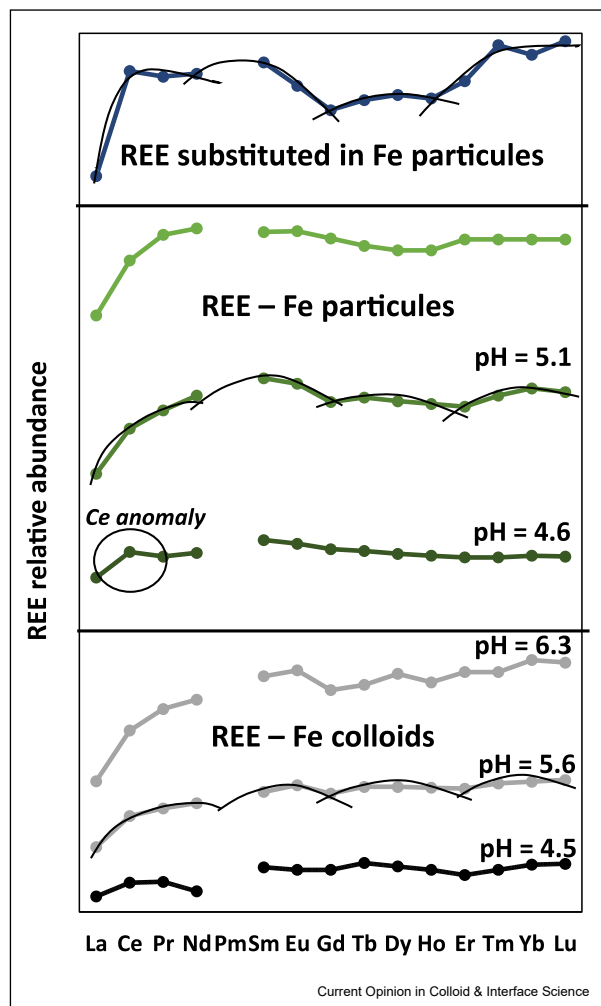
REE pattern developed onto organo-mineral colloid result from their adsorption onto the reactive binding sites occurring on their surface. Their type, density, and distribution mainly depend on crystallinity and hydration for mineral phases, and production mechanisms for organic phases [28]. Several parameters can, however, modify or even reverse REE patterns, such as REE loading and physicochemical conditions. Currently, only field data exist on REE patterns developed at the organo-mineral colloid's surface. No laboratory or modelling studies have described the REE distribution between mineral and organic phases constitutive of colloids. Therefore, in the following section, we consider mineral and organic colloids separately.

Mineral phases of organo-mineral colloids can be made of various minerals, mainly Fe or Al oxyhydroxides and clays. However, regarding literature, colloids composed of Fe and OM are the most highlighted. Moreover, REE affinity for Fe-oxyhydroxides is higher than for Al oxides or clays [76,77]. We therefore choose to focus only on REE binding to Fe colloids and oxyhydroxides in the following section.

Mechanisms of REE binding onto Fe-colloids

Liu et al. [70] demonstrated that Fe hydroxide colloids adsorb more HREE than LREE (Figure 2). This adsorption is pH-dependent, demonstrating that REE are bound to the OH^- groups on the colloidal Fe oxyhydroxides surface. At low pH, REE distribution coefficient patterns exhibit a pronounced M-Type REE tetrad effect and enrichment of HREE compared to other REE. Although no other laboratory studies specifically focused on REE binding to Fe colloids, the REE pattern described by Liu et al. [70] is similar to those developed on particulate Fe oxyhydroxides phases [24,79,80] (Figure 2). To gain a more detailed understanding of REE binding mechanisms by Fe colloids, we used literature focused on particulate Fe oxyhydroxides. According to modelling calculations by H. Liu et al.

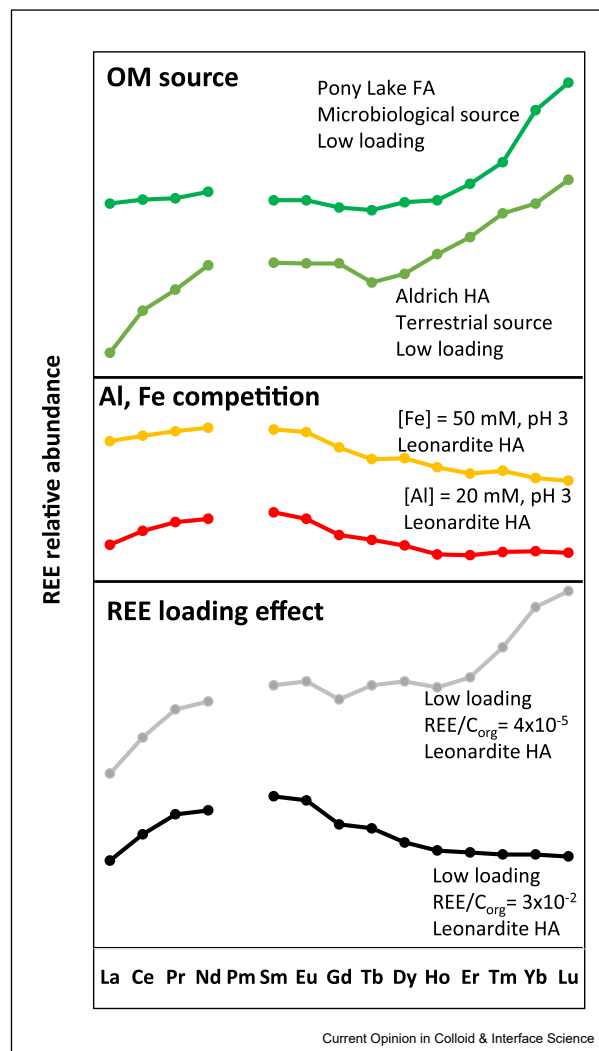
Figure 2



Variation of the REE patterns relative to the pH for REE adsorbed onto Fe-colloids ($<1 \mu\text{m}$) [78], onto particulate Fe oxyhydroxides ($>1 \mu\text{m}$) [24] or as substituted in particulate Fe-oxyhydroxide [83], REE tetrad effect is highlighted by the black curves.

[80], REE adsorption onto Fe oxyhydroxides follows the order of HREE $>$ MREE $>$ LREE. At low pH, HREE adsorption becomes dominant, with REE binding as both strong and weak complexes on Fe-oxyhydroxides surface. HREE enrichment can be progressively suppressed by the increasing carbonate concentration [26,81]. The same M-Type tetrad effect and HREE enrichment were observed for schwermanite [82]. REE can also be substituted in the Fe oxyhydroxide structure. Yang *et al.* [83] determined a substitution of REE in ferrihydrite as high as $\sim 550 \text{ mg kg}^{-1}$ (Figure 2). They also demonstrated that HREE are more prone to substitution than LREE and MREE, and this substitution is so significant to stabilize the Fe oxyhydroxide as ferrihydrite. Whether REE are substituted or adsorbed onto Fe oxyhydroxides surface sites, a positive Ce anomaly

Figure 3



Variation of the REE pattern for REE adsorbed onto organic-colloids (FA: fulvic acid, HA: humic acid) relative to the REE loading [52,74], to the major ion competition [88,89] and to the OM sources [90].

may appear on the REE pattern (Figure 2). This anomaly corresponds to surface precipitation of CeO_2 or preferential adsorption of Ce(VI) , the only REE capable of oxidizing in surface conditions [24,79,84,85]. Cerium(VI) oxidation can be driven by the Fe oxide oxidative surface or by adsorption at the Fe oxyhydroxides surface, decreasing the standard potential of the Ce(III/IV) [84,85].

