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Supplementary Information

The role of x-ray irradiation on the arsenic photo-oxidation and nucleation of arsenic-bearing phases in water

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EXPERIMENTAL DETAILS

Fe *K*-edge XANES Analysis:

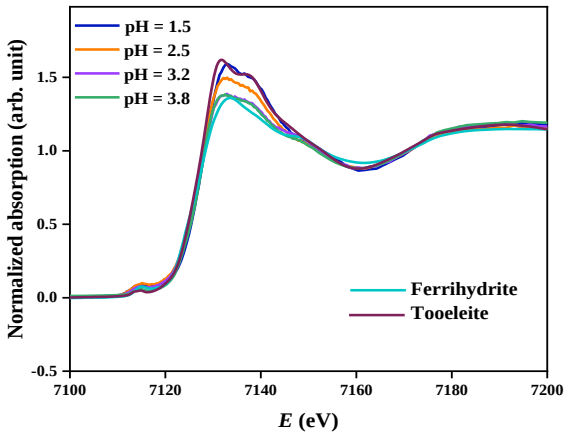


Fig. S1 Fe *K*-edge XANES spectra of Fe−As solutions measured at ESRF (BM-08) beamline in the pH range 1.5−3.8.

when the same spectra are plotted without vertical offset, the absorption edge position remains unchanged across the entire pH range. The absence of any measurable shift in the edge energy confirms that the oxidation state of iron remains Fe(III) throughout the experiment.

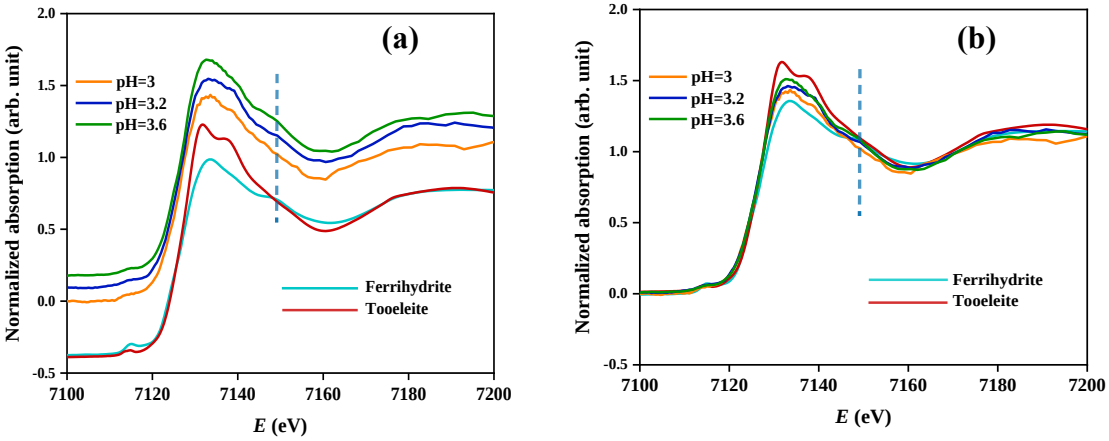


Fig. S2 Fe *K* edge XANES spectra measured on Fe–As solutions at INDUS2 (BL-09) beamline in the pH range 3–3.6.

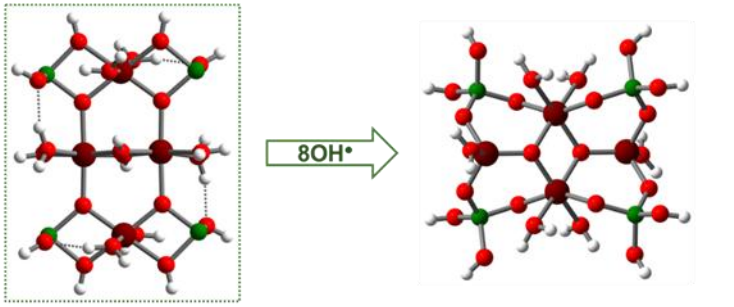
When the spectra are vertically offset (Fig. S2a), subtle changes in the post-edge region become more clearly visible. In particular, the shoulder feature around 7150 eV at pH 3.2 and 3.6 highlights the gradual evolution of ferrihydrite-like phases. Based on the evolution of the XANES features, the observed changes are consistent with the coexistence of both tooeleite-like and ferrihydrite-like environments that supported our previous study, where increasing pH governed to the development of mixed structural characteristics as further supported by *ex situ* measurements of the corresponding precipitates.[1,2] In contrast, when the same spectra are plotted without vertical offset (Fig. S2b), the absorption edge position remains unchanged across the entire pH range. The absence of any measurable shift in the edge energy confirms that the oxidation state of iron remains Fe(III) throughout the experiment.

