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New Insight into the Local Structure of Hydrrous Ferric Arsenate Using Full-Potential Multiple Scattering Analysis, Density Functional Theory Calculations, and Vibrational Spectroscopy

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1 **New insight into the local structure of hydrous ferric arsenate using**
2 **full-potential multiple scattering analysis, density functional theory calculations,**
3 **and vibrational spectroscopy**

4

5 Shaofeng Wang¹, Xu Ma¹, Guoqing Zhang¹, Yongfeng Jia^{2,*}, Keisuke Hatada³

6

7 1. Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of
8 Applied Ecology, Chinese Academy of Sciences, Shenyang, 110016, China

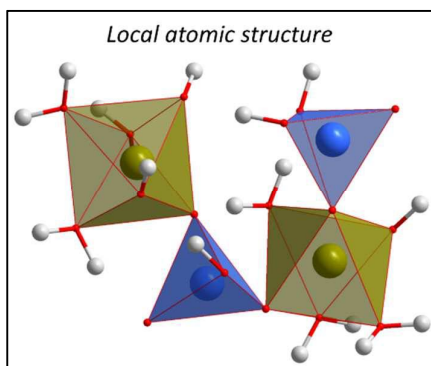
9 2. Institute of Environmental Protection, Shenyang University of Chemical
10 Technology, Shenyang, 110142, China

11 3. Département Matériaux Nanosciences, Institut de Physique de Rennes, UMR
12 UR1-CNRS 6251, Université de Rennes 1, 35042 Rennes Cedex, France

13 * Corresponding author, Prof. Yongfeng Jia, Email: yongfeng.jia@iae.ac.cn, Tel: +86
14 (24) 83970503

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19 **ABSTRACT:** Hydrous ferric arsenate (HFA) is an important arsenic-bearing
20 precipitate in the mining-impacted environment and hydrometallurgical tailings.
21 However, there is no agreement on its local atomic structure. The local structure of
22 HFA was re-probed by employing a full-potential multiple scattering (FPMS)
23 analysis, density functional theory (DFT) calculations, and vibrational spectroscopy.
24 The FPMS simulations indicated that the coordination number of the As-Fe and/or
25 Fe-As in HFA was approximately two. The DFT calculations constructed a structure
26 of HFA with the formula of $\text{Fe}(\text{HAsO}_4)_x(\text{H}_2\text{AsO}_4)_{1-x}(\text{OH})_y \cdot z\text{H}_2\text{O}$. The presence of
27 protonated arsenate in HFA was also evidenced by vibrational spectroscopy. The As
28 and Fe *K*-edge XANES spectra of HFA were accurately reproduced by FPMS
29 simulations using the chain structure, which was also a reasonable model for EXAFS
30 fitting. The FPMS refinements indicated that the interatomic Fe-Fe distance was
31 approximately 5.2 Å, consistent with that obtained by Mikutta et al. (*ES&T*, 2013)
32 using wavelet analysis. All of the results suggested that HFA was more likely to
33 occur as a chain with AsO_4 tetrahedra and FeO_6 octahedra connecting alternately in
34 an isolated bidentate-type fashion. This finding is of significance for understanding
35 the fate of arsenic and the formation of ferric arsenate minerals in an acidic
36 environment.
37

38 INTRODUCTION

39 Hydrous ferric arsenate (HFA) is one of the important secondary arsenic
40 precipitates in the mining-impacted environment and hydrometallurgical tailings,¹⁻⁵
41 such as acidic mining drainage⁶ and gold⁷ and uranium mine tailings.^{4, 8, 9} In the
42 Fe-As coprecipitation process, a widely employed method for the removal and
43 fixation of arsenic from hydrometallurgical raffinates, HFA precipitates as a major
44 arsenic-bearing phase at acidic pH values.¹⁰ The adsorbed arsenate on ferrihydrite
45 was also observed to transform into HFA at pH values of 3-5.^{2, 3} HFA is
46 thermodynamically metastable and can convert to scorodite during prolonged aging
47 at ambient temperature⁵ or elevated temperatures.^{3, 11} Therefore, precipitation of HFA
48 followed by heat treatment was also employed for the synthesis of scorodite,^{1, 4, 12-14}
49 and this could provide an alternative method for the removal and fixation of arsenic
50 in hydrometallurgical solutions with conventional autoclave¹⁵ and ambient pressure
51 scorodite precipitation technology.¹⁶⁻¹⁸

52 The local atomic structure of HFA controls its environmental behaviors and
53 recrystallization process. Although various techniques, including X-ray diffraction
54 (XRD),^{2, 3} Fourier transform infrared (FTIR) spectroscopy,³ total X-ray scattering
55 (TXS),¹⁹ synchrotron-based extended X-ray absorption fine structure spectroscopy
56 (EXAFS),^{6, 8, 20-22} and wavelet analysis,²² have been utilized to characterize the
57 structure of HFA, there is still no agreement on its atomic structure.^{8, 19-26} Current
58 views regarding the local atomic structure include the framework model,^{8, 25} similar
59 to the structure of scorodite, and the chain model,^{20, 21, 23, 24} similar to the structures

60 of butlerite and/or fibroferrite. Both models were proposed mainly based on
61 coordination numbers (CNs) and the interatomic distance of the As-Fe single
62 scattering path derived from shell-fit analysis of As and Fe *K*-edge EXAFS spectra.
63 However, the As-Fe CNs of HFA calculated from EXAFS spectra could vary
64 significantly (1.7 – 4), depending on the fitting strategies and initial model (See
65 Table S1, Supporting Information), thus leading to different conclusions about the
66 local structure of HFA. Chen et al.⁸ obtained CNs of 3.2 (As-Fe) and 3.8 (Fe-As) by
67 fitting the EXAFS spectra of HFA and proposed the scorodite-like structure, i.e.,
68 arsenate tetrahedra connecting to four FeO₆ octahedra and vice versa. In comparison,
69 Paktunc and coworkers obtained CNs of approximately 1.8 for both the As-Fe and
70 Fe-As paths, hence suggesting that the local structure of HFA is better described by
71 the chain model, i.e., single chains of corner-sharing FeO₆ octahedra bridged by
72 AsO₄ tetrahedra.²⁰ Mikutta et al. obtained a Fe-Fe interatomic distance of
73 approximately 5.3 Å according to the wavelet transform analysis and the total X-ray
74 scattering results, which is in agreement with the crystallographic data of scorodite
75 and significantly longer than that of the chain model (approximately 3.8 Å) as in
76 butlerite or fibroferrite.^{19,22} They proposed that HFA was composed of isolated FeO₆
77 octahedra bridged by AsO₄ tetrahedra.

