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Focus on speciation assessment in marine radiochemistry with X-ray Absorption Spectroscopy

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Abstract

The solubility, migration behavior and bioavailability of radionuclides in the marine environment strongly depend on their speciation. This focus article reviews the state-of-the-art and recent advances in the determination of radionuclide speciation in seawater, which is still challenging because of the very high ionic strength of the medium associated with ultra-trace concentrations of these elements in the oceans. In particular, we have highlighted the contribution and usefulness of synchrotron-based techniques such as X-ray Absorption Spectroscopy. Within this scope, we overview some major radionuclides in seawater, their natural or anthropogenic origin, their reactivity and natural concentrations. We outline the theoretical speciation models currently used, based on thermodynamic stability constants, and compare them to published experimental data recently obtained from spectroscopic investigation of radionuclides in natural seawater samples. Finally, we discuss some leading perspectives on radionuclide speciation using X-ray Absorption Spectroscopy in environmental samples at concentrations that must deal with spectroscopy detection limits.

The Hydrosphere covers the majority of the earth's surface and is a primary source of biodiversity. It can be defined as the surface on earth that is occupied by water or ice (and snow). Hence, seawater represents the largest proportion of the hydrosphere (*ca* 96.5 %) and covers by itself about 71% of the earth's surface. Ice caps, glaciers and permanent snow are the second compartment with about 1.74 % of total water on earth while other sources of fresh water represent only 1.76 % of total water.¹ As a consequence, oceans act as a long-term repository for pollution such as organics, heavy stable metals or radionuclides. Oceans can also be considered as the ultimate receptacle of rivers and catchment areas. For this reason, the marine environment has often been monitored as a pollution landmark.

Radionuclides are radioactive isotopes of the periodic table such as fission products (⁹⁰Sr, ¹²⁹I, ¹³⁷Cs, ⁹⁹Tc...), activation products (⁶⁰Co, ^{110m}Ag...) or actinides (Th, U, Pu, Am,...). They are involved in human nuclear activities since radioactivity has been developed in the middle of the 20th century. Radionuclides may be of anthropogenic origin (atmospheric nuclear tests since the end of the Second World War or releases from nuclear facilities) or natural (such as uranium and thorium from the earth's crust). Natural radionuclides may in turn be classified under cosmogenic radionuclides (like ³H for instance) and primordial radionuclides originating from radioisotopes with a half-life larger than the age of the earth ($4.5 \cdot 10^9$ years): ⁴⁰K, ⁸⁷Rb, ²³²Th, ²³⁵U and ²³⁸U (including their decay series). Radionuclides produced for medical applications are of minor concern in this respect and will not be discussed in this review article.

Concerning anthropogenic radionuclides, nuclear weapons testing in the atmosphere is considered the most significant contribution of radioactivity for the oceans during the period between 1945 to 1980. (The first test at the Trinity site in New Mexico, USA and the last atmospheric test, Lop Nor site, China). During this period, 543 nuclear atmospheric tests have been conducted, much more in underground conditions until 1998 as summarized in Figure 1.² For the plutonium element itself, it is estimated that approximately 6.52 PBq (1 Peta Bq = 10^{15} Bq) of ²³⁹Pu, 5.35 PBq of ²⁴⁰Pu, and 1.42 PBq of ²⁴¹Pu have been released into the atmosphere from nuclear weapons testing.^{3,4} It is estimated that 16 PBq of this element (all isotopes) have been deposited in the oceans from the atmospheric military nuclear tests⁵. Other contributions of radioactivity to the oceans are the following: underwater island tests, discharge from the nuclear industry, vessel accidents (satellite fall, submarines), nuclear power plant accidents (Chernobyl, 1986 and Fukushima, 2011). The presence of primordial radionuclides (⁴⁰K, ²³⁸U, ²³⁵U and ²³²Th) in the oceans also contributes to the global average radioactivity.⁶ Among the fission products that may be also released in case of a nuclear accident, cesium (¹³⁴Cs and ¹³⁷Cs) and iodine (¹³¹I, ¹²⁹I) are leading issues as in the case of Fukushima, for which ¹³⁴Cs and ¹³⁷Cs were detected throughout waters 30 - 600 km offshore.^{7,8} Due to its short half-life (8d), ¹³¹I is only detected for a short period of time. As a general rule, fallout quantities of anthropogenic radionuclides are highly dependent on the geographic zone and this makes general conclusions very difficult to assess, especially for anthropogenic radionuclides.⁶ For plutonium, values are scattered and it would be beyond the scope of this article to propose an exhaustive report. For instance, in 1989 Choppin reviewed some estimated

values for surface Pacific seawater: $3.0 \cdot 10^{-17}$ mol.L⁻¹ for North Pacific and $1.0 \cdot 10^{-17}$ mol.L⁻¹ for South Pacific.⁹ Ten years ago, Hirose and co-workers summarized the levels of ^{239,240}Pu in the Pacific Ocean.¹⁰ It has also been observed that surface concentrations (in the order of several mBq.m⁻³) are similar in the North and South Pacific. On the other hand, concentrations in deep waters of the South Pacific are significantly lower than those in the North Pacific, keeping in mind that concentrations decrease with depth. Overall, the ^{239,240}Pu inventories (down to 2300 m) are larger in the North Pacific than in the South Pacific because of the geographical anisotropy of global fallout. Hirose and Aoyama have also reported the determination of concentrations of particulate plutonium in surface seawater of the Western North Pacific.¹¹ The Pu concentration seems to be controlled by organic ligands that originate from marine microorganisms. The radioactivity of the Atlantic Ocean comes essentially from the primordial radionuclides of the uranium and thorium decay series. The most significant additional source of radioactivity comes from reprocessing plants of North West Europe (Sellafield, UK and La Hague, Fr). Discharge figures from both reprocessing plants have been reported by several studies and summarized by Runde and Neu.⁴ For the Arctic Ocean, atmospheric, underwater and underground nuclear testing from the Russian test site of Novaya Zemlya island resulted in severe contamination of the Chernaya Bay zone, which feeds into the Barents Sea. Data obtained from arctic kelp or sediments of the Novaya Zemlya archipelago and Chernaya Bay has been reviewed.^{12,13} The role of sea ice in transporting radionuclides from the Arctic Sea to the North Atlantic has also been addressed.^{14,15} Inventories of Pu atom ratios ²⁴⁰Pu/²³⁹Pu in bottom sediments suggested that plutonium from the Novaya Zemlya archipelago may be transported by sea ice towards the North Atlantic.¹⁶

