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Thomas Dumas, Mireille Guigue, Philippe Moisy, Roberto Colina-Ruiz, Jose Mustre de Leon, et al.. Experimental Speciation of Plutonium(IV) in Natural Seawater. *ChemistrySelect*, 2018, 3 (7), pp.2021-2024. <hal-03596685>

HAL Id: hal-03596685

<https://hal.science/hal-03596685v1>

Submitted on 3 Mar 2022

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Experimental Speciation of Plutonium(IV) in Natural Seawater

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Abstract Solubility, migration, and bioavailability of plutonium is lacunar because experimental evidences are missing. We report here on X-ray Absorption Spectroscopy of plutonium in natural seawater. The observed valence state is +IV and its speciation corresponds to PuO₂ type colloids. Furthermore, aging of the solution shows a gradient of ordering from hydroxide colloidal species to more crystalline PuO₂ colloids.

Among all the environmental compartments that serve as repositories for various heavy metals, seawater may be considered as the ultimate destination for rivers and catchment areas. As a consequence, seawater and associated biotopes have always been monitored as indicators of heavy element pollution. In the specific case of radionuclides, their origins are either anthropogenic (atmospheric nuclear tests from the cold war of the 1950s and 1960s, or accidental releases) or natural (mainly uranium and thorium). The latest event involving the Fukushima accident has demonstrated that seawater might be the first major repository in the long term, due to the potential impact of the numerous radionuclides present within the reactors, although drastic dilution factors will apply. In any case, the solubility, migration behaviour, and bioavailability of radionuclides strongly depend on their speciation (physical-chemical forms depending on different oxidation states or complex formation). Hence, understanding the speciation of radionuclides is essential for predicting and controlling their behaviour at the largest scales in the environment.

Plutonium (various isotopes) is a valuable energy resource that arises from civilian and military industries in a number of chemical and physical states. But the toxicity of plutonium is high whatever the isotope, because it is both chemically toxic (as a heavy metal) and mainly radiotoxic (as all its isotopes are radioactive). It is therefore crucial to maintain the lowest possible levels of releases into the environment and limit the impact of any accident conditions on workers, public and environment. It is estimated for instance that 1.6×10^{16} Bq of this element have been deposited in the oceans from military atmospheric nuclear tests.^[1] The recent historical report from Thakur and co-workers describes the various sources of plutonium from its discovery (in 1945) to now and its contribution to the global release in the atmosphere.^[2] Several attempts to describe the speciation of plutonium in seawater have been reported. Authors have addressed the question from thermodynamic considerations^[3,4,5] and have attempted to specify the oxidation-state distribution in relation to pH and E_H of the medium.^[6,7] Experimental evidence is lacking in all cases because concentrations in natural conditions are far too low to allow any spectroscopic measurements. One possibility to overcome this intrinsic difficulty is to dope the medium with a salt of the element of interest at a concentration that is a compromise between the spectroscopic detection limit and above all the avoidance of any significant modification of the chemical equilibria. Previously, this method was successfully applied to the study of uranium, neptunium and americium in natural seawater. X-ray Absorption Spectroscopy (XAS) was performed together with Time Resolved Laser Fluorescence Spectroscopy for uranium(VI).^[8,9]

We report on the spectroscopic investigation (using XAS) of the chemical form of plutonium colloids in natural seawater. To prepare the mother solution, the initial doping concentration of plutonium was equal to 5×10^{-5} mol.L⁻¹ (using ²³⁹Pu isotope, see sample preparation in S.I.). The seawater potential was measured and equal to 210 mV/NHE), while the pH was equal to 7.8(8). 500 μ L of the 30 days old mother solution were injected into an EXAFS cell 1 (spectrum **I**). The concentration of Pu in the EXAFS cell 1 was estimated from α spectrometry to be equal to 7×10^{-7} mol.L⁻¹. The difference from the mother solution (doped at 5×10^{-5} mol.L⁻¹) is attributed to the formation of heterogeneous physicochemical forms of plutonium colloids in the mother solution (see sample preparation in S.I.).

