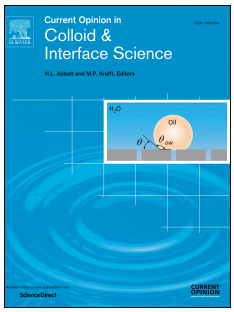
Equilibrium surface complexation modeling with metastable natural colloids: the key to predict the oxidation state distribution of trace elements?

Rémi Marsac, Charlotte Catrouillet, Mathieu Pédrot, Marc F Benedetti, Aline Dia, Eric D van Hullebusch, Mélanie Davranche, Yann Sivry, Anne-Catherine Pierson-Wickmann, Mickael Tharaud, et al.

Journal Pre-proof



Equilibrium surface complexation modeling with metastable natural colloids: the key to predict the oxidation state distribution of trace elements?

Rémi Marsac, Charlotte Catrouillet, Mathieu Pédrot, Marc F. Benedetti, Aline Dia, Eric D. van Hullebusch, Mélanie Davranche, Yann Sivry, Anne-Catherine Pierson-Wickmann, Mickael Tharaud, Frank Heberling

PII: S1359-0294(24)00038-4

DOI: https://doi.org/10.1016/j.cocis.2024.101820

Reference: COCIS 101820

To appear in: *Current Opinion in Colloid & Interface Science*

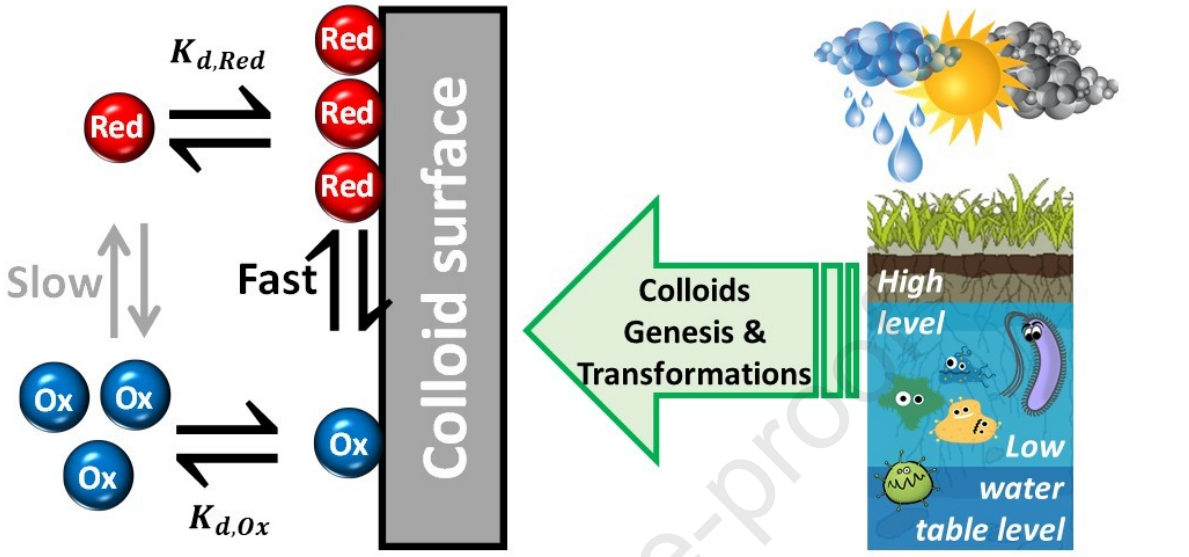
Received Date: 29 October 2023

Revised Date: 18 April 2024

Accepted Date: 4 June 2024

Please cite this article as: Marsac R, Catrouillet C, Pédrot M, Benedetti MF, Dia A, van Hullebusch ED, Davranche M, Sivry Y, Pierson-Wickmann A-C, Tharaud M, Heberling F, Equilibrium surface complexation modeling with metastable natural colloids: the key to predict the oxidation state distribution of trace elements?, *Current Opinion in Colloid & Interface Science*, https://doi.org/10.1016/j.cocis.2024.101820.

$$\frac{[Ox]_{aq}}{[Red]_{aq}} = \frac{[Ox]_{surf}}{[Red]_{surf}} \times \frac{K_{d,Ox}}{K_{d,Red}} = f(\text{Hydro/bio/ pedological and climatic conditions})$$



Equilibrium surface complexation modeling with metastable natural colloids: the key to predict the oxidation state distribution of trace elements?

Rémi Marsac[1,2]*, Charlotte Catrouillet[1], Mathieu Pédrot[2], Marc F. Benedetti[1], Aline Dia[2], Eric D. van Hullebusch[1], Mélanie Davranche[2], Yann Sivry[1], Anne-Catherine Pierson-Wickmann[2], Mickael Tharaud[1], Frank Heberling[3]

[1] Université Paris Cité, Institut de Physique du Globe de Paris, CNRS, F-75005 Paris, France

[2] Univ Rennes, CNRS, Géosciences Rennes - UMR 6118, F-35000, Rennes, France

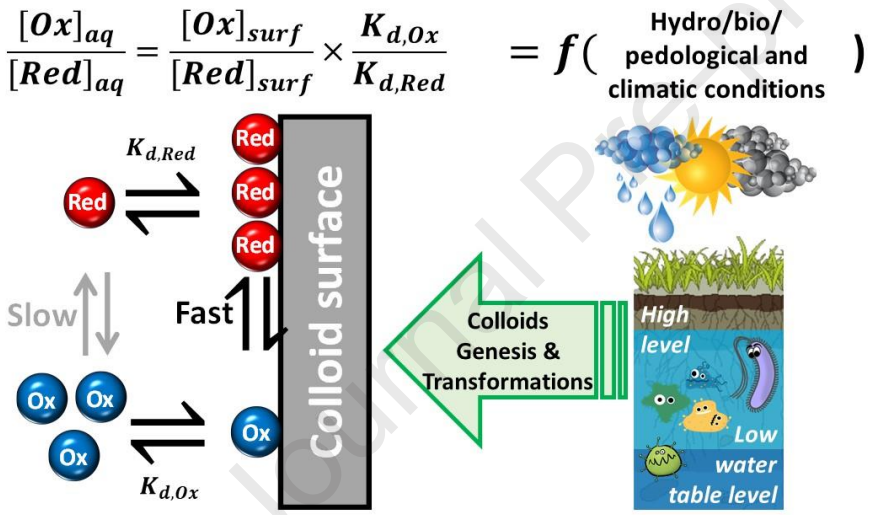
[3] Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany

* Corresponding author: remi.marsac@cnrs.fr

Abstract

Predicting the behavior and fate of redox-sensitive trace elements (TEs; e.g., As, U, Cu, Cr) in natural systems is challenging. Colloids have been reported to control TEs speciation and catalyze TEs redox reactions in many environments. We hypothesize that the lack of accurate thermodynamic models that account for the role of colloids in TEs speciation explains our inability to predict their redox state distribution in the environment. The slow evolution of the colloidal compartment in response to prevailing bio/hydro/pedo/climatological conditions needs to be decoupled from the fast TEs redox reactions promoted by colloidal surfaces. Further progress is hampered by experimental and theoretical challenges associated with capturing the extreme physical and chemical heterogeneity of colloids, their metastable structures, and their dynamic transformation behavior.

Graphical abstract



1 Introduction

Redox reactions play a key role on the biogeochemical cycles of many elements in the environment. These include C, with effects on climate change or soil quality, and nutrients of paramount importance for living organisms such as N or Fe. It also applies for many trace elements (TEs), from metals (e.g., Cr, Cu, Ce), radionuclides (e.g., U, Pu, Tc), to metalloids or non-metals (e.g., As, Sb, Se) displaying negative effects on the environment and/or human health. For instance, As, Cr and Cu are generally considered as toxic (at least above certain concentrations), but As(III), Cr(VI), and Cu(I) are much more toxic for living organisms compared to As(V), Cr(III) and Cu(II), respectively [1–3]. Actinides and Tc in their tetravalent state (U/Np/Pu/Tc(IV)) exhibit very low solubilities and may be considered much less mobile and bioavailable than the oxidized forms (i.e. U(VI)/Np/Pu(V)/Tc(VII)) [4,5]. Therefore, predicting the redox state and speciation of TEs is crucial to understand their behavior and fate in the environment, for risk assessments for health, ecosystems and development of remediation strategies.

