Identification of NpO_{2+x} in the Binary Np-O System

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ABSTRACT: In contrast to UO_2 and PuO_2 , there is no consensus on the existence of mixed valence NpO_{2+x} , resulting in a gap between NpO_2 and Np_2O_5 (the highest binary oxide of Np) in the Np-O phase diagram. We now show NpO_{2+x} via Np L_{III} Extended X-ray Absorption Fine Structure (EXAFS) spectra of three samples of NpO_2 that, analogous to U and Pu, exhibit multisite Np-O distributions with varying numbers of oxygen atoms at 1.87-1.91 Å. This is supported by the diffraction pattern of the sample with the largest amount of this oxo-type species that can be refined with both the simple fluorite structure and a trigonal one related to $\alpha\text{-U}_4\text{O}_9$. The implied Np(V)-bridging oxo moieties as well as possible indications of OH^- found by detailed EXAFS analysis suggest that NpO_{2+x} more closely resembles PuO_{2+x} than UO_{2+x} . An additional common characteristic suggested by the EXAFS and X-Ray Diffraction (XRD) is the phase separation into NpO_2 and what would be previously unreported $\text{Np}_4\text{O}_{9(-\delta)}$, indicative of O clustering.

1. INTRODUCTION

The oxides and oxyhydroxides of the light actinides are arguably their most important compounds because of their stability in the presence of air and water and their consequent roles in nuclear fuel, reprocessing, storage, disposition, and as potential and actual environmental contaminants[1-5]. Over the last fifteen years, however, local structure experiments have shown substantial complexity in their structural chemistry[6-13]. Combined with thermodynamic and other measurements, these newer results have caused UO_2 and PuO_2 to be less well understood than had previously been assumed. Two recent examples in environmental samples are the identification of cation substitution to form alteration compounds and unexpected variability in the resistance of UO_2 to oxidation[7, 14]. This complexity begins with their binary An-O phase diagrams. That of uranium is one of the most complicated known, even lacking consensus on the

actual number or crystallographic phases, but at least more than twenty[15, 16]. An interesting sidelight is that for the Mott insulator, fluorite structured UO_2 [17], partial filling is not known to produce any metallic phases. There are therefore no insulator-metal transitions, and the only known low temperature transformation is the 3- $\mathbf{k}$ spin ordering that produces the antiferromagnetic phase[18] at 30.8 K[19, 20]. Nevertheless, charge inhomogeneities give highly unusual, often unique behaviors.

In contrast, in part because valences $\geq V$ for binary Np-O compounds and ≥ 4.5 for binary Pu-O are unstable, the Np- and Pu-O phase diagrams are trivial by comparison. The original belief that the highest oxide for Pu was PuO_2 was overturned in 2000 with the confirmation of PuO_{2+x} with $x \leq 0.26$ [13]. Although the fluorite lattice constant was shown to display a very small expansion with increasing x (the opposite trend to UO_{2+x}), no results were given on the degree of ordering or structure of the possible Pu_4O_9 phase. Similarly, with contradictory reports of both the possibility[21] and impossibility[22] of NpO_{2+x} there is no consensus on whether such a fluorite-derived species fills in the gap between NpO_2 and the terminal Np_2O_5 oxide with its layered structure. This omission poses the question that, if fluorite structured UO_2 [7, 23] and PuO_2 [1, 8] add O continuously, why not Np as well? And if so, what are the atomic and mesoscale mechanisms and speciation? In UO_2 the adventitious O clusters at moderate temperatures so that UO_{2+x} consists of separated domains of the isomorphous, crystallographically single phase compounds[7, 24, 25] UO_2 with the <1% smaller U_4O_9 for $x < 0.25$, and U_4O_9 with the <1% larger, -1–2% tetragonally distorted U_3O_7 for $0.25 < x < 0.33$ -0.5. beyond which occurs layered U_3O_8 [15, 16, 26, 27]. In the absence of any comparable systematic studies this type of cooperative behavior has not been identified for Pu and Np.

On the atomic scale, neutron scattering and calculations as well as simply a consideration of the geometrical constraints have indicated that the O adds to the cubic holes in the open lattice concomitant with displacements of one or two of the original O ions at neighboring cube vertices into adjacent holes[28]. This mechanism gives the ordered cuboctahedral[29, 30] or less ordered di- and quad-interstitial structures[10, 12] containing U(V) and no U-O pairs with distances less than around 2.2 Å[10, 25, 29, 31, 32]. EXAFS[1, 6, 8, 33] and x-ray scattering measurements[34], however, identified O neighbors at 1.75Å in UO_{2+x} [2, 7]. These distances are indicative of the oxo-type, multiply bonded, terminal O ligands with very short An-O distances that are the defining characteristic of the trans-dioxo complexes of U(VI). This putative contradiction between x-rays and neutrons actually demonstrates that UO_{2+x} contains tunneling polarons[35]. When combined with results from many other experiments, these findings have been interpreted as signifying a coherent polaronic quantum phase with many of the properties of a Fröhlich-type Bose-Einstein condensate[34, 36]. In contrast, the EXAFS of PuO_{2+x} exhibits two independent types of multisite Pu-O distributions. One would result from oxidation, producing O neighbors at 1.8-1.9 Å[1] that are indicative of terminal and/or bridging Pu(V)-oxo groups. O neighbors at around 2.2 Å that are found both with and without oxo moieties from oxidation signify a second type of reaction. This would most likely be hydrolysis of sorbed H_2O , so that the most accurate description of PuO_2 could be $\text{PuO}_{2+x-y}(\text{OH})_{2y} \cdot z(\text{H}_2\text{O})$ [6]. Alternatively, it could be oxidation as well, but with the end product being the interstitial-type structures, possibly because the tendency for the O to cluster is less for Pu than U. There is then, in addition to the possibility of NpO_{2+x} , also the question of whether NpO_2 behaves more like U or Pu, a question difficult to answer because the structural chemistry of PuO_{2+x} is only beginning to be understood. Insofar as we now have extensive experience identifying and characterizing AnO_{2+x} (An=U, Np,

Pu) for U and Pu, it is of value to apply this expertise to reexamine the existing NpO_2 data[37] even if only very limited new data are available.

That NpO_{2+x} is unrecognized has resulted in an absence of studies of its preparation and specifically the relationship between the excess O content and the O activity or potential during preparation. The thermogravimetric study detected Np_4O_9 by heating Np(VI) hydroxide under vacuum or O_2 without observing a separate diffraction pattern at elevated temperature[21], whereas the XRD one failed to see a separate diffraction pattern after heating NpO_2 with O_2 [22]. As with PuO_{2+x} , the evaluation of the mixed valence material therefore depends upon measurements of multiple samples that, unfortunately, are very limited in number. Systematic or comprehensive studies are not feasible at this time because, unlike UO_{2+x} , of the difficulty and expense of preparing samples in a controlled way and, unlike PuO_{2+x} , a large number of archived samples is not available. However, given the current disagreement in the literature, it is useful to clarify the original XAFS study of NpO_2 that was not intended to identify disorder and whether it does or does not support compositions intermediate between NpO_2 and Np_2O_5 .