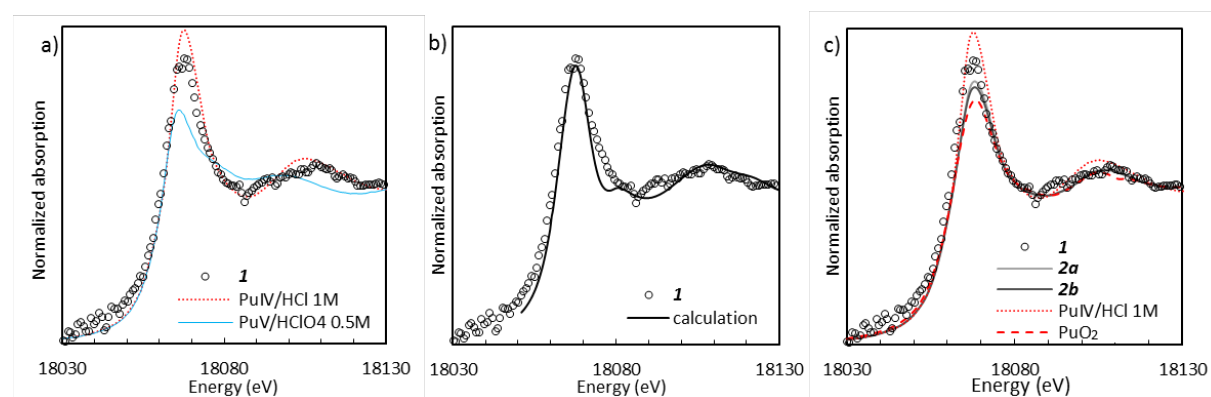


Fig. 1: a. XANES spectrum at the Pu L_{III} edge of plutonium in doped natural seawater (spectrum **I**, cell 1) compared to reference Pu(IV) and Pu(V) in acidic conditions. The estimated concentration in cell 1

is equal to $7 \cdot 10^{-7} \text{ mol.L}^{-1}$; b. XANES spectrum at the Pu L_{III} edge of spectrum **1** compared to XANES simulated using a simple model of PuO_2 (cubic form) in Full Multiple Scattering mode using Feff9 code; c. Comparison between the XANES spectra **1** (cell 1), **2a** and **2b** (cell 2) and references Pu(IV) aqua in HCl 1 mol.L^{-1} and pure solid PuO_2 .

XAS measurements were carried out on the MARS beam line of the SOLEIL synchrotron at the Pu L_{III} edge (experimental details in S.I.). At this concentration and because of the closeness of the $L\alpha_1$ emission line of plutonium (14279 eV) to the $K\beta_1$ emission line of bromine in seawater (13292 eV), the signal to noise ratio can be expected to be very low. The XANES spectrum of plutonium in this solution is shown in Figure 1a in comparison to the aqua forms of Pu(IV) (Pu^{4+}) and Pu(V) ($\{\text{PuO}_2^+\}$). It clearly shows the absence of O-Pu-O multiple scattering features about 15 eV after the edge maximum observed as a usual fingerprint of the transdioxo actinide species for Pu(V). Simulation of the XANES spectrum was also performed from a simple model of PuO_2 (cubic form) in Full Multiple Scattering mode using Feff9 code (Figure 1b).^[10] The data and simulation are in very good qualitative agreement. The EXAFS spectrum (Figure 2bc, EXAFS and corresponding Fourier transform) was also obtained, although data must only be considered until $k = 8 \text{ \AA}^{-1}$ (in $k^2\chi(k)$). Best fit parameters are given in Table 1. Because of the noise level (0.054), only one shell of a fixed number of oxygens (8, as in PuO_2) has been injected in the fit. The average bond length (2.28(15) Å) reflects the average environment of Pu in its first coordination sphere and is in good agreement with the average of the Pu-O distances in reported $\text{Pu}_n(\text{OH})_m(\text{O})_x\text{H}_2\text{O}$ species initiating colloid formation.^[11,12,13]

