

Supplemental Information for “Uranium incorporation into amorphous silica”

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Number of figures: 4

This supplement contains sample descriptions, x-ray fluorescence maps of natural samples, x-ray powder diffractograms, normalization information for EXAFS spectra, and “shell-by-shell” fitting of EXAFS spectra from structural models discussed in the main text. The supplementary information also includes a comparison of the EXAFS spectrum of uranyl adsorbed on ferrihydrite with the EXAFS spectrum of the synthetic U/Fe/Si solid. Based on these spectra it can be concluded that the local structure around U in the U/Fe/Si solid is not the same as that of U simply adsorbed on ferrihydrite. Finally, there is a comparison between the EXAFS spectrum of the synthetic U/Si solid and that of a U EXAFS spectrum taken from the Opal Butte opal. The U/Si spectrum resembles the EXAFS spectrum of the Opal Butte opal, but data limitations limit the possibility of conclusive comparison. Nonetheless, the Opal Butte opal provides some evidence of U coordinated by Si only, rather than Si and Fe, in a natural sample. Equilibrium chemical speciation was also included, to supplement the experiments in the main text.

SI1. Photographs of natural samples

Photographs of the Opal Butte opal showing the distinct zones (hyalite, fire opal, mixed, and parent material), as well as subsamples, are shown in Figure SI1.

SI2. Micro-scale synchrotron x-ray fluorescence mapping

Figure SI2 shows an x-ray fluorescence map of samples in Figures SI1 and SI3. With the exception of the NIST 611 standard reference material (marked), observed counts in the U/Rb fluorescence region (marked in red) were almost attributable to Rb, rather than U. As noted in the main text, U concentrations in these samples were very low ($< 5 \text{ mg kg}^{-1}$), which is below the detection limit of ca. $10\text{-}20 \text{ mg kg}^{-1}$ for this technique. No U “hot spots” were found using x-ray fluorescence mapping.

SI3. X-ray powder diffractograms

High-resolution synchrotron x-ray powder diffraction was used to identify crystalline solid phases in the natural opal samples. The diffractograms are shown in Figure SI3. No crystalline solid phases other than opal-CT were observed in the natural samples, and no crystalline phases could be identified over the capillary background in the synthetic samples.

SI4. Uranium L₃-edge EXAFS normalization and fitting

SI4.1. Calibration, averaging, and normalization of EXAFS spectra

Energy calibration was achieved using simultaneous collection an in-line metal foil in transmission geometry. A Y foil was used for energy calibration for U L₃-edge. The first peak in the first derivative of the metal foil XAS spectrum was calibrated to 17038.4 eV. The co-collected unknown XAS spectra were then referenced against the standard spectrum. Calibration was performed using the SixPack software package ¹.

Data were collected using a multi-element solid state detector, so each individual channel was inspected for data quality and removed if there were obvious data quality issues (such as a Bragg peak, poor signal-to-noise, etc.) Channels with good data were summed to obtain each individual spectrum. Multiple (usually 2-6, as many as 10+ for low-concentration samples) spectra were averaged to improve data quality. Averaging was also performed using the SixPack software package ¹.

SI4.1.1. Uranium L₃-edge EXAFS normalization parameters

After averaging, spectra were normalized to a total absorption of unity (as defined by the post-edge envelope), and fit using the Athena data normalization and analysis package (Ravel and Newville, 2005). For U L₃-edge EXAFS, the background was subtracted using pre-edge linear range of -200 to -50 eV (relative to E₀) and a linear post-edge region of 150 to ~720 eV (relative to E₀). E₀ was set at the top of the “white line” (top of the edge peak) of the XAS spectrum (ranging from 17,177.7 eV to 17,178.6 eV). A spline function was used to describe the absorption envelope using a range of $k=1.8$ to $k=13-14.6 \text{ \AA}^{-1}$, and a spline (background removal) k -weight of 2. The spline function had an r-background (“Rbkg” parameter) of 1.0-1.1 to remove low frequencies corresponding to non-physical interatomic distances.