Mechanism of REE binding to organic colloids

Pourret *et al.* [25] studied the binding of REE to colloidal OM (humic acid, HA) by combining ultrafiltration and ICPMS analysis. The amount of REE bound to OM colloid increased strongly with rising pH. Moreover, a MREE downward concavity was developed

on REE patterns at acidic pH (Figure 3). Modelling of the experimental dataset with Model VI and VII provided a set of $\log K_{MA}$ (i.e., the REE–HA stability constants specific to Model VI and VII) for the entire REE series [25,86]. $\log K_{MA}$ values reproduced the MREE downward concavity. The hypothesis of PHREEQC/MODEL VI and VII provided evidence that REE were mainly bound as bidentate complexes to COOH sites on colloidal OM. However, Sonke and Salters [54] and Sonke [87] in similar studies of REE binding to colloidal OM (humic acid as well), obtained a different pattern, and exhibited a continuous increase from La to Lu. The major difference between both studies was the REE loading onto OM colloids. To test the hypothesis of the impact of REE loading, Marsac et al. [52] performed REE–HA binding experiments relative to REE concentrations (REE/C molar ratios ranging from 4×10^{-4} to 2.7×10^{-2}) (Figure 3). At high REE loading, a MREE downward concavity developed, which progressively decreased with decreasing REE loading at the expense of a HREE enrichment (Figure 3). Experimental datasets modelling demonstrated that REE pattern variations with REE loading arise because REE binding to OM-colloids occurs through two binding sites in different densities: (i) at low REE loading, a few strong sites that preferentially complex HREE and form multidentate complexes, and (ii) at high REE loading, a larger amount of weak binding sites (–COOH) that preferentially form bidentate complexes with MREE. This modelling hypothesis and the various complexes formed relative to REE loading were later confirmed through X-ray absorption spectroscopy (EXAFS) by Marsac et al. [53]. Hence, REE loading exerts a major effect on REE binding with OM-colloids, which could explain the diversity of REE patterns in natural rich organic matter.

The source of OM can also control the REE pattern at the surface of organic colloids. Catrouillet et al. [90] investigated the potential of REE as tracers of organic colloid's sources using three different colloidal OM with terrestrial and microbiological origins. For Leonardite humic acid (LHA) and Aldrich humic acid (AHA), the REE patterns in the <10 kDa fraction were consistent with REE binding to strong but low-density sites at low REE loading. In contrast, Pony Lake fulvic acid (PLFA) exhibited a strong HREE enrichment similar to patterns obtained at the surface of bacteria cells [75]. Fluorescence and Py-GC–Ms analyses showed that the <10 kDa fraction was the fraction with the stronger microbiological character suggesting that REE were bound to PLFA through REE–phosphate complexes as onto the bacteria cells surface [75,90,91].

The REE pattern at the surface of organic colloids is also controlled by competition with major ions. Pourret et al. [92] studied the competition between colloidal HA and carbonates for REE binding at various pH and alkalinity.

They showed that the REE occur as binary humate or carbonate complexes but not as ternary REE–carbonate–humate as previously proposed. They also revealed the strong pH and alkalinity dependence of the mechanism resulted in a systematic fractionation across the REE series. Specifically, carbonate complexation is at a maximum at pH 10 and increases with the increasing alkalinity and atomic number of REE ($\text{LuCO}_3 \gg \text{LaCO}_3$). Marsac et al. [88] investigated the competition between REE and Al for binding to colloidal OM. Their results indicated that Al^{3+} competes more efficiently with HREE than with LREE at acidic pH (pH = 3) and low REE/HA ratios, providing evidence for the high affinity of Al for the few HA multidentate sites. At pH 5 to 6 and for high REE/C ratios, Al was more competitive for LREE, suggesting that Al is bound to HA carboxylic rather than phenolic sites. Under circumneutral pH conditions, such as in natural waters, Al is expected to lead to LREE-depleted patterns onto organic colloids. Marsac et al. [89] also tested the competitive effect of Fe(III) on the REE binding to organic colloids. At acidic pH, Fe^{3+} strongly competes with HREE for their binding to the few but strong multidentate sites of the colloidal OM. By contrast at pH 6, hydrolyzed Fe species compete equally with all REE, thereby demonstrating that LREE and HREE have the same affinity for carboxylic and phenolic sites as Fe. These studies suggest that major cations can compete with REE for their binding to organic colloids. Marsac et al. [78] using PHREEQC–Model VII tested the effects of divalent ions, specifically Cu^{2+} and Ca^{2+} , on REE binding to organic colloids. Cu is not able to compete with REE. Because Ca binds weakly to strong sites, they have a smaller competitive effect on HREE than on LREE.

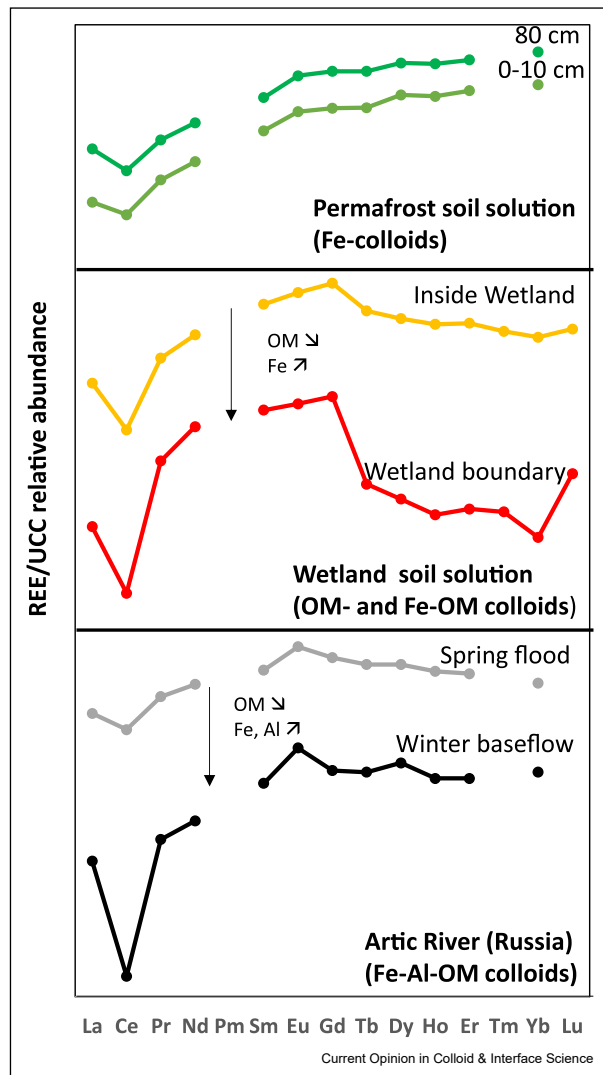
Thus, the REE pattern, speciation, and subsequent mobility and transfer are strongly controlled by: 1) organic colloid's sources and surface properties, and 2) the presence of competing ions, which impact REE pattern depending on their affinity for the strong or weak sites of the organic colloids. However, the primary driving factor remains pH, which controls organic colloid formation in response to redox fluctuation, the REE loading, and the solubility of competitive cations.