Concerning primordial uranium and thorium radionuclides present in seawater, in 1989 Choppin reviewed several average values for Th and U concentrations in surface seawater of both the Atlantic and Pacific oceans. Note that although uranium can have natural or anthropogenic origins,^{17,18} thorium is mostly natural (from U/Th decay series). Average reported values are around $1.3 \cdot 10^{-8}$ mol.kg⁻¹ for U and $4.3 \cdot 10^{-13}$ mol.kg⁻¹ for Th.^{19,20} For uranium, Pates and Muir proposed a revised relation based on empirical data in the Mediterranean Sea linking salinity and ²³⁸U concentration.²¹ For thorium, Krishnaswami proposed the average value of few tens of pg L⁻¹ of dissolved ²³²Th in seawater.²²

In conclusion, the above summary shows that most studies on marine radioecology are based on radioactive surveys at the largest scales. Those are necessary to map radionuclide inventories in specific compartments (sand, sediments, water, marine organisms....) or drifts. This large field approach is very useful in order to follow fluxes of transfer, mass balances and accumulation rates in specific compartments over large areas and large periods of time (follow up of contamination drifts). However, the specific chemical mechanisms that underline those processes are largely unknown and difficult to access because they depend on speciation at the molecular scale and because large-scale factors will apply (like dilution or time). Indeed, because of the very low content of radionuclides in seawater (due

to very large dilution factors), direct speciation probes (spectroscopy) are impossible to implement at environmental concentrations.

This focus article outlines the need for speciation data in marine radioecology and reviews the various approaches reported until today in this field using synchrotron-based X-ray Absorption Spectroscopy (XAS). In particular, the aim of this article is to present a survey of recent advances on radionuclide speciation in seawater. It is also worth noting that the spectroscopic approaches reviewed in this article can be applied, more generally, to the speciation assessment of many other metals in the hydrosphere.²³ One selected recent example is the work by Sundman *et al.*²⁴, which shows the essential role of XAS for the structural characterization of iron species in natural waters.

Finally, the present article will also discuss some leading perspectives in order to combine the ultra-trace levels of radionuclides in environmental samples with direct speciation studies that must deal with spectroscopy detection limits.

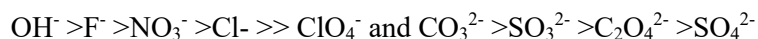
1 What about actinide speciation from thermodynamics models?

Seawater is characterized by a very high ionic strength which averages around 0.6 mol L⁻¹. Table 1 reports the concentrations of the major seawater inorganic constituents compared to concentrations of the same ions in lake basins. There has been some controversy about the Eh and pH of seawater. In 2011, Marion *et al.* reviewed the question of the pH of seawater and concluded that discrepancies in reported values come from pH definitions and conventions that are variable.²⁵ For example, at SA = 35.165 g kg⁻¹ soln, T = 25 °C, P = 1.0 atm, and fCO₂ = 3.33·10⁻⁴ atm, calculated pH values range from 8.08 to 8.33. Eh values have also been discussed by Silver, who predicted an average value of 0.35 V at pH = 8.0.²⁶ The value of 0.21 V has also been reported recently, showing that large variations may apply.²⁷

The solubility, migration behavior and bioavailability of radionuclides in the hydrosphere strongly depend on their speciation (physico-chemical forms depending on different oxidation states or complex formation). The radionuclides to be considered in nuclear activities (I, Sr, Cs, Tc, actinides, etc.) may have very simple or very complex redox chemistry that can be governed by media characteristics. At one end, actinides exhibit oxidation states that range from +III to +VI depending on the element and chemical conditions. At the other end, elements like Cs or Sr exhibit very simple redox behavior with only one available oxidation state. In any case, it is clear that understanding the speciation of radionuclides is necessary for predicting and controlling their behavior from the smallest to the largest scales in the hydrosphere and associated biotopes.

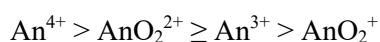
Several attempts to address the question of the speciation of radionuclides in seawater have been reported using simple thermodynamics models and considering RedOx potentials and complexation constants.^{19,28} From these models, oxidation state distributions in relation to pH and E_H of the medium may be postulated. A first qualitative approach based on the hardness (from Pearson's theory) of the basicity of common ligands present in the natural environment allows for the ranking of the affinity for

actinide complexation as follows:⁴



A quick comparison with Table 1 suggests that in seawater hydrolysis and carbonato complex formation may compete.