We have therefore analyzed in more detail the data from[37] to support the claims that NpO_{2+x} exists. In addition, like U and Pu, its EXAFS shows oxo species and phase separation into NpO_2 and what would then be $\text{Np}_4\text{O}_{9(-\delta)}$ with the details of the disorder more like Pu than U. The structural chemistry and positive identification of the various species is the initial step in elucidating their chemical and physical properties. These are crucial in their applications as well as understanding the role of the 5f electrons as their relative energy levels and size changes across the actinide row. The original suggestion that the Pu(V) ions in PuO_{2+x} would increase its solubility – the most important parameter in its environmental radiotoxicity – by analogy with its molecular species was shown to not to be the case by correlating the XAFS results with the preparations and histories of the samples. Of course, this also raises the issue for the future of how being in the solid state would so substantially modify the properties of Pu, and possibly U and Np, from those in molecular complexes in a material considered to be ionic.

2. EXPERIMENTAL AND ANALYTICAL PROCEDURES

Np is highly radiotoxic and must only be handled by trained personnel in laboratories designed for this level of hazard. Measurements at the light sources are performed using approved containments and procedures developed especially for transuranic-containing samples. The X-Ray Absorption Fine Structure (XAFS) measurements at the Stanford Synchrotron Radiation Lightsource and the XRD measurement in the laboratory that was performed with Cu radiation using film to record the pattern have been described in detail[37]. For the three samples, consistency with the earlier report is obtained by labeling the solid, crystalline, reference NpO_2 sample as “calcined (a)” or “(a)” and the one prepared by autoradiolytic reductive precipitation from an Np(V) aqueous solution as “ppt”. This process would lower the concentration of the Np(V) that was already below its solubility limit, making it highly unlikely that Np(V) compounds would be in the solid fraction. Coprecipitation would produce the NpO_{2+x} that is the objective of this study. The shorter spectrum from a third sample that was also an archived NpO_2 sample is labeled “calcined (b)” or “(b)”. Data analysis was performed using the same approaches as were successful for U and Pu that involved a thorough evaluation of the effects of the background on the low frequency features, fitting all of the features in the spectra, and comparison of the calculated waves with those in the data that they were fitting. The calcined (a) and ppt samples were curve-fit and transformed over both $k=2.6\text{--}12.0\text{ \AA}^{-1}$ and $2.6\text{--}10\text{ \AA}^{-1}$, while the shorter calcined (b) spectrum was analyzed over only the more limited range. Fourier

transforms were all performed using a sine window function. Metrical parameters were obtained by nonlinear least-squares curve-fitting using amplitudes and phases calculated by the feff code[38-40] from the crystal structures of NpO_2 and Np_2O_5 .

Figure.1 a) The moduli of the Fourier transforms of the EXAFS, $|\chi(R)|$, and the real components, $\text{Re}[\chi(R)]$, of the data, and in the insets $|\chi(R)|$ of the data, the fit, and the difference, and (inverted) the separated components, for $\text{PuO}_{2.0}$ and PuO_{2+x} with large x . b) $|\chi(R)|$ and $\text{Re}[\chi(R)]$ of the EXAFS of calcined (a), with the upper inset showing $k^3\chi(k)$ (the EXAFS weighted by k^3) of the data and fit and the lower inset $|\chi(R)|$ of the data, fit, difference, and (inverted) the separate components of the fit for calcined (a). c) The same for the EXAFS of ppt. All calculations were performed over the range $k=2.6-12.0 \text{ Å}^{-1}$.

The refinement of the XRD data from the ppt sample to the fluorite structure was repeated using the FULLPROF-2K code[41]. The diffraction pattern was fit assuming the pure fluorite-type structure of NpO_2 with the Fm-3m space group. The difference between the observed and calculated patterns is small and the goodness of fit of the refined XRD dataset is 1.65. The refined lattice constants were found to be $a=b=c=5.4289(3)$. The uniqueness of this refinement, especially with respect to more recent experience with the complicated structures of U_4O_9 that are derived from the fluorite structure by multiplying the unit cell and introducing small displacements of some of the atoms, was tested by subsequently also fitting the same data with the trigonal structure as in U_4O_9 [21].

3. RESULTS

Identification of neptunyl species and NpO_{2+x} . In the absence of a series of systematically prepared compounds – as for UO_{2+x} – or a large number of samples prepared using different approaches – as for PuO_{2+x} – the Fourier transforms of the k^3 -weighted EXAFS spectra, $\chi(R)$, from the three NpO_{2+x} samples can be interpreted via recourse to the XAFS from the isostructural oxides of its neighboring elements. The X-ray Absorption Near Edge Structure (XANES) spectra of the three compounds that will be shown to cover a wide range of x (Fig. SII) behave similarly to U and Pu. They do not display any significant shifts in shape or energy of the features but do exhibit changes in the white line amplitude that in this case, like U, decreases with increasing x . The response of the EXAFS to O addition and the formation of PuO_{2+x} were identified by comparing the spectra from the maximally ordered $\text{PuO}_{2.0}$ sample that will have negligible excess O with a sample known to have a significant amount of excess O. This excess was definitively shown in that preparing it by equilibrating it with air containing 80% relative humidity maximized the amplitude of “oxo” feature fit by an O shell at 1.88 Å. The EXAFS of the ordered material is very well fit through 4.5 Å with only the first three crystallographic near neighbor shells (Fig. 1a). This includes the small shoulder on the nearest neighbor O contribution around $R=1.1$ Å that is easily visible in the Fourier transform taken over this data range (Fig 1a upper right inset) and is a side lobe of the peak from the single, ordered O shell. In contrast, the oxidized sample does not exhibit this small shoulder and requires an additional O shell at 1.85 Å to not leave a large residual in this region (Fig. 1a lower right inset). This multisite Pu-O distribution not only eliminates the $R=1.1$ Å feature but also causes the base of this peak to broaden to be wider than the $\text{PuO}_{2.0}$ spectrum despite the proportionately larger reduction in the relative amplitude of this modulus peak.

