Supporting Information

Relevance of Formation Conditions on the Size, Morphology and Local Structure of Intrinsic Plutonium Colloids

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I. Fitting models

**Guinier form factor**

\[ I(Q) = I_0 \exp \left( - \frac{(QR_c)^2}{3} \right) \]

where, \( R_c \) is the gyration radius of the particle. \( I_0 \) can be expressed with the following equation:

\[ I_0 = \phi V \Delta \rho^2 \]

For a sphere with a radius \( R \)

\[ R_c = R \sqrt{3} \]

**Sphere form factor**

\[ I(Q) = I_0 P(Q) \]

\[ I_0 = \phi V_{sphere} \Delta \rho^2 \]

where, \( V_{sphere} \) is the volume of the sphere (cm\(^3\)) that is equal to \( \frac{4}{3} \pi R^3 \), \( \Delta \rho^2 \) is the contrast between the sphere and the solvent (cm\(^{-4}\)), calculated from the eletronic scattering length density \( \rho_{sphere} \) and \( \rho_{solvent} \) of the particle and the solvent respectively (cm\(^{-2}\)), and \( \phi \) is the volume fraction of the particle.

\[ P(Q) = \left( \frac{3(\sin (QR) - QR \cos (QR))}{(QR)^3} \right)^2 \]

where, \( Q \) is the wave vector (nm\(^{-1}\)), \( R \) is the radius of the sphere (nm\(^{-1}\)).
Core-shell form factor

\[ I(Q) = \frac{\phi_{\text{cluster}}}{V_{\text{shell}}} \left( 3 \left( V_{\text{shell}} (\rho_{\text{shell}} - \rho_{\text{solvent}}) \frac{\sin (QR_{\text{shell}}) - QR_{\text{shell}} \cos (QR_{\text{shell}})}{(QR_{\text{shell}})^3} \right) + 3 \left( V_{\text{core}} (\rho_{\text{core}} - \rho_{\text{shell}}) \frac{\sin (QR_{\text{core}}) - QR_{\text{core}} \cos (QR_{\text{core}})}{(QR_{\text{core}})^3} \right) \right) \]

where, \( \phi_{\text{cluster}} \) is the volume fraction of the cluster

\[ V_{\text{shell}} = \frac{4}{3} \pi R_{\text{shell}}^3 \]

where, \( V_{\text{shell}} \) the volume of the shell and \( R_{\text{shell}} \) the radius of the shell, \( \rho_{\text{shell}} \) the scattering length density of the shell;

\[ V_{\text{core}} = \frac{4}{3} \pi R_{\text{core}}^3 \]

where, \( V_{\text{core}} \) the volume of the core and \( R_{\text{core}} \) the radius of the core, \( \rho_{\text{shell}} \) the scattering length density of the shell;

Infinitely large lamella form factor

\[ I(Q) = \frac{8 \pi \phi \Delta \rho^2}{Q^4 L \sin^2 \left( \frac{QL}{2} \right)} \]

where, \( L \) is the thickness of the lamella.

Disk form factor \((R_D \gg L)\)

\[ I(Q) = 4 \phi V_{\text{disk}} \Delta \rho^2 \int_0^{\pi} \left[ \sin \left( \frac{1}{2} Q L \cos \alpha \right) J_1 \left( \frac{1}{2} Q R_D \sin \alpha \right) \right]^2 \sin \alpha \, d\alpha \]

where, \( V_{\text{disk}} \) the disk volume, \( L \) its thickness, \( R_D \) its radius, \( \alpha \) the angle between the disk and the wave vector \( \hat{Q} \) and \( J_1 \) the first order \textit{Bessel} function.
II. ESI Figures

**Fig S1** Lab pictures showing the synchrotron SAXS/XAS analytical bench.

**Fig. S2** UV-Vis absorption spectra of stable hydrolytic Pu(IV) colloidal suspensions diluted in milli-Q H₂O at different concentrations: 10 mM (no dilution; black line), 5 mM (blue line) and 1 mM (green line).
**Fig. S3** UV-Vis absorption spectra of stable hydrolytic Pu(IV) colloidal suspensions diluted in HNO₃ 42 mM at different concentrations: 10 mM (no dilution; blue line), 5 mM (black line), 1 mM (green line), 0.5 mM (orange line) and 0.1 mM (red line).