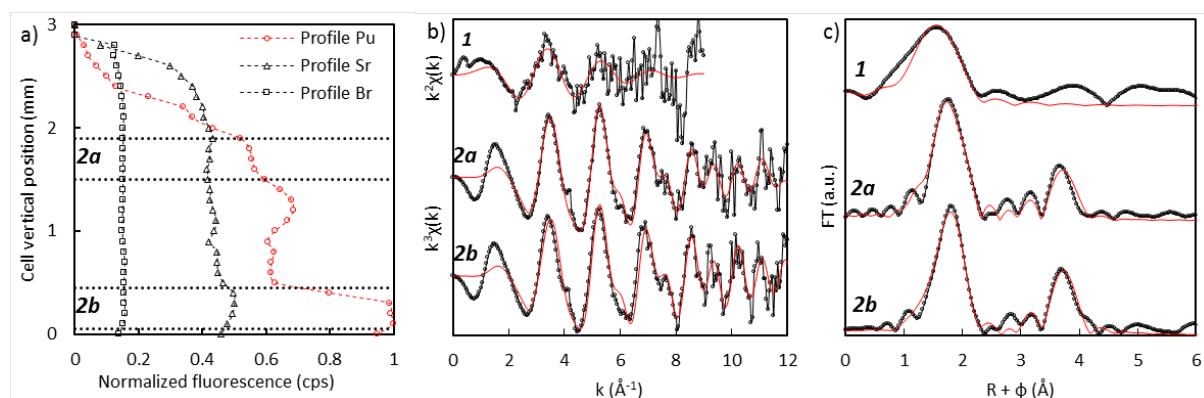


Fig. 2: a. Vertical profile in the EXAFS cell 2, red circles for plutonium ($L\alpha_1$ recorded for incident beam at 17900 eV and 18068), black triangles for strontium ($K\alpha_1$ recorded for incident beam at 16100 eV and 16120) and black squares for bromide (sum of $K\alpha_1$ fluorescence counts). Dotted lines indicate the vertical beam position for recording the EXAFS spectra **2a** and **2b**; b. k^3 -weighted EXAFS spectra (open circles) and best fit (red lines) of spectrum **1** (cell 1), **2a** and **2b** (cell 2); c. corresponding Fourier transformed (FT) of spectra **1**, **2a** and **2b**. k^2 -weighted EXAFS spectrum for sample **1** was recorded in diluted conditions ($7 \cdot 10^{-7} \text{ mol.L}^{-1}$).

The remaining initially doped seawater solution was kept in the same vessel as the mother solution in the laboratory (Atalante facility of CEA) for six months. It yielded the formation of a yellow-green colloidal solution at the bottom of the vial. 250 μL of this colloidal solution were separated from the bulk solution (S.I. Figure S1), transferred into EXAFS cell 2 and measured on the MARS beam line. As the sampled solution stood in cell 2 without significant shaking on the beam line, the colloidal solution slowly separated again from the remaining clear solution. In order to probe this heterogeneity through the cell, it was vertically mapped in fluorescence mode using a focused X-ray beam with 100 μm steps. This resulted in elementary profiles mapping plutonium together with two elements that are present in seawater with emission fluorescence lines close to that of plutonium: strontium and bromine. The resulting vertical profiles for plutonium, strontium and bromide are presented in Figure 2a (experimental details in S.I.). From top to bottom, wide variations in the plutonium concentrations can be observed and three zones may be distinguished: a very slightly concentrated Pu solution at the top of the cell (+3 mm), an intermediate band (+2 mm to +0.8 mm) and a highly concentrated area at the very bottom of