Using these PuO_{2+x} spectra as a guide, direct inspection of the $\chi(R)$ spectra from (a) (Fig. 1b) and ppt (Fig. 1c and SI2) shows that both exhibit the contributions from the nearest neighbor O and Np plus the second nearest neighbor O as the peaks at, respectively, $R=2.0$ Å and $R=3.9$ Å[7]. These distances and their relative amplitudes are the EXAFS signature of the fluorite structure of AnO_2 and its An_4O_9 and U_3O_7 derivatives. In addition, however, the $R=2.0$ Å peak is wide at its base and does not display the small shoulder at $R=1.1$ Å exhibited by $\text{PuO}_{2.0}$ (and $\text{UO}_{2.00}$). The features at $R<1$ Å are Fourier ripple. This modified pattern caused by the oxo neighbor indicates that this moiety should also occur with NpO_2 , as with U and Pu. These indications of neptunyl species in the nearest neighbor O contribution are largest in the ppt spectrum. The signal from the putative oxo neighbor not only broadens the base of this peak but is so large that it causes a substantial shoulder on its low R side. The origin of this behavior is elucidated by the curve fits. This component of the data and fits was isolated by subtracting the Np-O (2.35 Å) and Np-Np (3.85 Å) waves of the NpO_2 structure (Fig. 2). The direct comparison that this procedure provides

shows that the correspondence between the calculated oxo-type Np-O waves and the ones in the spectra that are being fit is very good. It is evident from the shift of the positions of the two peaks that the Np-oxo distance in (a) will be longer than ppt, and curve-fits find distances of, respectively, 1.91 Å and 1.87 Å. These bond lengths indicate Np(V) and not (VI), and by comparison with Np_2O_5 these Np(V)-oxo moieties could be terminal or bridging asymmetrically. It is also apparent that, consistent with their overall spectra, the amount of Np(V)-oxo is higher in ppt than (a). Given that this sample was prepared by spontaneous, radiolytic reduction of Np(V) that converted it to insoluble Np(IV), a large amount of Np(V) could be expected in the resulting NpO_{2+x} solids isolated from the original solution.

Figure 2. Comparison of the fit of the Np-oxo EXAFS (dashed) with the spectral feature being fit (solid) for the two samples, separated from the spectra by subtracting the wave of the fit for all of the other shells from the data.

Multiple scattering contributions are unnecessary in these fits. The first one in the fluorite structure is a 3.8 Å triangular path involving two O near neighbors. It may be the origin of the small O shell often found in curve-fits with an An-O distance of 3.35 Å or higher. This wave in the EXAFS that overlaps with the low R shoulder from the U contribution can often improve the quality of the fit, but is irrelevant to the interpretation of the results. The highest amplitude multiple scattering feature in the EXAFS of the light actinides is the linear one from the transdioxo moiety of An(V) and (VI) that occurs around $R=3.0$ Å. However, it is only a small fraction of the amplitude of the single scattering oxo features, which in these spectra are already quite low. In addition it overlaps with other contributions from the multisite An-O distribution and so it cannot be used to validate the oxo shell nor obtain additional information on its geometry.

The EXAFS spectrum of the third NpO_2 sample, calcined NpO_2 from a different source, can only be analyzed to $k=10$ Å⁻¹. Over this range it completely fits with only the NpO_2 structural components with no residual that could be indicative of Np(V)-oxo (Fig. 3a), including most of the small shoulder that is at $R=1.0$ Å for this data range. Including this shell in the fit finds that it makes only a negligible contribution. The overall amplitude of the (b) spectrum is also somewhat larger than for the other two samples, consistent with more order (Fig. 3b). These characteristics make it likely that this sample is closest to $\text{NpO}_{2.0}$. The shoulder at $R=4.1$ Å that is not fit with this structural basis is common to all of the spectra fit when fit over this $k=2.6-10.0$ Å⁻¹ data range and would therefore originate in a rapidly damped multiple scattering wave.

Figure 3. a) As in Fig. 1, EXAFS data, fit, and fit components for the spectrum of calcined (b). The fitting and transform range is $k=2.6\text{--}10.0 \text{ \AA}^{-1}$. b) Comparison of $\chi(R)$ spectra of all three samples transformed over this same, shorter range.

More distant neighbor shells and possible identification of Np₄O₉ and O clustering. Another characteristic of the PuO_{2.0} (and UO_{2.00}) spectra is that, despite the difference in x , both of these spectra show the same pattern of features beyond $R=4.5 \text{ \AA}$ [1, 6-8, 10]. This combination of overlapping single and multiple scattering contributions constitute the signature of the fully ordered fluorite structure. For UO₂:U₄O₉, the phase separation is therefore evident in this region in that the amplitudes diminish evenly across R with increasing x . Randomly distributed O causes the amplitude of the spectral features in $\chi(R)$ to decrease more rapidly at higher R because the longer range order is lost faster than the order at shorter distances. This behavior therefore implies clustering of the adventitious O in UO_{2+x} to give domains with low U:O ratios separated from intact UO₂. It is of interest to note that this behavior indicates that the extended structure of U₄O₉ is fully disordered beyond the nearest neighbor shell in EXAFS because if it produced spectral features they would interfere and reduce or modify the UO₂ spectrum [7]. Only a few of the PuO_{2+x} spectra, and none prepared from aqueous solution, displayed this series of peaks, demonstrating that this longer range order is more easily disrupted in PuO_{2+x}. This could be either because of the putative hydrolysis or because with Pu the adventitious O ions do not

cluster to form separate Pu_4O_9 domains in PuO_{2+x} [1, 6]. A third reason could be disorder resulting from Pu vacancies, which would necessitate low density material with this pattern growing in as the material ages and densifies.

Over the larger $k=2.6\text{--}12.0\text{ \AA}^{-1}$ energy range the sensitivity to multisite vs. single site broadening disorder is better because the waves from Np-O shells whose frequency differs because they are at different distances will separate more at higher k . The $\chi(R)$ spectrum of (a) displays the pattern of features beyond $R=5\text{ \AA}$ associated with fluorite whereas the ppt spectrum exhibits a different one. The loss of resolution, however, results in some of these features being similar to those for (a) over the shorter data range (Fig. 3b). The spectrum from (b) shows these same features, modified in appearance over the shorter range (Fig. 3b). It would therefore also have the extended NpO_2 structure, consistent with its negligible level of oxidation. This is then analogous to the same correlation between the PuO_{2+x} spectra and whether they were prepared from aqueous solution or directly as solids. It would also be consistent with the larger amount of Np(V)-oxo species that will result in more disorder. Compared with $\text{PuO}_{2.0}$, however, the peaks at $R>5.0\text{ \AA}$ that constitute this pattern in the (a) spectrum are somewhat lower relative to the principal, nearest neighbor O and Pu contributions at $R<4.0\text{ \AA}$. This not only implies partial oxidation of (a) because of the loss of ordered NpO_2 , but the similarity of the relative amplitudes across R would also be consistent with the $\text{UO}_2\text{:U}_4\text{O}_9$ phase separation model. Reiterating, distributing the adventitious O evenly throughout the material would reduce the amplitude of the higher R peaks of this pattern faster than the lower R ones because the longer range order is lost more quickly. Clustering of the O to give phase separation between NpO_2 and Np_4O_9 as in UO_{2+x} would cause the observed decrease in amplitude of the peaks in the pattern to be proportionately the same over the entire range in R . It therefore implies both the existence of Np_4O_9 and O clustering in NpO_{2+x} .