As previously explained, there are currently no experimental datasets detailing REE distribution and controlling binding phases in composite Fe–OM colloids. However, the comparison of REE patterns from natural colloids with experimental pattern on each Fe and OM colloid could provide some information and valuable insights into these interactions.

REE pattern in natural Fe–OM colloids

In this section, patterns of REE expected to be bound to natural OM/Fe and Fe–OM colloids were compared and discussed. For this purpose, we have selected studies

Figure 4



REE-natural colloids patterns normalized to upper continental crust (UCC) for permafrost soil solutions collected at 80 and 0–10 cm [35], for wetland soil solution relative to the location in the wetland [42,46,47] and in Arctic river relative to the season [36].

from contrasting organic and Fe-rich waters under various sources and pedo-climatic conditions. References from the early 2000s are considered pertinent for this discussion, as they provide Fe and DOC concentrations as well as colloidal fractions.

For Arctic River (Siberia, Russia), Pokrovsky *et al.* [37] observed that around 75% of the REE was with large-size colloids (10 kDa–0.22 μm) (Figure 4). In the spring period, LREE and HREE were in quite similar amount with La/Yb ratio = 0.9 ($\text{La/Yb} < 1$, HREE enrichment). In the winter, this ratio decreased to 0.77 in response to an increase in HREE. From spring to winter, the DOC concentration decreased from

15 mg L^{-1} to 5 mg L^{-1} , and its proportion in large colloids dropped from 75 to 40%. In the spring flood, no significant Ce anomaly was developed with $\text{Ce/Ce}^* = 0.93$ while a negative Ce anomaly occurred in the winter period with $\text{Ce/Ce}^* = 0.68$ ($\text{Ce/Ce}^* = 2\text{Ce}/(\text{La} + \text{Pr})$, $\text{Ce/Ce}^* < 1$, negative Ce anomaly). Pokrovsky *et al.* [36] explained that the Ce anomaly was due to high concentration of dissolved and particulate Fe. In the spring flood period, REE concentration was higher than in winter, the colloids were enriched in OM, the HREE concentration decreased and the Ce anomaly was quite less significant. All these observations demonstrated that soil flooding produced OM colloids that were then mixed with the colloidal fraction of the river (colloids of the winter period). REE were therefore bound to more mineral Fe-colloids in winter and to OM-enriched colloids in spring. The source of colloids and their mixing thus control the REE speciation and mobility. However, is the resulting REE pattern only due to colloids mixing or is it influenced by a structural rearrangement of the colloids between both periods?

From inside to the boundary of a wetland (Brittany, France), Dia *et al.* Poret *et al.* and Pédrot *et al.* [42,46,47] showed that OM concentration in the colloidal fraction decreased while Fe concentration increased. These variations were concomitant with an increase of HREE as showed by the La/Yb ratio ($\text{La/Yb} = 0.87$ and 1.03 from inside to the boundary, respectively) and an increase of the MREE downward concavity as showed by the La/Sm ratio ($\text{La/Sm} = 0.79$ and 0.71 from the inside to the boundary, respectively; $\text{La/Sm} < \text{MREE}$ enrichment) (Figure 4). However, this variation was not due to a HREE or a MREE increase but rather to a La decrease. The Pr/Yb ratio (indicating HREE enrichment) and Pr/Sm ratio (indicating MREE downward concavity) varied indeed inversely from 0.94 to 1.18 and from 0.87 to 0.92, respectively. Both ratio variations indicated an insignificant HREE enrichment but a more pronounced MREE downward concavity inside the wetland. This La depletion generally occurs when REE are bound to Fe colloids or particles, as shown in Figure 2. This observation is supported by the negative Ce anomaly, whose calculation provided the same value, with $\text{Ce/Ce}^* = 0.86$, inside and in the boundary of the wetland. All these observations demonstrate that inside wetlands, REE were mainly bound to OM colloids, although the occurrence of Fe-colloids at the boundary modified the REE pattern. However, as previously questioned, does the REE pattern correspond to only colloids mixing or a structural re-arrangement of colloids and subsequent binding properties modification due to the Fe phases increase inside the colloids?

In a permafrost soil solution [35], the REE patterns exhibited the same REE distribution at the surface and in the deep layer of the permafrost (Figure 4). The Ce

anomaly had a consistent size, with $Ce/Ce^* = 0.87$. A quite similar HREE enrichment with La/Yb varying from 0.71 to 0.75 was also observed from the surface to the deep soil. The authors attributed the HREE enrichment to the basalt bedrock and explained the Ce anomaly as a result of Ce oxidation during REE coprecipitation/adsorption onto Fe hydroxides. However, they determined a high concentration of DOC in the permafrost soil solution ranging from 20 to 30 mg L⁻¹. Additionally, they observed HREE enrichment in the REE pattern of the soil larch litter. However, because no direct correlation was observed between REE and OM, they ruled out that REE could be linked to organic colloids. Nevertheless, this hypothesis could not be excluded. The pattern could correspond to a low-loading REE pattern onto OM colloids, as suggested by Marsac et al. [52] (Figure 3).

Field studies revealed some uncertainties regarding the distribution of REE among the different phases that constitute the colloidal pool. It raises the question of whether REE patterns result from the mixing of colloids from various sources and components or from a rearrangement of the colloidal pool due to changes in hydrologic and physicochemical conditions. Generally, the colloidal pool is not described as a simple mixture of various colloids but rather as a complex system in which Fe and OM are strictly entangled [93–95].

What we know about the Fe-OM colloid structural organization and reactivity

Comparisons between experimental and natural REE patterns onto Fe-OM colloids have highlighted how the structural organization and evolution of colloids affect the REE distribution between the OM and Fe phases, with implications for resulting REE patterns.

In natural OM, the most reactive colloidal fraction regarding chemical elements is typically the colloidal humic substances, though this terminology should be considered operational. Colloidal humic substance structure can exist in two forms: (i) macromolecular polyelectrolytes that can form molecular aggregates [96], and (ii) supramolecular assemblies (molecular aggregates) of small molecules without macromolecular character, joined together by weak attraction forces [97]. Pédrot et al. [98], who support the idea of supramolecular assemblies, provided evidence that the REE distribution varied with the HA structural destabilization depending on pH. As pH decreased, humic associations were destabilized, leading to an enrichment in organic small molecules in the fraction <3 kDa, as highlighted by an increase of REE concentrations but without any REE pattern variation. These variations were interpreted as disruption of the supramolecular assemblies. While no REE pattern modifications were observed, the solubilization of small organic molecules

will therefore enhance the mobility of REE and their subsequent transfer in environmental systems.