Additional DFT results

I. Transformation of tooeleite clusters to ferrihydrite-like Fe_4 tetrameric clusters with high oxidant ($OH^{\bullet}$) concentration:

During the transformation of tooeleite to ferrihydrite-like Fe_4 tetrameric clusters, the coordinated As(III) ions are released into the solution in the presence of the hydroxyl radicals ($OH^{\bullet}$) generated from the water radiolysis under photoirradiation. The released As(III) ions remain as free $As^{III}(OH)_3$, while a few ions are oxidized to As(V) by the strong oxidant hydroxyl radicals ($OH^{\bullet}$). Detailed theoretical studies of this transformation under different conditions are already included in the main manuscript under (Theoretical Study on the conversion of tooeleite to ferrihydrite). In this section, we have considered another possible condition to further support both the experimental findings and theoretical studies.

In this special case, we considered very high concentration of hydroxyl radicals (OH•) and all the free As(III) ions are oxidized to As(V) ions and are readily adsorbed on the ferrihydrite-like Fe_4 tetrameric cluster. The corresponding resultant cluster structure shows a larger amount of distortion and does not preserve the structural symmetry or connectivity characteristic of ferrihydrite-like clusters. In addition, two of the Fe centres adopt tetra-coordinated environments, which are inconsistent with ferrihydrite clusters, where most of the Fe centres are hexa-coordinated with only few Fe ions are in tetrahedral environment.[3] This distortion would most likely prevent further aggregation of Fe_4 clusters into larger ferrihydrite nanoparticles. Besides, the Fe(III): As(V) ratio is also different from adsorbed As(V) scenario. This situation contradicts the experimental observations for the formation of ferrihydrite phases, and is not discussed in the main manuscript. The corresponding structures and reaction are presented in Fig. S3 below.



$$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 8OH^{\bullet} \rightarrow [Fe_4O_{10}As^V_4(OH)_8(H_2O)_6]^{4+} + 2H_3O^+ + 4H_2O \ , \ \Delta G_{aq} = -364.5 \text{ kcal/mol}$$

Fig. S3 Optimized structure of tooeleite $Fe_4^{III}As_4^{III}$ cluster and four As(V) ions adsorbed on $[Fe_4O_6As^V_2(OH)_6(H_2O)_8]^{4+}$ (Ferrihydrite like cluster). Colour scheme: the large dark red balls: Fe, green balls :As, small red balls: O, and small white balls: H.

II. Transformation of tooeleite clusters to ferrihydrite-like Fe_4 tetrameric clusters with H_2O_2 as oxidant:

During water radiolysis processes, the hydroxyl radicals (OH•) can easily recombine to from hydrogen peroxide (H_2O_2) molecule, which may also acts as oxidizing agent for the transformation of tooeleite to ferrihydrite with oxidation of As(III) to As(V) ion, consequently the reactions for such oxidation processes and respective free energies are different. Below, we also examined the oxidation of the removed As(III) ions to As(V) during the conversion of tooeleite to ferrihydrite like Fe_4 tetramer clusters in an analogous manner presented in the main text. The corresponding reactions are included in Table S1 below, which shows that the calculated free energies are less negative, thus less spontaneous thermodynamically, but, overall conclusions remain unchanged.

Table S1. Calculated reaction free energy for the various reactions considered and studied with different oxidant (H_2O_2) concentrations. The oxidation states of arsenic are written as superscripts for clarity. All Fe centers are considered as III oxidation states.

Cases examined	Conversion of Tooeleite clusters to Ferrihydrite clusters	(ΔG_{aq}) kcal/mol
I	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + H_2O_2 + 5H_2O \rightarrow [Fe_4O_2(OH)_4(H_2O)_{10}]^{4+} + 3As^{III}(OH)_3 + 2H_3O^+$	- 10.60
II	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 2H_2O_2 + H_2O \rightarrow [Fe_4O_4As^{V}(OH)_5(H_2O)_9]^{4+} + 2H_2As^{V}O_4^- + 2\ As^{III}(OH)_3 + 4H_3O^+$	-6.34
III	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 2H_2O_2 + 5H_2O \rightarrow Fe_4O_4\ As^{V}(OH)_5(H_2O)_9]^{4+} + H_2As^{V}O_4^- + 2\ As^{III}(OH)_3 + 3H_3O^+$	-36.53
IV	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 3H_2O_2 + 2H_2O \rightarrow [Fe_4O_6\ As^{V}_2(OH)_6(H_2O)_8]^{4+} + 2As^{III}(OH)_3 + 2H_3O^+$	-78.93
V	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 3H_2O_2 + 8H_2O \rightarrow [Fe_4O_2(OH)_4(H_2O)_{10}]^{4+} + 3H_2As^{V}O_4^- + As^{III}(OH)_3 + 5H_3O^+$	-32.33
VI	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 3H_2O_2 + 5H_2O \rightarrow [Fe_4O_4\ As^{V}(OH)_5(H_2O)_9]^{4+} + 2H_2As^{V}O_4^- + As^{III}(OH)_3 + 4H_3O^+$	-62.58
VII	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 3H_2O_2 + 2H_2O \rightarrow [Fe_4O_6As^{V}_2(OH)_6(H_2O)_8]^{4+} + H_2As^{V}O_4^- + As^{III}(OH)_3 + 3H_3O^+$	-104.92
VIII	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 4H_2O_2 + 8H_2O \rightarrow [Fe_4O_2(OH)_4(H_2O)_{10}]^{4+} + 4H_2As^{V}O_4^- + 6H_3O^+$	-58.32
IX	$[Fe_4O_4As^{III}_4(OH)_{10}(H_2O)_8]^{6+} + 4H_2O_2 + 2H_2O \rightarrow [Fe_4O_6As^{V}_2(OH)_6(H_2O)_8]^{4+} + 2H_2As^{V}O_4^- + 4H_3O^+$	-129.01