Curve-fit results. The metrical parameters (Table S1) were obtained by curve-fits of the EXAFS (Figs. 1 and 3). As noted above, as the end point of the analysis is increased the sensitivity to disorder is enhanced because the contributions of low amplitude shells separate more. Therefore, insofar as disordered systems are difficult to describe uniquely and definitively, these results are not necessarily unique or final. However, the curve-fits do provide the basis for identifying and characterizing differences in the speciation between the different samples and for comparing with the U and Pu systems. In addition to the oxo O at $1.91\text{ \AA}$ and $1.87\text{ \AA}$ for, respectively, the ref and ppt samples, other non-crystallographic distances are found. Specifically, there are significant contributions assigned to O neighbors at 2.99 and $3.27\text{ \AA}$. These distances are within the range of distant O neighbor shells found for PuO_{2+x} [1, 6], implying a similar arrangement of atoms. Another finding of interest is the Np-Np distances of $3.84\text{--}3.85\text{ \AA}$ that are intermediate between the $3.88\text{ \AA}$ for UO_{2+x} and the $3.82\text{--}3.82\text{ \AA}$ for PuO_{2+x} , consistent with their lattice constants. In addition, the curve fits extending to $k=14\text{ \AA}^{-1}$ (Table S1) find O shells at $2.46\text{ \AA}$ for (a) and $2.19\text{ \AA}$ for ppt. The $0.13\text{--}0.16\text{ \AA}$ separations from the principal O shell place the location of the maximum interference between these waves at the end of the data range. This behavior indicates that, rather than signifying distinct neighbor shells, the overall Np-O distributions are anharmonic and asymmetric. That of (a) would be wider on the high R side of the main Np-O peak, while that of ppt would be wider on the low R side. This is another result similar to the U and Pu compounds. Speculating from the single spectrum available, the difference in the behavior of the two samples could signify that the Np-O nearest neighbor distribution in the ppt sample could have more atom density around $2.2\text{ \AA}$. This distance would be consistent with Np-hydroxides in the precipitated NpO_{2+x} , giving the overall formula $\text{NpO}_{2+x-y}(\text{OH})_{2y}$ as in PuO_{2+x} .

Refinement of X-ray diffraction of sample ppt in the NpO_2 fluorite structure. Because of the very limited sample quantities and the radiological constraints, the x-ray diffraction pattern from ppt[37] exhibits a significant background. This impedes the analysis of the weak reflections that would be related to any eventual superstructure associated with ordering of the O anions. Nevertheless, the peaks that belong to a prototype NpO_2 fluorite reference lattice can be easily analyzed. Our previous approach to fit the diffraction pattern was with the Fm-3m fluorite structure[37]. This will not include any of the disorder found in the EXAFS that, if not periodic, will average out because it occurs within the unit cells while conserving the overall crystal lattice. Reanalyzing the data in this mode, utilizing anisotropic broadenings of the profile lineshape that would result from anisotropic microstrain, Rietveld refinement (Fig. 4) confirms $a=5.4289 \text{ \AA}$ (Table 1). Two small unindexed peaks at around $2\theta \sim 27.52$ and 30.81 are not fit. If the fluorite structure is correct they could be attributed to impurities from the preparation of the precipitated NpO_{2+x} sample.

Figure 4. Rietveld refinement of the XRD pattern of the ppt sample to the NpO_2 fluorite structure. Red open symbols are the observed data, the black solid line is the calculated data, green vertical symbols depict Bragg reflections, and the blue line represents the difference between the two.

Refinement of X-ray diffraction of sample ppt in the trigonal Np_4O_9 structure. There is a problem with concluding the analysis of the XRD of ppt with the fluorite structure. The EXAFS shows the expected O and U nearest neighbors. However, the $\chi(R)$ features beyond $R=4.5 \text{ \AA}$ (Fig. 1c), while displaying large amplitudes that indicate a high degree of order and a dominant single phase, display a pattern that is not that of AnO_2 . These results pose the question of whether there are alternative structures that could fit both the XRD and EXAFS better. This was addressed by refining the pattern with another structure derived from U_4O_9 and then calculating its EXAFS for comparison with the ppt spectrum. The EXAFS of ppt: 1) shows a very large amount of Np-oxo species; 2) unlike sample (a), does not show the fluorite pattern past $R=4.4 \text{ \AA}$; and 3) the preparation method is consistent with this material being saturated with Np(V). If NpO_{2+x} is presumed then this sample is close to being single phase Np_4O_9 . The analysis of its diffraction profile line-shape provides evidence of an anisotropic broadening of the diffraction peaks. Though this effect is significant from a statistical point of view, its extent is not enough to produce a visible splitting of the diffraction peaks, even at high angles. The same effect occurs in most U_4O_9 samples that are in the α phase at room temperature. In addition, the relative intensity ratios of the Bragg peaks deviate from the ideal fluorite model. The characteristics of the error in the peak intensities indicate that the structural motif should involve ordered displacements of the Np atoms that are not compatible with a (distorted) fluorite cell, suggesting models that involve

supercells derived from the fluorite structure. Analysis of higher order reflections suggests a trigonal distortion of the fluorite lattice.

Table 1. Crystal parameters for refinement of ppt diffraction pattern in Fm-3m space group

Fm-3m					
R _{wp}	3.32%	R _B	10.25%	S	1.65
a	5.4289(3)				
Widths					
W	0.0143(7)	Lx	0.145(6)		
Atoms	x	y	z	occ	Uiso
Np (3a)	0	0	0	1	0.0096(3)
O (8c)	1/4	1/4	1/4	1	0.0096

Table 2. Crystal parameters for refinement of ppt diffraction pattern in R3c space group

R3c (hex)					
R _{wp}	3.19%	R _B	10.22%	S	1.60
a	30.725(2)	c	18.779(2)		
Widths					
W	0.0149(7)	Lx	0.127(6)		
Atoms	x	y	z	occ	Uiso
Np7d	0	0	0.242(13)	1	0.0090(6)
Np6c	0.165(3)	0.082(4)	0.082(7)	1	0.0090
Np4c	0.043(5)	0.085(4)	0.087(7)	1	0.0090
O1d	0.06	0.03	0.0119	1	0.0090
O1b	0	-0.09	0	1	0.0090
O0	0	0	0	1	0.0090

A trial structure was derived from U₄O₉ based on the cuboctahedral arrangement of O ions found by neutron diffraction and pair distribution function analysis (pdf)[26, 42-44]. This structure does not exhibit the uranyl type distances found by x-ray absorption and pdf[34]. Taking into consideration the small lattice distortion, we have derived the possible structural models for the room temperature phase of Np₄O₉ using group theory and the hypothesis that the additional O atoms in the structure cluster as in UO_{2+x} to form the cuboctahedra. Assuming a prototype structure of symmetry $I\bar{4}3d$, as for the beta phase of U₄O₉, the most symmetric trigonal subgroup is then R3c (no. 161). A detailed discussion of this model is provided in the supplementary information. The calculated superstructure peaks are very weak, although their intensity slowly increases at high angle (Fig. 5), in agreement with the mainly displacive nature of this motif variation. The number of atomic parameters is large and the marginal superlattice reflections are

at or below the noise level. The refinement is therefore driven primarily by the change of the intensities of the main fluorite reflections that determine the displacement amplitudes (but not their phases) of the Np atoms surrounding each cuboctahedron. The relative phases of the displacements need to be constrained using chemical information.