the cell. Lastly, the bromide profile is constant over the three zones. This indicates that seawater is present in the three zones without any depletion in the plutonium colloidal zone. The slight increase of strontium in the last zone where the Pu colloid is present may be an indication of its trapping in the colloidal structure (vide infra for discussion on this point). To establish a correlation between the plutonium profile and the corresponding speciation, plutonium EXAFS spectra were recorded in both positions **2a** and **2b** (corresponding to spectra **2a** and **2b** of cell 2) indicated by dotted lines in the sample profile of Figure 2a. The resulting experimental k^3 -weighted EXAFS spectra **2a** and **2b** (note that due to noise, spectrum **1** is k^2 -weighted) are presented in Figure 2b, together with the best fit spectra and the corresponding Fourier transformed spectra (FT) in Figure 2c. Both spectra **2a** and **2b** are dominated by low frequency oscillations at k values ranging from 2 to 8 \AA^{-1} and higher frequency oscillations at k values ranging from 8 to 12 \AA^{-1} . This typically corresponds to two coordination shells, respectively at $R+\phi = 1.9 \text{ \AA}$ and $R+\phi = 3.7 \text{ \AA}$. This type of spectrum is known to be associated with a PuO_2 fluorite structure type (Fm3m). This crystal structure was previously used to model an EXAFS plutonium nanocrystal stabilized by an organic ligand and can reproduce satisfactorily well-ordered plutonium dioxide nanocrystals.^[14] Nevertheless, in seawater the plutonium hydrolysis process seems too chaotic to form such crystalline compounds. A fitting model made of only one oxygen shell either failed to accurately reproduce the spectra or led to unrealistic Debye Waller factors. To overcome this issue with disordered plutonium colloids, several authors have used complementary oxygen shell(s) and adjusted the Pu coordination number to take into account both the average particle size and the short-range disorder.^[15,16,17,18] The best fit spectra reported in Figure 2bc were obtained applying the same procedure with two oxygen shells.

A similar spread in oxygen bond distances is reported in the only crystallographic data available representative of plutonium colloids.^[19] Thereby, the Pu-Os shell accounts for short plutonium hydroxide bonds or surface $\mu^3\text{oxo}$ bonds, and Pu-Ol for long plutonium oxygen interactions (bulk plutonium oxide $\mu^4\text{oxo}$ or water molecules). Finally, it is worth mentioning that any attempt to include a chlorine contribution to the fit model ended with a less accurate fit. Best fit metrical parameters reported in Table 1 for spectra **2a** and **2b** are in same order of magnitude as those previously reported for plutonium colloids prepared by hydrolysis of Pu(IV) under acidic conditions. Nevertheless, a more careful analysis suggests that for spectrum **2b** a significant increase of the “crystalline” parameters occurs, with an increase of coordination numbers Ol and Pu together with a decrease of coordination number Os compared to that of spectrum **2a**. This change in the local structure moving down the cell is indicative of a maturing of plutonium particles toward more crystalline PuO_2 colloids that become denser.

Table 1: Best fit parameters for the EXAFS spectra **1**, **2a** and **2b** at the Pu L_{III} edge. Spectrum **1** correspond to the soluble part of the doped mother solution (cell 1), spectrum **2a** corresponds to acquisition in position 2a of cell 2 after 6 months of aging of the mother solution and sample **2b** corresponds to acquisition in position 2b in the same cell (cell 2). S_0^2 is the EXAFS global amplitude factor, e_0 is the energy threshold and R-factor (%) is the agreement factor of the fit. **1** : $S_0^2 = 1.0$, $e_0 = -5.7 \text{ eV}$, R-factor = 1.9%. **2a** : $S_0^{2*} = 0.9$, $e_0 = 0.1 \text{ eV}$, R-factor = 3.7%. **2b** : $S_0^{2*} = 0.9$, $e_0 = 0.4 \text{ eV}$, R-factor = 2.9%. * = fixed parameter.