78 Compared to the EXAFS spectra, XANES has much stronger oscillation and is
79 more sensitive to the structural details of the absorbing atoms. Based on full multiple
80 scattering (FMS) calculations, XANES features have been widely adopted to probe
81 the interatomic distance and angle of the local structure during the last two

82 decades.²⁷⁻³³ Hatada et al. developed the full-potential multiple scattering (FPMS)
83 theory and successfully simulated the XANES spectra of tetrahedrally coordinated
84 cations in GeCl_4 or quartz.³⁴⁻³⁶ In this study, we used FPMS analysis, in combination
85 with density functional theory (DFT) calculations, EXAFS, and vibrational
86 spectroscopy, to probe the local atomic structure of HFA. This would aid in the
87 understanding of its formation and transformation processes in the environment and
88 hydrometallurgical arsenic removal/fixation operations.

89

90 **EXPERIMENTAL**

91 **Synthesis of Hydrous Ferric Arsenate and Scorodite.** HFA was synthesized
92 using sodium arsenate and ferric sulfate solutions according to a previously reported
93 method.^{2, 3} In brief, 0.01 mol of As (from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) and 0.01 mol of Fe
94 (from $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$) were added to 500 mL of double distilled water, and the pH
95 of the mixture was adjusted from 1.3 to 1.8 with a 1 M NaOH solution. Then, the
96 mixture was maintained at that pH and room temperature for 3 hours. The resultant
97 solid product was separated by filtration, washed with HCl solution (pH 1.8), and
98 freeze-dried. Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) was also prepared as a reference material by
99 heating a mixture of 0.3 M Fe(III) and 0.3 M As(V) solutions in an autoclave at
100 175°C for 10 h followed by filtering, rinsing four times with HCl solution (pH 1.8)
101 and freeze drying.³⁷ Both synthesized materials were characterized using a Rigaku
102 D/Max 2500 X-ray diffractometer with graphite monochromatized $\text{CuK}_{\alpha 1}$ radiation.
103 The XRD patterns of synthetic HFA showed two broad diffraction peaks at 2θ values

104 of approximately 28° and 58° (Figure S1 in the Supporting Information), which were
105 consistent with previously reported results.^{3, 20} After digestion with concentrated
106 hydrochloric acid, the Fe/As molar ratio of HFA was determined to be 1.02±0.01 (n
107 = 3), and the sulfate concentration was lower than 0.01%. The XRD pattern of
108 synthetic scorodite matched well with the standard in the Joint Committee on
109 Powder Diffraction Standards (JSPDS) database (Figure S1).

110 **X-ray Absorption Spectroscopy (XAS) Measurements.** To collect the XAS
111 spectra, approximately 0.1 g of the synthesized solid was pressed as a disc with a
112 diameter of approximately 1 cm after grinding with an agate mortar and pestle. The
113 As and Fe *K*-edge XAS spectra were obtained on the XAFS beamline at the Beijing
114 Synchrotron Radiation Facility (BSRF). The storage ring was operated at 2.5 GeV
115 and a ring current of 250 mA. A fixed double crystal monochromator with Si(111)
116 crystals was used to monochromatize the white beam. The absolute position of the
117 monochromator was calibrated to 7112 eV for Fe measurements at the first inflection
118 point in the *K*-edge absorption spectrum of Fe foil and at 11919 eV for As
119 measurements by setting the first inflection point in the *L*_{III}-edge absorption
120 spectrum of Au foil. The absorption spectra were collected in the energy range of
121 6910-7910 eV for the Fe *K*-edge spectra and in the range of 11660-12680 eV for the
122 As *K*-edge spectra in the transmission mode at room temperature. The scan steps
123 were set to 5 eV/step for the pre-edge, 0.5 eV/step for the XANES, and 3-5 eV/step
124 for the EXAFS regions. Each individual sample was scanned three times, and the
125 averaged results are reported.

126 The pre-processing of spectra was performed by using the Athena program in
127 the Demeter package (version, 0.9.20).³⁸ The pre-edge of all spectra was fitted with a
128 straight line in the range of 150 – 50 eV before the absorption edge. The post-edge
129 absorption background was subtracted by fitting a cubic polynomial spline to the
130 data in the energy range of 0 – 750 eV after the absorption edge. For Fourier
131 transform, the background cutoff parameter (R_{bkg}) was set to 0.9 and 1.0 for As and
132 Fe, respectively.

133 **EXAFS Analysis.** EXAFS data analysis was performed by fitting the Fourier
134 transformed experimental data with the theoretical amplitude and phase functions
135 calculated by FEFF code. The crystallographic structure of scorodite³⁹ was used as
136 the FEFF input structure for the EXAFS data of scorodite, whereas the structure of
137 HFA optimized by DFT calculations was used as the model structure of HFA. The
138 least-squares fitting was performed in the k ranges of 3–14 Å⁻¹ for As and 2–14 Å⁻¹
139 for Fe K -edge spectra with Artemis (Demeter package, version 0.9.20) by using a
140 Kaiser–Bessel window function. Based on the fitting results of scorodite, the
141 amplitude reduction factor, S_0^2 , was set to 1.0 and 0.9 for the As and Fe K -edge
142 EXAFS data, respectively.