Therefore, we have enforced a -3 local symmetry for the O cuboctahedron and immediately surrounding Np atoms (Fig. SI2). This choice also further reduces the number of parameters of the model. In this constrained model, only 3 independent Np atoms are required for describing this structural block: Np4c, that generates 6 Np atoms bonded with the square faces of the cuboctahedron, each one located in a square antiprism environment, and two other independent atoms, Np6c and Np7d bonded with the trigonal faces of the cuboctahedron, both of them 10-fold coordinate with the surrounding O atoms. Np7d is on the local threefold axis so it only generates two atoms on the opposite sides of the cuboctahedron along the c-axis direction, while Np6c is in a general position and it generates the remaining 6 Np atoms.

Figure 5. Rietveld refinement of the XRD pattern of the ppt sample (same data as Fig. 4) to the Np_4O_9 R-3c structure structure. Experimental data are the black circles, the red line is the refinement, and the blue line is the difference. The inset shows the calculated diffraction patterns for the Fm-3m NpO_2 and R3c Np_4O_9 structures and the difference between them for comparison with the two refinements.

Table 2 summarizes the parameters used in the refinement. It only reports the coordinates of the O atoms forming the cuboctahedron motif and the three independent Np atoms around it. Their coordinates are given relative to the cuboctahedron center (the O0 atom) that is at $(1/2, 3/8, 1/4)$ in the crystal lattice frame. All the other atoms in this large structure are kept in their ideal fluorite positions and not refined. Also, the atomic coordinates of the O atoms composing the cuboctahedron are not refined. Only the Np coordinates in the cuboctahedron extended motif and an overall thermal displacement parameter Uiso for all atoms are refined. Therefore, only 7 atomic coordinates defining the relaxation of the Np atoms surrounding the cuboctahedron were refined in this model. The trigonal lattice obtained from the structural refinement using all the fluorite reflections has $a=30.725(2)\text{\AA}$ and $c=18.779(2)\text{\AA}$, giving a calculated density of $11.325(2)\text{ g cm}^{-3}$. The c/a ratio is 0.6112 that corresponds to a very small yet significant departure from the ideal value ($\sqrt{3/8}\approx 0.6124$) for a cubic lattice.

The refinement of this model that only uses 8 structural parameters (7 for the atomic coordinates and 1 for the thermal displacement parameter) converges to $R_{\text{wp}}=3.19\%$ ($\text{GoF}=1.60$) and $R_{\text{B}}=10.22\%$. A large value of the Bragg error is related to the very large number of the small reflections that are almost unobserved because of the high background noise. The observed data,

fits and difference are shown in Fig. 5. The reliability factor is improved (Tables 1 and 2), although there are still discrepancies between the measured intensities of several reflections and the intensities calculated by this model. The fluorite motif is therefore likely to be an oversimplification of the actual structure of this highly oxidized sample. The details of the Np environments obtained from this constrained structural refinement are provided in the supplementary information.

Nearly similar R values are obtained with the refinements using both models, indicating ambiguity in using diffraction to discern between the two. This value can be reduced by refining the O positions, but this procedure is not robust with the data set we have. As for Np, the amplitudes of the O displacements could be determined from the main fluorite reflections, but the relative phases of those displacements require the measurement of the superstructure peaks that unfortunately do not have the required statistical quality in this experiment. Also, the contribution of O atoms to the fluorite main reflections decrease faster than the Np one, reducing further the sensitivity of the refinement on the O displacements amplitudes to a smaller set of low order reflections. Therefore, development of a more accurate structure requires a neutron diffraction data set. Nevertheless, this structural model we obtained from this constrained Rietveld refinement can be used and improved against the EXAFS experiments that have a better statistical quality.

Figure 6. Calculated EXAFS ($\chi(R)$) for Fm3m NpO_2 (blue) and the trigonal Np_4O_9 (red) structures discussed in the text.

The Fm-3m and R3c structures were subsequently used to calculate the EXAFS, averaging all of the Np sites on the basis of their relative populations. Comparison with the calculated EXAFS of NpO_2 (Fig.6) shows that the primary pattern is maintained, including the nodes of the real component $\text{Re}[\chi(R)]$ under the principal modulus peaks ($|\chi(R)|$). Apart from the amplitudes, the differences therefore reside in the same locations where they occur in the spectra (Fig. 1b, 1c, and SI2), the low R side of the feature from the nearest neighbor O shell, the low amplitude region between this and the Np peaks, and the extended region beyond the Np-second near neighbor O feature. This is an intriguing result vis-à-vis not only these NpO_2 spectra but also for PuO_2 . Insofar as the high R region $> 4.5 \text{ \AA}$ does not display the same pattern as the measured one, this exact trigonal structure most likely does not describe the actual arrangement of atoms in Np_4O_9 . Nevertheless, this trend does indicate that these types of unit cell multiplications coupled to displacements of the atoms from their NpO_2 lattice positions can duplicate the observed retention of the main spectral features with the concomitant modification of the others. This

includes the features at higher R that indicate the presence of longer range order that is neither Fm-3m nor this exact trigonal structure, although it could be a variant. The answer to the question of whether there can be alternatives to the Fm-3m structure that better fit the XRD and EXAFS simultaneously is then a qualified “yes,” with the EXAFS perhaps being a better guide because its features originating in more distant neighbors are more sensitive to these differences.

4. DISCUSSION

These results demonstrate that: 1) like U and Pu, NpO_{2+x} occurs continuously over a relatively wide range of x approaching or up to ~ 0.25 ; 2) that there likely is a Np_4O_9 phase; and 3) like UO_{2+x} , the O clusters at ambient and lower temperatures so that NpO_{2+x} is actually a mixture of separated domains of NpO_2 and Np_4O_9 . Np_4O_9 would be close to isomorphous with NpO_2 , with the Np sublattice conserved so that the disorder is mostly confined to the O ions, and the difference in lattice constant would be even smaller than the several ppt found for U_4O_9 relative to UO_2 . Confirmation of NpO_{2+x} by XAFS is consistent with the thermogravimetric analysis of the decomposition of (VI) hydroxides[21]. In addition, our XRD analysis that shows that the difference in the lattice constant between NpO_2 and the postulated Np_4O_9 would be negligible explains why the opposite conclusion might have been drawn in the XRD-based Np-O phase diagram study[22]. A point for further theoretical study would then be why over the An_4O_9 series from U through Pu the lattice constant is, respectively, slightly lower, the same, and slightly higher than the parent AnO_2 . This second study also used a different preparation method, giving another reason why consensus on NpO_{2+x} is lacking. We have found similar behavior with UO_2 , differences in reacting it with O_2 vs. H_2O and sensitivity to impurities, and multiple types of reactions are implied in PuO_2 .