III. Transformation of As(III) to As(V) in water with •OH as oxidant:

We also investigated the oxidation of the As(III) ions to As(V) in the absence of Fe(III) ions, considering only the hydroxyl radicals ($OH^{\bullet}$) as oxidant. The highly negative free energy of this reaction as shown below indicates that the process is highly spontaneous, suggesting that the role of Fe(III) in the oxidation of $As^{III}(OH)_3$ to $H_2As^{V}O_4^-$ is not essential.

$$As^{III}(OH)_3 + 2OH^{\bullet} \rightarrow H_2As^{V}O_4^- + 4H_3O^+, \Delta G_{aq} = -62.33 \text{ kcal/mol}$$

IV. Validation of the computational methodology adopted with a different functional and basis-set:

The reactions that are included in Table 1 of the main manuscript are validated by performing the single point calculation using a different functional TPSSH and basis set cc-pVTZ for As, O, and H atoms, and LanL2DZ, for

Fe.[4] The corresponding free energy changes in aqueous medium are given below Table S2. The results follow a similar trend to that obtained with the B3LYP functional discussed in the main manuscript, with more negative values, indicating a more spontaneous process. From this we can conclude that our methods were adequate in determining the energies of the oxidation reactions.

Table S2. Calculated reaction free energy for the various reactions considered and studied with different oxidant ($OH^{\bullet}$) concentrations. The oxidation states of arsenic are written as superscripts for clarity. All Fe centers are considered as III oxidation states.

Cases examined	Conversion of Tooeleite clusters to Ferrihydrite clusters	(ΔG_{aq}) kcal/mol
I	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 2OH^{\bullet} + 5H_2O \rightarrow [Fe_4O_4As^{V}(OH)_5(H_2O)_9]^{4+} + 3As^{III}(OH)_3 + 2H_3O^{+}$	- 65.62
II	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 4OH^{\bullet} + H_2O \rightarrow [Fe_4O_2(OH)_4(H_2O)_{10}]^{4+} + 2H_2As^{V}O_4^{-} + 2As^{III}(OH)_3 + 4H_3O^{+}$	-105.03
III	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 4OH^{\bullet} + 5H_2O \rightarrow [Fe_4O_4As^{V}(OH)_5(H_2O)_9]^{4+} + H_2As^{V}O_4^{-} + 2As^{III}(OH)_3 + 3H_3O^{+}$	-132.35
IV	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 6OH^{\bullet} + 2H_2O \rightarrow [Fe_4O_6As^{V}{}_2(OH)_6(H_2O)_8]^{4+} + 2As^{III}(OH)_3 + 2H_3O^{+}$	-169.72
V	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 6OH^{\bullet} + 8H_2O \rightarrow [Fe_4O_2(OH)_4(H_2O)_{10}]^{4+} + 3H_2As^{V}O_4^{-} + As^{III}(OH)_3 + 5H_3O^{+}$	-171.65
VI	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6++} + 6OH^{\bullet} + 5H_2O \rightarrow [Fe_4O_4As^{V}(OH)_5(H_2O)_9]^{4+} + 2H_2As^{V}O_4^{-} + As^{III}(OH)_3 + 4H_3O^{+}$	-198.87
VII	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 6OH^{\bullet} + 2H_2O \rightarrow [Fe_4O_6As^{V}{}_2(OH)_6(H_2O)_8]^{4+} + H_2As^{V}O_4^{-} + As^{III}(OH)_3 + 3H_3O^{+}$	-236.64
VIII	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 8OH^{\bullet} + 8H_2O \rightarrow [Fe_4O_2(OH)_4(H_2O)_{10}]^{4+} + 4H_2As^{V}O_4^{-} + 6H_3O^{+}$	-302.97
IX	$[Fe_4O_4As^{III}{}_4(OH)_{10}(H_2O)_8]^{6+} + 8OH^{\bullet} + 2H_2O \rightarrow [Fe_4O_6As^{V}{}_2(OH)_6(H_2O)_8]^{4+} + 2H_2As^{V}O_4^{-} + 4H_3O^{+}$	-238.28

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