

Quantification of rapid environmental redox processes with quick-scanning x-ray absorption spectroscopy (Q-XAS)

Matthew Ginder-Vogel, Gautier Landrot, Jason S. Fischel, and Donald L. Sparks¹

Delaware Environmental Institute, Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716

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Quantification of the initial rates of environmental reactions at the mineral/water interface is a fundamental prerequisite to determining reaction mechanisms and contaminant transport modeling and predicting environmental risk. Until recently, experimental techniques with adequate time resolution and elemental sensitivity to measure initial rates of the wide variety of environmental reactions were quite limited. Techniques such as electron paramagnetic resonance and Fourier transform infrared spectroscopies suffer from limited elemental specificity and poor sensitivity to inorganic elements, respectively. Ex situ analysis of batch and stirred-flow systems provides high elemental sensitivity; however, their time resolution is inadequate to characterize rapid environmental reactions. Here we apply quick-scanning x-ray absorption spectroscopy (Q-XAS), at sub-second time-scales, to measure the initial oxidation rate of As(III) to As(V) by hydrous manganese(IV) oxide. Using Q-XAS, As(III) and As(V) concentrations were determined every 0.98 s in batch reactions. The initial apparent As(III) depletion rate constants ($t < 30$ s) measured with Q-XAS are nearly twice as large as rate constants measured with traditional analytical techniques. Our results demonstrate the importance of developing analytical techniques capable of analyzing environmental reactions on the same time scale as they occur. Given the high sensitivity, elemental specificity, and time resolution of Q-XAS, it has many potential applications. They could include measuring not only redox reactions but also dissolution/precipitation reactions, such as the formation and/or reductive dissolution of Fe(III) (hydr)oxides, solid-phase transformations (i.e., formation of layered-double hydroxide minerals), or almost any other reaction occurring in aqueous media that can be measured using x-ray absorption spectroscopy.

arsenic | extended x-ray absorption fine structure | manganese oxide | x-ray absorption near-edge structure | kinetics

In the environment, chemical reactions at the mineral/water interface occur over a range of temporal scales, ranging from microseconds to years. Many important mineral surface processes (e.g., adsorption, oxidation-reduction, precipitation) are characterized by a rapid initial reaction on time scales of milliseconds to minutes in which a significant portion of the reaction process may occur (1). Knowledge of these initial reaction rates is critical to determining chemical kinetic rate constants and reaction mechanisms, both of which are required to fully understand environmental chemical processes. Kinetic measurements with traditional techniques, such as batch or stirred-flow techniques, typically yield only a few data points during the initial phases of the reaction and cannot capture important reaction rates occurring on time-scales of seconds or faster. Chemical relaxation techniques, such as pressure jump and concentration jump (i.e., stopped-flow) techniques, allow rapid data collection on time scales of milliseconds. However, rate “constants” are calculated from linearized rate equations, which include parameters that are determined from equilibrium and modeling studies. Consequently, the rate constants are not directly determined.

Direct, in situ, molecular-scale measurement of rapid reactions has until recently been quite limited. Mn(II) sorption to birnessite was studied on a time scale of milliseconds by using stop-flow electron paramagnetic resonance (EPR) spectroscopy (2). More recently, in situ, Fourier transform infrared spectroscopy was used to measure As(III) oxidation rates by hydrous manganese(IV) oxide (HMO) at a time scale of approximately 2.5 s (3). However, both of these techniques suffer from significant limitations. EPR can be used to measure only EPR-active nuclei, and Fourier transform infrared spectroscopy requires both IR active functional groups and a relatively high concentration of the reactants being examined.

Quick-scanning x-ray absorption spectroscopy (XAS; Q-XAS) overcomes both of these limitations. Depending on beamline instrumentation and x-ray flux, Q-XAS can be used to probe most of the elements on the periodic table to relatively low concentrations. Previously, the majority of quick-scanning beamlines collect a complete extended x-ray absorption fine structure (EXAFS) spectra in approximately 1 min, by slewing the monochromator from low to high energy and repeating the process (4). An alternative method for rapidly collecting EXAFS data is to perform energy-dispersive measurements; however, this technique generally suffers from poor sensitivity (5) and is therefore not generally applicable to examining environmental systems. Additionally, energy-dispersive measurements require that the incident x-rays pass completely through the sample to reach the detector, which severely limits the types of samples that can be analyzed.