A significant portion of the studies included in this research demonstrated that OM colloid are associated with Fe and Al phases [35,43,58,66]. To understand this structural arrangement of OM, Al, and Fe phases, and particularly Fe-OM colloids, several authors have conducted experimental investigations [99–102]. They demonstrated that Fe phases have a fractal organization, with small Fe nanobeads (or oligomers) that aggregate as Fe primary aggregates (Fe NPs). These primary aggregates can further aggregate as larger Fe secondary aggregates, forming associations of Fe nano-oxides. Iron nanobeads (or oligomers), primary and secondary aggregates coexist within the heterogeneous colloid system. The primary aggregate (~6 nm) growth is controlled by the adsorption of organic molecules, while secondary aggregates are associated to a large OM colloid (~700 nm) [102]. The addition of Ca and Al leads to the opening of the colloid structure, in which Ca acts as dimer that bridges between organic molecules, while Al acts as oligomers that bridge between all OM and Fe phases. Both elements contribute to the formation of a large network, where OM molecules are interconnected by Ca, and both Fe and OM phases are interconnected by Al [99,100]. The impact of the structural organization of Fe-OM colloids was evaluated with arsenic (As). X-ray absorption analysis (XAS) demonstrated that As was exclusively bound to Fe phases [102]. The quantity of adsorbed As depended on the density of available sites, which was not controlled by the specific surface area of Fe NPs. Instead, it was governed by the Fe concentration and the degree of interaction between Fe and OM. These factors affected both the number and size of Fe NPs. When Fe NPs had reduced interaction with OM, due to either increased NP size or the global structure opening (Ca and Al connection between colloid phases), the density of available sites increased, leading to a greater amount of adsorbed As. Unlike As, which is an anion, REE are primarily cations. REE can bind to both Fe and OM phases in these mixed colloids, which complicates their binding dynamics compared to As. Unfortunately, no data currently exist for REE, although such data are crucial to understanding REE mobility/transfer between environmental compartments. The fate, mobility, and transfer of REE will be contingent on the nature of their binding—whether to OM, Fe, or both—highlighting the importance of further research in this area.

Conclusion, outlook, and recommendations

REE are increasingly becoming a major environmental concern due to their growing use in human activities and their subsequent release into the environment. However, our understanding of the parameters expected to control their transfer between the various environmental

compartment, which is crucial for determining the REE exposome, remains limited. An extensive review of a large literature database demonstrated that transfer of REE in the environment is mainly controlled by colloids and notably by Fe-OM colloids. The affinity of REE for these peculiar colloids is partly explained by their affinity to the organic molecules (even at low concentration $\leq 1 \text{ mg L}^{-1}$ in water) and Fe phases. This behaviour is a consequence of the ability of REE to form strong complexes, including bidentate complexes with the OH-site for Fe phases, and bidentate and chelate with the carboxylic and phenolic groups of OM. Literature on single organic colloids demonstrated that REE fractionation depends on factors such as the adsorbed REE loading, the OM sources, the resulting type and density of the chemical surface group, and the presence of competitive ions. For single Fe colloids, REE fractionation is mainly controlled by pH, the adsorbed REE loading, and the presence of inorganic ligands (ex. carbonate). However, the size of the particle (whether colloidal or particulate) does not influence the REE pattern. Unfortunately, no information exists for Fe-OM colloids, which are the most encountered in the environment. Studies of the REE patterns of natural Fe-OM colloids in various pedoclimatic contexts demonstrated that the REE patterns were mainly ascribed to the mixing of various sources of OM colloids with Fe-colloids. However, several authors have recently demonstrated that the structural organization of the Fe-OM colloids is complex, involving oligomer and Fe-nano-oxides that are more or less associated with organic molecules, with the majority being linked to OM colloid. Moreover, this structural organization is modified in the presence of major ions. The reviewed studies also demonstrated that this structure and its dynamic control the ability of Fe-OM colloids to bind metalloid and their subsequent distribution between Fe and OM phases. The review has therefore identified several gaps in our understanding, suggesting the need for further research and making the following recommendations based on the current state of knowledge for future studies.

- It is imperative to determine how REE are distributed among the different Fe and OM phases within these colloids. Since the structure of Fe-OM colloids is dynamic and affects their reactivity, identifying the main phases that carry REE within the colloids is crucial for anticipating their mobility and subsequent environmental transfer.
- It is essential not only to quantify the concentration of the OM but also to characterize its sources and therefore the type of chemical groups developed at this surface. Understanding the stability of the formed REE-OM complexes is crucial. This is particularly important in regions known as producers of colloids (such as wetland, dust storm, permafrost thawing, etc.).
- While bedrock and OM sources control the occurrence of Fe and OM colloids as well as the reactive surface group, prevailing physicochemical conditions control the structural arrangement between Fe and OM phases and their subsequent reactivity against chemical elements. More information is needed about the parameters that control the Fe-OM structure. Experimental studies are required, but they have to be completed by more detailed characterization (beyond size fractions) of colloids produced under environmental conditions and collected in the field.
- Colloids mixing was advanced to explain the REE pattern variation. However, during mixing, physicochemical conditions vary, and OM- and Fe-colloids are modified or can be rearranged. Understanding the structure and properties of colloids resulting from mixing is thus requisite to anticipate their reactivity regards REE and more generally chemical elements.
- Progress in sampling and analytical techniques is essential for accurately determining environmental REE concentrations and to be able to conduct further studies. Collecting a sufficient quantity of colloids without modifying their properties while allowing the determination of low REE concentration remains a challenge. The latest generation of ICP-MS, such as QQQ-ICP-MS or HR-ICP-MS equipped with a collision chamber, now allows for lower REE detection limits and could therefore be a solution. To circumvent the colloid sampling issue, several authors have synthesized Fe-OM colloids representative of those observed in the field [99,101,102]. With this protocol, enough amount is produced allowing REE measurement and the study of the impact of physicochemical parameters. For heterogeneous Fe-OM colloids, the challenge lies in determining the REE distribution between the Fe and OM phases. Coupling high-sensitivity and selective analytical techniques is now available for the accurate determination of the REE distribution. These techniques involve size fraction on the colloids and determining the co-occurrence of REE, Fe and OM. Asymmetric flow field fractionation (A4F) equipped with UV and multiple-angle light scattering (MALS) detectors, and coupled with a QQQ-ICP-MS is an example of such techniques [103,104].
- To understand the control exerted by Fe-OM colloids on REE speciation and mobility, and to establish the REE exposome, all eco-toxicological studies must be performed using Fe-OM colloid. This is essential for estimating the actual impact that REE could have on living organisms, trophic webs, communities, and ecosystems.

Funding

This project has received funding from the European Union Horizon 2020 research and innovation program

under the Marie Skłodowska-Curie Grant Agreement N°857989.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Melanie Davranche reports financial support was provided by European Commission.