Thermodynamic models are thought to provide inaccurate predictions in the environment [6–8]. Indeed, as far as thermodynamics is concerned, many important redox reactions should proceed in the environment (involving redox couples e.g. CO_2/organic C, $Fe(OH)_{3(s)}/Fe^{2+}$, O_2/H_2O, $NO_3^-/NH_4^+/N_2$, SO_4^{2-}/HS^-), but, in reality many compounds persist due to strong kinetic constrains [1,3,7,9]. In addition, under the influence of combined effects of bio/hydro/pedo/climatological conditions [9,10], large fluctuations or gradients of pH and redox potential (E_H) might occur over too short time scales in the environment, which may prohibit the attainment of thermodynamic equilibria, and instead cause the formation of metastable compounds. These include for example amorphous nano-phases/colloids such as clay minerals, metal oxides or sulfides, and organic colloids with a large heterogeneity of reactive sites, and thus a broad variety of redox potentials [9,11–13] with varying electron donating/accepting capacities [14]. In addition, coupling between the biogeochemical cycles of elements must be considered, such as the impact of organo-mineral associations on C preservation in soils or the role of Fe in the C and N redox cycles [15–17]. In view of the extreme complexity of natural systems, characterized by a high degree of chemical and physical heterogeneity, with processes occurring over various spatial and temporal scales, and the lack of numerical models to take this complexity into account, predicting the redox state

distribution of TEs, whose biogeochemical cycle is dictated by major elements (e.g. C/S/N/Fe/Mn/Al/Si), seems currently not achievable. Therefore, new ideas and conceptual frameworks are urgently needed to better understand the driving parameters of TEs dynamics and trajectories in natural environments, and to provide efficient predictive tools for understanding and constraining their behavior and fate.

Colloids are ubiquitous in aquatic environmental systems and, with their small size (typically ranging from a few nanometers to a few micrometers), large and highly reactive surface towards TEs, they largely control the speciation of TEs. For instance, they can transport TEs over long distances in groundwaters [18], from soils to water bodies, in tropical [19,20], temperate [21] and subarctic [22,23] regions, or from continents to oceans, because colloid flocculation in estuaries traps many TEs in sediments [24]. Accordingly, the impact of colloids on the redox state distribution of TEs must correctly be considered in geochemical speciation models. Like engineered nanoparticles, natural colloids can catalyze chemical reactions, including redox transformations. Indeed, there is plethora of scientific articles reporting the catalytic activity of nanoparticles and colloids towards redox transformation of TEs in environmentally relevant conditions [3,25–28]. Colloids may even be compared to enzymes for their catalytic activities [29,30], and have sometimes been shown more efficient than biotic processes [31]. The fact that TEs redox reactions at colloid-water interface proceed rapidly might encourage the use of equilibrium speciation modelling, but this rarely the case. Only few studies, often dedicated to actinide, successfully used equilibrium modelling to predict TEs oxidation state distribution [26,32–38].

The limitations of equilibrium speciation models for predicting the oxidation state distribution (or "redox speciation") of TEs are discussed here, as well as recent results that support a broader use of these tools to unravel some important aspects hidden behind the complexity of natural environments. The fact that colloids are metastable nanophases, whose composition and structure is impacted by combined effects of bio/hydro/pedo/climatological conditions, suggests that equilibrium models are of little help as far as colloids are concerned. However, as pointed out by Alexandra Navrotsky: "*we ourselves are metastable with respect to CO_2, H_2O, and a small pile of ash, but that does not matter for most of our lives*" [39]. In other words, over a relevant time scale where metastable phases persist, their thermodynamic properties can be studied. For instance, equilibrium calculations are the most relevant to predict radionuclide migration in the context of nuclear waste disposal in deep

geological environments, because reaction rates (time scales from seconds to years) are law compared to the half-life of relevant radionuclides (up to thousands or millions of years) [4,5]. Recent thermodynamic investigations of metastable phases provide evidence that many of the behaviors that we have previously ascribed to kinetics are, in fact, thermodynamically driven, such as the polymorphism of metal oxides, dehydration and redox reactions [40,41]. Under kinetic constraints, thermodynamics may still guide the processes, such as in the case of the redox reactions involving Fe-oxides [27,28,42]. More generally, thermodynamics allows us to judge which reactions are possible or in which direction they may be expected to proceed. Because thermodynamics clearly point to the oxidation of colloidal organic matter to CO_2 in the presence of O_2, we can claim that this system is constrained by kinetics. The same reasoning can be applied to any mixture of a strong reductant and an oxidized form of a TE (or the contrary). However, this may not be so straightforward in all natural systems where TEs can experience a wide range of redox conditions and where TEs are indeed intimately associated with colloids. Accordingly, the appropriate description of the influence of colloids and surfaces on the redox speciation of TEs is presently discussed as an important key for a holistic understanding and modeling of the fate and behavior of TEs in environmental systems.

2 Reasons for the inefficiency of previous equilibrium modeling approaches

The distribution of the redox states of an element should be predicted using the Nernst equation as follows:

$$E_H = E^0_{Ox/Red} + \frac{RT}{nF}\log\left(\frac{[Ox]\times\gamma_{Ox}}{[Red]\times\gamma_{Red}}\right) + \frac{m}{n}pH \quad (1)$$

Where E_H is the redox potential, *T* is absolute temperature, *F* is the Faraday constant and *R* is the gas constant, "Ox" and "Red" are oxidized and reduced species of an element, γ_{Ox} and γ_{Red} are their respective activity coefficients, brackets denote concentrations, $E^0_{Ox/Red}$ is the standard redox potential of the Ox/Red couple, *n* and *m* are the number of electrons and protons, respectively, involved in the redox reaction that can be written as follows:

$$Ox + n\ e^- + m\ H^+ \rightleftharpoons Red \quad (2)$$

Equation 1 relies on concentrations of chemical species (e.g. [Fe^{2+}] and [Fe^{3+}]), which often differ from their total concentrations ([Fe(II)] and [Fe(III)], keeping the Fe example)) that are detected in natural samples using spectrophotometry, mass spectrometry or electrochemistry when the instruments are calibrated against total element concentration. The relationship between total and species concentrations of an element under a given oxidation state can be written, using the example of Fe(II), as follows:

$$[Fe(II)] = [Fe^{2+}] + \sum_i [FeL_i] \quad (3)$$

Where L_i is a *i*-th ligand in solution (including, e.g., OH^-, Cl^-, organic acids), which can form complexes with Fe^{2+}. For the sake of simplicity, equation 3 does not show other Fe:L stoichiometries than 1:1 and it omits charges of the complexes. Nevertheless, it shows that knowing the Fe speciation in the sample precisely is a mandatory prerequisite to use the Nernst equation. This includes concentrations of all ligands and the corresponding complexation reactions and constants with both Fe^{2+} and Fe^{3+}. Popular geochemical speciation software (e.g. PHREEQC [43], Visual Minteq [44]), include extensive aqueous chemical reaction databases for this purpose.

As discrepancies between measurements and equilibrium calculations are common [3,6–8], the Nernst equation is very often used to conclude that the system has not reached equilibrium. Alternatively, failure in the use of the Nernst equation might be attributed to the extreme sensitivity of the calculations to uncertainties related, for instance, to E_H determination, which is subjected to numerous limitations and artifacts [6,7,45], or the accuracy of the chemical reaction database. However, the fact that filtered natural samples (e.g. <0.2µm) are no more than colloid suspensions [18–23,46] is a major limitation that should be considered. In principle, such nano-phases are solid particles that should be ideally removed from the solution by filtration however this is hardly achieved, unless much more rigorous separation procedures are applied. For Fe, it is well known that the presence of (hydr)oxide nanophase must be taken into account to predict its solubility and redox speciation [46]. Similarly, application of the Nernst equation to predict TE redox speciation should consider adsorption processes (e.g. cation exchange, surface complexation) occurring at the colloids-water interfaces, but this is generally overlooked in geochemical speciation calculations.