However, by using a unique, cam-operated, continuous-scanning monochromator (Fig. 1) at beamline X18B, located at the National Synchrotron Light Source (NSLS), it is possible to collect complete x-ray absorption near edge structure (XANES) or EXAFS spectra in as little as 300 ms and 600 ms, respectively, while maintaining sensitivity to low elemental concentrations.

In environmental settings, manganese oxide minerals commonly occur as coatings and fine-grained aggregates with large surface areas (6) and exert chemical influences far out of proportion to their prevalence. Manganese oxide minerals act as potent sorbents of heavy metals and nutrients, serving as natural sinks for environmental contaminants. Additionally, they participate in a wide variety of environmental redox reactions; for example, birnessite (δ -MnO₂) directly oxidizes Se(IV) to Se(VI), Cr(III) to Cr(VI), and As(III) to As(V). The mobility and toxicity of these contaminants is directly determined by their oxidation state. For example, arsenite [As(III)] is more mobile and toxic than its oxidized counterpart, arsenate [As(V)]. Conversely, chromate [Cr(VI)], the oxidized form of Cr, is more

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¹To whom correspondence should be addressed. E-mail: dlsparks@udel.edu.

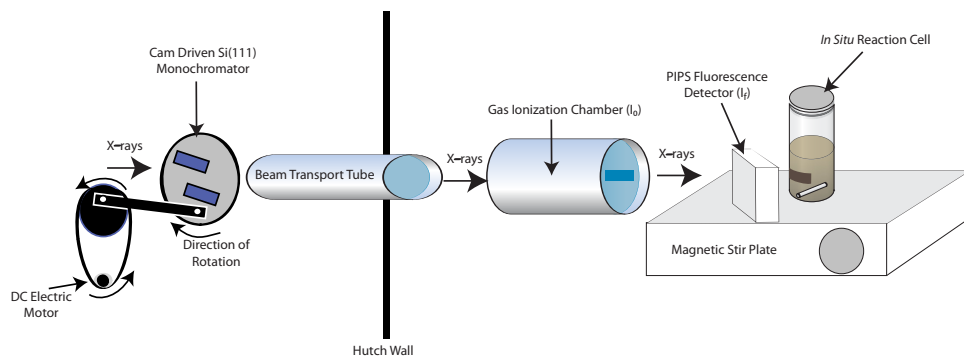


Fig. 1. Experimental setup used to collect Q-XAS data.

mobile and toxic than its reduced counterpart Cr(III). Determining the initial rates and mechanisms of oxidation reactions is critical to predicting environmental mobility of these types of environmental contaminants.

Here we use Q-XAS to measure an environmental redox reaction at a time scale of ones of seconds. We determine that the initial apparent As(III) depletion rate constant ($t < 30$ s) measured with Q-XAS is nearly twice as large as the reaction rate constant measured with traditional analytical techniques. Our results demonstrate the importance of developing analytical techniques capable of analyzing environmental reactions on the same time scale as they occur.

Results

Before initiation of the batch reactions, the As(III) stock solution was measured using liquid chromatography-inductively coupled plasma MS (LC-ICP-MS) and was found to contain 50.03 mM As(III) with no detectable As(V). Traditional batch reactions measured the oxidation of As(III) by HMO at pH 7 by removal of a 1-mL aliquot of the reaction slurry, followed immediately by filtration with a 0.2- μ m polypropylene filter to separate the reaction phases. Depletion of As(III) by HMO proceeds rapidly; after 15 s of reaction the concentration of dissolved As(V) is 0.55 mM (Fig. 2). The As(V) concentration continues to increase while As(III) decreases over the course of the 5-min reaction, with As(V) reaching 1.4 mM and As(III) reaching 3.2 mM after 300 s (Fig. 2). The total dissolved As concentration at all time points was measured by addition of the As(III) and As(V) concentrations determined by LC-ICP-MS analysis. Little change in the total dissolved As concentration is observed over the course of the reaction; however, the total dissolved As concentration is approximately 4.6 mM, lower than the initial total As concentration of 5.0 mM.

Q-XAS was used as an in situ technique to directly monitor the arsenic oxidation state. At the energy used to collect the arsenic XANES data (≈ 12 keV) the x-ray penetration depth into water is approximately 3 cm. Therefore, the arsenic oxidation state in both the solution and at the mineral/water interface is probed. The average oxidation state in the system is then determined by fitting each individual XANES spectra with a linear combination of 5 mM As(III) and As(V) standard solutions (Fig. 3). These fits provide the molar ratio of As in the solution, from which the concentrations of As(III) and As(V) in the reaction system were calculated, using the initial arsenic concentration. After 1 s of reaction, the As(V) concentration reaches 0.37 mM (Fig. 2) and continues to increase rapidly for 45 s to reach a concentration of 1 mM. The As(V) concentration continues to slowly increase for the remainder of the reaction, reaching 1.5 mM after 300 s of reaction (Fig. 2).