Plutonium is the actinide element with the most complex chemistry since four oxidation states might be found in natural conditions (+III, +IV, +V and +VI). Note that additional complication with plutonium comes also from the fact that Pu(V) will disproportionate at low pH values while Pu(IV) will disproportionate at high pH values. In any case, the extremely low solubility of Pu(IV) comes from its very strong tendency to hydrolyze at moderate pH values, as discussed in the review on plutonium transport in the environment by Kersting.²⁹ Indeed the reported solubility constant for plutonium hydroxide (Pu(OH)₄) is equal to $\log K_{\text{sp}}^0 = -58.3 \pm 0.5$ (where K_{sp}^0 stands for the solubility product of the hydrolysis reaction calculated from the standard molar Gibbs energy).³⁰ Uranium is ubiquitous at oxidation state +VI under its so-called uranyl form {UO₂²⁺} but may also be present more rarely at oxidation +IV in reducing conditions. At seawater redox potential, uranium occurs mostly under its hexavalent oxidation state in the form of the uranyl cation and is known to form essentially soluble species (unless hydrolysis occurs). Neptunium has an intermediate behavior but is mostly present at oxidation state +V under the form {NpO₂⁺} where it is mainly soluble. Finally, thorium and americium exhibit a unique oxidation state behavior in environmental conditions: +IV for Th and +III for americium. In any case, the most up to date thermodynamics models need to take into account complexation constants for simple ligands as hydroxide, carbonate or sulfate. These general trends have been fully reviewed, for instance, by Choppin in 2007.³¹ A very complete and more recent review on the speciation of actinides in the environment is also provided by Maher *et al.*³² As a general trend, it is commonly accepted that the ability of actinide ions to form complexes follows their effective charge as:



Nevertheless, the specific case of seawater is somewhat complex since it combines very high ionic strength, large carbonate amounts, high pH with the presence of particles, organic ligands and microorganisms.

In the case of plutonium, for instance, Silver and Choppin have approached the question considering equilibrium equations derived from disproportionation or other oxidation-reduction reactions.^{33,26} Hirose and co-workers have discussed the complexation of Pu(IV) with strong organic ligands in competition with hydrolysis.¹¹ But they also estimated that the fraction of insoluble complexes of Pu(IV) associated with particulate matter is minor compared to soluble species. The presence of Pu(V) under the form {PuO₂⁺} has been under debate and would clearly compete with the complexation of plutonium at other oxidation states as extensively discussed by Silver.³³ More recently, Topin and Aupiais have revisited the solution chemistry of An(V) in the environment.³⁴ They reported a prediction from thermodynamics constants, suggesting that under average seawater conditions ($I = 0.6 \text{ mol.L}^{-1}$ and pH

= 8.2) the main Pu(V) species would be distributed as: PuO_2^+ (69.9%), PuO_2Cl (18.3%), $\text{PuO}_2\text{SO}_4^-$ (6.0%) and $\text{PuO}_2\text{CO}_3^-$ (5.3%).

For uranium (uranyl), during the last two decades, all of the speciation models have reported on the formation of carbonate species as predominant. According to Choppin, carbonate complexes represent 90-100% of the total uranium in seawater.³⁵ Atwood reported $\text{UO}_2(\text{CO}_3)_3^{4-}$ as the major and most stable complex at seawater pH (between 8 and 8.5).⁶ Other studies have shown the influence of the calcium ion on uranyl speciation in seawater, with the formation of calcium-uranyl-carbonate ternary complexes of different stoichiometries. These ternary complexes were already observed by Bernhard *et al.* in artificial seepage water by TRLIFS.³⁶ They found the complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ as the predominant species. For a more general review on the thermodynamic stabilities of uranyl complexes in natural waters, see the work by Berto *et al.*³⁷ and the recent review on uranium recovery from seawater.³⁸

Although this information is very important for the building of speciation diagrams, it often lacks experimental evidence and in particular "direct" speciation data ("direct" meaning here that the radionuclide itself and its environment are directly probed). In addition, kinetics is affected by diffusion phenomena at the ultra-trace scales that may modify significantly the thermodynamics predictions. Clearly, molecular speciation in natural seawater has rarely been addressed because concentrations in natural conditions are far too low to allow any direct spectroscopic measurements. In conclusion, if thermodynamics assessment of equilibrium equations is essential as a predictive tool, then experimental data are a bottleneck for speciation in natural media and in marine radioecology in particular.

2 A move towards direct speciation in natural systems

2.1 General considerations

As mentioned in the previous paragraph, seawater is a complex medium, containing several inorganic and organic species. Concentrations of the major inorganic species (Cl^- , Na^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , K^+) in the oceans are relatively constant, because of water mixing and sea currents. In contrast, minor species concentrations strongly depend on geographic zone and seawater depth. Forty percent of organic matter in seawater is composed of humic substances (HS) that are able to complex several metal ions, including the actinides, having an influence on their mobility and fate in seawater.³⁹ The remaining 60% of organic matter is made of living organisms and their metabolites.⁴⁰ Numerous inorganic and organic seawater species can act as ligands for actinides, which consequently occur in seawater under different physico-chemical forms: from small inorganic complexes, through HS complexes, to higher molecular mass species, such as colloids and polynuclear species.

The high ionic strength of seawater compared to other natural aqueous compartments makes speciation studies more complicated by preventing the use of many spectroscopic techniques. ICP-MS or ICP-OES, for example, would need significant sample dilutions or prior separation of the element of interest from the saline matrix. Such a separation step may have an influence on thermodynamic equilibria and speciation in the analyzed medium. On top of that, radionuclide concentrations in seawater (see

introduction) are often lower than detection limits of the techniques commonly used for most spectroscopic techniques. Time Resolved Laser Induced Fluorescence Spectroscopy (TRLIFS) is a sensitive technique for speciation assessment as it allows direct determination of the chemical species in solution, given that the analyzed element is fluorescent. Furthermore, TRLIFS allows analysis of natural samples and has very low detection limits compared to other spectroscopic techniques (typically around 10^{-8} mol L⁻¹ for U(VI), and Cm(III), 10^{-6} mol L⁻¹ for Am(III))⁴¹. However, among the actinides, only uranium, americium and curium can be analyzed by this technique.