The results also raise two the additional issues stated in the introduction: 1) the similarities among and differences between NpO_{2+x} , UO_{2+x} , and PuO_{2+x} ; and 2) the consequences of the presence of the oxo in NpO_{2+x} . For UO_{2+x} the oxo group was observed at bond distances ($1.74\text{\AA}$) shorter than those found for Np in the present study[7, 34], whereas the Pu-oxo distances are comparable to NpO_{2+x} or somewhat shorter. The short distance for U demonstrates the (VI) valence for the oxo species, whereas these longer ones for Np and Pu are more consistent with (V). In particular, based on the structure of Np_2O_5 [45], the specific moieties could be the $\text{Np}=\text{O}-\text{Np}$ asymmetric bridges between but possibly also within the planes of Np_2O_5 [45]. This can be contrasted with the symmetric bridging oxo groups in U_3O_8 that link the planes where the U-O distance is $2.08\text{\AA}$ [46], and also the longer distances in U_2O_5 that mostly tend to be more equal to each other and therefore more octahedron-like. Np_2O_5 may therefore serve as a model for the EXAFS-derived sites of the O-enriched, An_4O_9 -type domains in PuO_{2+x} and NpO_{2+x} , whereas $\alpha\text{-UO}_3$ [47] is a better basis for these in UO_{2+x} . It is perhaps therefore not surprising that NpO_2 appears to also show in common with PuO_2 evidence for the second reaction with H_2O , the postulated hydrolysis, in addition to oxidation that gives Np-oxo moieties. Hydrolysis would form hydroxides within the lattice with Np/Pu-O distances that must be around $2.2\text{\AA}$. The presence of hydroxide raises the issue of the possibility of ordered oxyhydroxide phases vs. protonation limited to defects. However, as with PuO_2 , XPS[48], NMR, or neutron scattering would be more definitive in this regard than EXAFS that must infer hydroxide from the Np-O bond length. In this context, insofar as U_4O_9 displays a slightly contracted U sublattice, the reported slow expansion of the PuO_2 lattice[13] with oxidation that is the opposite to this trend may reflect this possible hydrolysis as well as the longer plutonyl-type bonds. Pu should not only be similar to its actinide neighbors so that a $\text{PuO}_2\text{-Pu}_4\text{O}_9$ mixture should be smaller on average,

but was also reported to have shoulders on the high angle side of its diffraction peaks[49]. In UO_{2+x} [7] these originated in the phase separated U_4O_9 domains with their smaller lattice constant. Although it was suggested that the Pu(V) component of PuO_{2+x} would increase its solubility and environmental hazard[13], this has not been found[1, 6], and it is likely that NpO_{2+x} will behave similarly in that the chemistry of molecular species is not a good basis for predicting the behavior of the solid state compounds.

Of equal significance, however, is that like $\alpha\text{-UO}_3$, Np_2O_5 is also a planar structure with highly oblate Np sites, neither of which are compatible with the fluorite lattice. In UO_{2+x} , the formation of these planes via coupling of the tunneling polaron to a (111) phonon suggests the mechanism for the coherence and other properties that provide the evidence for the coherent polaronic quantum phase in UO_{2+x} that displays a number of the properties expected for a Bose-Einstein condensate[34]. Although the only results to date that might point to this phenomenon in NpO_{2+x} and PuO_{2+x} are this demonstration of the oxo groups and implied planar substructures, their formation does pose the question of whether they signify tunneling polarons as found in UO_{2+x} [34, 36]. The long distance tunneling in the UO_{2+x} system associated with this polaron is attributed to the presumed superfluidity of the condensate[34, 36]. The proposed mechanism is a disproportionation reaction of two fermionic U(V) sites to form bosonic U(IV) + planar U(VI), with the associated strain reduced by this process occurring collectively over a large U_4O_9 -type domain and the coherence resulting from this synchronization. The EXAFS results for Pu and Np imply a corresponding transformation from the cuboctahedral type of Pu/Np(V) site to an asymmetrically bridging Pu/Np(V)-oxo, but without charge transfer. This type of oxo bonding in these compounds allows the adventitious O to form these moieties with less lattice strain than terminal ones, so that even if the polaron is tunneling its facilitated formation may not be associated with a collective effect over the entire domain. If the tunneling polaron does occur in these systems there is then the issue of what process might drive its formation in the absence of condensate formation. The transformation between NpO_2 and Np_2O_5 would, however, require a shift of an entire plane of atoms to render the Np sites collinear, requiring an even larger overall displacement. As in UO_{2+x} , confirmation would follow from comparing neutron pdf with x-ray pdf and absorption results.

5. CONCLUSIONS

XAFS and XRD data have been reanalyzed on the basis of methods used to reveal the structures of UO_{2+x} and PuO_{2+x} . With this approach and by comparison with the behavior PuO_{2+x} the XAFS shows an O shell with Np-O around 1.85-1.9 Å that would be a Np(V) oxo or neptunyl group, demonstrating the existence of NpO_{2+x} . It also shows multisite Np-O and disordered but single site Np-Np neighbor distributions. The XRD data from a sample prepared in a way that could maximize the Np(V) content, corroborated by its EXAFS, has been refined in both the Fm-3m structure and an R3c one derived from U_4O_9 , with both giving good fits. The lattice constant of the postulated Np_4O_9 would therefore be more similar to that of its parent NpO_2 than even for U and Pu. Although the EXAFS calculated with the R3c structure does not match the spectrum measured for this sample, both display a pattern of higher R features different from those produced by the AnO_2 fluorite structure. This finding demonstrates that multiplying the unit cell and displacing some of the atoms from their fluorite lattice positions can give a structure that retains the geometry of the nearest neighbor O and An while giving a different but still ordered arrangement of atoms at longer distances. Like U_4O_9 , Np_4O_9 (and Pu_4O_9) may be difficult to identify and refine using laboratory XRD. In addition, although spectra from only three samples

are available, NpO_{2+x} appears to behave less like U and more like Pu, so that in addition to the (V) valence NpO_{2+x} may also be more accurately described as $\text{NpO}_{2+x-y}(\text{OH})_{2y}\cdot z(\text{H}_2\text{O})$. A more definitive characterization of NpO_{2+x} - Np_4O_9 will require a more systematic approach in synthesizing compounds over a range of O potential with the expectation of obtaining a range of x. These results that identify NpO_{2+x} as a material similar to PuO_{2+x} , abetted by the importance of the Np-O- H_2O system in actinide environmental chemistry, nuclear fuels, and repository licensing, should stimulate this effort.