143 **XANES Analysis.** The X-ray absorption cross sections from the rising edge
144 energy region to 150 eV for As and 200 eV for Fe K -edge XANES spectra after the
145 absorption edge have been analyzed using the recently developed FPMXAN
146 software. For the Fe XANES spectra analysis, the muffin-tin (MT) approximation
147 was used for the shape of the potential.^{27, 28, 30} For the As K -edge XANES spectra, a

148 Wigner-Seitz cell was constructed by adding 10 empty spheres around the As atom
149 (Figure S3) based on the FPMS theory.³⁴⁻³⁶ The real part of self energy was
150 calculated by using the Hedin-Lunqvist (H-L) potential. Multiple scattering of
151 hydrogen atoms was not considered during the calculations except for the hydrogen
152 atom linked to the central As-O bond. The program used a Monte-Carlo search to
153 alternatively optimize the structure and non-structural parameters (e.g., Fermi energy,
154 energy shift, normalization factor, energy independent broadening, energy dependent
155 broadening, overlapping factor, etc.) until the global minimum of the square residue
156 was achieved. The fitting quality was evaluated using the goodness-of-fit parameter
157 square residue function (S^2), which is defined by the following equation:^{27, 28}

$$158 \quad S^2 = n \frac{\sum_{i=1}^m w_i [(y_i^{th} - y_i^{exp}) \epsilon_i^{-1}]^2}{\sum_{i=1}^m w_i} \quad (1)$$

159 where n is the number of independent parameters, m is the number of data points, y_i^{th}
160 and y_i^{exp} are the theoretical and experimental values of the absorption, respectively, ϵ_i
161 is the error in each point of the experimental data set, and w_i is a statistical weight. In
162 this study, $w_i = 1$ was assumed and the square residual function S^2 was equaled to the
163 statistical χ^2 function.

164 **Molecular Orbital Theory Calculations.** The structure of HFA cluster was
165 optimized by performing DFT calculations using ORCA program (V3.0.3) in the gas
166 phase.⁴⁰ All energy minimization calculations were carried out without symmetry
167 and atomic constraints. After preliminary tests, hybrid functional B3LYP and
168 def2-TZVP basis set⁴¹ were utilized for geometric optimization, using the resolution

169 of identity (RI) method. The atom-pairwise dispersion correction with the
170 Becke-Johnson damping scheme (D3BJ)⁴² was also applied for all calculations.
171 High-spin Fe³⁺, with each 3d electron occupying one of the five *d*-orbitals, was used
172 for energy minimization. The spin multiplicity of the HFA cluster model (containing
173 two Fe atoms) was set to 11 according to multiplicity = 2*S* + 1, where *S* is the spin of
174 the unpaired electrons.⁴³ Harmonic vibrational frequencies of the geometrically
175 optimized HFA was also calculated.

176 **Raman Spectroscopy.** The Raman spectra of synthetic HFA and scorodite were
177 collected on a Raman microscope (Thermo Scientific™ DXR™ xi) equipped with a
178 solid state laser diode operating at 785 nm. A 50X objective lens and 0.8 mW laser
179 were applied. Approximately 50 mg of freeze-dried ground sample was mounted on
180 a glass slide. All samples were measured from 60 to 3300 cm⁻¹ in the line focus
181 confocal mode with a detector exposure time of 8 s with the accumulation of 30
182 spectra. The wavenumber resolution was set at 4 cm⁻¹. All of the scans were
183 measured at 10% of the laser output at the microscope exit to avoid radiation damage.
184 Before the measurements, the instrument was calibrated to 520 cm⁻¹ by using a
185 standard silicon sample.

186 **Infrared Spectroscopy.** FTIR spectra were scanned on a Nicolet 6700 Fourier
187 transform infrared spectrometer (Thermo Fisher Scientific, USA). The spectra were
188 collected in a range of 400–4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and 200
189 co-added scans. Each sample of less than 0.050 mg was mixed with high-purity KBr
190 and then pressed into a disk. Immediately, samples were recorded in the transmission

191 mode. Peak fitting of infrared spectra was performed using a Lorentzian-Gaussian
192 cross function with the minimum number of peaks. All infrared and Raman spectra
193 were manipulated using the software OMNIC (v 8.2).

194

195 RESULTS AND DISCUSSION

196 **XANES Analysis.** The normalized As and Fe *K*-edge XANES spectra of
197 scorodite and HFA are compared in Figure 1a and 1b. The figures show obvious
198 differences at 11876-11888 eV and 11934-11980 eV for As as well as 7126-7135 eV
199 and 7183-7300 eV for Fe *K*-edge XANES spectra, indicating that the structure of
200 HFA is different from that of scorodite. The As and Fe *K*-edge XANES spectra of
201 scorodite were simulated using FPMS calculations (Figure 1c and 1d). The
202 crystallographic data of scorodite with the space group *Pcab* ($a = 8.937 \text{ \AA}$, $b =$
203 10.278 \AA , $c = 9.996 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$) were used as the starting simulation model.³⁹
204 The cluster radius used is 8 \AA , containing 166 and 150 atoms for the As and Fe
205 *K*-edge XANES spectra simulations, respectively. The results show that the
206 experimental spectra of scorodite were accurately reproduced ($S^2 = 7.7$ for As and S^2
207 $= 3.9$ for Fe). The small discrepancy between the theoretical and experimental
208 spectra in the first 20 eV from the edge is possibly due to the limited cluster size or
209 an overestimation of the inelastic losses.²⁸

210 The controversy for the local atomic structure of HFA focused on the number
211 and positions of FeO₆ octahedra/AsO₄ tetrahedra coordinating with the central atoms.
212 Since HFA is the precursor of crystalline scorodite,^{3,5} it could be intuitively assumed