3 Recently developed approaches to model the redox speciation of TEs on the surface of particles and colloids

3.1 Thermodynamics at the colloid-water interface

For many redox-sensitive TEs (e.g. V, Cr, Mn, Cu, As, Se, Mo, Tc, Sb, Ce, actinides), whose speciation can be affected by colloids in natural waters [4,18,20–23], the term [Ox]/[Red] in equation 1 should include colloid-bound species. This observation offers new perspectives to explore unforeseen thermodynamic effects related to interfacial processes. Figure 1, schematically depicts the adsorption and redox reactions of a TE's oxidized and reduced forms ("Ox" and "Red"). The cartoon in Figure 1 showcases four Red and four Ox ions. The change in Gibbs free energy in the oxidation reaction of the aqueous species Red to Ox (ΔG_{aq}) is in many cases tabulated in thermodynamic databases, however, the free energy of the corresponding reaction at the surface (ΔG_{surf}) will be different, because different species are involved (i.e. aqueous species *versus* surface complexes), and is usually unknown. The relationship between the two distinct redox reaction can be calculated if the Gibbs free energy of the respective adsorption reactions of Ox ($\Delta G_{ads,Ox}$) and Red ($\Delta G_{ads,Red}$) are known:

$$\Delta G_{surf} = \Delta G_{aq} + \Delta G_{ads,Ox} - \Delta G_{ads,Red} \quad (4)$$

This relationship provides a quantitative measure for the difference between ΔG_{surf} and ΔG_{aq} (as well as the corresponding $E^0_{Ox/Red}$ values in eq. 1), depending on the affinity of Ox and Red for the surface. This situation very-likely applies to the vast majority of TEs, whose oxidation state primarily dictate their chemical behavior, and thus, also their adsorption behavior. For instance, actinides and Tc in their tetravalent state (U/Np/Pu/Tc(IV)) are known to bind much more strongly with colloids than their oxidized forms (i.e. U(VI)/Np/Pu(V)/Tc(VII)), [4] as illustrated for Np adsorption onto a clay (illite) in Figure 1b [32]. Note that irreversibility of adsorption reactions, which can be attributed to additional reactions such as surface precipitation or incorporation, and may lead to additional complications, will not be discussed here to keep the focus of this article.

The thermodynamic parameters of the adsorption reactions of Ox and Red can be either determined experimentally, e.g. by measuring the amount of adsorbed the TE under sufficiently oxidizing or reducing conditions, respectively, or predicted by surface

complexation models (SCM), provided that relevant parameters are available and trustworthy. For instance, missing SCM parameters associated with a redox-sensitive TE can be estimated by using relevant chemical analogues [4,33] or linear free energy relationships [47]. The choice of the SCM (e.g. with or without explicit description of electrostatic effects) has no real importance for the present calculations, provided that the model predictions are equal, which should in principle be the case when SCM are calibrated using the same experimental dataset. Experimental or model results can be provided as solid-liquid distribution coefficients (K_d, taken here in its unitless form):

$$K_{d,Ox} = \frac{[Ox]_{surf}}{[Ox]_{aq}} \quad \text{and} \quad K_{d,Red} = \frac{[Red]_{surf}}{[Red]_{aq}} \tag{5}$$

which is a conditional thermodynamic parameter, describing adsorption phenomena in the specific physico-chemical conditions (surface loading, pH, ionic strength, *T*, etc.). Including it in equation 4 leads to the following equation:

$$\frac{[Ox]_{aq}}{[Red]_{aq}} = \frac{[Ox]_{surf}}{[Red]_{surf}} \times \frac{K_{d,Red}}{K_{d,Ox}} \tag{6}$$

The consequences of equation 6 are illustrated in Figure 1, in which Red adsorbs more strongly to the surface ($K_{d,Red}$ = 3/1) than Ox ($K_{d,Ox}$ = 1/3). For an initially stoichiometric mixture of Ox and Red (4 ions each in total), adsorption processes imply that $[Ox]_{aq}/[Red]_{aq}$ is 9-fold larger than $[Ox]_{surf}/[Red]_{surf}$ (i.e. 3 *versus* 1/3). The above statements are further illustrated with modeling results in a more realistic system (Np-illite), for which the model was derived from batch experiments and spectroscopic investigations [32]. The adsorption of Np(IV) to illite is much larger than that of Np(V) (Figure 1b) whatever the pH. Therefore, the apparent redox potential of the Np(V)/Np(IV) couple in solution ($Np(V)_{aq}/Np(IV)_{aq}$) is lower than at the illite surface ($Np(V)_{surf}/Np(IV)_{surface}$). In other words, Np(V) is more easily reduced to Np(IV) at the illite surface. A comparison of the predominance pH-E_H ("Pourbaix") diagrams of Np in the aqueous phase or at the illite surface evidence an intermediate pH-E_H domain where Np(V) dominates in the aqueous phase whereas Np(IV) dominates at the illite surface (Figure 1c).