**Fig. S4** UV-Vis absorption spectra of stable sonolytic Pu(IV) colloidal suspensions in water at different concentrations: no dilution (0.8 mM, red line) and dilution 10 times in milli-Q water (0.08 mM, black line).
Fig. S5 Fit models applied to SAXS spectra of hydrolytic and sonolytic intrinsic Pu(IV) colloids at different conditions: (i) sonochemical colloid in water diluted 10 times (SC-D10) [disk form factor (red line)], (ii) hydrolytic colloid diluted in HNO$_3$ 42 mM to obtain a final Pu concentration of 10 mM (HC-10-HNO$_3$), 5 mM (HC-5-HNO$_3$) and 0.5 mM (HC-0.5-HNO$_3$) [Guinier model (blue line), sphere form factor (red line), spherical core-shell form factor (green line), sphere form factor with polydispersity (purple line), sphere with SLD gradient (orange line)]; and (iii) hydrolytic colloid diluted in H$_2$O to obtain a final Pu concentration of 5 mM (HC-5-H$_2$O) and 1 mM (HC-1-H$_2$O) [Guinier model (blue line), sphere form factor (red line) and spherical core-shell form factor (green line)]. Insert picture for HC-10-HNO$_3$ represent the scattering length density profile of each fitting model.
Fig. S6 Scattered SAXS intensity normalized by the theoretical volume fraction ($\phi_{th}$) of 10 mM hydrolytic Pu(IV) colloid (42 mM HNO$_3$): a) diluted in 42 mM HNO$_3$ at different concentrations: 10 mM (no dilution; blue squares), 5 mM (black circles) and 0.5 mM (orange triangles); and b) diluted in H$_2$O at different concentrations: 10 mM (no dilution; blue square), 5 mM (black circle) and 1 mM (green triangle).

Fig. S7 HR-TEM pictures measured on sonolytic colloids (red) and hydrolytic colloids (blue) with their corresponding electron diffraction patterns. Adapted from Dalodiere et al.$^1$
**Fig. S8** Normalized Pu L\textsubscript{III} XANES spectra acquired on a selection of hydrolytic and sonolytic colloids

![Normalized Pu L\textsubscript{III} XANES spectra](image)

**Fig. S9** Pu L\textsubscript{III} XANES spectra acquired on 10 mM hydrolytic colloid (HNO\textsubscript{3}) after several cycles measuring ca. 60 to 90 min per scan. Both figures (a) large view; b) magnification of the area of interest) show the absence of significant variations between the experimental run.

![Pu L\textsubscript{III} XANES spectra](image)
**Fig. S10** Derivatives of the normalized Pu L\textsubscript{III} XANES spectra acquired on a selection of hydrolytic and sonolytic colloids.

**Fig. S11** Normalized Pu L\textsubscript{III} XANES spectra acquired on a selection of hydrolytic (HC-10-HNO\textsubscript{3}) and sonolytic (SC-0.8-H\textsubscript{2}O) colloids compared to a) Pu(IV), Pu(III), b) Pu(V) and Pu(VI) references.
Fig. S12 Modulus (black lines), real (green lines) and imaginary (red lines) parts of the FT for the experimental $k^3$-weighted EXAFS spectra for a selection of samples.
Fig S13. FT of the experimental $k^3$-weighted EXAFS spectra (black line) superimposed to the best fit results (red line) and the single Pu-O (green line) and Pu-Pu (blue line) scattering paths.

References