SI4.2. “Shell-by-shell” fitting of adsorbed U EXAFS standard spectrum, synthetic U/Si, and synthetic U/Fe/Si spectra

“Shell-by-shell” fitting of U L₃-edge EXAFS spectra was conducted using the Athena software package ^{2,3} and FEFF 6 ⁴. The adsorbed U spectrum was fit in k -space, R-space, and q -space with a k -range of 3-13.5 \AA^{-1} , an R range of 1.0 to 3.6 \AA , and a fit k -weight of 3. The Fourier transform and inverse Fourier transform used a Hanning function for windowing, with a dk of 3 and a dr of 0.1 for smoothing. The U/Si spectrum was fit in k -space, R-space, and q -space with a k -range of 3 to 10.3 \AA^{-1} , an R range of 1.0 to 4.0 \AA , and fit k -weight of 3. The Fourier transform and inverse Fourier transform used a Hanning function for windowing, with a dk of 0.5 and a dr of 0.1 for smoothing. The U/Fe/Si was fit in k -space, R-space, and q -space with a k -range of 2.97 to 12.1 \AA^{-1} , an R range of 1.0 to 3.7 \AA , and fit k -weights of 2 and 3. The Fourier transform and inverse Fourier transform again used a Hanning function for windowing, with a dk of 0.5 and a dr of 0.2 for smoothing.

The adsorbed uranyl spectrum was dominated by axial and equatorial O atoms at ~1.8 \AA and ~2.3-2.5 \AA , respectively, as well as Fe at ~3.4-3.5 \AA , consistent with previous reports ⁵. Tabulated results for the shell-by-shell fitting of the adsorbed U spectrum are given in Table SI1, and results from the synthetic U/Si and U/Fe/Si fits are discussed at length in the main text. Statistics for each additional second-neighbor shell (U-Si_{near}, U-Si_{far}, U-U, and U-Fe) are given in Table SI2.

SI5. Chemical equilibrium modeling

Visual MINTEQ 3.0 was used to model the equilibrium aqueous speciation and aqueous chemical concentrations in the experiment. At experimental conditions (including atmospheric equilibrium with CO₂ and a fixed pH of 5.6), the equilibrium Si concentration was ~1.8 mM, indicating that ~85% of the initial 12 mM Si formed an amorphous Si precipitate. This is close to the observed experimental concentrations, suggesting the system was near equilibrium.

Equilibrium speciation of uranyl (without allowing uranyl precipitation or adsorption, so the “after” column should be taken as a lower bound for uranyl-silicate complexation) is given in Table SI3.

References

- (1) Webb, S. M. SIXPack: a Graphical User Interface for XAS Analysis Using IFEFFIT. *Physica Scripta* **2005**, 1011.
- (2) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* **2005**, 12, 537–541.
- (3) Ravel, B. ATOMS: crystallography for the X-ray absorption spectroscopist. *Journal of Synchrotron Radiation* **2001**, 8, 314–316.
- (4) Zabinsky, S.; Rehr, J.; Ankudinov, A.; Albers, R.; Eller, M. Multiple-scattering calculations of x-ray-absorption spectra. *Phys. Rev. B* **1995**, 52, 2995–3009.
- (5) Bargar, J.; Reitmeyer, R.; Davis, J. Spectroscopic Confirmation of Uranium(VI)-Carbonato Adsorption Complexes on Hematite. *Environ. Sci. Technol.* **1999**, 33, 2481–2484.

Tables

Table SII. Uranium L₃-edge EXAFS shell-by-shell fitting results for synthetic U-bearing solids. Uranyl was adsorbed on ferrihydrite in order to obtain a reference spectrum.

| | Coordination number | Distance (Å) | σ^2 | ΔE_0 (eV) |
|------------------------------|---------------------------------|--------------------|----------------------|--------------------|
| U adsorbed on Fe | | | | |
| U-O _{axial} | 2.00* | 1.81 (\pm 0.02) | 0.003 (\pm 0.001) | 5.49 (\pm 4.14) |
| U-O _{axial} MS | 2.00 [†] | 3.64 [†] | 0.005 [†] | 5.49 [†] |
| U-O _{equatorial, 1} | 3.21 (\pm 0.91) [‡] | 2.32 (\pm 0.04) | 0.007 (\pm 0.004) | 5.49 [†] |
| U-O _{equatorial, 2} | 2.79 (\pm 0.91) [‡] | 2.49 (\pm 0.07) | 0.008 [†] | 5.49 [†] |
| U-Fe | 1.39 [†] | 3.48 (\pm 0.10) | 0.015 (\pm 0.012) | 5.49 [†] |
| U-C | 2.27 (\pm 2.56) | 2.90 (\pm 0.08) | 0.009 [†] | 5.49 [†] |

* Parameter was set as a constant value in the fit.