Data availability

Data will be made available on request.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

** of outstanding interest

- Mclennan SM: *Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes*. 1989.
 - Balaram V: **Rare earth elements: a review of applications, occurrence, exploration, analysis, recycling, and environmental impact**. *Geosci Front* 2019, **10**:1285–1303, <https://doi.org/10.1016/j.gsf.2018.12.005>.
 - Hedrick G: *Towards mining rare earth elements on the moon*. *IEEE Aerosp. Conf.*, **2023**; 2023:1–11, <https://doi.org/10.1109/AERO55745.2023.10116027>.
 - Hu Z, Richter H, Sparovek G, Schnug E: **Physiological and biochemical effects of rare earth elements on plants and their agricultural significance: a review**. *J Plant Nutr* 2004, **27**: 183–220.
 - Tao Y, Shen L, Feng C, Qu J, Ju H, Yang R, *et al.*: **Distribution of rare earth elements (REEs) and their roles in plants growth: a review**. *Environ Pollut* 2021, 118540.
 - Wen B, Yuan D, Shan X, Li F, Zhang S: **The influence of rare earth element fertilizer application on the distribution and bioaccumulation of rare earth elements in plants under field conditions**. *Chem Speciat Bioavailab* 2001, **13**: 39–48.
 - Zhuang M, Zhao J, Li S, Liu D, Wang K, Xiao P, *et al.*: **Concentrations and health risk assessment of rare earth elements in vegetables from mining area in Shandong, China**. *Chemosphere* 2017, **168**:578–582, <https://doi.org/10.1016/j.chemosphere.2016.11.023>.
 - Bau M, Knappe A, Dulski P: **Anthropogenic gadolinium as a micropollutant in river waters in Pennsylvania and in Lake Erie, northeastern United States**. *Geochemistry* 2006, **66**:143–152, <https://doi.org/10.1016/j.chemer.2006.01.002>.
 - Kulaksöz S, Bau M: **Contrasting behaviour of anthropogenic gadolinium and natural rare earth elements in estuaries and the gadolinium input into the North Sea**. *Earth Planet Sci Lett* 2007, **260**:361–371.
 - Kulaksöz S, Bau M: **Rare earth elements in the Rhine River, Germany: first case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere**. *Environ Int* 2011, **37**:973–979, <https://doi.org/10.1016/j.envint.2011.02.018>.
 - Abdelnour SA, Abd El-Hack ME, Khafaga AF, Noreldin AE, Arif M, Chaudhry MT, *et al.*: **Impacts of rare earth elements on animal health and production: highlights of cerium and lanthanum**. *Sci Total Environ* 2019, **672**:1021–1032.
 - Miao L, Xu R, Ma Y, Zhu Z, Wang J, Cai R, *et al.*: **Geochemistry and biogeochemistry of rare earth elements in a surface environment (soil and plant) in South China**. *Environ Geol* 2008, **56**:225–235.
 - Li X, Chen Z, Chen Z, Zhang Y: **A human health risk assessment of rare earth elements in soil and vegetables from a mining area in Fujian Province, Southeast China**. *Chemosphere* 2013, **93**:1240–1246.
 - Abbasi S, Rezaei M, Keshavarzi B, Mina M, Ritsema C, Geissen V: **Investigation of the 2018 Shiraz dust event: potential sources of metals, rare earth elements, and radionuclides; health assessment**. *Chemosphere* 2021, **279**, 130533, <https://doi.org/10.1016/j.chemosphere.2021.130533>.
 - Gwenzi W, Mangori L, Danha C, Chaukura N, Dunjana N, Sanganyado E: **Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants**. *Sci Total Environ* 2018, **636**:299–313.
 - Sordello F, Berruti I, Gionco C, Paganini MC, Calza P, Minero C: **Photocatalytic performances of rare earth element-doped zinc oxide toward pollutant abatement in water and wastewater**. *Appl Catal B Environ* 2019, **245**:159–166.
 - Yang Q, Cheng M, Zhou Q, Wang L, Jiao Y, Liu Y, *et al.*: **Sharply and simultaneously increasing pollutant accumulations in cells of organisms induced by rare earth elements in the environment of Nanjing**. *Chemosphere* 2023, **311**, 136823.
 - Viana LN, Soares APS, Guimarães DL, Rojano WJS, Saint-Pierre TD: **Fluorescent lamps: a review on environmental concerns and current recycling perspectives highlighting Hg and rare earth elements**. *J Environ Chem Eng* 2022, **10**, 108915, <https://doi.org/10.1016/j.jece.2022.108915>.
 - Burlakovs J, Jani Y, Kriipsalu M, Vincevica-Gaile Z, Kaczala F, Celma G, *et al.*: **On the way to 'zero waste' management: recovery potential of elements, including rare earth elements, from fine fraction of waste**. *J Clean Prod* 2018, **186**:81–90.
 - Gutiérrez-Gutiérrez SC, Coulon F, Jiang Y, Wagland S: **Rare earth elements and critical metal content of extracted land-filled material and potential recovery opportunities**. *Waste Manag* 2015, **42**:128–136.
 - Jowitt SM, Medlin CC, Cas RA: **The Rare Earth Element (REE) mineralisation potential of highly fractionated rhyolites: a potential low-grade, bulk tonnage source of critical metals**. *Ore Geol Rev* 2017, **86**:548–562.
 - Jowitt SM, Werner TT, Weng Z, Mudd GM: **Recycling of the rare earth elements**. *Reuse Recycl UN SGDs Can Sustain Chem Contrib Green Chem Educ* 2018, **13**:1–7, <https://doi.org/10.1016/j.cogsc.2018.02.008>.
 - Mudd G, Jowitt S: **Rare earth elements from heavy mineral sands: assessing the potential of a forgotten resource**. *B Appl Earth Sci* 2016, **125**:107–113.
 - Bau M: **Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect**. *Geochem Cosmochim Acta* 1999, **63**:67–77, [https://doi.org/10.1016/S0016-7037\(99\)00014-9](https://doi.org/10.1016/S0016-7037(99)00014-9).
 - Pourret O, Davranche M, Gruau G, Dia A: **Rare earth elements complexation with humic acid**. *Chem Geol* 2007, **243**: 128–141.
- Paper explaining the sorption mechanism at the surface of OM colloids.
- Quinn KA, Byrne RH, Schijf J: **Sorption of yttrium and rare earth elements by amorphous ferric hydroxide: influence of solution complexation with carbonate**. *Geochem Cosmochim Acta* 2006, **70**:4151–4165, <https://doi.org/10.1016/j.gca.2006.06.014>.
 - Schijf J, Marshall KS: **YREE sorption on hydrous ferric oxide in 0.5M NaCl solutions: a model extension**. *Mar Chem* 2011, **123**: 32–43, <https://doi.org/10.1016/j.marchem.2010.09.003>.
 - Stumm W, Morgan JJ: *Aquatic Chemistry: chemical equilibria and rates in natural waters*. John Wiley & Sons; 2012.
 - Buffle J, Leppard GG: **Characterization of aquatic colloids and macromolecules. 2. Key role of physical structures on analytical results**. *Environ Sci Technol* 1995, **29**:2176–2184, <https://doi.org/10.1021/es00009a005>.
- Founding paper of the presence of colloids in surface waters.