213 that FeO_6 octahedra connect with AsO_4 tetrahedra in a similar structure to that of
214 scorodite during the formation of the HFA. Therefore, we extracted the local
215 structure of AsO_4 tetrahedra and FeO_6 octahedra from the crystallographic data of
216 scorodite as the initial structure to distinguish which structure is proximal to the
217 local structure of HFA (Figure 2). The interatomic distances and angles of the
218 extracted local structure are summarized in Table S2 in the Supporting Information.
219 The theoretical As and Fe *K*-edge XANES spectra of different clusters of AsO_4
220 tetrahedra and FeO_6 octahedra were calculated. Only the non-structural parameters
221 were optimized by fixing the atomic positions of each cluster. The comparisons
222 between the theoretical spectra and experimental data are illustrated in Figure 2c and
223 2d. For As *K*-edge XANES spectra, it can be observed that the calculated spectrum
224 of the configuration A1, representing one AsO_4 tetrahedron connecting with four
225 FeO_6 octahedra, has significantly stronger oscillations than other clusters in the
226 energy range of 50-80 eV, where it is strongly influenced by the backscattering of Fe
227 atoms. As a result, the S^2 of 6.9 for configuration A1 is higher than those derived
228 from clusters A5, A6, and A7 (one AsO_4 tetrahedron connects with two FeO_6
229 octahedra), indicating that the A1 configuration is not the best. Consistently, the Fe
230 *K*-edge XANES spectra showed that the configuration F1 (one FeO_6 octahedron
231 connects with four AsO_4 tetrahedra) did not give the smallest S^2 either, implying that
232 the FeO_6 octahedron is less likely to connect with 4 AsO_4 tetrahedra in a manner
233 similar to that of scorodite. These results suggested that in HFA, one AsO_4
234 tetrahedron/ FeO_6 octahedron is more likely to connect with two FeO_6

235 octahedra/ AsO_4 tetrahedra as a chain rather than a scorodite-like structure.

236 Furthermore, the XANES spectra are also very sensitive to the Fe-O-As angle
237 between AsO_4 tetrahedra and FeO_6 octahedra.^{28, 44} It can be clearly observed from
238 Figures 2c and 2d that the clusters of AsO_4 tetrahedra and FeO_6 octahedra with
239 different angles showed different goodness-of-fit parameters, S^2 . Simulations for
240 three Fe (As) second-shell neighbors of As (Fe) were also performed (Figure S4,
241 Supporting Information). The clusters A5 ($S^2 = 4.6$) and F5 ($S^2 = 1.0$) showed the
242 best simulation for the experimental data, indicating that the structure of HFA may
243 correspond to a chain structure with AsO_4 tetrahedra connecting to two FeO_6
244 octahedra at vertices through atoms O2 and O3.

245 **Density Functional Theory Calculation Results.** Given that the average
246 crystallite size of the initial HFA precipitates was estimated to be approximately 0.8
247 – 1 nm,^{19, 20} the initial structure of HFA cluster with 2 AsO_4 tetrahedra and 2 FeO_6
248 octahedra connecting at vertices through atoms O2 and O3 was constructed based on
249 the XANES simulation results above. Some hydrogen atoms were added to Fe-O
250 bond to achieve charge balance. After energy minimization, the optimized HFA
251 structure showed that the AsO_4 groups occurred as HAsO_4^{2-} group in the middle of
252 the chain and as H_2AsO_4^- at the end of the chain, suggesting a structural formula of
253 $\text{Fe}(\text{HAsO}_4)_x(\text{H}_2\text{AsO}_4)_{1-x}(\text{OH})_y \cdot z\text{H}_2\text{O}$ (hydrous basic ferric hydrogen arsenate,
254 $0.5 < x < 1, y = 2 - x$) (Figure 3). This result is reasonable because arsenate prefers to exist
255 as protonated arsenate species (i.e., H_3AsO_4^0 and H_2AsO_4^-) at acidic pH values (pH 1
256 – 2) where HFA precipitates. The calculated bond lengths of As-O in optimized HFA

257 cluster were in the range of 1.62–1.77 Å, with an average of 1.69±0.048 Å. The
258 calculated bond lengths of Fe-O were in the range of 1.85–2.15 Å, with a mean value
259 of 2.01±0.11 Å. The interatomic distance of Fe-Fe was approximately 5.25 Å.

260 Based on the DFT-optimized structure, the As and Fe *K*-edge XANES spectra
261 of HFA were simulated. It can be observed that the XANES spectra were accurately
262 simulated with $S^2 = 3.3$ for As and $S^2 = 1.3$ for Fe (Figure 4a & 4b), indicating that
263 our chain model is reasonable. Then, the interatomic distances between absorbing
264 atoms and back scattering atoms were optimized for As and Fe *K*-edge XANES
265 spectra to achieve the best of the As-O and Fe-O bonds. Excellent agreement
266 between the theoretical data and experimental spectra was achieved for both the As
267 ($S^2 = 3.2$) and Fe ($S^2 = 0.19$) *K*-edge XANES spectra (Figure 4c and 4d). The
268 structural optimization of the XANES spectra gave As-O bond lengths of 1.61 – 1.74
269 Å, with an average of 1.67±0.046 Å, which was comparable to the values derived
270 from DFT calculations and EXAFS data (Table 1). The refined Fe-O bond lengths
271 ranged from 1.84 to 2.15 Å, with an average of 1.99±0.11 Å, which was slightly
272 shorter than those from DFT calculations and EXAFS data (Table 1). In addition, the
273 FPMS optimization of the Fe *K*-edge XANES spectra gave an average interatomic
274 Fe-Fe distance of 5.22 Å, which is highly consistent with the DFT result (~ 5.25 Å)
275 and the value of approximately 5.3 Å derived from the wavelet analysis reported by
276 Mikutta et al.⁷ These results further implied that our chain structure was reasonable
277 for HFA.