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REFERENCES

- [1] S.D. Conradson, B.D. Begg, D.L. Clark, C. Den Auwer, F.J. Espinosa-Faller, P.L. Gordon, N.J. Hess, R. Hess, D.W. Keogh, L.A. Morales, M.P. Neu, W. Runde, C.D. Tait, D.K. Veirs, P.M. Villella, Speciation and Unusual Reactivity in PuO_{2+x} , *Inorg. Chem.* 42(12) (2003) 3715-3717.
- [2] F. Weigel, Chapter Five, Uranium, in: J.J. Katz, L.R. Morss, G.T. Seaborg (Eds.), *The Chemistry of the Actinide Elements*, Methuen, Inc., New York, 1986.
- [3] R.G. Haire, L. Eyring, Comparison of the Binary Oxides, in: K.A. Gschneidner, Jr., L. Eyring, G.R. Choppin, G.H. Lander (Eds.), *Handbook on the Physics and Chemistry of the Rare Earths*, Elsevier Science, B. V., New York, 1994, pp. 413-505.
- [4] S. Cotton, *Lanthanide and actinide chemistry*, John Wiley & Sons 2013.
- [5] B. Allard, U. Olofsson, B. Torstenfelt, Environmental actinide chemistry, *Inorg. Chim. Acta* 94(1) (1984) 37.
- [6] S.D. Conradson, B.D. Begg, D.L. Clark, C. den Auwer, M. Ding, P.K. Dorhout, F.J. Espinosa-Faller, P.L. Gordon, R.G. Haire, N.J. Hess, R.F. Hess, D.W. Keogh, L.A. Morales, M.P. Neu, P. Paviet-Hartmann, W. Runde, C.D. Tait, D.K. Veirs, P.M. Villella, Local and nanoscale structure and speciation in the $\text{PuO}_{2+x-y}(\text{OH})_{2y}\oplus z\text{H}_2\text{O}$ System, *J. Am. Chem. Soc.* 126(41) (2004) 13443-13458.
- [7] S.D. Conradson, D. Manara, F. Wastin, D.L. Clark, G.H. Lander, L.A. Morales, J. Rebizant, V.V. Rondinella, Local structure and charge distribution in the UO_2 - U_4O_9 system, *Inorg. Chem.* 43(22) (2004) 6922-6935.
- [8] S.D. Conradson, B.D. Begg, D.L. Clark, C. den Auwer, M. Ding, P.K. Dorhout, F.J. Espinosa-Faller, P.L. Gordon, R.G. Haire, N.J. Hess, R.F. Hess, D.W. Keogh, G.H. Lander, D. Manara, L.A. Morales, M.P. Neu, P. Paviet-Hartmann, J. Rebizant, V.V. Rondinella, W. Runde, C.D. Tait, D.K. Veirs, P.M. Villella, F. Wastin, Charge distribution and local structure and speciation in the UO_{2+x} and PuO_{2+x} binary oxides for $x \leq 0.25$, *J. Solid State Chem.* 178(2) (2005) 521-535.
- [9] C. Fillaux, J.-C. Berthet, S.D. Conradson, P. Guilbaud, D. Guillaumont, C. Hennig, P. Moisy, J. Roques, E. Simoni, D.K. Shuh, T. Tyliszczak, I. Castro-Rodriguez, C. Den Auwer, Combining

Theoretical Chemistry and XANES Multi-Edge Experiments to Probe Actinide Valence States, *C.R. Chim.* 10(10-11) (2007) 859-871.

[10] D.A. Andersson, J. Lezama, B.P. Uberuaga, C. Deo, S.D. Conradson, Cooperativity Among Defect Sites in AO_{2+x} and A_4O_9 ($\text{A}=\text{U}, \text{Np}, \text{Pu}$): Density Functional Calculations, *Phys. Rev. B* 79(2) (2009) 024110/1-12.

[11] Y.Q. An, A.J. Taylor, S.D. Conradson, S.A. Trugman, T. Durakiewicz, G. Rodriguez, Ultrafast hopping dynamics of 5f electrons in the Mott insulator UO_2 studied by femtosecond pump-probe spectroscopy, *Phys. Rev. Lett.* 106(20) (2011) 207402/1-4.

[12] D.A. Andersson, F.J. Espinosa-Faller, B.P. Uberuaga, S.D. Conradson, Stability and Migration of Large Oxygen Clusters in UO_{2+x} : Density Functional Theory Calculations, *J. Chem. Phys.* 136(23) (2012) 234702.

[13] J.M. Haschke, Allens H., M.L. A., Reaction of Plutonium Dioxide with Water: Formation and Properties of PuO_{2+x} , *Science* 287 (2000).

[14] T.R. Griffiths, V.S.A. Hubbard, M.J. Davies, Electron-Transfer Reactions in Nonstoichiometric Ceria and Urania, *Inorg. Chim. Acta* 225(1-2) (1994) 305-317.

[15] G.C. Allen, P.A. Tempest, J.W. Tyler, The formation of U_3O_8 on crystalline UO_2 , *Philos. Mag. B* 54(2) (1986) L67-L71.

[16] G.C. Allen, N.R. Holmes, A mechanism for the UO_2 to $\alpha\text{-U}_3\text{O}_8$ phase-transformation, *J. Nucl. Mater.* 223(3) (1995) 231-237.

[17] S.W. Yu, J.G. Tobin, J.C. Crowhurst, S. Sharma, J.K. Dewhurst, P. Olalde Velasco, W.L. Yang, W.J. Siekhaus, f-f Origin of the Insulating State in Uranium Dioxide: X-Ray Absorption Experiments and First-Principles Calculations, *Phys. Rev. B* 83(16) (2011) 165102/1-8.

[18] R. Caciuffo, G. Amoretti, P. Santini, G.H. Lander, J. Kulda, P.D. Du Plessis, Magnetic Excitations and Dynamical Jahn-Teller Distortions in UO_2 , *Phys. Rev. B* 59(21) (1999) 13892-13900.

[19] B.T.M. Willis, R.I. Taylor, Neutron diffraction study of antiferromagnetism in UO_2 , *Phys. Lett.* 17(3) (1965) 188-190.

[20] B.C. Frazer, G. Shirane, D.E. Cox, C.E. Olsen, Neutron-diffraction study of antiferromagnetism in UO_2 , *Phys. Rev.* 140(4A) (1965) 1448-1452.

[21] J.A. Fahey, R.P. Turcotte, T.D. Chikalla, Decomposition, stoichiometry and structure of neptunium oxides, *J. Inorg. Nucl. Chem.* 38(3) (1976) 495-500.

[22] K. Richter, C. Sari, Phase relationships in the neptunium-oxygen system, *J. Nucl. Mater.* 148(3) (1987) 266-271.

[23] R.A. Jackson, A.D. Murray, C.R.A. Catlow, Theoretical-Studies of the Point-Defect Properties of UO_2 , *Ann. Chimie. Sci. Materiaux* 10(3) (1985) 227-237.

[24] G.C. Allen, P.A. Tempest, J.W. Tyler, Coordination model for the defect structure of hyperstoichiometric UO_{2+x} and U_4O_9 , *Nature* 295(5844) (1982) 48-49.

[25] A.D. Murray, B.T.M. Willis, A Neutron-Diffraction Study of Anion Clusters in Nonstoichiometric Uranium-Dioxide, *J. Solid State Chem.* 84(1) (1990) 52-57.

[26] L. Desgranges, G. Baldinozzi, D. Simeone, H.E. Fischer, Refinement of the $\alpha\text{-U}_4\text{O}_9$ crystalline structure: new insight into the $\text{U}_4\text{O}_9 \rightleftharpoons \text{U}_3\text{O}_8$ transformation, *Inorg. Chem.* 50(13) (2011) 6146-6151.