30. Brito P, Caetano M, Martins MD, Caçador I: **Effects of salt marsh plants on mobility and bioavailability of REE in estuarine sediments.** *Sci Total Environ* 2021, **759**, <https://doi.org/10.1016/j.scitotenv.2020.144314>.
31. Han G, Liu M, Li X, Zhang Q: **Sources and geochemical behaviors of rare earth elements in suspended particulate matter in a wet-dry tropical river.** *Environ Res* 2023, **218**, 115044, <https://doi.org/10.1016/j.envres.2022.115044>.
32. Traore M, He Y, Wang Y, Gong A, Qiu L, Bai Y, *et al.*: **Research progress on the content and distribution of rare earth elements in rivers and lakes in China.** *Mar Pollut Bull* 2023, **191**, 114916, <https://doi.org/10.1016/j.marpolbul.2023.114916>.
33. Dupré B, Viers J, Dandurand J-L, Polve M, Bénézech P, Vervier P, *et al.*: **Major and trace elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solutions.** *Chem Geol* 1999, **160**:63–80, [https://doi.org/10.1016/S0009-2541\(99\)00060-1](https://doi.org/10.1016/S0009-2541(99)00060-1).
- One of the first papers to use ultrafiltration to study colloid-metal associations directly in the field.
34. Pokrovsky O, Shirokova L, Kirpotin S, Audry S, Viers J, Dupré B: **Effect of permafrost thawing on organic carbon and trace element colloidal speciation in the thermokarst lakes of western Siberia.** *Biogeosciences* 2011, **8**:565–583.
35. Pokrovsky OS, Schott J, Dupré B: **Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basaltic terrain in Central Siberia.** *Geochem Cosmochim Acta* 2006, **70**:3239–3260, <https://doi.org/10.1016/j.gca.2006.04.008>.
36. Pokrovsky OS, Viers J, Shirokova LS, Shevchenko VP, Filipov AS, Dupré B: **Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary.** *Chem Geol* 2010, **273**:136–149, <https://doi.org/10.1016/j.chemgeo.2010.02.018>.
37. Pokrovsky OS, Viers J, Dupré B, Chabaux F, Gaillardet J, Audry S, *et al.*: **Biogeochemistry of carbon, major and trace elements in watersheds of northern Eurasia drained to the Arctic Ocean: the change of fluxes, sources and mechanisms under the climate warming prospective.** *Compt Rendus Geosci* 2012, **344**:663–677, <https://doi.org/10.1016/j.crte.2012.08.003>.
38. Sholkovitz ER: **Chemical evolution of rare earth elements: fractionation between colloidal and solution phases of filtered river water.** *Earth Planet Sci Lett* 1992, **114**:77–84, [https://doi.org/10.1016/0012-821X\(92\)90152-L](https://doi.org/10.1016/0012-821X(92)90152-L).
- First paper dedicated to the interaction between REE and natural colloids.
39. Sholkovitz ER: **The geochemistry of rare earth elements in the Amazon River estuary.** *Geochem Cosmochim Acta* 1993, **57**:2181–2190, [https://doi.org/10.1016/0016-7037\(93\)90559-F](https://doi.org/10.1016/0016-7037(93)90559-F).
40. Sholkovitz ER: **The aquatic chemistry of rare earth elements in rivers and estuaries.** *Aquat Geochem* 1995, **1**:1–34, <https://doi.org/10.1007/BF01025229>.
41. Pédrot M, Dia A, Davranche M, Bouhnik-Le Coz M, Henin O, Gruau G: **Insights into colloid-mediated trace element release at the soil/water interface.** *J Colloid Interface Sci* 2008, **325**:187–197, <https://doi.org/10.1016/j.jcis.2008.05.019>.
42. Dia A, Gruau G, Olivé-Lauquet G, Riou C, Molénat J, Curmi P: **The distribution of rare earth elements in groundwaters: assessing the role of source-rock composition, redox changes and colloidal particles.** *Geochem Cosmochim Acta* 2000, **64**:4131–4151, [https://doi.org/10.1016/S0016-7037\(00\)00494-4](https://doi.org/10.1016/S0016-7037(00)00494-4).
43. Guénet H, Demangeat E, Davranche M, Vantelon D, Pierson-Wickmann A-C, Jardé E, *et al.*: **Experimental evidence of REE size fraction redistribution during redox variation in wetland soil.** *Sci Total Environ* 2018, **631–632**:580–588, <https://doi.org/10.1016/j.scitotenv.2018.03.005>.
44. Johannesson KH, Tang J, Daniels JM, Bounds WJ, Burdige DJ: **Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA.** *Chem Geol* 2004, **209**:271–294, <https://doi.org/10.1016/j.chemgeo.2004.06.012>.
45. Munemoto T, Ohmori K, Iwatsuki T: **Distribution of U and REE on colloids in granitic groundwater and quality-controlled sampling at the Mizunami underground research laboratory.** *Prog Earth Planet Sci* 2014, **1**, <https://doi.org/10.1186/s40645-014-0028-z>.
46. Pédrot M, Dia A, Davranche M, Gruau G: **Upper soil horizons control the rare earth element patterns in shallow groundwater.** *Geoderma* 2015, **239**:84–96.
47. Pourret O, Gruau G, Dia A, Davranche M, Molénat J: **Colloidal control on the distribution of rare earth elements in shallow groundwaters.** *Aquat Geochem* 2010, **16**:31–59.
48. Tang J, Johannesson KH: **Speciation of rare earth elements in natural terrestrial waters: assessing the role of dissolved organic matter from the modeling approach.** *Geochem Cosmochim Acta* 2003, **67**:2321–2339, [https://doi.org/10.1016/S0016-7037\(02\)01413-8](https://doi.org/10.1016/S0016-7037(02)01413-8).
49. Blancho F, Davranche M, Marsac R, Léon A, Dia A, Grassl B, *et al.*: **Metal-binding processes on nanoplastics: rare earth elements as probes.** *Environ Sci Nano* 2022, <https://doi.org/10.1039/D2EN00048B>.
50. Davranche M, Grybos M, Gruau G, Pédrot M, Dia A, Marsac R: **Rare earth element patterns: a tool for identifying trace metal sources during wetland soil reduction.** *Chem Geol* 2011, **284**:127–137.
51. Kautenburger R, Hein C, Sander JM, Beck HP: **Influence of metal loading and humic acid functional groups on the complexation behavior of trivalent lanthanides analyzed by CE-ICP-MS.** *Anal Chim Acta* 2014, **816**:50–59, <https://doi.org/10.1016/j.aca.2014.01.044>.
52. Marsac R, Davranche M, Gruau G, Dia A: **Metal loading effect on rare earth element binding to humic acid: experimental and modelling evidence.** *Geochem Cosmochim Acta* 2010, **74**:1749–1761, <https://doi.org/10.1016/j.gca.2009.12.006>.
53. Marsac R, Davranche M, Morin G, Takahashi Y, Gruau G, Briant N, *et al.*: **Effect of loading on the nature of the REE–humate complexes as determined by Yb³⁺ and Sm³⁺ LIII-edge EXAFS analysis.** *Chem Geol* 2015, **396**:218–227, <https://doi.org/10.1016/j.chemgeo.2014.12.024>.
- This paper demonstrated the impact of the REE loading on the REE speciation and pattern at the surface of OM colloids.
54. Sonke JE, Salters VJM: **Lanthanide–humic substances complexation. I. Experimental evidence for a lanthanide contraction effect.** *Geochem Cosmochim Acta* 2006, **70**:1495–1506, <https://doi.org/10.1016/j.gca.2005.11.017>.
55. Andersson K, Dahlgvist R, Turner D, Stolpe B, Larsson T, Ingri J, *et al.*: **Colloidal rare earth elements in a boreal river: changing sources and distributions during the spring flood.** *Geochem Cosmochim Acta* 2006, **70**:3261–3274, <https://doi.org/10.1016/j.gca.2006.04.021>.
56. Barroux G, Sonke JE, Boaventura G, Viers J, Godderis Y, Bonnet M-P, *et al.*: **Seasonal dissolved rare earth element dynamics of the Amazon River main stem, its tributaries, and the Curuai floodplain: REE dynamics of the Amazon River.** *Geochem Geophys Geosystems* 2006, **7**, <https://doi.org/10.1029/2006GC001244>. n/a-n/a.
57. Heydon M, Perez Serrano L, Schreck E, Causserand C, Pokrovsky OS, Behra P, *et al.*: **Role of colloids in the transfer and dispersion of trace elements into river waters through a former mining district.** *Appl Geochem* 2023, **155**, 105736, <https://doi.org/10.1016/j.apgeochem.2023.105736>.
58. Krickov IV, Pokrovsky OS, Manasyov RM, Lim AG, Shirokova LS, Viers J: **Colloidal transport of carbon and metals by western Siberian rivers during different seasons across a permafrost gradient.** *Geochem Cosmochim Acta* 2019, **265**:221–241.
59. Lafrenière M-C, Lapierre J-F, Ponton DE, Guillemette F, Amyot M: **Rare earth elements (REEs) behavior in a large river across a geological and anthropogenic gradient.** *Geochem Cosmochim Acta* 2023, **353**:129–141, <https://doi.org/10.1016/j.gca.2023.05.019>.