278 Paktunc and coworkers argued that the local structure of HFA is similar to those

279 of the ferric sulfates butlerite ($\text{FeSO}_4(\text{OH})\cdot 2\text{H}_2\text{O}$) and fibroferrite
280 ($\text{FeSO}_4(\text{OH})\cdot 5\text{H}_2\text{O}$), which consist of corner-sharing FeO_6 octahedra single chains
281 bridged by SO_4 tetrahedra.^{20, 23, 24} To verify this hypothesis, the structures of butlerite
282 and fibroferrite were modified by replacing the S atoms with As atoms, and were
283 optimized using DFT calculations. The optimized structures are shown in Figure S5
284 in the Supporting Information. The Fe-Fe interatomic distances in optimized
285 butlerite-like and fibroferrite-like structures were 3.78 Å and 3.65 Å on average,
286 respectively, which were significantly shorter than those from the DFT calculations
287 (5.25 Å), the FPMS refinement (5.22 Å) and the wavelet analysis of the Fe *K*-edge
288 EXAFS data (~5.3 Å).²¹ Furthermore, the theoretical As and Fe *K*-edge XANES
289 spectra calculated using FPMS theory based on the optimized structures were
290 compared with the experimental data. Significant differences were observed for both
291 As ($S^2 = 10.3$ for butlerite and $S^2 = 7.9$ for fibroferrite) and Fe ($S^2 = 2.2$ for butlerite
292 and $S^2 = 4.2$ for fibroferrite) (see Figure S6 in the Supporting Information). These
293 results indicated that the chain structure of corner sharing FeO_6 was unlikely to be a
294 reasonable model to describe the local atomic structure of HFA.

295 **EXAFS Analysis.** Fourier transforms of As and Fe *K*-edge EXAFS data of
296 synthetic scorodite and HFA are compared in Figure 5. Consistent with previous
297 reports,^{8, 22} the magnitudes of the Fourier transform peaks of HFA at $R + \Delta R \sim 2.9$ Å
298 for the As *K*-edge EXAFS spectra and $R + \Delta R \sim 3.0$ Å for the Fe *K*-edge EXAFS
299 spectra, with both attributed to the As-Fe oscillations, are less than half of those of
300 crystalline scorodite. This was thought to be the result of lower CNs of the nearest

301 Fe/As atoms around the absorbers or large variation in the Fe-As interatomic
302 distance.²² The As and Fe *K*-edge EXAFS spectra were fitted by using the DFT
303 optimized cluster structure of HFA as a model structure. The detailed least-square
304 fitting results are summarized in Table S3 in the Supporting Information. The
305 satisfactory goodness-of-fit parameters, *R*-factor (0.008 for As and 0.006 for Fe) and
306 reduced χ^2 (110 for As and 28 for Fe), were obtained for both the As and Fe *K*-edge
307 EXAFS data. As described above, comparisons in Table 1 show that the mean
308 interatomic distances of As-O (1.68 Å, CN = 4), Fe-O (2.00 Å, CN = 6), and As-Fe
309 (3.30 Å, CN = 1.5) are comparable to those derived from DFT calculations and
310 FPMS analysis. These data further demonstrated that the chain structure of HFA
311 proposed in this study is reliable.

312 **Infrared and Raman Spectroscopy.** Figure 6, Figure S7 and Figure S8
313 illustrate the infrared and Raman spectra of synthetic HFA and scorodite. The
314 assignments of infrared and Raman bands for scorodite and HFA are listed in Table
315 S4 in the Supporting Information.

316 The deconvoluted bands of infrared (400 – 1200 cm^{-1}) and Raman spectra (60 –
317 1200 cm^{-1}) for HFA are consistent (Figure 6). Due to the poorly crystalline nature,
318 the bands on infrared and Raman spectra of HFA are poorly resolved and may
319 represent composite of different vibrations. The shape and positions of the infrared
320 and Raman bands of HFA are different from those of scorodite indicating that the
321 protonation and/or metal complexation of AsO_4 tetrahedra in HFA was different from
322 in scorodite.^{41, 43, 45} According to the DFT calculated frequencies and previously

323 reported infrared and Raman spectra of (hydrogen) arsenate group-bearing solids
324 (Figure S9 and Table S4),⁴⁵⁻⁵¹ the intense HFA infrared bands at 827 and the Raman
325 bands at 825 may be attributed to the composite of ν_1 AsO_3 symmetric stretching
326 vibration from HAsO_4^{2-} groups and As-OFe stretching vibrations from H_2AsO_4^-
327 groups.⁵² The infrared band at 877 cm^{-1} and Raman band at 889 cm^{-1} could be
328 assigned to the ν_3 AsO_3 antisymmetric stretching vibration from HAsO_4^{2-} groups.⁴⁷⁻⁴⁹
329 The infrared band at 951 cm^{-1} is possibly attributed to the ν_3 AsO_2 antisymmetric
330 stretching vibration from H_2AsO_4^- group.⁵¹ The Raman bands at 985 cm^{-1} and weak
331 infrared bands at 1048 and 1108 cm^{-1} may be attributed to the ν_1 symmetric
332 stretching vibration of SO_4^{2-} impurity.^{50, 53} The shoulder bands at 748 cm^{-1} (infrared)
333 and 766 cm^{-1} (Raman), locating in the range of As-OH stretching vibrations (707 –
334 772 cm^{-1})^{45-48, 50}, could be assigned to the composite of As-OH stretching vibrations
335 from H_2AsO_4^- groups and As-OFe stretching vibrations from HAsO_4^{2-} groups. Other
336 observed bands were assigned to the following vibrations: 213 and 271 cm^{-1} in the
337 Raman spectrum to the lattice vibrations; 424 cm^{-1} of the infrared spectrum and 360
338 and 412 cm^{-1} in the Raman spectrum to the composite of the ν_2 $\text{HAsO}_4^{2-}/\text{H}_2\text{AsO}_4^-$
339 symmetric bending; 481 cm^{-1} of the infrared spectrum and 469 cm^{-1} of the Raman
340 spectrum to the ν_4 $\text{HAsO}_4^{2-}/\text{H}_2\text{AsO}_4^-$ antisymmetric bending; and a broad weak band
341 at 605 cm^{-1} in the infrared spectrum to the FeOH/ OH_2 stretching vibrations and/or
342 As-OH stretching vibrations from H_2AsO_4^- groups.^{46-49, 51} Although these results
343 cannot provide clear information on the $\text{HAsO}_4^{2-}/\text{H}_2\text{AsO}_4^-$ ratios, the presence of
344 protonated AsO_4 groups in HFA is evidenced by the As-OH stretching vibration

345 bands.