In contrast, X-ray Absorption Spectroscopy (XAS) is a technique that is ideally adapted to metals. It is a powerful tool for the speciation of radionuclides and, more generally, metal ions speciation in complex matrices like environmental ones. In fact, XAS gives direct information on the local structure around the investigated element (ligands, interatomic distances), its oxidation state, its symmetry. XAS measurements of environmental samples can be performed without previous separation steps that could modify the thermodynamic equilibria and therefore the chemical speciation. XAS is almost exclusively a synchrotron-based technique because of the need of an energy continuous high flux X-ray source. It is not the purpose of this article to review this spectroscopy in depth, so we will just give some general information on the XAS spectra and detection limits below. To have a broader view concerning instrumentation, theory, analysis and applications of XAS the reader may refer to the recent book by van Bokhoven, C. Lamberti.⁴² Also, a very recent review on the use of XAS in the field of biomedical chemistry including some basic theoretical background of data analysis is also provided by Porcaro *et al.*⁴³ Finally, some less recent reviews dedicated to the use of XAS for speciation of actinides have been provided by Denecke⁴⁴ and by Antonio and Soderholm.⁴⁵ In short, a typical XAS spectrum at a given element edge is formally composed of two parts:

- (i) the XANES (X-ray Absorption Near Edge Structure) region goes from the pre-edge region (energies below energy threshold E_0) to energies 50-100eV above E_0 . XANES (also called NEXAFS, depending on the edge) gives important structural and electronic information, such as the symmetry and filling of the valence states. It is also related to the oxidation state of the absorbing element and its symmetry.⁴⁴
- (ii) the EXAFS (Extended X-ray Absorption Fine Structure) region corresponds to the interferences of the scattered photoelectron between the central atom and its neighbors (ligands). EXAFS gives information on the local structure around the central atom, the nature and number of coordination, the interatomic distances between the central atom and its neighbors.⁴⁶ Figure 2 reports an example of an EXAFS spectrum at uranium L_{III} edge and its Fourier Transform.

To acquire XAS signals on samples with diluted absorbing elements ($< 10^{-2}$ - 10^{-3} mol L⁻¹), measurements have to be performed in fluorescence mode generally using an energy resolving solid-state detector (SSD).

Although XAS allows direct measurements in natural matrixes (without previous chemical or physical separations in most cases) it is not sensitive enough to detect radionuclides in seawater at environmental

concentrations. Indeed, the detection limits of fluorescence XAS using SSD detectors may span from 10^{-6} mol L⁻¹ to 10^{-4} mol L⁻¹ but strongly depend on the matrix composition and the edge energy. To overcome these technical limitations, some recent studies have been performed by doping natural seawater samples with the radionuclide of interest.^{27,47,48} Figure 3 illustrates that in these studies the doping concentrations were chosen higher than the detection limits for this experiment ($5 \cdot 10^{-5}$ M), but still low enough to maintain the chemical equilibria in solution unperturbed.

We propose below a selection, as updated as possible, of reported studies on radionuclide speciation in seawater, for which the contribution of XAS has been essential. Note that this domain of environmental chemistry is very restrictive and very few data are available in the literature. For most of these studies, XAS (alone or coupled with other analytical techniques) has been essential to obtain definitive information about the investigated radionuclide speciation. Table 2 recapitulates the results obtained in these studies.

It should be kept in mind that despite the low concentrations of the radionuclides in samples investigated with XAS, the radioactivity levels for some of the samples can be higher than the usual national exemption limits and thus require the performance of the studies on specific synchrotron beamlines dedicated to radioactive samples, such as in France the MARS beamline at SOLEIL⁴⁹ and the ROBL beam line at ESRF⁵⁰. Since this kind of specific beamlines is only present at a few synchrotron facilities, it is evident that such studies are difficult to implement for radioelements having all isotopes with high specific activities (like plutonium, americium, curium etc...) and no stable isotope.

2.2 Uranium

At environmental water pH (between 6.9 and 8.0), the structural identification of the carbonato complex by EXAFS was attempted by Bernhard in 2001⁵¹ and by Kelly *et al.* in 2007⁵² at micro molar concentration. These EXAFS studies revealed that, in environmental waters, the uranyl cation is coordinated by three carbonate groups in a bidentate way, resulting in six equatorial oxygen ligands. In contrast, assessing the presence of the calcium ion in such carbonate complex was more challenging. In fact, EXAFS could not give accurate information on the presence of calcium in this particular complex because the calcium signal overlaps the distal oxygen signal of the carbonate ligands. Maloubier *et al.* have more recently analyzed the uranyl speciation in natural seawater doped with $\text{UO}_2(\text{NO}_3)_2$, at 10^{-5} and $5 \cdot 10^{-5}$ M. They reported the neutral carbonato calcic complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, as the main species in solution, together with $\text{CaUO}_2(\text{CO}_3)_3^{2-}$.²⁷ Although the EXAFS data obtained at 10^{-5} M were significantly noisy, they were similar to that obtained at $5 \cdot 10^{-5}$ M. This comparison is important since it validates the doping approach and may open perspectives for even more dilute samples. In the same work, the presence of these carbonato calcic complexes was confirmed by TRLIF spectroscopy. These results are essential in terms of environmental and biological impact because these ternary complexes were previously shown to be non-toxic or non-bioavailable species.⁵³ Further investigation on the role of the alkaline earth cation in uranyl-carbonate complexes in seawater has recently been performed by