[†] Parameter was defined as a function of other parameters in the fit.

[‡] Parameter was constrained to sum to U-O_{equatorial, total} = 6 in the fit.

Table SI2. Statistical test (F -test) results for the addition of each additional second-neighbor distance (U-Si, U-U, and U-Fe) to the EXAFS fits of the U/Si and U/Fe/Si solids. The listed “ r -factors” were calculated by the Athena software package, and used to calculate the F -score of the fit improvement by the addition of the second-neighbor atoms in question.

| Second-neighbor paths | “ r -factor” of best fit | | |
|---------------------------|----------------------------|-------------------------------|-------------------------------|
| | or test fit without path | F -score of fit improvement | p -value of fit improvement |
| U/Si solid best fit | 0.002042 | | |
| U-Si _{near} path | 0.007331 | 4.40 | $p < 0.01$ |
| U-Si _{far} path | 0.040117 | 142.4 | $p << 0.001$ |
| U-U path | 0.014767 | 18.98 | $p << 0.001$ |
| U/Fe/Si solid best fit | 0.007709 | | |
| U-Si _{near} path | 0.016636 | 2.67 | $p < 0.05$ |
| U-Si _{far} path | 0.060765 | 44.63 | $p << 0.001$ |
| U-Fe path | 0.0307276 | 10.87 | $p << 0.001$ |

Table SI3. Equilibrium speciation of uranyl in solution at the beginning and end of the U/Si incubation experiment. Uranyl was not allowed to adsorb or precipitate in the modeled geochemical speciation, so the “after” column should be interpreted as a lower bound of aqueous uranyl-silicate complexation.

| U aqueous species | Beginning of experiment (%) | After Si precipitation (%) |
|---------------------------------------|--------------------------------|-------------------------------|
| $\text{UO}_2\text{H}_3\text{SiO}_4^+$ | 89.5 | 32.3 |
| $\text{UO}_2(\text{OH})^+$ | 3.4 | 8.1 |
| $(\text{UO}_2)_3(\text{OH})_5^+$ | 3.1 | 42.2 |
| UO_2^{2+} | 2.3 | 5.5 |
| $(\text{UO}_2)_2(\text{OH})_2^{2+}$ | 0.9 | 4.9 |
| Other [*] | 0.8 | 7.0 |

^{*} Includes polymeric uranyl hydroxy complexes, as well as uranyl carbonato complexes and minor uranyl silicate complexes.