346

347 **IMPLICATIONS**

348 The local atomic structure of synthetic HFA was re-probed using FPMS
349 calculations, EXAFS spectra, DFT calculations, and vibrational spectroscopy. The
350 short chain structure with $\text{HAsO}_4^{2-}/\text{H}_2\text{AsO}_4^-$ tetrahedra and FeO_6 octahedra alternately
351 connected at vertices was found to be a reasonable model for HFA. The butlerite
352 and/or fibroferrite-like chain modes proposed by Paktunc et al.²⁰ and the
353 scorodite-like model proposed by Chen et al.⁸ are unlikely reasonable. The structural
354 information obtained in this study is of significance for understanding the fate of
355 arsenic in some surface environments because HFA is a widely occurring precipitate
356 in the mining-impacted environment and engineered systems, e.g., acid mine drainage
357 and hydrometallurgical tailings,^{2, 3, 54} and is the precursor of various crystalline ferric
358 arsenate compounds (i.e., $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, $\text{FeH}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$, and
359 $\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5.5\text{H}_2\text{O}$) at 25°C depending on the pH values.⁵ It would be easier for the
360 HFA with our model structure to convert to ferric hydrogen arsenate minerals
361 ($\text{FeH}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$, and $\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5.5\text{H}_2\text{O}$) than the scorodite model which
362 consists of isolated AsO_4 tetrahedron connecting to four FeO_6 octahedra, and vice
363 versa. It is also easier for the structure we proposed to transform to scorodite than the
364 butlerite and/or fibroferrite-like structure consisting of single chains of corner-sharing
365 FeO_6 octahedra bridged by AsO_4 tetrahedra which needs breakage of Fe-O-Fe bonds.
366 The findings of the present work could also explain the reason why HFA showed

367 significantly higher solubility than scorodite⁴ which needs to break four covalent
368 bonds to dissolve.

369

370 ASSOCIATED CONTENT

371 **Supporting Information.** Additional information contains the XRD patterns, the
372 SEM images, the Wigner-Seitz cell, the DFT-optimized butlerite-like and
373 fibroferrite-like chain structures and their the theoretical As and Fe K-edge XANES
374 spectra, infrared and Raman spectra, previously reported As-Fe CNs, interatomic
375 distance and bond angle in the local scorodite structure, the EXAFS fitting
376 parameters, and frequency assignments.

377

378 AUTHOR INFORMATION

379 Corresponding Author

380 *Telephone: Tel: +86 (24) 83970503. Email: yongfeng.jia@iae.ac.cn.

381 Present Address

382 No.72, Wenhua Road, Shenyang, China, 110016.

383 Notes

384 The authors declare no competing financial interest.

385

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396

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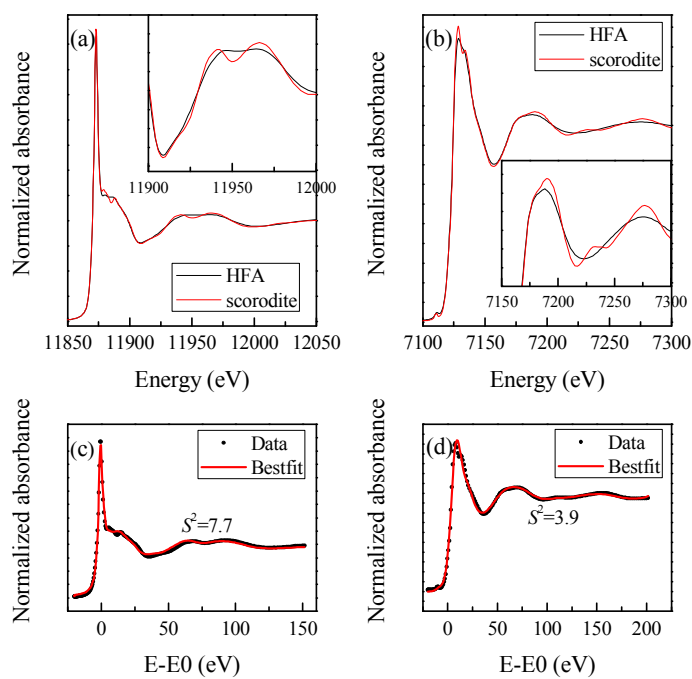
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580

581 Table 1. Comparison of interatomic distance (Å) (coordination number) of scorodite
 582 and HFA among the results derived from crystallographic data (XRD), total X-ray
 583 scattering (TXS), As and Fe *K*-edge EXAFS spectra analysis, DFT calculations, and
 584 full-potential multiple scattering analysis (FPMS) of As and Fe *K*-edge XANES
 585 spectra

	XRD ^a	DFT ^b	XANES ^b	EXAFS ^b	TXS ⁱ
Scorodite					
As-O	1.67-1.69 (4)	1.68-1.69 (4)	No data	1.69 ^c (4)	No data
As-Fe	3.33-3.38 (4)	3.35-3.41 (4)	No data	3.36 ^{c,d} (4)	No data
Fe-O	1.94-2.11 (6)	1.94-2.14 (6)	No data	2.01 ^d (6)	No data
Fe-Fe	5.13-5.35 (4)	5.19-5.45 (4)	No data	No data	No data
HFA					
As-O	No data	1.62-1.76 (4)	1.61-1.74 (4) ^e	1.68 ^c (4)	1.68
As-Fe	No data	3.21-3.36 (2)	3.16-3.38 (1.5) ^f	3.30 ^c , 3.33 ^d (1.5)	3.32
Fe-O	No data	1.85-2.15 (6)	1.84-2.15 (6) ^g	2.00 ^d (6)	1.97
Fe-Fe	No data	5.25 (1)	5.22 ^g (1)	5.3 ^h	No data