using EXAFS at two different edges.⁴⁷ This work has experimentally asserted the presence of the alkaline earth ions in ternary uranyl-carbonate complex structures, by replacing Ca^{2+} with Sr^{2+} . The authors recorded and analyzed the EXAFS spectrum at uranium L_{III} edge for an artificial seawater solution containing Sr^{2+} (5 mM) instead of Ca^{2+} and doped at $[\text{U}] = 5 \cdot 10^{-5}$ M. The spectrum and the corresponding Fourier transform were adjusted using a $\text{SrUO}_2(\text{CO}_3)_3^{2-}$ model (Figure 2).

Moreover, the role of the alkaline earth ion, with its nature and size, on the complex structure has been revealed, showing that the major complex presents only one alkaline earth ion and is negatively charged when Ca^{2+} is replaced by Sr^{2+} ($\text{SrUO}_2(\text{CO}_3)_3^{2-}$).

Uranyl complexes with other anions present in seawater are far less stable than those including carbonate ligands.

2.3 Neptunium

The first direct experimental speciation study on neptunium in natural seawater was reported in 2015, by using XAS.²⁷ A Few EXAFS studies were previously performed on groundwater environments, which detected the presence of three carbonate complexes ($\text{NpO}_2(\text{CO}_3)^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$) in synthetic carbonate solution and elucidated their structures.⁵⁴ In the work of Maloubier *et al.* a natural seawater sample was doped with $5 \cdot 10^{-5}$ M Np(V) and analyzed by EXAFS at the Np L_{II} edge. The structural data revealed the presence of at least one carbonate ligand in the coordination sphere of Np, even if the presence of several carbonate complexes with different stoichiometries could not be excluded. In the absence of other species in solution, working at Np L_{III} edge would have probably improved the count rate contrast, leading to a higher signal to noise ratio of the EXAFS spectrum. However, in the specific case of seawater working at Np L_{III} edge was not possible because of the presence of bromine dissolved in seawater (the $\text{K}\beta_1$ emission line of bromine, 13292 eV, interferes with the $\text{L}\alpha_1$ emission line of neptunium, 13946 eV).

2.4 Americium

In environmental waters, americium is able to form complexes mainly with hydroxides, carbonates and humic acids. Actually, carbonate complexes formation becomes important at pH higher than 8 and pCO_2 higher than 0.1 atm.⁶ Theoretical predictions of americium speciation in seawater using thermodynamic constants in aqueous solution shows that the main Am species at seawater pH and redox potential is AmCO_3^+ .⁴⁰ To our knowledge, the only experimental study on Am(III) speciation in seawater was performed in 2015⁵⁵, by using XAS. In this work, the presence of carbonate ligands was confirmed, and the main identified americium species was a ternary sodium-biscarbonato complex ($\text{NaAm}(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$).

2.5 Cesium

Radio-caesium is one of the major radioelements dispersed in seawater in 2011, during the Fukushima-Daiichi nuclear accident. It is present at its oxidation state I (Cs^+) in aqueous solution. Hydrated Cs^+ is highly stable and does not show reactivity with humic and fulvic acids.⁵⁶ Cesium migration in seawater is therefore strongly dependent on suspended particles, which adsorb this element between the layers of clay minerals, forming inner-sphere complexes. For this reason, describing sorption-desorption phenomena is fundamental in order to understand cesium speciation in seawater. In the Baltic Sea, the link between cesium mobility and mineral composition of suspended sediments has been investigated.⁵⁷ Onodera *et al.* have also recently shown how Na^+ and K^+ ions, both abundant in seawater, can affect cesium sorption-desorption processes. In particular, hydrated Na^+ ions expand the interlayer distances of the particulate minerals, improving the desorption of cesium. In contrast, dehydrated K^+ ions inhibit this desorption process by reducing the interlayer distance.⁵⁸ To the best of our knowledge, no XAS study on cesium complexation by ligands naturally present in seawater has been performed. Due to the position of Cs in the periodic table, both L and K edges are possible. However, the L_{II} and L_{III} edges are separated by only 350 eV and this drastically reduces the potential resolution of the spectrum. The Cs L_{III} edge (5 012 eV) is also close to I L_{III} edge. At this energy, the absorption length is also lowered by the high salinity of the medium. For all these reasons Cs K edge (35 985 eV) might be preferred although it is broadened by its very short core hole life time. It is also difficult to achieve for most XAS beam lines.

2.6 Plutonium

Plutonium is an element of particular concern in terms of global inventory. As mentioned in the introduction, direct speciation is difficult because, at the pH of seawater, hydrolysis of Pu(IV) and formation of colloid species may be dominating. On the other hand, XAS data on plutonium contaminated environmental samples has recently been recorded, as summarized by Batuk *et al.*⁵⁹ A recent attempt to better describe the speciation of plutonium colloids in seawater has been done by the authors of this article, by using the doping strategy described above for uranium and analyzing the doped sample by XAS.⁴⁸ In this case, the observed valence for plutonium in natural seawater is +IV in its majority and its speciation corresponds to $\{\text{PuO}_2\}$ -like colloids. Aging of the solution shows a gradient of ordering from oxo-hydroxo species to more crystalline PuO_2 type of colloids that become denser and less soluble.