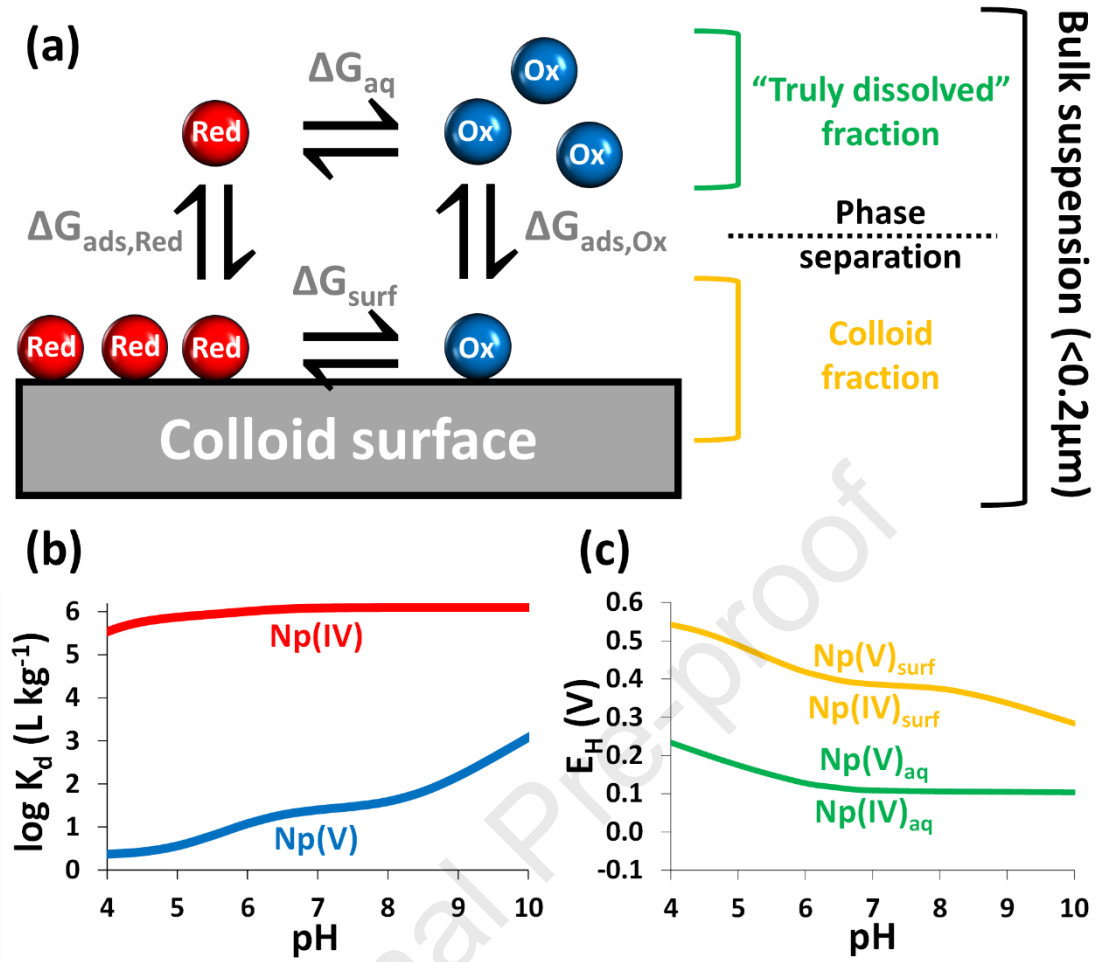


Figure 1. (a) Cartoon of the adsorption and redox reactions involving the oxidized and the reduced forms of a TE ("Ox" and "Red") in solution and at the surface of a colloid. Aqueous samples filtered at 0.2 µm are bulk colloid suspension that, upon further phase separation, split into so-called "truly dissolved" and colloid fractions. (b) Adsorption of Np(IV) (red) and Np(V) (blue) onto illite, quantified as solid-liquid distribution coefficients (K_d). (c) Predominance pH-E_H ("Pourbaix") diagrams of Np either in the aqueous phase (green) or at the illite surface (orange). Modeling results in (b) and (c) where obtained for $[Np]_{tot} = 10^{-9}$ M, 2 g L^{-1} of illite in 0.1 M NaCl in reference [32].

Field samples passed through a 0.2 or 0.45 µm filter, referred to as "bulk suspension" in Figure 1, do not provide data that can easily be interpreted by numerical modeling. Equations 4 or 6 show the importance of colloids in the redox speciation calculations using the Nernst equation. Neglecting colloids, leads to erroneous conclusions because a mismatch between observation and calculation is inevitable. Solution analysis after further phase separation (e.g. by ultrafiltration, ultracentrifugation or some chromatographic techniques) might allow investigating the colloid-free, so-called "truly dissolved fraction" [19,21,22]. Such data should be better suited to the application of the Nernst equation, provided that (i) the original redox

state and speciation are maintained, and (ii) speciation of the TE in the truly dissolved fraction can accurately be calculated or measured (i.e. in relation to equation 3). Therefore, appropriate sample preparation and determination of the redox state distribution of the element is required, and a consistent model must be adopted, i.e. accounting or not for the colloid compartment depending on the sample filtration.

3.2 Odd TE redox speciation explained by interfacial thermodynamics

The above calculations are corroborated by the results of several studies dedicated to TE-colloid interactions which have revealed the existence of an unforeseen oxidation state, that can be explained by thermodynamic factors [26,32–38]. These results were obtained under controlled laboratory conditions using purified colloids or synthetic materials that mimicked natural colloids. This ensured that a steady-state was reached, that phase separation was efficient and that geochemical speciation modeling may be accurate, thanks to the simplicity of the system in relation to natural waters. Plutonium, with four oxidation states, ranging from +III to +VI, and the capacity to disproportionate, as well as radiolytic processes induced by the high activity of some of its isotopes, it is very easy to invoke any kind of kinetically controlled process when thermodynamics appears to fail in predicting its complex chemistry. However, several examples exist for which the Pu oxidation state distribution could be explained accounting for the impact of colloids and surfaces:

- Pu(V) can be reduced to Pu(IV) at the surface of quartz in the presence of atmospheric O_2, which is highly counter-intuitive but, in fact, this is due to the thermodynamic stability of a Pu(IV) surface complex [35].
- Pu(V) reduction occurred in the presence of magnetite (Fe_3O_4) and mackinawite (FeS) under anoxic conditions. Although the E_H values were similar in both cases, reduction only proceeded to Pu(IV) where it precipitated as $PuO_{2(s)}$ with mackinawite, because Pu has weak affinity for surface S sites, whereas Pu(III) was found stabilized through surface complexation on magnetite [37].
- Pu(III) oxidized to Pu(IV) at the surface of kaolinite and illite under reducing conditions. Under oxidizing conditions, Pu(IV) prevailed on the surface of kaolinite but it partially oxidized and prevailed as Pu(V) in the aqueous phase. These processes could be explained using surface complexation modeling to account for the effects of adsorption on Pu redox

speciation under various physico-chemical conditions (e.g. pH, ionic strength, surface loadings) [33,34].

As discussed above, similar observations were made for Ce, U and Np [32,36,38], which are chemical analogues of Pu, with respect to their tetravalent oxidation state having a higher affinity for the surface. Stabilization of one oxidation state with respect to others has not only been observed not only for actinides but also for other TE such as Cu. It is expected to prevail as Cu(II) and Cu(0) in oxidizing and reducing conditions, respectively, as Cu(I) is expected to disproportionate. However, the presence of NOM can reduce the stability field of Cu(0) and promote of the formation of Cu(I) complexes [26].

4 Current challenges regarding the modelling of colloidal effects on the redox speciation of trace elements in natural systems.

4.1 Redox potential determination

All the approaches discussed above rely on the accurate determination of the E_H, which is a considerable challenge to achieve. The simplest approach involves Pt-electrodes, but it cannot be recommended due to the occurrence of several widely documented artifacts [6–8,45]. This situation is likely discouraging for numerous scientists and, as other potential techniques are more difficult to apply, in the vast majority of the studies focused on the redox speciation of elements, no attempt is made to even measure an E_H value. However, there are also several favorable outcomes, that should motivate hydro/bio/geochemists to attempt an E_H measurement. In several studies, E_H measurements were corroborated by both independent measurements and geochemical speciation modeling [13,32,48,49]. Recently [13,48], two independent research teams measured consistently the E_H of 10 nm-sized magnetite nanoparticles suspension, which provided key data for the understanding and the modeling of the redox behavior of this highly reactive mineral. This is in line with the previous demonstration that small iron oxide nanoparticles interact with the Pt-electrode, thus, facilitating the E_H measurement [49]. Other electrodes can be efficient depending on the studied system (e.g. using other metals such as Au-electrodes, or specifically designed electrodes such as powder disk electrodes) [7,50], and electron mediators can be used to facilitate the measurement [27]. The redox potential can also be determined indirectly by performing redox state analysis of quinone-like compounds [28], or of a TE in the aqueous

phase and subsequent calculation using the Nernst equation, provided that phase separation was efficient and the reaction database is complete enough to reach this aim [33]. Therefore, the determination of the E_H is probably not impossible, but alternative methods have to be developed, especially for the application in field studies [9]. Measurement by several independent methods is encouraged to ensure reliable results, as the simple comparison between E_H measurement with a Pt-electrode and calculations with the Nernst equation is clearly not enough to do so.

4.2 The complex structure and heterogeneity of colloids, and the various related TE-binding mechanisms

The large heterogeneity and diversity of colloids is clearly an important bottleneck, limiting the prediction of TE-colloid interactions in the environment. One of the common characteristics of natural systems is the simultaneous presence of a wide variety of minerals (such as Fe/Al/Mn (oxy)hydroxides, clays, etc.) and organic compounds (natural organic matter (NOM): fresh biological compounds, humic substances, etc.), which can be released into water bodies as colloids and may potentially be associated as heteroagreggates (e.g. Fig. 2a,b,c) [19,51,52]. Because TEs binding mechanisms mainly depend on the type of colloid, and related TEs surface species formed, this requires to understand whether TEs (i) adsorb through purely electrostatic attraction generated by either the variable surface charge or the permanent charge of a mineral, (ii) form surface complexes with either organic or inorganic moieties of colloids, (iii) incorporate into the bulk colloid structure or (iv) form precipitates onto the colloid surface (see some examples in Fig. 2). Unfortunately, distinct mathematical formalisms are required for each of these different processes, in order to simulate their impact under various physico-chemical conditions encountered in natural systems (e.g., pH, ionic strength, E_H, temperature). This issue is even more complex for redox-sensitive TEs, for which the binding mechanisms must be elucidated for every oxidation state, as they behave as distinct chemical elements. Great progresses are currently being made in predicting the ions binding with nanoparticles and colloids, by accounting more accurately for interfacial processes, surface site reactivity, and the information from the molecular to the aggregate scale [53–56].