586 ^a The crystallographic data reported by Hawthorne. ^b This study. ^c Data calculated
 587 from As *K*-edge EXAFS spectrum. ^d Data calculated from Fe *K*-edge EXAFS
 588 spectrum. ^e Data calculated from As *K*-edge XANES spectrum. ^f Averaged value of
 589 As-Fe distance from multiple scattering calculation of As and Fe *K*-edge XANES
 590 spectrum. ^g Data calculated from Fe *K*-edge XANES spectrum. ^h Data from wavelet
 591 analysis of Fe *K*-edge EXAFS data reported by Mikutta et al.⁹ ⁱ Data from total X-ray
 592 scattering analysis reported by Mikutta et al.



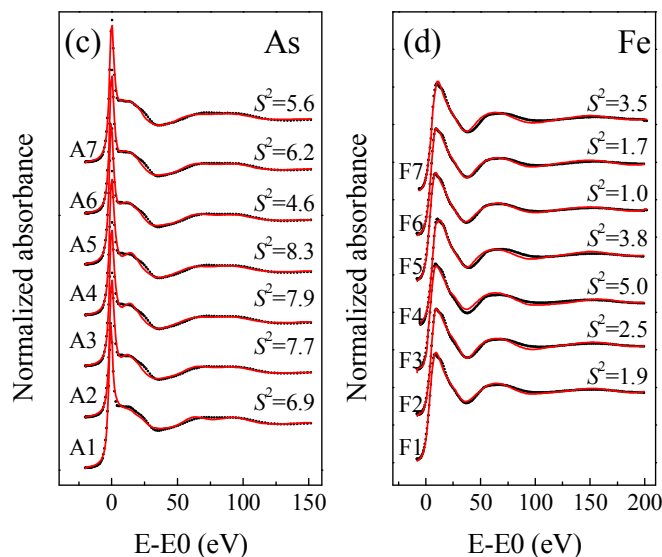
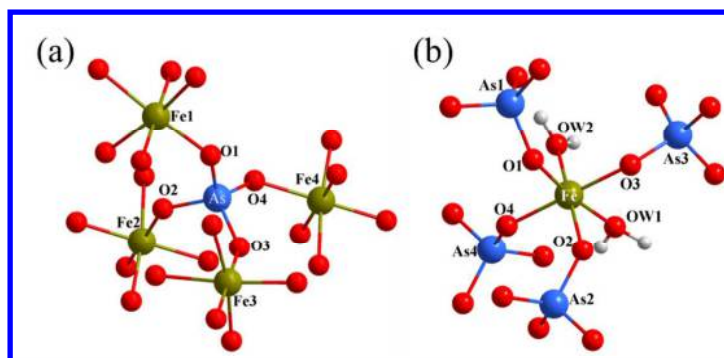
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594 Figure 1. Arsenic (a) and iron (b) *K*-edge XANES spectra of HFA (black lines) and595 scorodite (red lines) and the best-fits for As (c) and Fe (d) *K*-edge XANES spectra of

596 scorodite using non-structure optimizations.

597

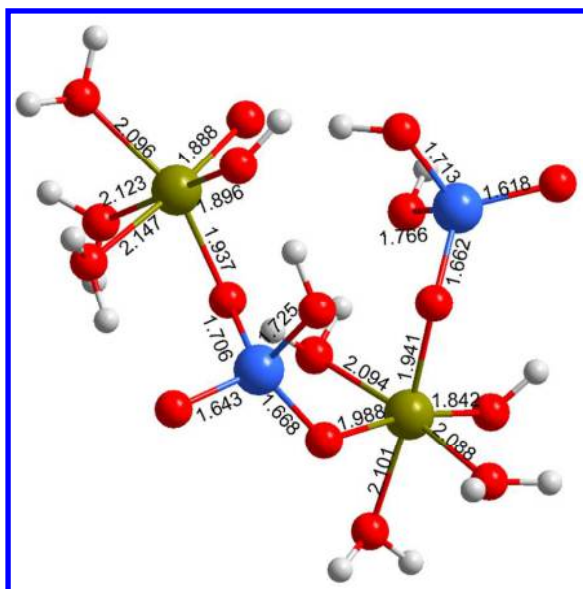
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600 Figure 2. Local atomic structure of scorodite. (a) One arsenate tetrahedron coordinates
 601 with four Fe(III)-O octahedra. (b) One Fe(III) octahedron coordinates with four
 602 arsenate tetrahedra. Comparison between theoretical arsenic (c) and iron (d) *K*-edge
 603 XANES spectra (red solid lines) according to the extracted clusters from scorodite
 604 and experimental data (black dotted lines) of HFA. For As *K*-edge spectra, cluster
 605 A1-A7 represent As+4Fe, As+Fe1+Fe2, As+Fe1+Fe3, As+Fe1+Fe4, As+Fe2+Fe3,
 606 As+Fe2+Fe4, and As+Fe3+Fe4, respectively. For Fe *K*-edge spectra, cluster F1-F7
 607 represent Fe+4As, Fe+As1+As2, Fe+As1+As3, Fe+As1+As4, Fe+As2+As3,
 608 Fe+As2+As4, and Fe+As3+As4, respectively.