	Path	CN	$\sigma^2 (\text{\AA}^2)$
1	Pu-O	8*O at 2.28(15) \AA	0.0184
2a	Pu-Os	3.4(5) O at 2.24(1) \AA	0.004 (1)
	Pu-Ol	3.2(6) O at 2.39(1) \AA	0.003 (1)
	Pu...Pu	3.6(6) O at 3.82(2) \AA	0.008 (1)
2b	Pu-Os	2.7(7) O at 2.24(1) \AA	0.004 (1)
	Pu-Ol	3.6(6) O at 2.37(2) \AA	0.005 (1)
	Pu...Pu	4.7(5) O at 3.83(2) \AA	0.008 (1)

This effect, already described as an aging process of plutonium colloids, is associated here in seawater with a slight increase in strontium content. But further interpretation of the role of Sr cations in the colloidal structure is impossible at this stage. The same conclusions can be drawn from the comparison

of the XANES spectra of **1**, **2a** and **2b** with references for aqueous Pu(IV) (in hydrochloric acid) and solid state PuO₂ (Figure 1c). This shows a decrease of the white line intensity concomitant with a spread in energy between the maximum of the white line and the inflexion point (S.I. Table S1). This decrease in white line intensity is in agreement with previously reported values on plutonium colloidal species compared with aqueous Pu(IV) and PuO₂.^[20] It qualitatively confirms this evolution of the structure from the bulk solution to colloidal form.

Finally, in similar conditions to those for the preparation of the solution ([Pu] = 5 · 10⁻⁵ M, Eh = 210 mV/NHE), the predictive species diagram was calculated between pH 4 and 10 using JCHESS code (experimental details in S.I.).^[21] Table S2 reports the ionic species concentrations used for the calculation model, corresponding to seawater chemical composition. Figure S2a shows the corresponding speciation diagram. Redox state fluctuations and solid species formation have been enabled in the calculation. The predominant species at seawater pH and redox potential is unambiguously hydrated PuO₂, in agreement with EXAFS analyses for spectra **1**, **2a** and **2b** that indicates the presence of time dependent hydrated {PuO₂}-like colloids. Figure S2b is a zoomed-in portion of Figure S2a, showing that a number of Pu(III) species are also expected in the investigated conditions (but no Pu(V)), at nanomolar concentrations. Such concentrations are below the spectroscopic detection limits, which explains why if any, Pu(III) species have not been experimentally observed in our conditions.

As a conclusion, the valence state of experimentally detected plutonium in seawater (under these experimental conditions) is purely +IV and the speciation corresponds to {PuO₂}-like colloids. Aging of the solution shows a gradient of ordering from Pu_n(OH)_m(O)_l.xH₂O species to more crystalline PuO₂ colloids that become denser and less soluble.

Supporting Information Summary: Supporting Information file includes details about sample preparation, XAS data acquisition and treatment, and thermodynamics simulation.

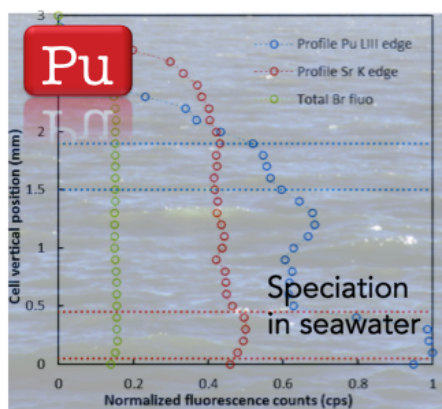
Acknowledgements: XAS data were recorded at the French synchrotron facility SOLEIL, MARS beam line. This work was partially supported by partially by CEA/DAM/DPN and CNRS and partially by ECOS-Nord project under grant n° M12P01.

Keywords:

Environmental chemistry, Plutonium, Radiochemistry, X ray Absorption Spectroscopy

TOC

Solubility, migration, and bioavailability of plutonium is lacunar because experimental evidences are missing. The present article reports on X-ray Absorption Spectroscopy of plutonium in natural seawater. The observed valence state is +IV and the speciation corresponds to PuO_2 type colloids. Furthermore, aging of the solution shows a gradient of ordering from hydroxide colloidal species to more crystalline PuO_2 colloids.



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