In natural colloidal heteroaggregates, composed of organomineral (e.g. Fe-oxides + NOM [51]) or inorganic assemblages (e.g. clays + Fe/Mn-oxides), each of the constitutive phases can

behave drastically differently from its individual counterparts. This is due to so-called "non-additive" effects caused by the interactions between components, which requires further experimental investigations and modelling development to be accurately taken into account in surface speciation models [54,57,58]. Appropriate description of the surface speciation of TEs might be required in order to identify the rate limiting reaction and to implement its rate law expression in kinetic surface reaction modeling. If spectroscopic tools have widely been used to determine the speciation of TEs in naturally heterogeneous samples, isotopic tools have become very popular to probe interaction mechanisms between TEs and colloids. The TEs isotopic fractionation can be driven by redox-dependent or independent processes (adsorption). For instance, reduction of Cr(VI) to Cr(III) leads to significant isotopic fractionation. During reactions, Cr isotopes fractionation happens because the Cr-O bonds with light Cr isotopes are more easily broken compared to those of heavy isotopes, leading to higher reaction rates of the lighter Cr isotope composition and consequent enrichment of Cr(III) in the product [59]. But isotope fractionation at the mineral-water interface as also been reported in the absence of redox processes or in the case of redox-inert TEs [60,61]. There is still much to discover how TEs isotopes fractionate at the colloids-water interfaces as this tool can be applied to various redox sensitive TEs. In addition, further experimental approaches can take advantage of TE isotopes. Isotopic dilution techniques have been acknowledged as a valuable tool for investigating various surface processes associated with the mobility of TEs while determining the concentration of elements capable of isotopic exchange [62]. When two compartments with distinct isotopic signatures (i.e. one natural and one artificially modified) come into contact, isotopes tend to reach an equilibrium between solid and liquid phases through isotopic exchange, without disturbance of the chemical equilibrium. Recent studies specifically focused on the use of isotopic dilution to study the fate TEs in colloidal suspension (e.g. [63]), while kinetic modelling of isotopic exchanges conducted to significant scientific breakthrough in the understanding of additivity/non-additivity effects of TEs/bearing phases interactions [64].

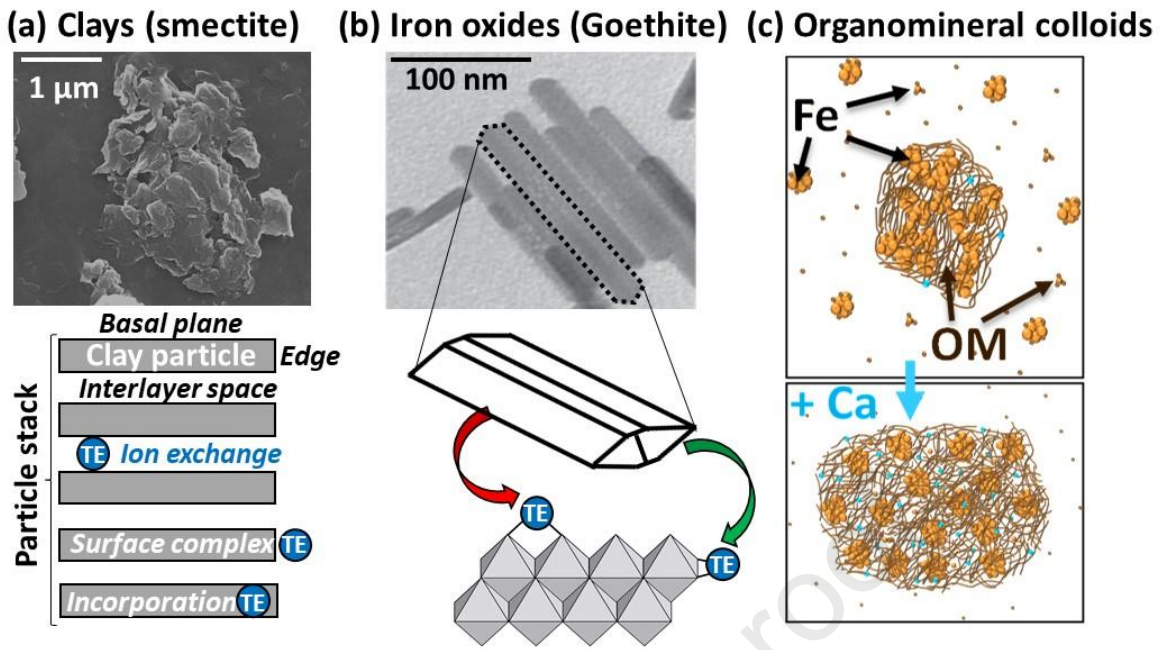


Figure 2. Examples of different constituents of colloids and binding mechanisms with TE: (a) clays (scanning electron microscopy image from [65]) and (b) iron oxides (transmission electron microscopy image from [66]) and some of the various possible interaction mechanisms with TEs. (c) Colloids structure is dynamic as illustrated here with a simple example: the impact of Ca^{2+} on the aggregation of organomineral colloids (illustration adapted from [51]).

4.3 Genesis and dynamics within the colloid compartment

Colloids are small particles that can easily change in size and shape due to, e.g., recrystallization processes or aggregation phenomena (see e.g., Fig. 2c), or in composition due to matter transfer from or to the biota or soil/sediment compartments. Changes in the physical and chemical state of colloids inevitably affect TEs-colloid binding mechanisms and the driving forces of electron-transfer processes between TEs and colloids. Evolution of the colloid compartment occur, notably, through microbial activity being reductive or oxidative toward colloids, fluctuations or gradients of the E_H (e.g., in temporarily flooded soils such as, wetlands or coastal sediments), temperature (e.g., leading to ice melting in permafrost or to accepting or donating electron capacity changes), pH (e.g., in podzols or soils contaminated by mining activities) or salinity (e.g., in estuaries). Therefore, the concomitant evolution of the colloidal compartment and TEs redox speciation under the influence of bio/hydro/pedo/climatological constraints is a major obstacle to the understanding and prediction of related processes. It is necessary to comprehend the evolution of the colloidal

compartment in order to understand and predict its impact on TE redox speciation. This concerns not only the redox potential and capacity (i.e. electron donating or accepting capacity) of colloids [11–14], but also the binding capacity for TEs, as discussed above.

Due to their small size and high degree of heterogeneity, characterization of natural colloids remains an important challenge, although great progress has been made during the past years. For example, the use of ultrafiltration to separate the truly dissolved phase from the colloidal phase, and to separate different ranges of colloidal sizes, has made it possible to distinguish different behaviors with respect to trace elements [18,19,21,22]. To go further, field flow fractionation (FFF) techniques combined with inductively coupled mass spectrometry (ICP-MS) or time of flight ICP-MS used in single particle mode (spICP-ToF-MS) coupled with machine learning algorithm [67–69], are particularly powerful techniques to determine the size and composition of colloids, as well as to quantify the associated TEs. Scanning transmission electron microscopy (STEM) with electron energy loss detection (EELS) provides the atomic resolution suitable to identify traces of TEs at the surface of colloids, and EELS spectra allow distinguishing not only elements but also their oxidation states [70].

However, if these tools allow investigating the heterogeneity within the colloid compartment, new approaches are required to elucidate their dynamic behavior. Further developments of *in situ* microscopic techniques, such as *in situ* STEM, would provide better understanding of microbial effects on nanoparticle and colloid formation [71]. New *in situ* and *operando* spectroscopic approaches inspired from the chemical catalysis community, might allow to follow the transformation of colloids during wetting or drying of soils, and during the activity of micro-organisms, by following the speciation of soil constituents with time. For instance, oxidation processes of Fe(II) to Fe(III) by O_2 in the presence of NOM could be studied by Quick-X ray absorption spectroscopy (XAS) [52]. Hyperspectral imaging adds spatial information to time-resolved XAS data, which can be expected as highly valuable to investigate the formation and transformation of colloids in soils [72]. Finally, isotopic tools could also probe the formation and transformations of colloids, as it can be applied to elements like carbon, nitrogen, sulfur, and other metals, as shown, for instance, in the case of natural Fe-NOM heteroaggerates and complexes [73,74].