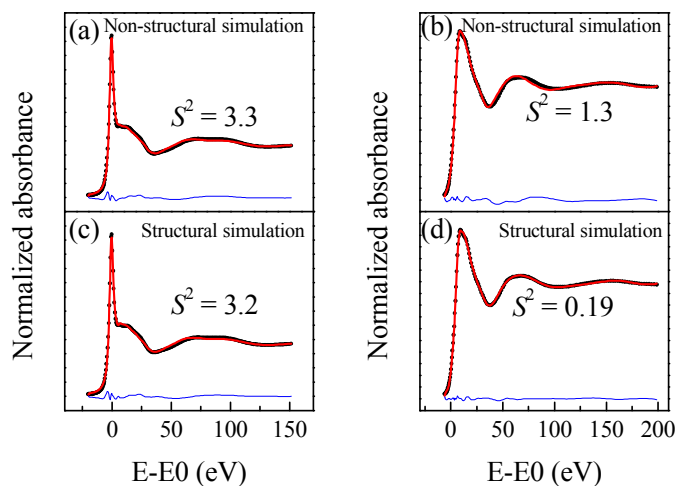
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610 Figure 3. The DFT optimized structure of hydrous ferric arsenate (HFA) cluster.

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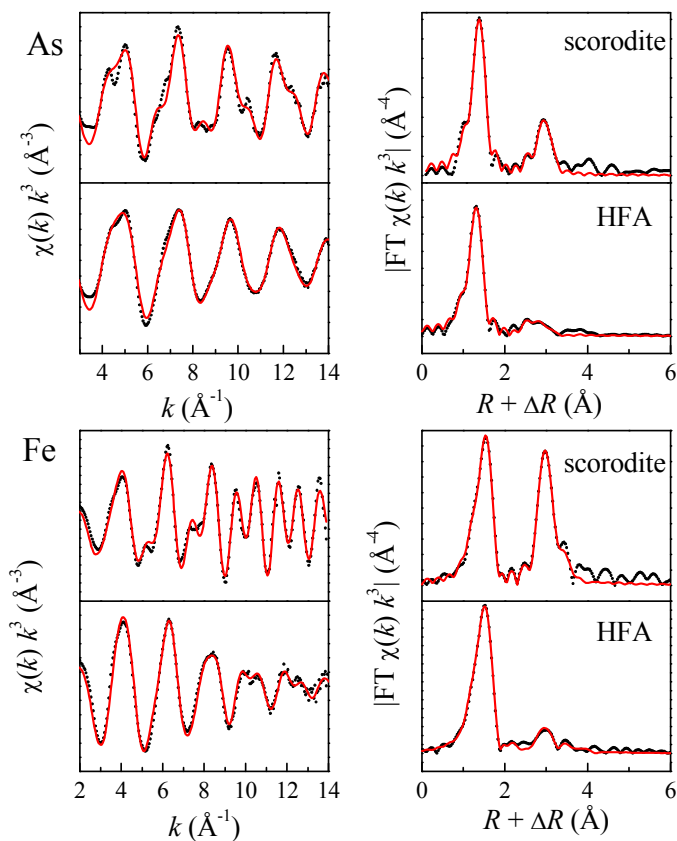
613 Figure 4. Comparison of the experimental and theoretical data of non-structural

614 simulation and structural optimized As (left column) and Fe (right column) *K*-edge

615 XANES spectra of HFA. Experimental data, best fits, and residual are shown as black

616 dots, red lines and blue lines, respectively.

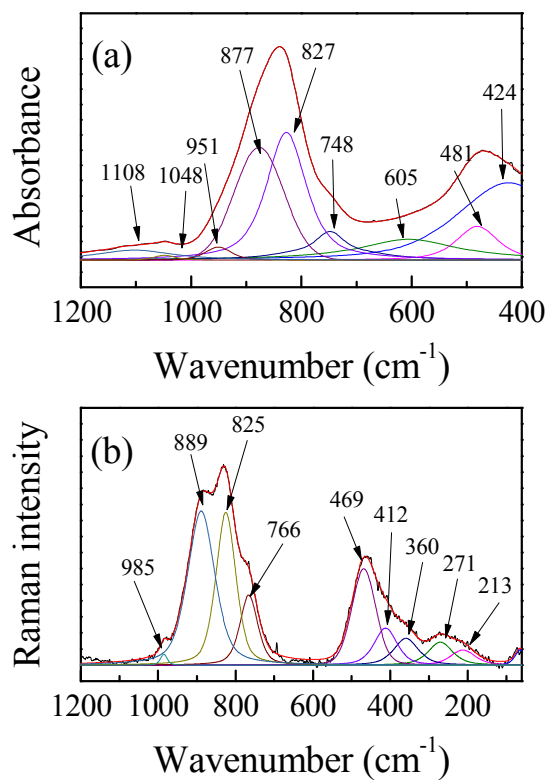
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619 Figure 5. Arsenic and iron K -edge k^3 -weighted EXAFS spectra (left) and the
620 corresponding Fourier transforms (right) of scorodite and HFA based on DFT
621 optimized structure. Experimental data and fits are shown as black dots and red lines,
622 respectively. The fitting results are summarized in Table S5.

623



624

625 Figure 6. Deconvoluted infrared (400 – 1200 cm⁻¹) (b) and Raman (60 – 1200 cm⁻¹) (c)

626 spectra of synthetic scorodite and HFA. Black and red line represent the experimental

627 and fitted spectra, respectively.

628

629 Supporting information to
630 **“New insight into the local structure of hydrous ferric arsenate using**
631 **full-potential multiple scattering analysis, density functional theory calculations,**
632 **and vibrational spectroscopy”**

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634 Shaofeng Wang¹, Xu Ma¹, Guoqing Zhang¹, Yongfeng Jia^{1,2,*}, Keisuke Hatada³

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636 1. Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of
637 Applied Ecology, Chinese Academy of Sciences, Shenyang, 110016, China

638 2. Institute of Environmental Protection, Shenyang University of Chemical
639 Technology, Shenyang, 100049, China

640 3. Département Matériaux Nanosciences, Institut de Physique de Rennes, UMR
641 UR1-CNRS 6251, Université de Rennes 1, 35042 Rennes Cedex, France

642 * Corresponding author, Prof. Yonfeng Jia, Email: yongfeng.jia@iae.ac.cn, Tel: +86
643 24 83970503

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645 This supporting information contains 9 figures, 4 tables, and references.