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

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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 aquatic 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 the prevailing bio/hydro/pedo/climatological conditions need 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.

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Introduction

Redox reactions play a key role in 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 to many trace elements (TEs), from metals (e.g. Cr, Cu, Ce), radionuclides (e.g. U, Pu, Tc), to metalloids or nonmetals (e.g. As, Sb, Se) displaying negative effects on the environment and/or human health. For instance, As, Cr, and Cu are generally considered 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 the 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 equilibrium, 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 be correctly considered in geochemical speciation models. Like engineered nanoparticles, natural colloids can catalyze chemical reactions, including redox transformations. Indeed, there is a plethora of scientific articles reporting the catalytic activity of nanoparticles and colloids toward 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 to be 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 modeling, but this rarely the case. Only a few studies, often dedicated to actinide, successfully used equilibrium modeling 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 are impacted by the 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 small 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.

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:

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

where E_H is the redox potential, T is the 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:

$$\mathrm{Ox} + \mathrm{n\ e^-} + \mathrm{m\ H^+} \rightleftharpoons \mathrm{Red} \qquad (2)$$

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 the total and species concentrations of an element under a given oxidation state can be written, using the example of Fe(II), as follows:

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

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 softwares (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. <0.2 μm) are no more than colloid suspensions [18–23,46] is a major limitation that should be considered. In principle, such nanophases 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.

Recently developed approaches to model the redox speciation of trace elements on the surface of particles and colloids

Thermodynamics at the colloid–water interface

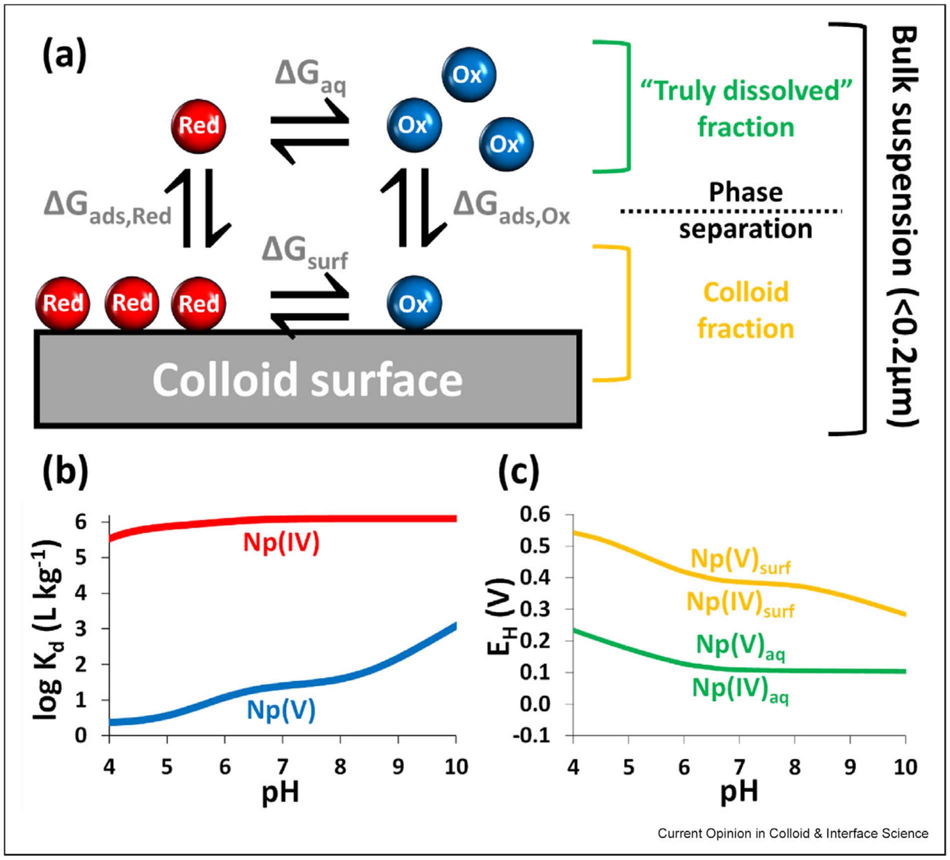
For many redox-sensitive TEs (e.g. V, Cr, Mn, Cu, As, Se, Mo, Tc, Sb, Ce, and actinides), whose speciation can be affected by colloids in natural waters [4,18,20–23], the term [Ox]/[Red] in equation (1) should include colloid-bound species. This observation offers new perspectives to explore unforeseen 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 it is usually unknown. The relationship between the two distinct redox reactions 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:

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

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 equation (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 dictates their chemical behavior and, thus, also their adsorption behavior. For instance, actinides and Tc in their tetravalent states (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 1(**b**) [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 TE under sufficiently oxidizing or reducing conditions, respectively, or predicted by surface complexation models (SCMs), 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 analogs [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 SCMs 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):

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 suspensions that, upon further phase separation, can be 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**) were obtained for $[Np]_{tot} = 10^{-9}$ M, 2 g L^{-1} of illite in 0.1 M NaCl in Ref. [32]. TE, trace element.