First-order rate plots were created using As(III) concentrations determined using traditional batch methods and Q-XAS

(Fig. 4). Similar to many environmental redox reactions, this reaction exhibited biphasic reaction kinetics; therefore, 2 sets of apparent, first-order rate constants were calculated using data from either the initial or final portion of the reaction. The number of data points used to analyze the kinetics during the initial portion of the reaction was chosen by inclusion of points providing a linear fit to the first-order kinetics model (4 for batch reaction, 30 for Q-XAS reaction). This analysis reveals that, independent of the analytical technique, rate constants for As(III) depletion are approximately an order of magnitude larger during the initial portion of the reaction than in the later portion of the reaction (Table 1 and Fig. 4). However, the initial rate constant of As(III) depletion measured using Q-XAS is nearly twice as large ($4.7 \times 10^{-3}/s$) as the rate constant measured using traditional techniques ($2.5 \times 10^{-3}/s$; Table 1).

Discussion

The oxidation of many environmental contaminants by manganese(IV) oxides has been the subject of much recent investigation (3, 11, 12). Among these contaminants, As(III) oxidation

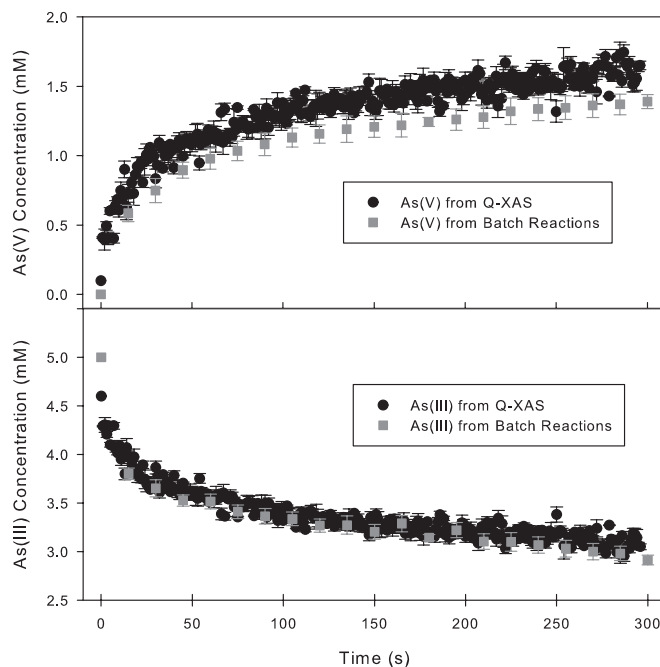


Fig. 2. As(V) and As(III) concentrations determined from traditional batch and Q-XAS reactions. Error bars represent the SD of 3 measurements made at each time point. XANES spectra and fits used to calculate Q-XAS As concentrations are shown in Fig. 3.