60. Hoyle J, Elderfield H, Gledhill A, Greaves M: **The behaviour of the rare earth elements during mixing of river and sea waters.** *Geochem Cosmochim Acta* 1984, **48**:143–149, [https://doi.org/10.1016/0016-7037\(84\)90356-9](https://doi.org/10.1016/0016-7037(84)90356-9).
61. Gerard M, Seyler P, Benedetti MF, Alves VP, Boaventura GR, Sondag F: **Rare earth elements in the Amazon basin.** *Hydrol Process* 2003, **17**:1379–1392, <https://doi.org/10.1002/hyp.1290>.
62. Davranche M, Pourret O, Gruau G, Dia A: **Impact of humate complexation on the adsorption of REE onto Fe oxyhydroxide.** *J Colloid Interface Sci* 2004, **277**:271–279, <https://doi.org/10.1016/j.jcis.2004.04.007>.
63. Davranche M, Pourret O, Gruau G, Dia A, Le Coz-Bouhnik M: **Adsorption of REE(III)-humate complexes onto MnO₂: experimental evidence for cerium anomaly and lanthanide tetrad effect suppression.** *Geochem Cosmochim Acta* 2005, **69**:4825–4835, <https://doi.org/10.1016/j.gca.2005.06.005>.
64. Davranche M, Gruau G, Dia A, Marsac R, Pédrot M, Pourret O: **Biogeochemical factors affecting rare earth element distribution in shallow wetland groundwater.** *Aquat Geochem* 2015, **21**:197–215, <https://doi.org/10.1007/s10498-014-9247-6>.
65. Grybos M, Davranche M, Gruau G, Petitjean P, Pédrot M: **Increasing pH drives organic matter solubilization from wetland soils under reducing conditions.** *Geoderma* 2009, **154**:13–19, <https://doi.org/10.1016/j.geoderma.2009.09.001>.
66. Pokrovsky OS, Manasypov RM, Loiko SV, Shirokova LS: **Organic and organo-mineral colloids in discontinuous permafrost zone.** *Geochem Cosmochim Acta* 2016, **188**:1–20.
67. Pokrovsky OS, Manasypov RM, Loiko SV, Shirokova LS: **Organic and organo-mineral colloids in discontinuous permafrost zone.** *Geochem Cosmochim Acta* 2016, **188**:1–20, <https://doi.org/10.1016/j.gca.2016.05.035>.
68. Lim AG, Loiko SV, Kuzmina DM, Krickov IV, Shirokova LS, Kulizhsky SP, et al.: **Dispersed ground ice of permafrost peatlands: potential unaccounted carbon, nutrient and metal sources.** *Chemosphere* 2021, **266**, 128953, <https://doi.org/10.1016/j.chemosphere.2020.128953>.
69. Åström ME, Österholm P, Gustafsson JP, Nystrand M, Peltola P, Nordmyr L, et al.: **Attenuation of rare earth elements in a boreal estuary.** *Geochem Cosmochim Acta* 2012, **96**:105–119, <https://doi.org/10.1016/j.gca.2012.08.004>.
70. Lecomte KL, Sarmiento AM, Borrego J, Nieto JM: **Rare earth elements mobility processes in an AMD-affected estuary: huelva Estuary (SW Spain).** *Mar Pollut Bull* 2017, **121**:282–291, <https://doi.org/10.1016/j.marpolbul.2017.06.030>.
71. Goldstein SJ, Jacobsen SB: **REE in the great whale river estuary, northwest quebec.** *Earth Planet Sci Lett* 1988, **88**:241–252, [https://doi.org/10.1016/0012-821X\(88\)90081-7](https://doi.org/10.1016/0012-821X(88)90081-7).
72. Davranche M, Grybos M, Gruau G, Pédrot M, Dia A: **Rare earth elements as a fingerprint of soil components solubilization.** 2009:7134.
73. Guénet H, Demangeat E, Davranche M, Vantelon D, Pierson-Wickmann A-C, Jardé E, et al.: **Experimental evidence of REE size fraction redistribution during redox variation in wetland soil.** *Sci Total Environ* 2018, **631–632**:580–588, <https://doi.org/10.1016/j.scitotenv.2018.03.005>.
74. Catrouillet C, Guenet H, Pierson-Wickmann A-C, Dia A, LeCoz MB, Deville S, et al.: **Rare earth elements as tracers of active colloidal organic matter composition.** *Environ Chem* 2020, **17**:133, <https://doi.org/10.1071/EN19159>.
- This paper demonstrated the role of the OM colloids sources on the type of surface reactive sites and subsequent REE pattern.
75. Takahashi Y, Yamamoto M, Yamamoto Y, Tanaka K: **EXAFS study on the cause of enrichment of heavy REEs on bacterial cell surfaces.** *Geochem Cosmochim Acta* 2010, **74**:5443–5462, <https://doi.org/10.1016/j.gca.2010.07.001>.
76. Aja SU: **The sorption of the rare earth element, nd, onto kaolinite at 25.** *Clays Clay Miner* 1998, **46**.
77. Gu Q, Liu J, Yang Y, Zhu R, Ma L, Liang X, et al.: **The different effects of sulfate on the adsorption of REEs on kaolinite and ferrihydrite.** *Appl Clay Sci* 2022, **221**, 106468, <https://doi.org/10.1016/j.clay.2022.106468>.
78. Liu C, Wu J, Yu W: **Controls of interactions between iron hydroxide colloid and water on REE fractionations in surface waters: experimental study on pH-controlling mechanism.** *Sci China Ser Earth Sci* 2002, **45**:449–458, <https://doi.org/10.1360/02yd9047>.
- Unique paper that provides the REE pattern developed at the surface of Fe-colloids relative to the pH.
79. Bau M: **Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect.** *Contrib Mineral Petrol* 1996, **123**:323–333, <https://doi.org/10.1007/s004100050159>.
80. Liu H, Pourret O, Guo H, Bonhoure J: **Rare earth elements sorption to iron oxyhydroxide: model development and application to groundwater.** *Appl Geochem* 2017, **87**:158–166, <https://doi.org/10.1016/j.apgeochem.2017.10.020>.
81. Koepfenkastro D, De Carlo EH: **Sorption of rare-earth elements from seawater onto synthetic mineral particles: an experimental approach.** *Chem Geol* 1992, **95**:251–263, [https://doi.org/10.1016/0009-2541\(92\)90015-W](https://doi.org/10.1016/0009-2541(92)90015-W).
82. Lozano A, Ayora C, Fernández-Martínez A: **Sorption of rare earth elements on schwertmannite and their mobility in acid mine drainage treatments.** *Appl Geochem* 2020, **113**, 104499, <https://doi.org/10.1016/j.apgeochem.2019.104499>.
83. Yang M, Liang X, Li Y, He H, Zhu R, Arai Y: **Ferrihydrite transformation impacted by adsorption and structural incorporation of rare earth elements.** *ACS Earth Space Chem* 2021, **5**:2768–2777, <https://doi.org/10.1021/acsearthspacechem.1c00159>.
84. Ohta A, Kawabe I: **REE(III) adsorption onto Mn dioxide (δ -MnO₂) and Fe oxyhydroxide: Ce(III) oxidation by δ -MnO₂.** *Geochem Cosmochim Acta* 2001, **65**:695–703, [https://doi.org/10.1016/S0016-7037\(00\)00578-0](https://doi.org/10.1016/S0016-7037(00)00578-0).
- The authors explained how a positive Ce anomaly can be form onto oxidative surface.
85. Ratié G, Zhang K, Iqbal M, Vantelon D, Mahé F, Rivard C, et al.: **Driving forces of Ce(III) oxidation to Ce(IV) onto goethite.** *Chem Geol* 2023, **633**, 121547, <https://doi.org/10.1016/j.chemgeo.2023.121547>.
86. Marsac R, Catrouillet C, Davranche M, Bouhnik-Le Coz M, Briant N, Janot N, et al.: **Modeling rare earth elements binding to humic acids with model VII.** *Chem Geol* 2021, **567**, 120099, <https://doi.org/10.1016/j.chemgeo.2021.120099>.
87. Sonke JE: **Lanthanide-Humic substances complexation. II. Calibration of humic ion-binding model V.** *Environ Sci Technol* 2006, **40**:7481–7487, <https://doi.org/10.1021/es060490g>.
88. Marsac R, Davranche M, Gruau G, Dia A, Bouhnik-Le Coz M: **Aluminium competitive effect on rare earth elements binding to humic acid.** *Geochem Cosmochim Acta* 2012, **89**:1–9.
89. Marsac R, Davranche M, Gruau G, Dia A, Pédrot M, Le Coz-Bouhnik M, et al.: **Effects of Fe competition on REE binding to humic acid: origin of REE pattern variability in organic waters.** *Chem Geol* 2013, **342**:119–127, <https://doi.org/10.1016/j.chemgeo.2013.01.020>.
90. Catrouillet C, Guenet H, Pierson-Wickmann A-C, Dia A, LeCoz MB, Deville S, et al.: **Rare earth elements as tracers of active colloidal organic matter composition.** *Environ Chem* 2019, **17**:133–139.
91. Takahashi Y, Hirata T, Shimizu H, Ozaki T, Fortin D: **A rare earth element signature of bacteria in natural waters?** *Chem Geol* 2007, **244**:569–583, <https://doi.org/10.1016/j.chemgeo.2007.07.005>.
92. Pourret O, Davranche M, Gruau G, Dia A: **Competition between humic acid and carbonates for rare earth elements complexation.** *J Colloid Interface Sci* 2007, **305**:25–31, <https://doi.org/10.1016/j.jcis.2006.09.020>.
93. Benedetti MF, Ranville JF, Allard T, Bednar AJ, Menguy N: **The iron status in colloidal matter from the Rio Negro, Brasil.** *Colloids Surf A Physicochem Eng Asp* 2003, **217**:1–9, [https://doi.org/10.1016/S0927-7757\(02\)00553-8](https://doi.org/10.1016/S0927-7757(02)00553-8).