5 Conclusions

To predict the redox state distribution of TEs more accurately, new conceptual and numerical models are needed. Over the past decades, the use of equilibrium thermodynamic models in environmental studies has become less attractive because major elements (e.g., C/S/N/Fe/Mn/Al/Si) can react slowly in the environment and tend to form metastable phases, including colloids. Recent scientific breakthroughs on the processes occurring at the interfaces between water and nanoparticles/colloids may have provided important keys to the appropriate use of thermodynamic models in a natural context. For example, they have been shown to provide key insights for predicting the kinetically limited redox transformation of organic pollutants. Equilibrium models accounting for TE adsorption processes on colloids also provided robust interpretations of pH- and E_H-dependent TE redox speciation under laboratory conditions. However, the colloidal compartment in field samples should be analyzed more accurately, as 0.2µm filtration does not allow the concentration of truly dissolved TEs and TEs bound to colloids to be distinguished, which would be of great help for accurate geochemical speciation calculations. Further work is needed to accurately describe and predict the binding of TEs to natural colloidal heteroaggregates, which will require the development of advanced tools for field application as well as more mechanistic models of the surface reactivity of these heterogeneous assemblages. Future models should decouple the slow evolution of colloidal compartments in response to prevailing bio/hydro/pedo/climatological conditions from the potentially faster redox transformation of TEs occurring at the surface of colloids; an important key to a holistic understanding and modeling of the fate and behavior of TEs in environmental systems.

Acknowledgements

This work was supported by the COLOSSAL project funded by ANR (project number ANR-23-CE01-0001; coordinator: R. Marsac).

Author contributions

Rémi Marsac: Writing - original draft; Charlotte Catrouillet: Writing - review & editing; Mathieu Pédrot: Writing - review & editing; Marc Benedetti: Writing - review & editing; Mélanie Davranche: Writing - review & editing; Eric D. van Hullebusch: Writing - review & editing; Aline Dia: Writing - review & editing; Yann Sivry: Writing - review & editing; Anne-Catherine Pierson-

Wickmann: Writing - review & editing; Mickael Tharaud: Writing - review & editing; Frank Heberling: Writing - review & editing.

References

[1] Borch T, Kretzschmar R, Kappler A, Cappellen PV, Ginder-Vogel M, Voegelin A, et al. Biogeochemical Redox Processes and their Impact on Contaminant Dynamics. Environ Sci Technol 2010;44:15–23. https://doi.org/10.1021/es9026248.

[2] Wang X, Wang W-X. Intracellular Biotransformation of Cu(II)/Cu(I) Explained High Cu Toxicity to Phytoplankton Chlamydomonas reinhardtii. Environ Sci Technol 2021;55:14772–81. https://doi.org/10.1021/acs.est.1c05408.

[3] Stumm W, Morgan JJ. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd ed. John Wiley&Sons, Inc., New York. 1996.

[4] Geckeis H, Lützenkirchen J, Polly R, Rabung T, Schmidt M. Mineral-water interface reactions of actinides. Chemical Reviews 2013;113:1016–62. https://doi.org/10.1021/cr300370h.

[5] Altmaier M, Gaona X, Fanghänel T. Recent Advances in Aqueous Actinide Chemistry and Thermodynamics. Chem Rev 2013;113:901–43. https://doi.org/10.1021/cr300379w.

[6] Lindberg RD, Runnells DD. Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling. Science 1984;225:925–7. https://www.jstor.org/stable/1693951.

[7] Sigg L. Redox Potential Measurements in Natural Waters: Significance, Concepts and Problems. In: Schüring J, Schulz HD, Fischer WR, Böttcher J, Duijnisveld WHM, editors. Redox: Fundamentals, Processes and Applications, Berlin, Heidelberg: Springer; 2000, p. 1–12. https://doi.org/10.1007/978-3-662-04080-5_1.

[8] Wilkin R, Ludwig R, Ford R. Workshop on monitoring processes for groundwater restoration. EPA Report 600/R-02/002; 2002.

[9] Peiffer S, Kappler A, Haderlein SB, Schmidt C, Byrne JM, Kleindienst S, et al. A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems. Nat Geosci 2021;14:264–72. https://doi.org/10.1038/s41561-021-00742-z.

[10] Lacroix EM, Aeppli M, Boye K, Brodie E, Fendorf S, Keiluweit M, et al. Consider the Anoxic Microsite: Acknowledging and Appreciating Spatiotemporal Redox Heterogeneity in Soils and Sediments. ACS Earth Space Chem 2023;7:1592–609. https://doi.org/10.1021/acsearthspacechem.3c00032.

[11] Klüpfel L, Piepenbrock A, Kappler A, Sander M. Humic substances as fully regenerable electron acceptors in recurrently anoxic environments. Nature Geosci 2014;7:195–200. https://doi.org/10.1038/ngeo2084.

[12] Gorski CA, Klüpfel L, Voegelin A, Sander M, Hofstetter TB. Redox Properties of Structural Fe in Clay Minerals. 2. Electrochemical and Spectroscopic Characterization of Electron Transfer Irreversibility in Ferruginous Smectite, SWa-1. Environ Sci Technol 2012;46:9369–77. https://doi.org/10.1021/es302014u.

[13] Jungcharoen P, Pédrot M, Heberling F, Hanna K, Choueikani F, Catrouillet C, et al. Prediction of nanomagnetite stoichiometry (Fe(II)/Fe(III)) under contrasting pH and redox conditions. Environ Sci: Nano 2022;9:2363–71. https://doi.org/10.1039/D2EN00112H.

[14] Burgin AJ, Loecke TD. The biogeochemical redox paradox: how can we make a foundational concept more predictive of biogeochemical state changes? Biogeochemistry 2023;164:349–70. https://doi.org/10.1007/s10533-023-01036-9.

[15] Kleber M, Bourg IC, Coward EK, Hansel CM, Myneni SCB, Nunan N. Dynamic interactions at the mineral–organic matter interface. Nat Rev Earth Environ 2021;2:402–21. https://doi.org/10.1038/s43017-021-00162-y.

[16] Kappler A, Bryce C, Mansor M, Lueder U, Byrne JM, Swanner ED. An evolving view on biogeochemical cycling of iron. Nat Rev Microbiol 2021;19:360–74. https://doi.org/10.1038/s41579-020-00502-7.

[17] Dong H, Zeng Q, Sheng Y, Chen C, Yu G, Kappler A. Coupled iron cycling and organic matter transformation across redox interfaces. Nat Rev Earth Environ 2023;4:659–73. https://doi.org/10.1038/s43017-023-00470-5.

[18] Kersting AB, Efurd DW, Finnegan DL, Rokop DJ, Smith DK, Thompson JL. Migration of plutonium in ground water at the Nevada Test Site. Nature 1999;397:56–9. https://doi.org/10.1038/16231.

[19] Allard T, Menguy N, Salomon J, Calligaro T, Weber T, Calas G, et al. Revealing forms of iron in river-borne material from major tropical rivers of the Amazon Basin (Brazil). Geochimica et Cosmochimica Acta 2004;68:3079–94. https://doi.org/10.1016/j.gca.2004.01.014.

[20] Ilina SM, Lapitskiy SA, Alekhin YV, Viers J, Benedetti M, Pokrovsky OS. Speciation, Size Fractionation and Transport of Trace Elements in the Continuum Soil Water–Mire–Humic Lake–River–Large Oligotrophic Lake of a Subarctic Watershed. Aquat Geochem 2016;22:65–95. https://doi.org/10.1007/s10498-015-9277-8.

[21] 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. Applied Geochemistry 2023;155:105736. https://doi.org/10.1016/j.apgeochem.2023.105736.