Figures

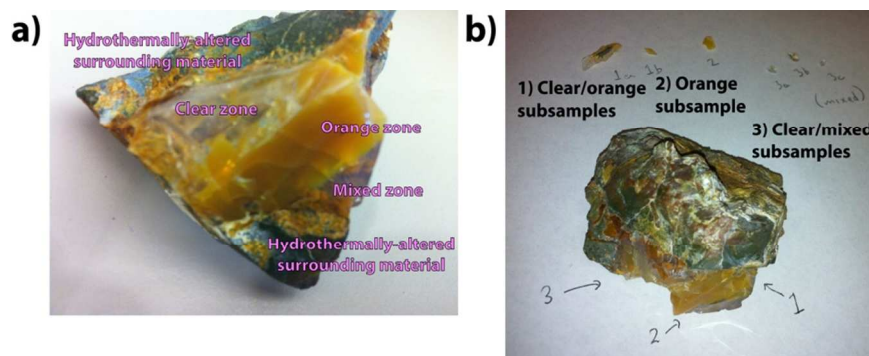


Figure SI1. *a)* Photograph of bulk commercial opal sample (OB-OR) attributed to Opal Butte mine in Oregon, United States. The opal has three distinct zones: a “clear” zone of “pure” opal-CT; an “orange” zone of opal-CT mixed homogeneously with small iron-bearing particles; and, a “mixed” zone of large iron-bearing clasts heterogeneously distributed in a matrix of pure/clear opal-CT. *b)* Photograph of bulk opal sample (OB-OR) in relation to small sub-samples for synchrotron micro-x-ray fluorescence mapping and SHRIMP-RG analysis. Samples were from three distinct zones: a “clear” zone of “pure” opal-CT; an “orange” zone of opal-CT mixed homogeneously with small iron-bearing particles; and, a “mixed” zone of large iron-bearing clasts heterogeneously distributed in a matrix of pure/clear opal-CT.

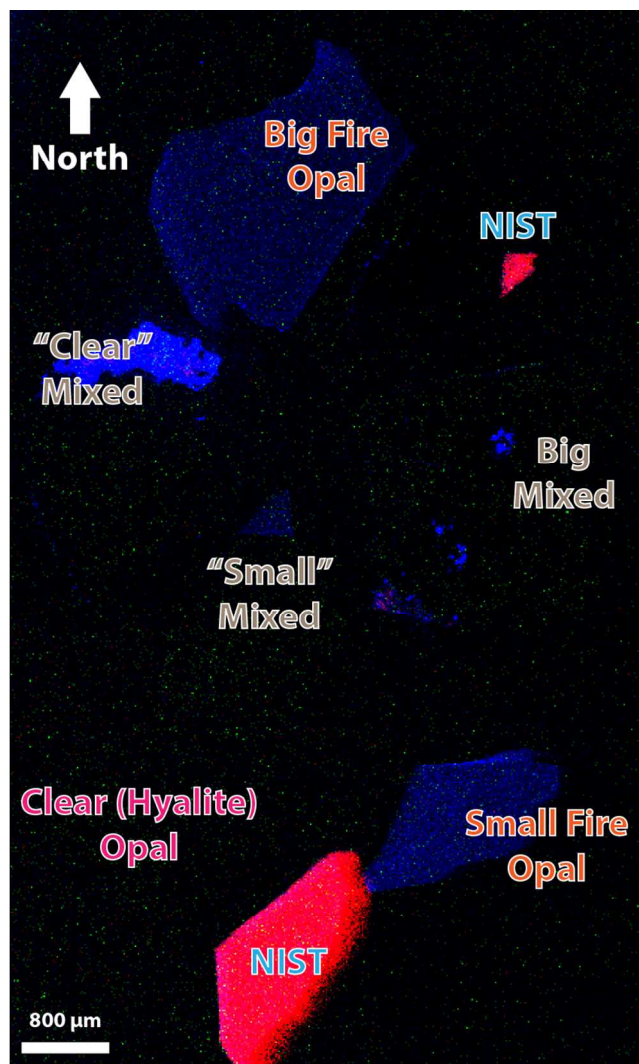


Figure SI2. X-ray fluorescence maps showing U/Rb (red), Fe (blue), and Si (green flecks) elemental associations in fragments of a natural opal with clear (hyalite, opal-CT), orange (fire opal, opal-CT homogeneously mixed with iron-bearing solids), and mixed zones (clear hyalite opal-CT with iron-bearing clasts heterogeneously distributed within the opaline material). The NIST SRM 611 analytical standard used for concentration determination is also labeled.