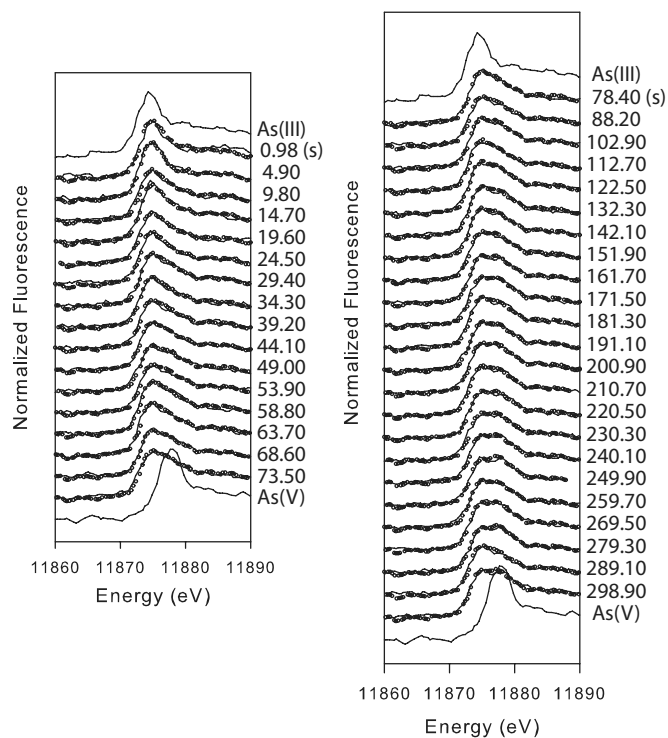


Fig. 3. Data (solid) and linear combination fits (dots) of individual As K-edge XANES spectra used to determine As(III) and As(V) concentrations during the batch reactions. Each spectrum was collected in approximately 980 ms, with the time (in s) next to each spectrum indicating the time the last data point of each spectrum was collected.

has received much of the attention, because environmental reactions that may result in the mobilization of As are of great concern. The overall oxidation reaction results in the production of 1 As(V) and 1 Mn(II) (Eq. 1).



However, the oxidation of As(III) by Mn(IV) oxides, such as HMO, likely proceeds via 2 successive 1-electron transfers that transform Mn(IV) into Mn(III). Nesbitt et al. (11) used x-ray photoelectron spectroscopy to demonstrate that As(III) oxidation proceeds through a Mn(III) intermediate (Eqs. 2 and 3), where MnOOH* is an intermediate Mn(III) reaction product:

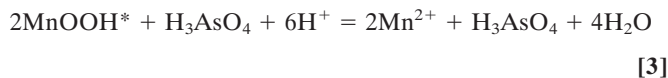
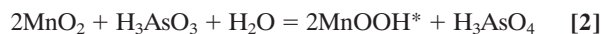


Table 1. Apparent, first-order rate constants determined from batch and Q-XAS experiments

Experiment type	Time period (s)	No. of data points	k (s^{-1})	r^2
As(III)-Batch	1-60	4	2.5 (3) $\times 10^{-3}$	0.96
As(III)-Batch	135-300	14	6.1 (4) $\times 10^{-4}$	0.82
As(III)-Q-XAS	1-30	30	4.7 (4) $\times 10^{-3}$	0.91
As(III)-Q-XAS	135-300	168	4.9 (4) $\times 10^{-4}$	0.74

The rate constants of As(III) depletion were determined by linear regression analysis of the noted time-periods for the plots in Fig. 4.

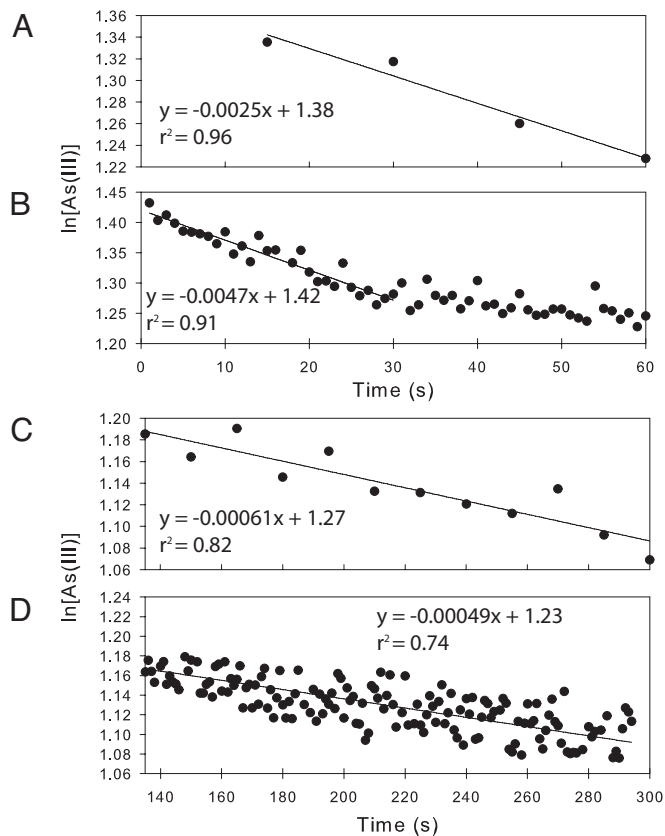


Fig. 4. First-order As(III) depletion rate plots determined from As(III) concentrations determined using batch (A and C) and Q-XAS (B and D). The time periods used for linear regression analysis are in Table 1.