[22] Krickov IV, Lim AG, Vorobyev SN, Shevchenko VP, Pokrovsky OS. Colloidal associations of major and trace elements in the snow pack across a 2800-km south-north gradient of western Siberia. Chemical Geology 2022;610:121090. https://doi.org/10.1016/j.chemgeo.2022.121090.

[23] Pokrovsky OS, Dupré B, Schott J. Fe–Al–organic Colloids Control of Trace Elements in Peat Soil Solutions: Results of Ultrafiltration and Dialysis. Aquat Geochem 2005;11:241–78. https://doi.org/10.1007/s10498-004-4765-2.

[24] Elderfield H, Upstill-Goddard R, Sholkovitz ER. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. Geochimica et Cosmochimica Acta 1990;54:971–91. https://doi.org/10.1016/0016-7037(90)90432-K.

[25] Liger E, Charlet L, Van Cappellen P. Surface catalysis of uranium(VI) reduction by iron(II). Geochimica et Cosmochimica Acta 1999;63:2939–55. https://doi.org/10.1016/S0016-7037(99)00265-3.

[26] Maurer F, Christl I, Fulda B, Voegelin A, Kretzschmar R. Copper Redox Transformation and Complexation by Reduced and Oxidized Soil Humic Acid. 2. Potentiometric Titrations and Dialysis Cell Experiments. Environ Sci Technol 2013;47:10912–21. https://doi.org/10.1021/es4024095.

*** [27] Chen G, Thompson A, Gorski CA. Disentangling the size-dependent redox reactivity of iron oxides using thermodynamic relationships. PNAS 2022;119:e2204673119. https://doi.org/10.1073/pnas.2204673119.**

The authors demonstrated a link between reduction potential values for the hematite/aqueous Fe^{2+} redox couple and the size of the particle, which explained the reduction rates of organic contaminants.

***[28] Aeppli M, Giroud S, Vranic S, Voegelin A, Hofstetter TB, Sander M. Thermodynamic controls on rates of iron oxide reduction by extracellular electron shuttles. PNAS 2022;119:e2115629119. https://doi.org/10.1073/pnas.2115629119.**

This article shows how free energy relationships aid in identifying controls on microbial iron oxide reduction by extracellular electron shuttles, hence the role played by thermodynamics in important biologically-mediated processes.

[29] Wei H, Wang E. Nanomaterials with enzyme-like characteristics (nanozymes): next-generation artificial enzymes. Chem Soc Rev 2013;42:6060–93. https://doi.org/10.1039/C3CS35486E.

[30] Gao L, Zhuang J, Nie L, Zhang J, Zhang Y, Gu N, et al. Intrinsic peroxidase-like activity of ferromagnetic nanoparticles. Nature Nanotech 2007;2:577–83. https://doi.org/10.1038/nnano.2007.260.

[31] Robinson TC, Latta DE, Notini L, Schilling KE, Scherer MM. Abiotic reduction of nitrite by Fe(II): a comparison of rates and N2O production. Environ Sci: Processes Impacts 2021;23:1531–41. https://doi.org/10.1039/D1EM00222H.

[32] Banik NL, Marsac R, Lützenkirchen J, Marquardt CM, Dardenne K, Rothe J, et al. Neptunium sorption and redox speciation at the illite surface under highly saline conditions. Geochimica et Cosmochimica Acta 2017;215:421–31. https://doi.org/10.1016/j.gca.2017.08.008.

[33] Marsac R, Banik NL, Lützenkirchen J, Buda RA, Kratz JV, Marquardt CM. Modeling plutonium sorption to kaolinite: Accounting for redox equilibria and the stability of surface species. Chemical Geology 2015;400:1–10. https://doi.org/10.1016/j.chemgeo.2015.02.006.

[34] Marsac R, Banik NL, Lützenkirchen J, Diascorn A, Bender K, Marquardt CM, et al. Sorption and redox speciation of plutonium at the illite surface under highly saline conditions. Journal of Colloid and Interface Science 2017;485:59–64. https://doi.org/10.1016/j.jcis.2016.09.013.

[35] Hixon AE, Arai Y, Powell BA. Examination of the effect of alpha radiolysis on plutonium(V) sorption to quartz using multiple plutonium isotopes. Journal of Colloid and Interface Science 2013;403:105–12. https://doi.org/10.1016/j.jcis.2013.04.007.

[36] Chakraborty S, Favre F, Banerjee D, Scheinost AC, Mullet M, Ehrhardt J-J, et al. U(VI) Sorption and Reduction by Fe(II) Sorbed on Montmorillonite. Environ Sci Technol 2010;44:3779–85. https://doi.org/10.1021/es903493n.

[37] Kirsch R, Fellhauer D, Altmaier M, Neck V, Rossberg A, Fanghänel T, et al. Oxidation state and local structure of plutonium reacted with magnetite, mackinawite, and chukanovite. Environmental Science and Technology 2011;45:7267–74. https://doi.org/10.1021/es200645a.

[38] 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. Chemical Geology 2023;633:121547. https://doi.org/10.1016/j.chemgeo.2023.121547.

[39] Navrotsky A. Energetics at the nanoscale: Impacts for geochemistry, the environment, and materials. MRS Bulletin 2016;41:139–45. https://doi.org/10.1557/mrs.2015.336.

[40] Navrotsky A, Mazeina L, Majzlan J. Size-Driven Structural and Thermodynamic Complexity in Iron Oxides. Science 2008;319:1635–8. https://doi.org/10.1126/science.1148614.

[41] Navrotsky A, Ma C, Lilova K, Birkner N. Nanophase Transition Metal Oxides Show Large Thermodynamically Driven Shifts in Oxidation-Reduction Equilibria. Science 2010;330:199–201. https://doi.org/10.1126/science.1195875.

[42] Aeppli M, Voegelin A, Gorski CA, Hofstetter TB, Sander M. Mediated Electrochemical Reduction of Iron (Oxyhydr-)Oxides under Defined Thermodynamic Boundary Conditions. Environ Sci Technol 2018;52:560–70. https://doi.org/10.1021/acs.est.7b04411.

[43] Parkhurst DL, Appelo CAJ. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. vol. 6-A43. Reston, VA: U.S. Geological Survey; 2013. https://doi.org/10.3133/tm6A43.

[44] Gustafsson JP. Visual MINTEQ Version 30 2005.

[45] Shi Z, Nurmi JT, Tratnyek PG. Effects of Nano Zero-Valent Iron on Oxidation−Reduction Potential. Environ Sci Technol 2011;45:1586–92. https://doi.org/10.1021/es103185t.

[46] Neal C, Lofts S, Evans CD, Reynolds B, Tipping E, Neal M. Increasing Iron Concentrations in UK Upland Waters. Aquat Geochem 2008;14:263–88. https://doi.org/10.1007/s10498-008-9036-1.

[47] Dzombak DA, Morel FMM. Surface Complexation Modeling: Hydrous Ferric Oxide. Wiley-Interscience, New York; 1990.

[48] Robinson TC, Latta DE, Leddy J, Scherer MM. Redox Potentials of Magnetite Suspensions under Reducing Conditions. Environ Sci Technol 2022;56:17454–61. https://doi.org/10.1021/acs.est.2c05196.

[49] Silvester E, Charlet L, Tournassat C, Géhin A, Grenèche J-M, Liger E. Redox potential measurements and Mössbauer spectrometry of FeII adsorbed onto FeIII (oxyhydr)oxides. Geochimica et Cosmochimica Acta 2005;69:4801–15. https://doi.org/10.1016/j.gca.2005.06.013.

[50] Gorski CA, Nurmi JT, Tratnyek PG, Hofstetter TB, Scherer MM. Redox Behavior of Magnetite: Implications for Contaminant Reduction. Environ Sci Technol 2010;44:55–60. https://doi.org/10.1021/es9016848.

[51] Beauvois A, Vantelon D, Jestin J, Rivard C, Coz MB-L, Dupont A, et al. How does calcium drive the structural organization of iron–organic matter aggregates? A multiscale investigation. Environ Sci: Nano 2020;7:2833–49. https://doi.org/10.1039/D0EN00412J.