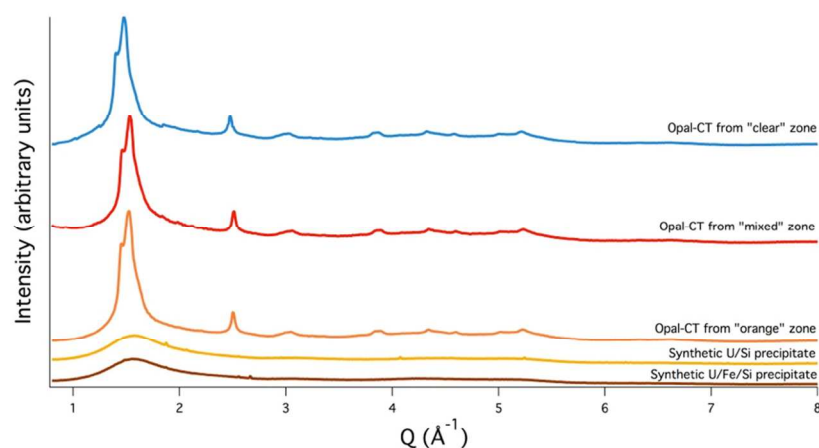


Figure SI3. Synchrotron x-ray high-resolution powder diffraction patterns of opal-CT from three distinct zones of opal from a commercially-obtained natural sample: a “clear” zone of hyalite opal-CT (*top*); an “orange” zone of fire opal-CT mixed homogeneously with small iron-bearing particles; and, a “mixed” zone of large iron-bearing clasts heterogeneously distributed in a matrix of clear hyalite opal-CT. The bottom two diffraction patterns are opal-A or amorphous silica (plus capillary background) from synthetic solids obtained by reacting 37 μM uranyl and 12 mM silicate for 28 days, at pH 5.6; the U/Fe/Si precipitate also contained ferrihydrite slurry.

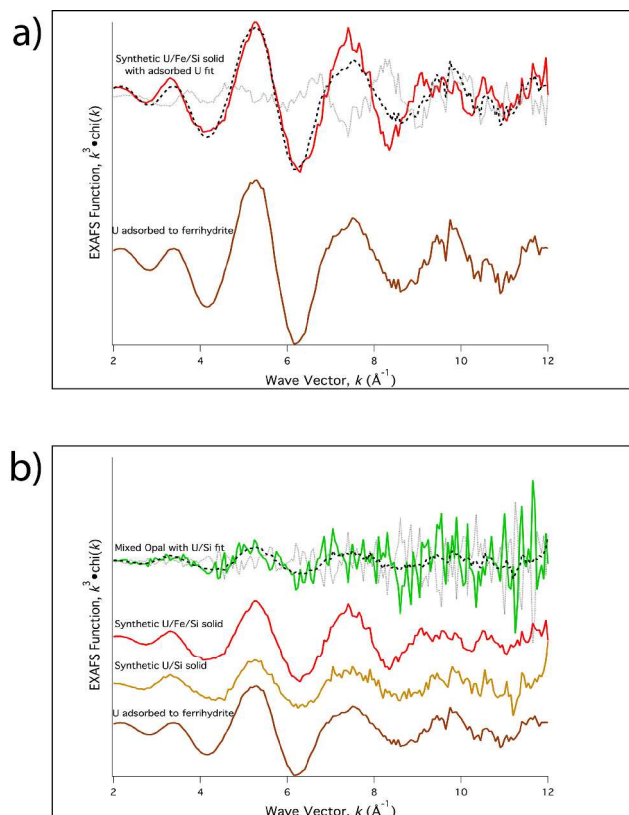


Figure SI4. *a)* Uranium L₃-edge EXAFS spectra and linear combination fitting results for synthetic U- and Fe-bearing silicate solid, and U(VI) adsorbed to ferrihydrite slurry. The U/Fe/Si spectrum was fit using a two-component model (adsorbed U(VI) and the U/Si solid spectrum), but only the adsorbed U(VI) spectrum had a non-zero coefficient in the fit. The synthetic U/Fe/Si solid was obtained from reacting 37 μ M uranyl with ferrihydrite slurry and 12 mM silicate for 28 days, at pH 5.6. The fit is shown with a black dotted line, and the fit residual is shown in grey. The U adsorbed to ferrihydrite spectrum is inadequate for describing the U(VI) in the synthetic U/Fe/Si solid; second-neighbor Si is necessary to explain the difference. *b)* Uranium L₃-edge EXAFS spectra and linear combination fitting results for the Opal Butte opal and synthetic U-bearing silicate solids. The Opal Butte “mixed” opal section was fit with a single component: the synthetic U/Si solid obtained from reacting 37 μ M uranyl 12 mM silicate for 28 days, at pH 5.6. Fit is shown with black dotted lines, and fit residuals are shown in grey. The EXAFS spectra of the synthetic samples and U adsorbed to ferrihydrite are shown for comparison.