After oxidation, some portion of the As(V) is likely adsorbed by the manganese oxide mineral surface (Eq. 4). In this reaction, Mn-OH represents reactive OH groups at the MnO₂ mineral surface, and (MnO)₂AsOOH represents an As(V) surface complex (10):



Mn(II) sorption at the MnO₂ mineral surface (Eq. 5) will likely affect the rate of As(III) oxidation and may ultimately determine the extent of As(III) oxidation (Eq. 5) by limiting the availability of As(III) reaction sites.



Eqs. 4 and 5 will likely limit the utility of determining kinetic parameters of this oxidation reaction using traditional methods (i.e., batch reactions). This is exemplified by comparing As(V) and As(III) concentrations determined using traditional methods and Q-XAS (Fig. 2). After 15 s of reaction, the As(V) concentration determined by traditional methods is approximately 0.1 mM lower than the concentration determined by Q-XAS. From 15 to 60 s, the average difference between the 2 methods is approximately 0.15 mM, and that difference increases to approximately 0.28 mM during the final 240 s of reaction. Interestingly, the As(III) concentrations determined by using the 2 techniques are nearly identical (Fig. 2). This comparison demonstrates that sorption of As(V) is the likely source of the discrepancy in the rate measurements obtained by using the 2 techniques.

The largest difference in the rate constants of As(III) depletion also occurs during the initial portion of the reaction, with the depletion rate constant observed using Q-XAS nearly twice as

large as the depletion rate constant observed using traditional batch reactions (Table 1 and Fig. 4). Additionally, the first 60 s of data obtained using traditional methods are in good agreement with the first-order rate model; however, when the same reaction is analyzed using Q-XAS, only the first 30 s of data are in good agreement with a first-order rate model (Fig. 4). The likely reason for this discrepancy is the fundamental difference in what the 2 techniques are measuring. As previously described, the batch reactions only measure dissolved As, whereas Q-XAS measures both the dissolved and sorbed As. This observation suggests that the oxidation reaction has reached a point where the number of reaction sites for As(III) oxidation are being controlled via the release of As(V) into solution (i.e., Eq. 4 in reverse).

Q-XAS Applications in Molecular Environmental Sciences. Development of in situ, molecular-scale probes that can be used to investigate both redox and other reactions occurring at the mineral/water interface is critical to furthering our understanding of the kinetics and mechanisms of these reactions. Here, we demonstrate the application of Q-XAS, with a time-resolution of approximately 1 s, to measure the kinetics of As(III) oxidation by HMO. Comparison of the oxidation rate measured using traditional batch techniques with the oxidation rate measured using Q-XAS reveals a twofold difference in the initial, apparent, first-order rate constants of As(III) depletion. Given the high sensitivity, elemental specificity, and time resolution of Q-XAS, it has many potential applications. They could include not only redox reactions but also measurement of dissolution/precipitation reactions, such as the formation and/or reductive dissolution of Fe(III) (hydr)oxides, solid-phase transformations (i.e., formation of layered-double hydroxide minerals), or almost any other reaction occurring in aqueous media that can be measured using XAS.

Materials and Methods

Ultrapure water (Barnstead) was used for all solutions. All chemicals used in this study met or exceeded American Chemical Society standards. HMO was synthesized by the drop-wise addition of 250 mL of 0.3 M Mn(II)(NO₃)₄·4H₂O to 250 mL of 0.2 M KMn(VII)O₄ in 0.4 M NaOH over 2 h (7). The reaction mixture was stirred rapidly during permanganate addition, and stirring was continued for 12 h. The mixture was centrifuged at 10 × g for 10 min; then the supernatant was removed and replaced with fresh Ultrapure water. These steps were repeated 6 times, after which the HMO was resuspended in Ultrapure water to reach a final concentration of 10 g HMO/L.

All As(III) oxidation reactions were performed in reaction media, which was buffered at pH 7 and consisted of 10 mM NaCl, and 5 mM Mops (C₇H₁₅NO₄S). "Traditional" batch experiments were performed using 80 mL of the reaction buffer, to which 10 mL of the 10 g/L HMO solution were added. The reaction was then initiated by the addition of 10 mL of 50 mM As(III), in reaction buffer, to achieve an initial As(III) concentration of 5 mM. The reaction was sampled every 15 s for 5 min by removal of 1.0 mL of the reaction mixture using a pipette. Within 2 s of removal, the reaction mixture was filtered through a 0.20- μ m polypropylene syringe filter to quench the reaction. As(III) and As(V) concentrations in the filtrate were determined using LC-ICP-MS. Arsenate and arsenite were separated using a Phenomenex Prodigy 5- μ m ODS-3 100 Å (150 × 4.6) column with a flow rate of 1 mL/min, using a 10- μ L sample injection before quantification by LC-ICP-MS. The mobile phase consisted of 5% methanol in 5 mM tetra-butyl ammonium hydroxide, and its pH was adjusted to 5.9 using malonic acid (final concentration of \approx 3 mM). Arsenic species separated by LC were directly introduced via a nebulizer into an Agilent 7500ce inductively coupled plasma mass spectrometer operated in helium mode.