[27] D.A. Andersson, G. Baldinozzi, L. Desgranges, D.R. Conradson, S.D. Conradson, Density functional theory calculations of UO_2 oxidation: Evolution of UO_{2+x} , U_4O_{9-y} , U_3O_7 , and U_3O_8 , *Inorg. Chem.* 52(5) (2013) 2769-2778.

- [28] B.T.M. Willis, Structures of UO_2 , UO_{2+x} and U_4O_9 by neutron diffraction, *Solid State Commun.* 2(1) (1964) 23-23.
- [29] B.T.M. Willis, Crystallographic Studies of Anion-Excess Uranium-Oxides, *J. Chem. Soc. Faraday Tras.* 83 (1987) 1073-1081.
- [30] F. Garrido, R.M. Ibberson, L. Nowicki, B.T.M. Willis, Cuboctahedral oxygen clusters in U_3O_7 , *J. Nucl. Mater.* 322(1) (2003) 87-89.
- [31] H.Y. Geng, Y. Chen, Y. Kaneta, M. Kinoshita, Stability Mechanism of Cuboctahedral Clusters in UO_{2+x} : First-Principles Calculations, *Phys. Rev. B* 77(18) (2008) 180101(R)/1-4.
- [32] L. Desgranges, G. Baldinozzi, G. Rousseau, J.-C. Niepce, G. Calvarin, Neutron diffraction study of the in situ oxidation of UO_2 , *Inorg. Chem.* 48(16) (2009) 7585-7592.
- [33] E. Schofield, A. Mehta, S. Webb, K.U. Ulrich, D.E. Giammar, J.O. Sharp, H. Veeramani, R. Bernier-Latmani, S. Conradson, D. Clark, J.R. Bargar, Molecular- and Nano-Scale Structure and Reactivity of Biogenic Uranium(IV) Oxide, *Geochim. Cosmochim. Acta* 72(12) (2008) A838-A838.
- [34] S.D. Conradson, T. Durakiewicz, F.J. Espinosa-Faller, Y.Q. An, D.A. Andersson, A.R. Bishop, K.S. Boland, J.A. Bradley, D.D. Byler, D.L. Clark, D.R. Conradson, L.L. Conradson, A.L. Costello, N.J. Hess, G.H. Lander, A. Llobet, M.B. Martucci, J. Mustre de Leon, D. Nordlund, J.S. Lezama-Pacheco, T. Proffen, G. Rodriguez, D.E. Schwarz, G.T. Seidler, A.D. Taylor, S.A. Trugman, T.A. Tyson, J.A. Valdez, Possible Bose condensate behavior in a quantum phase originating in a collective excitation in the chemically and optically doped Mott-Hubbard system, $\text{UO}_{2(+x)}$, *Phys. Rev. B* 88 (2013) 115315/1-21.
- [35] M.I. Salkola, A.R. Bishop, S.A. Trugman, J.M. Deleon, Correlation-function analysis of nonlinear and nonadiabatic systems - polaron tunneling, *Phys. Rev. B* 51(14) (1995) 8878-8891.
- [36] S.D. Conradson, S.M. Gilbertson, S.L. Daifuku, J.A. Kehl, T. Durakiewicz, D.A. Andersson, A.R. Bishop, D.D. Byler, P. Maldonado, P.M. Oppeneer, J.A. Valdez, M.L. Neidig, G. Rodriguez, Possible Demonstration of a Polaronic Bose-Einstein(-Mott) Condensate in $\text{UO}_{2(+x)}$ by Ultrafast THz Spectroscopy and Microwave Dissipation, *Sci. Rep.* 5 (2015) 15278.
- [37] K.E. Roberts, T.J. Wolery, C.E. Atkins-Duffin, T.G. Prussin, P.G. Allen, J.J. Bucher, D.K. Shuh, R.J. Finch, S.G. Prussin, Precipitation of crystalline neptunium dioxide from near-neutral aqueous solution, *Radiochim. Acta* 91(2-2003) (2003) 87-92.
- [38] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Real-Space Multiple-Scattering Calculation and Interpretation of X-Ray-Absorption Near-Edge Structure, *Phys. Rev. B* 58(12) (1998) 7565-7576.
- [39] J.J. Rehr, R.C. Albers, Theoretical Approaches to X-Ray Absorption Fine Structure, *Rev. Mod. Phys.* 72(3) (2000) 621-654.
- [40] J.J. Rehr, J.J. Kas, M.P. Prange, A.P. Sorini, Y. Takimoto, F. Vila, Ab Initio Theory and Calculations of X-Ray Spectra, *C. R. Phys.* 10(6) (2009) 548-559.
- [41] J. Rodriguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B: Condens. Matter* 192(1) (1993) 55-69.
- [42] D.J.M. Bevan, I.E. Grey, B.T.M. Willis, The Crystal-Structure of Beta- U_4O_9 , *J. Solid State Chem.* 61(1) (1986) 1-7.
- [43] R.I. Cooper, B.T.M. Willis, Refinement of the Structure of beta- U_4O_9 , *Acta. Crystallogr. Sect. A* 60 (2004) 322-325.
- [44] F. Garrido, A.C. Hannon, R.M. Ibberson, L. Nowicki, B.T.M. Willis, Neutron Diffraction Studies of U_4O_9 : Comparison with EXAFS Results, *Inorg. Chem.* 45(20) (2006) 8408-8413.

- [45] T.Z. Forbes, P.C. Burns, S. Skanthakumar, L. Soderholm, Synthesis, Structure, and Magnetism of Np_2O_5 , *J. Am. Chem. Soc.* 129 (2007) 2760-2761.
- [46] B.O. Loopstra, On the crystal structure of $\alpha\text{-U}_3\text{O}_8$, *J. Inorg. Nucl. Chem.* 39 (1977) 1714-1715.
- [47] C. Greaves, B.E.F. Fender, Structure of $\alpha\text{-UO}_3$ by Neutron and Electron-Diffraction, *Acta Crystallogr. Sect. B: Struct. Sci.* 28(DEC15) (1972) 3609-3614.
- [48] T. Gouder, A. Seibert, L. Havela, J. Rebizant, Search for higher oxides of Pu: A photoemission study, *Surf. Sci.* 601(14) (2007) L77-L80.
- [49] J.L. Stakebake, D.T. Larson, J.M. Haschke, Characterization of the plutonium-water reaction II: Formation of a binary oxide containing Pu(VI), *J. Alloys Compd.* 202(1-2) (1993) 251-263.

Graphical Abstract

Synopsis:

A reanalysis of the EXAFS of NpO_2 finds a multisite Np-O distribution with Np(V)-oxo moieties at 1.88-1.91 Å. The structure and behavior of NpO_{2+x} more closely resemble PuO_{2+x} than UO_{2+x} . In addition EXAFS and XRD results indicate phase separation into NpO_2 and previously unreported $\text{Np}_4\text{O}_{9(-\delta)}$, signifying O clustering.