Some hypothesis on plutonium speciation in seawater have also been done by analyzing thorium speciation in the same environment. In fact, Th(IV) is often considered a chemical analogue of Pu(IV) and other tetravalent actinides. In organic-free aqueous solutions, at seawater pH, Th(IV) mostly forms poly-hydroxy colloidal complexes. In natural seawater, the existence of mixed hydroxo-humate complexes has also been stated.⁴⁰ Santchi *et al.* provide a complete review of thorium speciation in seawater, analyzed by different experimental and theoretical methods.⁶⁰ However, any study on Th(IV) speciation in seawater has been performed by using synchrotron techniques.

3 Further trends (and challenges)

The above examples show the complexity of working on a natural medium because of the necessity of finding a compromise between reproducing the environmental conditions and overcoming technical limitations (Figure 3). The doping methodology reported by Maloubier *et al.*²⁷ is a case in point and could be extended to other fields of environmental chemistry. Of course, it suffers from the suspicion that chemical equilibria will be modified compared to the trace and ultra-trace scales, even if doping concentrations are set largely below the concentrations of the major elements of the medium. Nevertheless, careful doping just above the spectroscopic detection limit is the only way to obtain direct structural data. On top of that, Maloubier *et al.* showed that, for uranium and neptunium in seawater, theoretical speciation diagrams based on thermodynamic constants are identical for the radionuclide at doping concentration ($5 \cdot 10^{-5}$ M) and environmental concentrations (10^{-8} M for U and 10^{-14} M for Np).²⁷ There are of course a few sources of improvement with regards to the limitations of X-ray Absorption Spectroscopy to measure diluted samples.

A first simple possibility is to consider the region of the XANES spectrum, typically up to ~ 50 eV above the edge (post edge region). The photoelectron mean free path is maximal after the edge, therefore it is sensitive to the position of atoms beyond the nearest neighbor coordination sphere and can yield information about the hydration sphere around an absorbing atom. The main limitation of this approach is that, unlike the EXAFS region, the interpretation of the XANES features is not straightforward. It often requires a comparison with spectra of model compounds or spectra from models produced *in silico*. In the latter case, the determination of the local sphere of an ion in solution requires the use of theoretically generated configurations, obtained either from first principle quantum mechanical calculations or molecular dynamics. Several examples have been given, some concerning the actinide or lanthanide elements. For the lanthanide series for instance, the combination of XANES with simulation and the use of molecular dynamics has led to the full description of their coordination sphere in solution.^{61,62} One major advantage is that XANES spectra can be recorded at very low concentrations, around the ppm level, depending on the chemical system but in any case, at much lower concentration than EXAFS. Very recently, Zhang *et al.* have reviewed the analysis of uranyl XANES spectra in various model solutions down to 40 ppm.⁶³ Other examples are also given by the very comprehensive study of Batuk *et al.* on a large variety of contaminated solid samples.⁵⁹ They have compared XANES spectra at very low concentrations with model samples. Another limitation in the analysis of the XANES region is that the signal can be less informative than EXAFS due to instrumental and intrinsic broadening that is associated to the core hole. A possible improvement would be to increase the edge sharpening using a crystal analyzer spectrometer (CAS) at a resolution around the core hole widths instead of a SSD (see below).⁶⁴ This effect is particularly interesting for core levels of heavy atoms like the K or L_{III} edges of the third and fourth row elements.⁶⁵

Another possible improvement to measure diluted samples with XAS would be to increase the photon flux of the incoming beam. Usually XAS beamlines are installed on synchrotron bending magnets, since these sources allow for a more continuous energy domain for the generated X-rays, with fluxes around $10^{11} - 10^{12}$ ph/s for third generation synchrotrons. A step towards higher incoming beam flux (however in a narrower spot) should be achievable in the following years with the construction and operation of new high brilliance synchrotrons with Diffraction-limited storage rings (DLSR).⁶⁶ One must keep in mind, however, that the principal bottleneck related to the increase of photons is the stability of the samples. Indeed, more and more often, radiation damage of samples induced by X-rays is observed. This problem can be handled, for example, by freezing the samples with specific cryostats. It is clear that for seawater studies this is not conceivable because of a possible change of speciation induced by a phase change of water. Other possibilities that could be more suitable for this kind of study might be the use of liquid jet devices or microfluidic cells. In this case, difficulties may arise because of the need of a sealed containment (or double/triple containment) necessary for the study radioactive samples.

Another source of improvement for the study of diluted systems is in the area of detection. Hence, a first improvement would be to try to collect the X-ray fluorescence over the largest solid angle possible. This is possible with SSD systems by making use of multi-element (array) systems (also to avoid saturation effects, see below), which are usually set with tens of elements, but could be increased up to hundreds. However, there are intrinsic restraints in considering SSDs systems in relation to maximum count rate achievable and energy resolution, which can be particularly limiting when studying diluted elements in environmental matrices. Indeed, for this kind of sample the total count rate might be dominated by the elastic or inelastic scattering coming from the matrix or by the fluorescence signals of the elements of the matrix itself with a minority of counts coming from the fluorescence line of the element of interest. The high-count rates may lead to distortions or damping of the signals because of saturation of the detector. To reduce this effect, it is possible, as mentioned before, to use multi-element detectors, and in favorable cases to use specific filters or specific optical systems (such as bent Laue crystals) to damp or suppress the undesired signals.⁶⁷ In some other cases, what is limiting is the fluorescence peaks from other elements of the matrix or the scattered peaks that overlap with the fluorescence signal of the diluted element (the energy resolution of SDD systems is usually 150 and 300 eV).

