

# Shedding light on the transplutonium element (Am, Cm, Bk, Cf) solution chemistry using EXAFS - Beamline 11-2.

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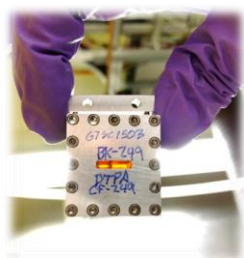
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The chemistry of trivalent transplutonium ions ( $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Bk}^{3+}$ ,  $\text{Cf}^{3+}$ ...) is usually perceived as monotonic and parallel to that of the trivalent lanthanide series. Herein, we report the very first extended X-ray absorption fine structure (EXAFS) study performed on a series of aqueous heavy actinide chelates, extending past Cm.

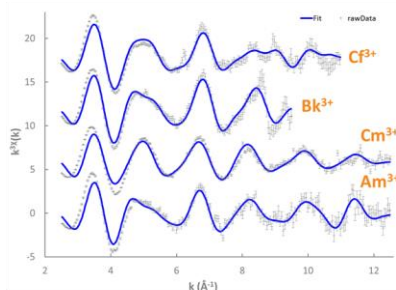
Taking advantage of the high photon flux and availability of a 100-element Ge detector at the *Stanford Synchrotron Radiation Lightsource* (SSRL – Beamline 11-2), we were able to measure the EXAFS  $L_{III}$  edge signature of these elusive and highly radioactive elements using as little as 1.7  $\mu\text{g}$  of  $^{249}\text{Bk}$ , 3.3  $\mu\text{g}$  of  $^{249}\text{Cf}$ , 10.9  $\mu\text{g}$  of  $^{248}\text{Cm}$ , and 27.1  $\mu\text{g}$  of  $^{243}\text{Am}$ .

The results obtained on the complexes of  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Bk}^{3+}$ ,  $\text{Cf}^{3+}$  with the flagship chelator of the nuclear chemistry field, namely diethylenetriaminepentaacetic acid ( $\text{DTPA}^{5-}$ ), show an unexpected break to a much shorter metal-oxygen nearest-neighbor bond lengths in the case of  $\text{Cf}^{3+}$ . Corroborating those results, density functional theory calculations, extended to  $\text{Es}^{3+}$ , suggest that the shorter Cf-O and Es-O bonds could arise from the departure of the coordinated water molecule and contraction of the ligand around the metal relative to the other  $[\text{M}^{III}\text{DTPA}(\text{H}_2\text{O})]^{2-}$  ( $\text{M} = \text{Am}, \text{Cm}, \text{Bk}$ ) complexes.

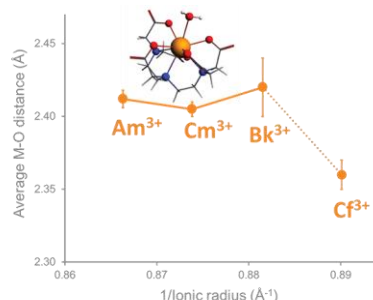
Taken together, these experimental and theoretical results demonstrate inhomogeneity within the trivalent transplutonium series that has been insinuated and debated in recent years, and that may also be leveraged for future nuclear waste reprocessing technologies. The techniques developed in this study also appear instrumental for probing elements with very limited availability and will be extended to other systems in the near future.



1) Sample preparation



2) EXAFS



3) Structural data

G. J-P. Deblonde, M. P. Kelley, J. Su, E. R. Batista, P. Yang, C. H. Booth, R. J. Abergel, "Spectroscopic and computational characterization of DTPA-transplutonium chelates: evidencing the californium pivot in the heavy actinide(III) series." Submitted to *Angewandte Chemie Int.*

M. P. Kelley, G. J-P. Deblonde, J. Su, C. H. Booth, R. J. Abergel, E. R. Batista, P. Yang, "Bond covalency and oxidation state of actinide ions complexed with therapeutic chelating agent 3,4,3-LI(1,2-HOPO)." Submitted to *J. Am. Chem. Soc.*