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

which is a conditional, thermodynamic parameter, describing adsorption phenomena in the specific physicochemical 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 1(**b**)), 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 pH-E_H predominance ("Pourbaix") diagrams of Np in the aqueous phase or at the illite surface evidences an intermediate pH-E_H domain where Np(V) dominates in the aqueous phase whereas Np(IV) dominates at the illite surface (Figure 1(**c**)).

Field samples do not 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 a 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.

Odd trace element 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 or surfaces. 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. When studying 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 by 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 analogs 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 TEs 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 limit the stability field of Cu(0) and promote the formation of Cu(I) complexes [26].

Current challenges regarding the modeling of colloidal effects on the redox speciation of trace elements in natural systems

Redox potential determination

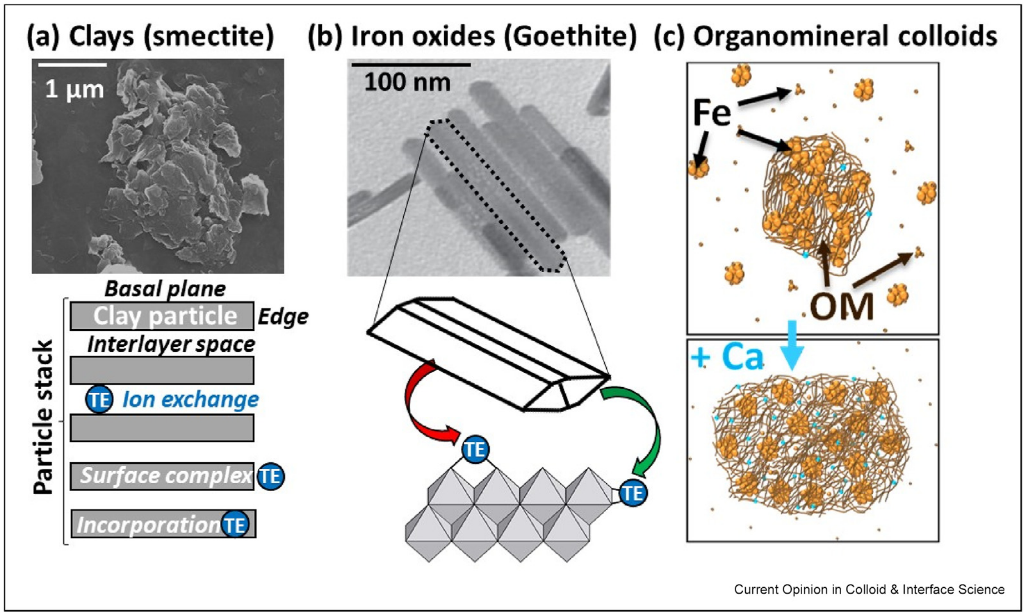
All the approaches discussed above rely on the accurate determination of the E_H, which is a considerable challenge to achieve. The simplest approach involves Pt-electrodes, but it cannot be recommended due to the occurrence of several widely documented artifacts [6–8,45]. This situation is likely discouraging 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, the 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 nanoparticle 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]. Measurements by several independent methods are 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.

The complex structure and heterogeneity of colloids, and the various related trace element-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 heteroaggregates (e.g. Figure 2(**a**–**c**)) [19,51,52]. Because TEs binding mechanisms mainly depend on the type of colloid and related TE 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 Figure 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 counterpart. This is due to so-called "nonadditive" effects caused by the interactions between components, which require further experimental investigations and modeling development to be accurately taken into account in surface speciation models [54,57,58]. Appropriate description of the surface

Figure 2



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Examples of different constituents of colloids and binding mechanisms with TE: (a) clays (scanning electron microscopy image from Ref. [65]) and (b) iron oxides (transmission electron microscopy image from Ref. [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 Ref. [51]). TE, trace element.

speciation of TEs might be required in order to identify the rate-limiting reaction and 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, the reduction of Cr(VI) to Cr(III) leads to significant isotopic fractionation. During reactions, Cr isotope fractionation happens because of the Cr—O bonds with light Cr isotopes are more easily broken compared to those with 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 is 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 about how TE 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 of TEs in colloidal suspension (e.g. Ref. [63]), while kinetic modeling of isotopic exchanges conducted to result in significant scientific breakthroughs in the understanding of additivity/nonadditivity effects of TEs/bearing phase interactions [64].

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. Figure 2(**c**)), 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 affects TEs-colloid binding mechanisms and the driving forces of electron-transfer processes between TEs and colloids. Evolution of the colloid single compartment occurs, 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), 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, the characterization of natural colloids remain 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 algorithms [67—69] are particularly powerful techniques to determine the size and composition of colloids, as well as to quantify the associated TEs. And, 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 for 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 the 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 they can be applied to elements like carbon, nitrogen, sulfur, and other metals, as shown, for instance, in the case of natural Fe-NOM heteroaggregates and complexes [73,74].

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 have 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 0.2 μm 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 aquatic environmental systems.

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.

Declaration of competing interest

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.

Data availability

No data were used for the research described in the article.

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