One possibility for overcoming this difficulty is to use a crystal analyzer spectrometer (CAS) for which energy resolutions of some eVs can be achieved and thus allow better selection of the fluorescence line of interest. This has been demonstrated for various examples by Llorens *et al.* using a high energy resolution five-crystal spectrometer of a Johann-type geometry. With this setup, the fluorescence or scattering of the matrix can be removed, resulting in higher signal to noise ratio for the edge of interest.⁶⁸ A more recent review from the same authors gives various examples from the field of environmental biogeochemistry.⁶⁵ However, the limit of the CAS systems is the low efficiency compared to SSD systems. Thus, it could be interesting in the future to develop different detection systems such as those

making use of superconducting transition-edge sensors (TES) which have narrower energy resolutions than SSDs and higher efficiency than CAS.⁶⁹

Table 1.

Average concentrations of inorganic constituents of seawater^{70, 71}, compared to concentrations of the same elements in lake basins.

	Seawater concentration (mM)	Lake basins concentration (mM)
Cl ⁻	535	0.054 - 0.68
SO ₄ ²⁻	9 - 28	0.03 - 0.53
HCO ₃ ⁻	2.3	0.31 - 1.85
Br ⁻	0.84	-
F ⁻	0.068	0.011 - 0.016
I ⁻	0.00047	-
SiO ₂	0.11	0.12 - 0.17
B	0.42	-
Na ⁺	465	-
Mg ²⁺	52.7	0.045 - 0.41
Ca ²⁺	10.0	0.11 - 0.95
K ⁺	9.7	0.033 - 0.074
Si ²⁺	0.15	-

Table 2. Compendium of radionuclide complexes experimentally detected by X-Ray Absorption Spectroscopy in seawater and in model solutions reproducing environmental water conditions. For each study, we report the used radionuclide concentration, the obtained information (nature of ligands and distance from the central atom) which led to the speciation assessment (detected complexes).

Radionuclide	Matrix	Radionuclide concentration	Ligands	Detected complexes	Ref.
U(VI)	natural seawater	$1 \cdot 10^{-5} \text{ M} - 5 \cdot 10^{-5} \text{ M}$	2 O at 1.80(1) Å 5.8(5) O at 2.43(1) Å 2.9(3) C at 2.90(1) Å	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ $\text{CaUO}_2(\text{CO}_3)_3^{2-}$	27
	$2 \cdot 10^{-3} \text{ M Ca}^{2+}$, $5 \cdot 10^{-5} \text{ M HCO}_3^-$, aqueous solution, pH 8	$2 \cdot 10^{-5} \text{ M} - 1 \cdot 10^{-4} \text{ M}$	2 O at 1.81 Å 6 O at 2.44 Å 3 C at 2.90 Å 3 O at 4.22 Å 2 Ca at 3.94 Å	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	51
	$5 \cdot 10^{-5} \text{ M NaHCO}_3$, aqueous solution, pH 6.9	$5 \cdot 10^{-5} \text{ M}$	2 O at 1.78(1) Å 6 O at 2.45(1) Å 3 C at 2.89(1) Å	$\text{Na/Ca-UO}_2\text{-CO}_3^{(a)}$	52
Np(V)	natural seawater	$5 \cdot 10^{-5} \text{ M}$	2 O at 1.84(1) Å 6(10) O at 2.54(2) Å 2 (20) C at 2.99(7) Å	$\text{NpO}_2(\text{CO}_3)^-$ $\text{NpO}_2(\text{CO}_3)_2^{3-}$ $\text{NpO}_2(\text{CO}_3)_3^{5-}$	27
Pu(IV)	natural seawater	$5 \cdot 10^{-5} \text{ M}$	8 O at 2.28(15) Å ^(b)	$\text{Pu}_n(\text{OH})_m\text{O}_1 \cdot x\text{H}_2\text{O}$	48
			3.4(5) O at 2.24(1) Å ^(c) 3.2(6) O at 2.39(1) Å ^(c) 3.6(6) O at 3.82(2) Å ^(c)	$\text{Pu}_n(\text{OH})_m\text{O}_1 \cdot x\text{H}_2\text{O}$	
			2.7(7) O at 2.24(1) Å ^(d) 3.6(6) O at 2.37(2) Å ^(d) 4.7(5) O at 3.83(2) Å ^(d)	$\text{Pu}_n(\text{OH})_m\text{O}_1 \cdot x\text{H}_2\text{O}$ PuO_2	
Am(III)	natural seawater	$5 \cdot 10^{-5} \text{ M}$	9 O at 2.48(1) Å 1 Na at 3.25(5) Å 2 C at 3.73(3) Å	$\text{NaAm}(\text{CO}_3)_3$	55

(a) undefined stoichiometry

(b) measure performed after sample preparation, soluble part.

(c) measure performed after 6 months of aging of the sample, soluble part.

(d) measure performed after 6 months of aging of the sample, colloidal precipitate.