94. Poggenburg C, Mikutta R, Sander M, Schippers A, Marchanka A, Dohrmann R, *et al.*: **Microbial reduction of ferrihydrite-organic matter coprecipitates by *Shewanella putrefaciens* and *Geobacter metallireducens* in comparison to mediated electrochemical reduction.** *Chem Geol* 2016, **447**:133–147, <https://doi.org/10.1016/j.chemgeo.2016.09.031>.
95. Rose J, Vilge A, Olivie-Lauquet G, Masion A, Frechou C, Bottero J-Y: **Iron speciation in natural organic matter colloids.** *Colloids Surf A Physicochem Eng Asp* 1998, **136**:11–19, [https://doi.org/10.1016/S0927-7757\(97\)00150-7](https://doi.org/10.1016/S0927-7757(97)00150-7).
96. Sutton R, Sposito G: **Molecular structure in soil humic substances: the new view.** *Environ Sci Technol* 2005, **39**: 9009–9015, <https://doi.org/10.1021/es050778q>.
97. Piccolo A: **The supramolecular structure of humic substances.** *Soil Sci* 2001, **166**:810.
98. Pédrot M, Dia A, Davranche M: **Dynamic structure of humic substances: rare earth elements as a fingerprint.** *J Colloid Interface Sci* 2010, **345**:206–213.
99. Beauvois A, Vantelon D, Jestin J, Rivard C, Bouhnik-Le Coz M, Dupont A, *et al.*: **How does calcium drive the structural organization of iron–organic matter aggregates? A multiscale investigation.** *Environ Sci Nano* 2020, **7**:2833–2849, <https://doi.org/10.1039/D0EN00412J>.
100. Beauvois A, Vantelon D, Jestin J, Dupont A, Briois V, Paineau E, *et al.*: **Aluminum-induced colloidal destabilization of iron-organic matter nanoaggregates.** *Geochem Cosmochim Acta* 2023, **344**:1–11, <https://doi.org/10.1016/j.gca.2023.01.005>.
101. Gentile L, Wang T, Tunlid A, Olsson U, Persson P: **Ferrihydrite nanoparticle aggregation induced by dissolved organic matter.** *J Phys Chem A* 2018, **122**:7730–7738, <https://doi.org/10.1021/acs.jpca.8b05622>.
102. Guénet H, Davranche M, Vantelon D, Gigault J, Prévost S, Taché O, *et al.*: **Characterization of iron–organic matter nano-aggregate networks through a combination of SAXS/SANS and XAS analyses: impact on as binding.** *Environ Sci Nano* 2017, **4**:938–954, <https://doi.org/10.1039/C6EN00589F>.
103. Gigault J, Pettibone JM, Schmitt C, Hackley VA: **Rational strategy for characterization of nanoscale particles by asymmetric-flow field flow fractionation: a tutorial.** *Anal Chim Acta* 2014, **809**:9–24, <https://doi.org/10.1016/j.aca.2013.11.021>.
104. Stolpe B, Guo L, Shiller AM: **Binding and transport of rare earth elements by organic and iron-rich nanocolloids in Alaskan rivers, as revealed by field-flow fractionation and ICP-MS.** *Geochem Cosmochim Acta* 2013, **106**:446–462, <https://doi.org/10.1016/j.gca.2012.12.033>.

This paper explained the impact of Ca on the structural organization of Fe-OM colloids.

this paper used for a first time FFF to study the interaction between metal and colloids with natural samples