Reactions studied using Q-XAS were performed in round, 50-mL polypropylene reaction vessels, into which a 8 × 30-mm slit was cut and sealed with Kapton tape, backed with Kapton film to prevent interaction of the tape adhesive with the reaction mixture (Fig. 1). This Kapton "window" minimized the

absorption of incident and fluorescent x-rays, allowing the collection of XAS data during the oxidation reaction. Each reaction consisted of 20 mL of reaction buffer, 2.5 mL of HMO stock solution, to which 2.5 mL of the 50-mM As(III) stock solution was added, yielding an initial As(III) concentration of 5 mM. The As(III) solution was added remotely, after XAS data collection had begun to ensure data collection during the entire oxidation reaction. X ray-induced redox reactions were checked for by collecting XAS data on HMO, As(III), and As(V) solutions at the same concentrations and durations used in the oxidation experiments. No change in the Mn or As oxidation state was observed.

Q-XAS Beamline. The NSLS at Brookhaven National Laboratory is a second-generation synchrotron operating at a current of between 200 and 300 mA and energy of 2.8 GeV. Beamline X18B at the NSLS is a bending magnet beamline equipped with a water-cooled, channel cut Si(111) monochromator that has an energy resolution of 0.5 eV at the As K-edge (11.9 keV), using 0.5 mm white-beam slits. To eliminate harmonics, the beam was de-tuned 30%. Energy selection of the incident x-rays was accomplished by continuously rocking the monochromator crystals between 11.7 and 12.2 keV. This continuous rocking motion allowed x-ray fluorescence spectra to be recorded as the monochromator moved from low to high and from high to low energy, thereby increasing the time-resolution of the XAS measurements. Changing the speed of the monochromator rocking motion varied the time required to collect each individual XAS scan.

Initial x-ray intensity was measured using a gas ionization chamber (Oxford), whereas fluorescence x-ray intensity was measured using a passivated implanted planar silicon detector (Fig. 1). The signals from the 2 x-ray detectors were amplified using SRS amplifiers with their filtration set at 1 ms. This signal was then read using a National Instruments A/D converter. The Bragg angle of the monochromator crystals was recorded using a Heidenhain IK220 encoder. These signals were sampled at 2,000 data points per second for 300 seconds, resulting in individual data files containing 600,000 data points. In these studies, the speed of the monochromator rocking motion was set so that a complete scan from 11.7 to 12.2 keV took 980 ms, resulting in the collection of a data point every 0.49 eV and collection of 306 individual scans in 300 seconds.

Data Analysis. To analyze Q-XAS data using traditional x-ray spectroscopic analytical techniques, the original, 600,000-data point file was split into 306 individual files, each containing 500 eV of data. At this point, it is possible to treat the data the same way that one would treat traditionally collected XAS data. For each individual file, the fluorescence signal was normalized to the intensity of the incidence x-rays. Using the Athena interface (8) to IFEFFIT (9), each spectrum was background corrected, and the edge jump was normalized to unity. Energy calibration was performed using a 5-mM arsenate solution, and the inflection point of the As(V) K-edge was set to equal 11.874 keV.

The oxidation state of As in the reaction solution was determined by fitting individual XANES spectra using a linear combination of spectra of 5-mM solutions of either As(III) or As(V) in reaction buffer (Fig. 3). The accuracy of the linear combination fitting was maximized by analyzing the "up" scans, in which the monochromator moved from low energy to high energy, separately from the "down" scans, in which the monochromator moved from high to low energy. Additionally, the background subtraction and normalization of standard and experimental spectra were performed using identical parameters. The As(V) detection limit of this method was determined to 5% by fitting a series of standards containing known ratios of As(III) and As(V) ranging from 0% to 10% As(V). The accuracy of the fitting method was determined to be 5% by fitting a series of standards containing known amounts of As(V). The error of each fit was calculated using the 95% CI provided by Athena (8).

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