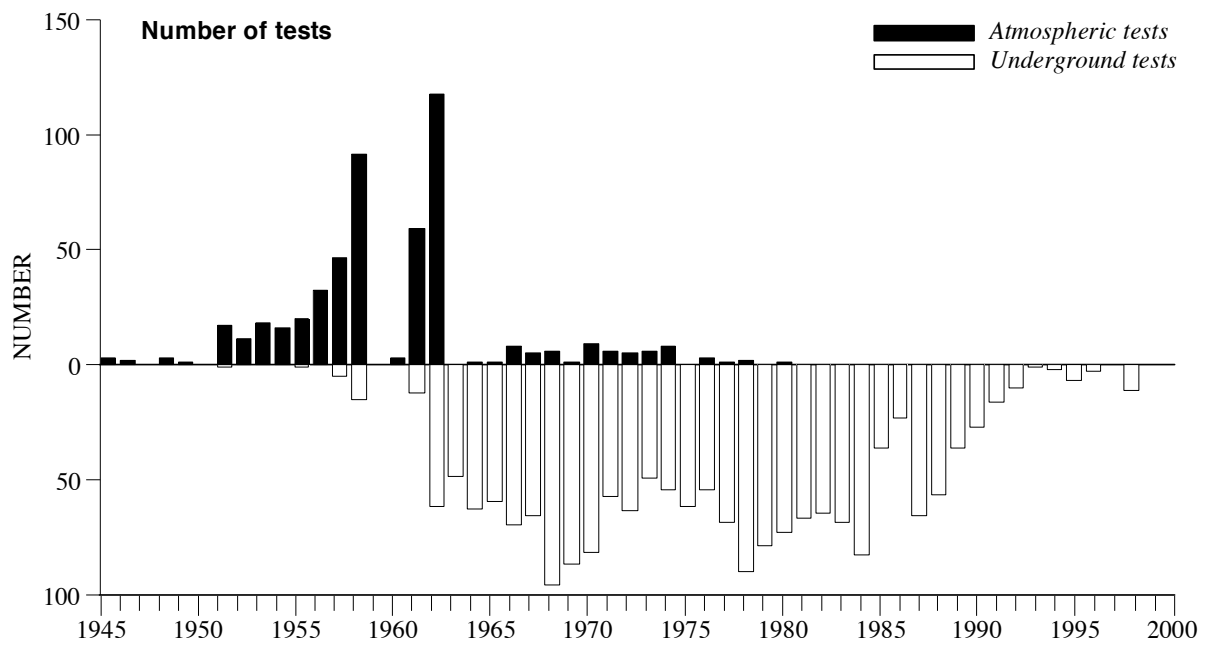


Figure 1: Number of nuclear weapon tests. From UNSCEAR Report, 2000²

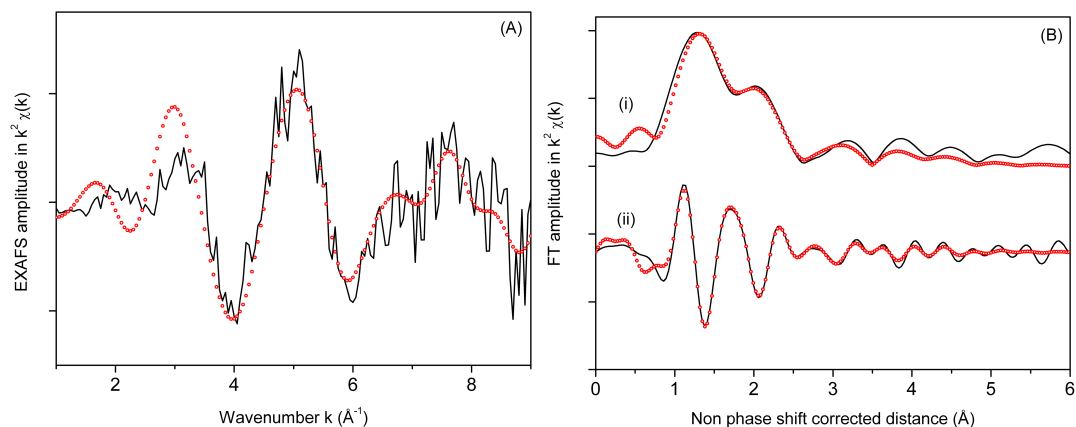


Figure 2: Adjustment of the EXAFS spectrum for artificial seawater solution containing Sr^{2+} ($5 \cdot 10^{-3}$ M) and UO_2^{2+} ($5 \cdot 10^{-5}$ M). Data fitting was performed with the contribution of a Sr^{2+} ion, in addition to two bidentate and one monodentate carbonate ligands around the uranyl ion. Panel (A): k^2 -weighted EXAFS spectrum and the U L_{III} edge; panel (B): corresponding Fourier transform ((i) magnitude, (ii) imaginary part). Experimental spectra in black solid line, adjustment in red dots.⁴⁷

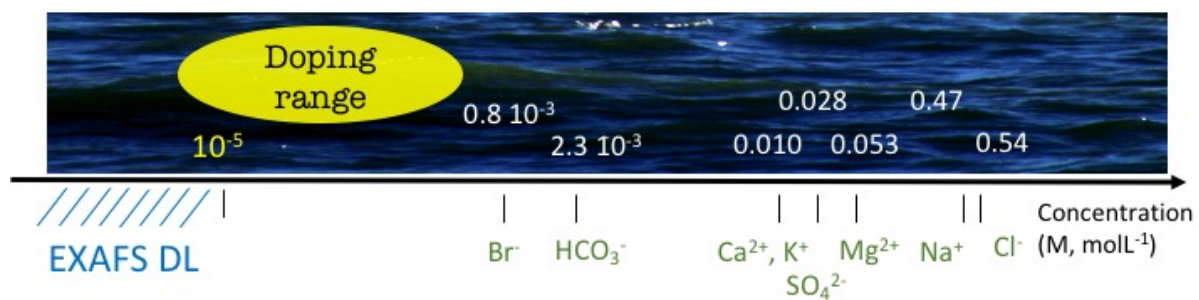


Figure 3: Schematic representation of the average concentrations of major inorganic constituents of seawater compared to EXAFS detection limit (DL, average value or below, depending on the experimental setup).

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