[52] Vantelon D, Davranche M, Marsac R, Fontaine CL, Guénet H, Jestin J, et al. Iron speciation in iron–organic matter nanoaggregates: a kinetic approach coupling Quick-EXAFS and MCR-ALS chemometrics. Environ Sci: Nano 2019;6:2641–51. https://doi.org/10.1039/C9EN00210C.

[53] Pinheiro JP, Rotureau E, Duval JFL. Addressing the electrostatic component of protons binding to aquatic nanoparticles beyond the Non-Ideal Competitive Adsorption (NICA)-Donnan level: Theory and application to analysis of proton titration data for humic matter. Journal of Colloid and Interface Science 2021;583:642–51. https://doi.org/10.1016/j.jcis.2020.09.059.

[54] Gil-Díaz T, Jara-Heredia D, Heberling F, Lützenkirchen J, Link J, Sowoidnich T, et al. Charge regulated solid-liquid interfaces interacting on the nanoscale: Benchmarking of a generalized speciation code (SINFONIA). Advances in Colloid and Interface Science 2021;294:102469. https://doi.org/10.1016/j.cis.2021.102469.

*** [55] Liu L, Legg BA, Smith W, Anovitz LM, Zhang X, Harper R, et al. Predicting Outcomes of Nanoparticle Attachment by Connecting Atomistic, Interfacial, Particle, and Aggregate Scales. ACS Nano 2023;17:15556–67. https://doi.org/10.1021/acsnano.3c02145.**

The authors successfully applied an upscaling approach, from the atomic to the macroscopic scale, to predict nanoparticle aggregation and attachment phenomena.

[56] Boily J-F, Song X. Direct identification of reaction sites on ferrihydrite. Commun Chem 2020;3:1–8. https://doi.org/10.1038/s42004-020-0325-y.

[57] Reiller PE. Modelling metal–humic substances–surface systems: reasons for success, failure and possible routes for peace of mind. Mineralogical Magazine 2012;76:2643–58. https://doi.org/10.1180/minmag.2012.076.7.02.

*** [58] Li J, Weng L, Deng Y, Ma J, Chen Y, Li Y. NOM-mineral interaction: Significance for speciation of cations and anions. Science of The Total Environment 2022;820:153259. https://doi.org/10.1016/j.scitotenv.2022.153259.**

This study provides explanation for some of the non-additive effects observed in the binding of cations and anions to iron oxides-natural organic matter.

[59] Schauble EA. Applying Stable Isotope Fractionation Theory to New Systems. Reviews in Mineralogy and Geochemistry 2004;55:65–111. https://doi.org/10.2138/gsrmg.55.1.65.

[60] Frank AB, Klaebe RM, Frei R. Fractionation Behavior of Chromium Isotopes during the Sorption of Cr (VI) on Kaolin and its Implications for Using Black Shales as a Paleoredox Archive. Geochemistry, Geophysics, Geosystems 2019;20:2290–302. https://doi.org/10.1029/2019GC008284.

*** [61] Yan X, Zhu M, Li W, Peacock CL, Ma J, Wen H, et al. Cadmium Isotope Fractionation during Adsorption and Substitution with Iron (Oxyhydr)oxides. Environ Sci Technol 2021;55:11601–11. https://doi.org/10.1021/acs.est.0c06927.**

In this article, Cd isotopes are used to probe the formation of different Cd species bound to iron oxides. This one excellent example using such approach.

[62] Collins RN, Tran ND, Bakkaus E, Avoscan L, Gouget B. Assessment of Isotope Exchange Methodology to Determine the Sorption Coefficient and Isotopically Exchangeable Concentration of Selenium in Soils and Sediments. Environ Sci Technol 2006;40:7778–83. https://doi.org/10.1021/es061528s.

[63] Bolaños-Benítez V, van Hullebusch ED, Garnier J, Quantin C, Tharaud M, Lens PNL, et al. Assessing chromium mobility in natural surface waters: Colloidal contribution to the isotopically exchangeable pool of chromium (EwCr value). Applied Geochemistry 2018;92:19–29. https://doi.org/10.1016/j.apgeochem.2018.02.007.

[64] Zelano IO, Sivry Y, Quantin C, Gélabert A, Maury A, Phalyvong K, et al. An Isotopic Exchange Kinetic Model to Assess the Speciation of Metal Available Pool in Soil: The Case of Nickel. Environ Sci Technol 2016;50:12848–56. https://doi.org/10.1021/acs.est.6b02578.

[65] Norrfors KK, Bouby M, Heck S, Finck N, Marsac R, Schäfer T, et al. Montmorillonite colloids: I. Characterization and stability of dispersions with different size fractions. Applied Clay Science 2015;114:179–89. https://doi.org/10.1016/j.clay.2015.05.028.

[66] Xu J, Marsac R, Costa D, Cheng W, Wu F, Boily J-F, et al. Co-Binding of Pharmaceutical Compounds at Mineral Surfaces: Molecular Investigations of Dimer Formation at Goethite/Water Interfaces. Environmental Science & Technology 2017;51:8343–9. https://doi.org/10.1021/acs.est.7b02835.

[67] Tharaud M, Schlatt L, Shaw P, Benedetti MF. Nanoparticle identification using single particle ICP-ToF-MS acquisition coupled to cluster analysis. From engineered to natural nanoparticles. J Anal At Spectrom 2022;37:2042–52. https://doi.org/10.1039/D2JA00116K.

[68] Meili-Borovinskaya O, Meier F, Drexel R, Baalousha M, Flamigni L, Hegetschweiler A, et al. Analysis of complex particle mixtures by asymmetrical flow field-flow fractionation coupled to inductively coupled plasma time-of-flight mass spectrometry. Journal of Chromatography A 2021;1641:461981. https://doi.org/10.1016/j.chroma.2021.461981.

[69] Ghotbizadeh M, Cuss CW, Grant-Weaver I, Markov A, Noernberg T, Ulrich A, et al. Spatiotemporal variations of total and dissolved trace elements and their distributions amongst major colloidal forms along and across the lower Athabasca River. Journal of Hydrology: Regional Studies 2022;40:101029. https://doi.org/10.1016/j.ejrh.2022.101029.

[70] Hao X, Yoko A, Chen C, Inoue K, Saito M, Seong G, et al. Atomic-Scale Valence State Distribution inside Ultrafine CeO 2 Nanocubes and Its Size Dependence. Small 2018;14:1802915. https://doi.org/10.1002/smll.201802915.

673 *** [71] Couasnon T, Alloyeau D, Ménez B, Guyot F, Ghigo J-M, Gélabert A. In situ monitoring of**
674 **exopolymer-dependent Mn mineralization on bacterial surfaces. Science Advances**
675 **2020;6:eaaz3125. https://doi.org/10.1126/sciadv.aaz3125.**

676 **The authors used, for the first time, liquid-cell scanning transmission electron microscopy to observe**
677 **mineral growth on bacteria and the exopolymers they secrete.**

678

679 [72] La Fontaine C, Belin S, Barthe L, Roudenko O, Briois V. ROCK: A Beamline Tailored for
680 Catalysis and Energy-Related Materials from ms Time Resolution to µm Spatial Resolution.
681 Synchrotron Radiation News 2020;33:20–5. https://doi.org/10.1080/08940886.2020.1701372.

682 [73] Oleinikova OV, Poitrasson F, Drozdova OY, Shirokova LS, Lapitskiy SA, Pokrovsky OS. Iron
683 Isotope Fractionation during Bio- and Photodegradation of Organoferric Colloids in Boreal Humic
684 Waters. Environ Sci Technol 2019;53:11183–94. https://doi.org/10.1021/acs.est.9b02797.

685 [74] Lotfi-Kalahroodi E, Pierson-Wickmann A-C, Rouxel O, Marsac R, Bouhnik-Le Coz M, Hanna K,
686 et al. More than redox, biological organic ligands control iron isotope fractionation in the riparian
687 wetland. Sci Rep 2021;11:1933. https://doi.org/10.1038/s41598-021-81494-z.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: