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# Selenium nanowire formation by reaction of selenate with magnetite

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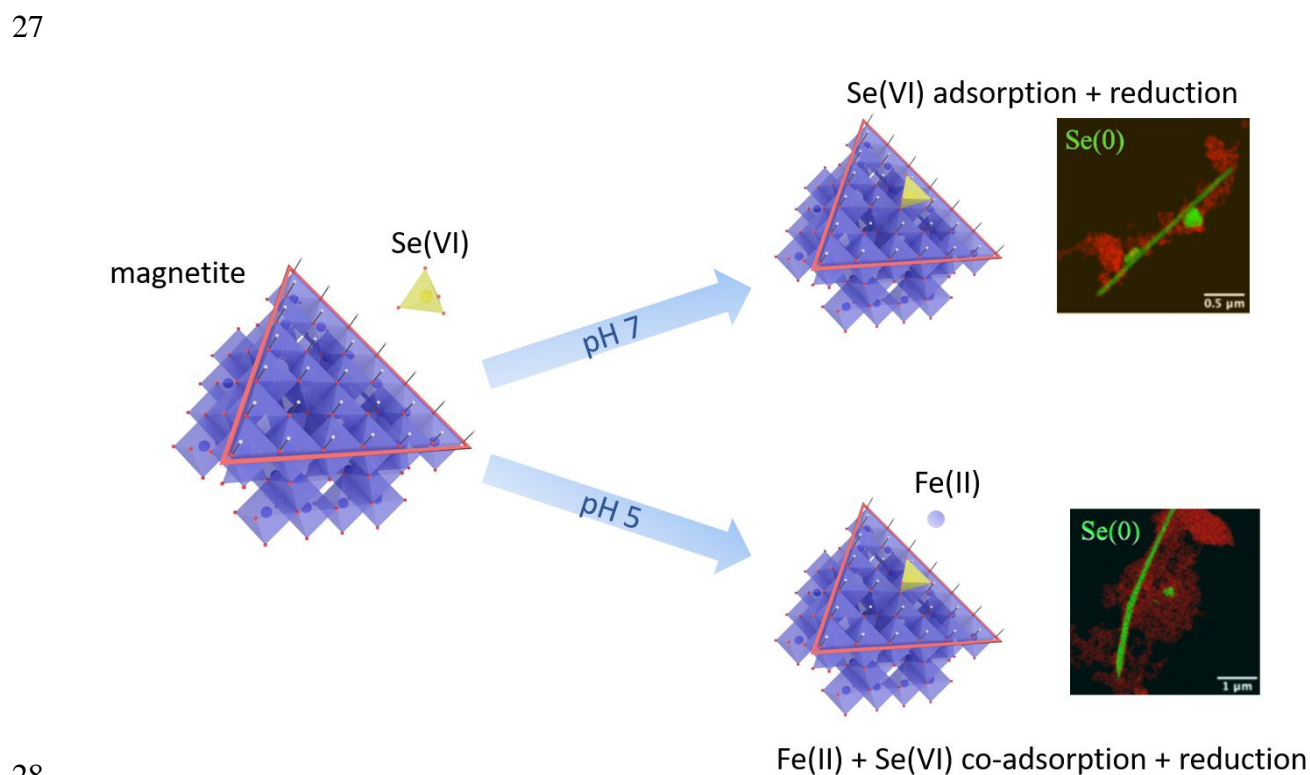
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4 19 **KEYWORDS:** Nuclear wastes, Selenium reduction, Sorption on magnetite, Selenium needles,  
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6 20 Magnetite to maghemite interconversion  
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9 21 **SYNOPSIS**

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12 22 Studies of selenate reduction on magnetite at neutral and acidic pH revealing different  
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15 23 mechanism of radionuclide retention.  
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26 26 **GRAPHICAL ABSTRACT**



## 29 ABSTRACT

30 The mobility of  $^{79}\text{Se}$ , a long half-life radioisotope and fission product of  $^{235}\text{U}$ , and contaminant of  
31 drainage waters from black shale mountains and from coal mines, is an important parameter in the  
32 safety assessment of radioactive nuclear waste disposal systems. Highly mobile and soluble in its  
33 high oxidation states ( $\text{Se(VI)O}_4^{2-}$ ,  $\text{Se(IV)O}_3^{2-}$ ), selenium oxyanions can interact with magnetite, a  
34 mineral present in anoxic natural environments and in steel corrosion products, and be precipitated  
35 by reduction, and thus immobilized. Here, the sorption and reduction capacity of synthetic  
36 nanomagnetite towards  $\text{Se(VI)}$  was investigated at neutral and acidic pH, under reducing, oxygen  
37 free conditions. The additional presence of  $\text{Fe(II)}_{\text{aq}}$ , released during magnetite dissolution at pH 5,  
38 is shown to have an effect on the reduction kinetics. XANES analyses revealed that, at pH 5,  
39 trigonal gray  $\text{Se(0)}$  formed, and that outer-sphere  $\text{Se(IV)}$  complexes existed at the nanoparticle  
40 surface at longer reaction times. The  $\text{Se(0)}$  nanowires grew during the reaction, which points to a  
41 complex transport mechanism of reduced species or to active reduction sites at the tip of the  $\text{Se(0)}$   
42 nanowires. The concomitant uptake of aqueous  $\text{Fe(II)}$  and  $\text{Se(VI)}$  ions is interpreted as a  
43 consequence of small pH oscillations that result from the  $\text{Se(VI)}$  reduction, leading to a re-  
44 adsorption of aqueous  $\text{Fe(II)}$  onto the magnetite, renewing its reducing capacity. This effect is not  
45 observed at pH 7, indicating that the presence of aqueous  $\text{Fe(II)}$  may be an important factor to be  
46 considered when examining the environmental reactivity of magnetite.

## 48 INTRODUCTION

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4 49 Selenium is an essential micronutrient often called ‘double-edged sword element’<sup>1</sup> or ‘essential  
5  
6 50 toxin’,<sup>2</sup> due to one of the narrowest tolerance limits (40 and 400 µg/day).<sup>3-4</sup> Its maximum allowed  
7  
8 51 concentration in drinking water has been set to 50 µg/L (US Environmental Protection Agency)  
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10  
11 52 and 40 µg/L (World Health Organization). Aqueous species of selenium show a variety of  
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13 53 oxidation states, the distribution of which depends strongly on the environmental conditions.  
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15  
16 54 Selenate (Se(VI)O<sub>4</sub><sup>2-</sup>) and selenite (Se(IV)O<sub>3</sub><sup>2-</sup>) are water-soluble species which account for 95 %  
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18 55 of selenium toxicity related to accumulation in plant and animal tissues,<sup>3</sup> reflecting its  
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21 56 concentration and bioavailability in soils. Se(VI) predominates at high redox potential and under  
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23 57 alkaline conditions and has a low adsorption and precipitation ability, while Se(IV) occurs at  
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26 58 moderate redox potentials and its mobility is mainly governed by sorption/desorption processes.<sup>4</sup>  
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28  
29 59 Elemental selenium [Se(0)], metals selenides [Se(-II) and Se(-I)] and selenium sulfides are  
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31 60 essentially insoluble and thus immobile in soils, hence selenium reduction strategies are used in  
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34 61 decontamination technologies.<sup>5</sup> The reduced forms predominate under strongly reducing and  
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36 62 acidic conditions with high amounts of organic matter.

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39 63 While selenium-deficient environments are much more common than seleniferous environments,  
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42 64 high natural concentrations are associated with crustal weathering of organic-rich shales, coals,  
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45 65 volcanic activity and sulfidic mineralization, and phosphate rocks.<sup>6</sup> For example an urban  
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47 66 development of a historical wetland in Upper Newport Bay, US<sup>7</sup> brought watershed contamination  
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49  
50 67 related to weathering of pyrite bearing black shale<sup>8</sup> flushing out from the vadose zone down to  
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52 68 Newport Bay with large impact on its bird wildlife.<sup>9</sup> Point pollution is usually associated with  
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55 69 human activity including coal and oil combustion facilities,<sup>10</sup> selenium refining factories, non-

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4 70 ferrous metal smelting and refining factories,<sup>11</sup> mining,<sup>12</sup> manufacturing and utilization of  
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6 71 agriculture products, irrigation,<sup>13</sup> flint soda-lime-silica glass production<sup>14-15</sup> and nuclear waste  
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8 72 disposal. These industrial effluents often exceed the selenium drinking water limits by 10-100  
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11 73 times.<sup>12,16-17</sup> Such anthropogenic emissions result in contamination at a regional scale of an  
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14 74 otherwise selenium deficient environment.

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17 75 The <sup>79</sup>Se radioisotope (half-life 2.95 x 10<sup>5</sup> years) is a <sup>235</sup>U fission product, which may affect the  
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20 76 total cumulative dose of radioactivity by an eventual release from waste repositories to the  
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22 77 biosphere.<sup>18</sup> Programs for radioactive waste storage focus nowadays on materials with high  
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24 78 radionuclide (RN) retention capacities. For example, clay-mineral rich formations show low  
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27 79 permeability and high capacity to retard the diffusion of most RNs in their cationic forms via  
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30 80 sorption processes, but are less effective to retard the migration of anions like selenate and  
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32 81 selenite.<sup>19</sup> Some nuclear glasses, e.g. the French ones, contain up to 0.04% total selenium by  
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35 82 weight, with a Se(VI) species fraction ranging from 0.05% to 20%, depending on f<sub>O2</sub> during the  
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37 83 glass production process.

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40 84 This highly mobile, long half-life selenium ion can be reductively precipitated in complex redox  
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43 85 reactions initiated at corroding steel waste canisters, surrounding compacted clay liners, and in  
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45  
46 86 deep anoxic aquifers.<sup>20-22</sup> Abiotic reduction of soluble selenium species by Fe(II)-bearing materials  
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48 87 (potential corrosion products) has been observed for several minerals such as green rust,<sup>23-25</sup>  
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50  
51 88 magnetite,<sup>26-28</sup> mackinawite and siderite,<sup>27</sup> pyrite,<sup>29,30</sup> troillite<sup>31</sup> and Fe(0).<sup>32</sup> The mixed-valence  
52  
53 89 Fe(II)/(III) oxide magnetite (Fe<sub>3</sub>O<sub>4</sub>) shows a high redox reactivity towards selenium species.<sup>26-28</sup>  
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56 90 Fe(II) desorb from magnetite at pH < 7 and has been shown to remain in solution and act as a

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4 91 reactive species when in close contact with the surface.<sup>33-35</sup> As such, the presence of aqueous Fe(II)  
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6 92 is an interesting parameter that needs to be further investigated to correctly assess the reactivity of  
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9 93 different mixed-valence oxides towards selenium oxyanions.

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12 94 The aim of this paper is to investigate sorption and reducing capacity of synthetic nanomagnetite  
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14 95 towards Se(VI), in the reducing, oxygen free environment at neutral and acidic pH. A recent study  
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17 96 by our group reported the reduction of selenite to elemental selenium by magnetite nanoparticles,  
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19 97 but the kinetics of the process as well as the influence of Fe(II) were not investigated.<sup>26</sup> Here, the  
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22 98 combination of two spectroscopy techniques helped to elucidate the redox mechanism: <sup>57</sup>Fe  
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24 99 Mössbauer spectrometry was used to quantify Fe(II)/Fe(III) and hence magnetite to maghemite  
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27 100 ratio, while K-edge X-ray Near-Edge spectroscopy (XANES) revealed oxidation states of Se  
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30 101 adsorbed on solid samples. X-Ray Diffraction (XRD) patterns confirmed the mineral oxidation  
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32 102 and presence of reduced crystalline Se form. Finally, Transmission Electron Microscopy (TEM)  
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35 103 analyses of the reacted mineral enabled examination of the morphology and size of the magnetite  
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37 104 particles and Se crystals.

## 40 105 **MATERIALS AND METHODS**

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44 106 All solutions were prepared with boiled, nitrogen-degassed Millipore 18.2 MΩ water. Reagent  
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46 107 grade NaOH (≥98 %, Sigma Aldrich) and HCl (37 %, Carl Roth) were used for preparation of 1  
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48  
49 108 M and 0.1 M stock solutions for pH control. A SENTRON pH meter was calibrated with VWR  
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51 109 buffers, and Pt redox electrode for Eh measurements with a 200 mV buffer solution. All  
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4 110 experiments and synthesis were conducted at room temperature in an Ar-filled Jacomex glovebox,  
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6 111 with a controlled oxygen partial pressure ( $< 2$  ppm).  
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10 112 **Magnetite synthesis and characterization**  
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12  
13 113 Magnetite was synthesized following original protocol of Jolivet et al.<sup>36</sup> 60 ml of 6 M  $\text{NH}_3$  (Sigma  
14  
15 114 Aldrich) was slowly added to 50 ml solution containing  $[\text{Fe}_{\text{tot}}] = 0.55$  M and  $[\text{Fe(II)}]/[\text{Fe(III)}] =$   
16  
17 115 0.5, prepared by adding 0.4 M  $\text{FeCl}_2$  (tetrahydrate, Sigma Aldrich) to 0.8 M  $\text{FeCl}_3$  (hexahydrate,  
18  
19 116 Merck). The solution turned black immediately upon mixing and was left for 24 h on a rotary  
20  
21 117 shaker. Afterwards a strong magnet was used to separate the magnetic particles and the supernatant  
22  
23 118 was filtered (0.22  $\mu\text{m}$  MF-Millipore). Magnetite was rinsed 4 times with water and 2 times with  
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25 119 0.1 mM NaCl solution, the latter one also used for the magnetite storage.  
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31 120 **XRD.** Samples were loaded inside the glove box into kapton capillaries, sealed with epoxy glue  
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33 121 and stored in anoxic conditions until measurement. X-ray powder diffraction data were collected  
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35 122 at room temperature at the ID31 beamline at the ESRF ( $\lambda = 0.1907$  Å) using a Pilatus3 X CdTe  
36  
37 123 2M detector with 172  $\mu\text{m} \times 172$   $\mu\text{m}$  pixel size. The detector calibration was done using NIST  
38  
39 124 certified  $\text{CeO}_2$  674b standard. Azimuthal integrations were performed using the pyFAI package.<sup>37</sup>  
40  
41 125 The lattice parameters, average crystallite sizes from Debye-Scherrer equation and phase fractions  
42  
43 126 were calculated using Rietveld analysis with the FullProf Suite.<sup>38</sup> The advantages of synchrotron  
44  
45 127 over laboratory X-ray source are: a better signal to noise ratio thanks to high photon flux and noise-  
46  
47 128 free detector (Figure S1), faster measurements (few seconds *vs* few hours) and the smaller amount  
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49 129 of powder required (beneficial for small-scale sorption experiments).  
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4 130 **BET.** The specific surface area (SSA) was determined by the Brunauer–Emmett–Teller adsorption  
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6 131 method (BET-N<sub>2</sub>) at 77 K, using a Belsorp-Max (Bel Japan) volumetric gas sorption instrument.

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8 132 A small amount (0.418 g) of magnetite was loaded in a glass cell inside the glovebox and then  
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11 133 dried under vacuum at 80 °C during 12 h. The SSA was calculated from the BET equation in the  
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14 134  $P/P_0$  range 0.052-0.307.

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17 135 **<sup>57</sup>Fe Mössbauer.** The spectra were collected at 300 and 77 K using a conventional constant  
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19 136 acceleration transmission spectrometer with a <sup>57</sup>Co(Rh) source and an α-Fe foil as calibration  
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21 137 sample. To obtain 5 mg Fe/cm<sup>2</sup> to satisfy the fine absorber conditions, 20 mg of the powder was  
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23 138 loaded inside the glovebox in flat round plastic holders, sealed with epoxy glue, and transported  
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27 139 in oxygen free conditions. The hyperfine structure was modeled by means of quadrupole doublets  
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29 140 and/or magnetic sextets with lorentzian lines using the homemade program MOSFIT.<sup>39</sup>

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33 141 **TEM.** A few milligrams of solid samples were placed in plastic tubes, filled with 10 mL of ethanol  
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35 142 (previously stored for several weeks in the glovebox), sealed with parafilm, and removed from the  
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37  
38 143 glovebox for 5 minutes for redistribution in an ultrasonic bath. Next, the solutions were  
39  
40 144 immediately transferred back to the glovebox, diluted with ethanol to a barely distinguishable  
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43 145 black color and drop-casted on pure carbon, 200 mesh Cu TEM grids (TED PELLA, INC.). The  
44  
45 146 samples were transferred to the microscope in anoxic conditions and were in contact with air only  
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47  
48 147 for few minutes during mounting on the microscope sample holder. Conventional Transmission  
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50 148 Electron Microscopy (TEM), High Angular Angle Dark Field imaging in scanning mode (STEM-  
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53 149 HAADF), X-ray energy-dispersive spectroscopy (XEDS) and Selected Area Electron Diffraction  
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55 150 (SAED) patterns were collected at IMPMC, Sorbonne University, Paris, using a JEOL 2100F

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4 151 microscope. Fast Fourier Transform on HR TEM images were carried out using ImageJ software  
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6 152 (<https://imagej.nih.gov/ij/>) and SAED pattern were indexed using SingleCrystal Software  
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8 153 (<http://www.crystalmaker.com/singlecrystal/index.html>).

#### 11 12 154 **Batch sorption experiments**

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15 155 Sorption experiments of  $\text{Se(VI)O}_4^{2-}$  on magnetite were performed in glass bottles at room  
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17 156 temperature in an Ar-filled glovebox. The concentration of dry magnetite in four batches was fixed  
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19 157 at 10 g/L in 0.1 mM NaCl background electrolyte. Due to stronger selenium adsorption on  
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21 158 magnetite in acidic conditions,<sup>26</sup> pH 5 and 7 were selected for comparison. The acidity of the initial  
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23 159 suspensions was adjusted during 4 days by adding HCl or NaOH stock solutions, until the pH was  
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25 160 not drifting from the desired value more than 0.2 unit within 24h. At the end of equilibration,  
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27 161 aliquots of Se(VI) stock solution were added to obtain the total target RN concentration equal to  
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29 162 8.6 mM (details in Table 1). This should cover 100% of the [-Fe-OH] surface reactive sites, as  
30  
31 163 calculated from the BET-determined specific surface area values and the magnetite theoretical  
32  
33 164 crystallographic site density of 8 sites/nm<sup>2</sup>.<sup>40</sup>

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35  
36 165 The addition of the Se(VI) to magnetite suspension stabilized at pH 5 (*Se(VI)\_pH5*) resulted in an  
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38 166 increase of the pH to 5.4, which was immediately readjusted. No change of pH was observed upon  
39  
40 167 addition of Se(VI) to the magnetite suspension stabilized at pH 7 (*Se(VI)\_pH7*). The pH of the  
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42 168 suspensions was monitored and readjusted, if necessary, throughout the experiment. The two  
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44 169 reactors were placed on a rotary shaker and 5 ml aliquots of the suspension were sampled at  
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46 170 selected time intervals. The solid was isolated by magnetic separation, dried using vacuum

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4 171 filtration system (0.22  $\mu\text{m}$ ), and left for further XAS, Mössbauer spectroscopy, TEM, XRD  
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6 172 characterization. The liquid was filtered through a syringe filter (0.22  $\mu\text{m}$ ) and left for ICP-AES,  
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8 173 IC and Eh analysis.

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12 174 **ICP-AES** and **IC**. The total concentrations of Se in the liquid samples were determined after  
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14 175 dilution by ICP-AES (Varian 720ES, detection range 0.05 - 50 ppm), while the concentrations of  
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16 176 Se(VI) and Se(IV) by Ion Chromatography (Dionex Inegriion HPIC, Thermo Scientific, detection  
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18 177 range 0.1 - 10 ppm). Difference between the initial selenium content ( $c_0$ ) and the measured value  
19  
20 178 ( $c_e$ ) provided the amount of adsorbed species.

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25 179 **XAS**. Pelletized samples (BN filler) were transported and kept in a liquid Nitrogen dewar until the  
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27 180 measurements in a closed-cycle He cryostat with He atmosphere at 15 K, to avoid photon-induced  
28  
29 181 oxidation and to exclude thermal disorder. X-ray Absorption Spectra were collected at the  
30  
31 182 Rossendorf Beamline (BM20)<sup>41</sup> at the ESRF, in fluorescence mode at the Se-K edge (12 657 eV),  
32  
33 183 using a pair of Rh-coated mirrors for suppression of higher harmonics The energy of the Si(111)  
34  
35 184 monochromator was calibrated using Au foil at L3 edge (11 918 keV). Fluorescence spectra were  
36  
37 185 acquired with an 18-element solid-state Germanium detector (Ultra-LEGe, GUL0055, Mirion  
38  
39 186 Technologies). Several spectra were measured to obtain sufficient signal quality. Energy  
40  
41 187 calibration and merging of individual scans was performed with SixPack,<sup>42</sup> normalization of  
42  
43 188 XANES spectra was done with WinXAS.<sup>43</sup> Derivation of the number of spectral components in  
44  
45 189 the complete data, their identification set as well as determination of their fractions in individual  
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47 190 samples was done with ITFA,<sup>44-45</sup> using spectra of selenium standards.

## 191 RESULTS AND DISCUSSION

### 192 Magnetite characterization before sorption experiments

193 Magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) have a similar inverse spinel structure with  
194 comparable unit cell parameters of 8.3963 Å and 8.347 Å in the microcrystalline state,<sup>46-47</sup> difficult  
195 to differentiate by laboratory XRD. Magnetite contains both  $\text{Fe}^{2+}$  (in octahedral sites) and  $\text{Fe}^{3+}$   
196 cations (in tetrahedral and octahedral sites), while maghemite is an oxidized form of spinel,  
197 containing only  $\text{Fe}^{3+}$  cations in the two types of sites. This leads to unit cell shrinking due to both  
198 the smaller size of the  $\text{Fe}^{3+}$  cation in relation to  $\text{Fe}^{2+}$ , and the formation of cationic vacancies  
199 necessary to maintain charge balance. Because of possible deviations from perfect magnetite  
200 stoichiometry corresponding to an  $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$ , a whole range of mixed phases is possible  
201 ( $\text{Fe}^{2+}/\text{Fe}^{3+} = 0$  for pure maghemite).<sup>48-49</sup>

202 Although phase identification by laboratory XRD is challenging, due to nearly identical  
203 contribution of the crystallographic planes, it is still feasible.<sup>48,50</sup> Several XRD patterns measured  
204 using laboratory device (Bruker D8) and synchrotron X-rays confirmed that the synthesized  
205 magnetite that was kept in the glovebox, as well as stabilized at  $\text{pH} \geq 7$ , represented the pure phase  
206 with  $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$  and  $a = 8.39$  Å (Figure S1). The average crystallite size of 15 nm was estimated  
207 using the Scherrer equation, while TEM image showed rather large distribution of particles ranging  
208 from 5 to 50 nm, aggregated in large clusters (Figure S2).

209 A typical Mössbauer spectrum of microcrystalline magnetite at room temperature consists of two  
210 magnetic sextets, one due to  $\text{Fe}^{3+}$  in tetrahedral positions and the other one due to  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in

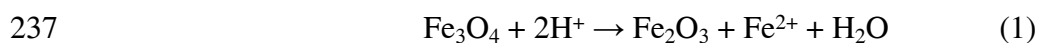
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4 211 octahedral positions, which are averaged as  $\text{Fe}^{2.5+}$  because of fast electron exchange above the  
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6 212 Verwey transition at about 125 K. The ratio between  $\text{Fe}^{3+}/\text{Fe}^{2.5+}$  is equal to  $1/2$ .<sup>53</sup> On the other hand  
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8 213 at 77 K, the spectrum differs from that at room temperature due to the Verwey transition observed  
9  
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11 214 at about 119 K, below which electron hopping is absent and the hyperfine structure must be  
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13 215 described by means of the superposition of different magnetic sextets. A structural change from  
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15  
16 216 cubic (300 K) to monoclinic (77 K) phase can be best fitted with three to five sextets.<sup>54-55</sup> In the  
17  
18 217 case of microcrystalline maghemite, the Mössbauer spectra consist of one magnetic sextet at  
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21 218 temperatures below its magnetic ordering temperature  $T_N$ , which must be described by means of  
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24 219 two magnetic components attributed to  $\text{Fe}^{3+}$  species, according to the values of isomer shift,  
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26 220 located in tetrahedral and octahedral positions. Therefore, the stoichiometry of magnetite can be  
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29 221 accurately estimated by Mössbauer measurements, which allow the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio to be  
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31 222 successfully determined from the least square data fitting, particularly from the mean value of the  
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34 223 isomer shift.<sup>51-52,56--57</sup>

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37 224 In the present study, the Mössbauer spectrum of the “pure” magnetite at 300K (Figure S3, left)  
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39 225 differs from the typical one, and shows broadened lines due to superparamagnetic relaxation  
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42 226 effects due to the presence of nanoparticles.

#### 43 44 45 227 **Stabilization of the background electrolyte at pH 5**

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48 228 Lowering the pH of the suspension consisting of only background electrolyte and magnetite, prior  
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51 229 to sorption experiments, brought substantial changes to the solid and liquid phases. As the iron  
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54 230 concentration at  $t_0$  in the following sorption experiments was accidentally not measured (first point

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4 231 at 10 min) an additional experimental runs with magnetite suspensions stabilized at pH 3-10 were  
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6 232 conducted. They proved that iron was released from magnetite at  $\text{pH} \leq 6$  through acidic dissolution  
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8 233 (see XRD patterns and Mössbauer spectra in Figures S1 and S3). Moreover, the magnetite to  
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10 234 maghemite conversion ratio obtained from Mössbauer spectrometry and from ICP-AES  
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12 235 measurements were consistent<sup>48</sup> and proved that the acidic dissolution / oxidation<sup>58-59</sup> follows the  
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14 236 reaction:



23 238 The short stabilization time (overnight) at pH 5 may explain why Goberna-Ferron<sup>26</sup> did not observe  
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25 239  $\text{Fe(II)}_{\text{aq}}$  in their solutions.

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28 240 Magnetite diffraction peak widths were similar for solids stabilized at pH 4 and 8 (Figure S1),  
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30 241 ruling out a significant change of magnetite crystal size in this pH range, in agreement with other  
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32 242 studies.<sup>58,60</sup> The two low intensity peaks at 2.9 and 3.2 °, however, which are visible only in  
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34 243 diffractograms measured at the synchrotron and not in the those measured with a laboratory source,  
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36 244 as well as peaks shifting to higher values due to a shorter unit cell parameter, demonstrate a  
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38 245 significant magnetite to maghemite transformation at pH 4 (62 %, Figure S1). As an example, the  
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40 246 Mössbauer spectra recorded for the mineral stabilized at pH 3 (Figure S3), which contained >80  
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42 247 % of maghemite, showed sharper and less bifurcated peaks than magnetite in positions typical of  
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44 248 maghemite. Indeed, the Mössbauer spectra show rather symmetrical hyperfine structures at 300 K  
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46 249 and 77 K, as maghemite does not undergo the Verwey transition that is consistent with a large  
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48 250 content of  $\text{Fe}^{3+}$  species.  
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4 251 This oxidation/conversion process driven by an adsorption reaction, which traps mobile electrons  
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6 252 on the surface sites,<sup>53</sup> is correlated with cation migration/electron hopping through the lattice,  
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8 253 creating cationic vacancies to keep the charge balance.<sup>49</sup> Mobility of electrons on the octahedral  
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10 254 magnetite sub-lattice renews the surface  $\text{Fe}^{2+}$ , but slows down with time, due to the increase in  
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12 255 thickness of the passivation layer.<sup>59,60</sup> Reaction (1) is known to be reversible in the absence of the  
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14 256 oxidizing agent:<sup>33,61</sup> by increasing the pH, aqueous iron re-adsorbs by epitaxial growth on the  
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16 257 surface, and results in 'spinel iron'.<sup>60</sup> No migration of iron ions towards the interior of the particle  
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18 258 occurs, but electrons and presumably protons are injected into the particle from the adsorbed  
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20 259 layer.<sup>62</sup>

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27 260 To conclude this section, batch sorption experiments with the initial magnetite concentration 10  
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29 261 g/L at pH 7 start with pure material, in line with iron concentration < 0.01 mmol/L measured  
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31 262 between 10 minutes and 5 months. 1.9 mmol/L of iron detected after 10 minutes of sorption  
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33 263 experiment in *Se(VI)\_pH5* solution corresponds to 4.4 % of the maghemite, if no Se(VI) was  
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35 264 introduced. Estimation of the initial value at time zero will be given in the next paragraphs.

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40 265 Such an elementary understanding of the magnetite/maghemite chemistry was needed before  
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42 266 discussing the sorption/reduction experiments on magnetite, because maghemite does not show  
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44 267 any reducing capacity towards selenate and selenite oxyanions,<sup>63-64</sup> and may perturb the electron  
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46 268 exchange if covering the magnetite core surface. It should be highlighted here that the exact  
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48 269 location of the oxidized layers (whether maghemite forms a shell around a magnetite core,<sup>52,65</sup> or  
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50 270 it is delocalized due to possible electron hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  positions) is not within  
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52 271 the scope of the present study.



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4 272 **Se(VI) sorption kinetics experiments on magnetite at pH 5 and 7**

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7 273 Results of the Se(VI) sorption experiments at pH 5 and 7 are given in Figure 1 and Table S1.

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9 274 Retention on magnetite was calculated from the ratio between the initial RN concentration ( $c_0$ ) and  
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12 275 the one measured by ICP-AES at a selected time interval ( $c_{aq}$ ).

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15 276 **Se(VI)** uptake was fastest during the first 10 days (240 h) in the two experimental series, while the  
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18 277 rate depended on the solution pH, as reported in the literature.<sup>28,66</sup> At pH 7 during the first 10 days,  
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21 278 22 % of selenate was removed from the solution, while at pH 5 only 43 %. Thus, sorption was 1.9  
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23 279 times higher at pH 5 than that at pH 7 in the corresponding series (3.67 vs 1.86 mmol/L).

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26 280 After the first 10 days, a plateau (within experimental error) was observed at pH 7 and the  
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29 281 corresponding final selenate sorption extent was about 1.5 molecule/nm<sup>2</sup> of Se(VI). At pH 5 the  
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32 282 removal process continued but at a much lower rate, reaching 53 % after 5 months, equivalent to  
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34 283 about 4.2 molecule/nm<sup>2</sup> of Se(VI). It indicates that the theoretical sorption capacity (8 sites/nm<sup>2</sup>)  
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36 284 calculated for [Fe-OH] groups on the {111} crystallographic faces of magnetite<sup>40</sup> was only  
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39 285 partially reached, with a level of 53 % at pH 5, and 22 % at pH 7, most probably due to the high  
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41 286 concentrations of the adsorbates.<sup>26,67</sup>

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45 287 ICP-AES results were confirmed by IC measurements, which can distinguish the two soluble  
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47 288 forms (Se(IV) and Se(VI)). The reduced, soluble (Se(IV)O<sub>3</sub><sup>2-</sup> oxyanion remained below the  
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50 289 detection limit at both pH values, suggesting that the reduction processes took place at the mineral  
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52 290 surface and not in solution during the 5 months of the reaction. However, due to the necessary  
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55 291 sample dilution (IC Se(VI) upper detection limit 10 ppm), low concentrations of selenite (for

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4 292 sample dilution equal 50, Se(IV) lower detection limit 0.5 ppm would give 25 ppm!) might not  
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6 293 have been detected.

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9 294 If no reduction occurred, we could have assumed that the negatively charged oxyanions were  
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12 295 exclusively adsorbed via electrostatic attraction to the positively charged surface sites of magnetite  
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14 296 or maghemite, below their isoelectric points ( $\text{IEP}_{\text{magnetite}} = 6.4-8$ ,  $\text{IEP}_{\text{maghemite}} = 5.5-7.5$ )<sup>68</sup>, as found  
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17 297 for selenate and selenite adsorbed on positively charged  $\text{FeOH}_2^+$  groups of maghemite.<sup>63-64</sup>

## 20 298 **Fe(II) aqueous**

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24 299 At pH 7 the concentration of  $\text{Fe(II)}_{\text{aq}}$  stayed below 0.01 mmol/L during 5 months, so we could  
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26 300 assume that the magnetite was fairly pure at  $t_0$  (as confirmed by Mössbauer spectrometry) and that  
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29 301 any further mineral transformation was the consequence of redox reactions between the mineral  
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31 302 and selenium species.

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34 303 At pH 5, after 10 minutes of reaction, 1.87 mmol/L of iron was detected in the solution as a result  
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37 304 of pH stabilization and acidic dissolution of magnetite, prior to selenate injection. While the re-  
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40 305 adsorption of  $\text{Fe(II)}_{\text{aq}}$  on magnetite is not favored at pH 5 due to the positively charged mineral  
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42 306 surface,<sup>33,35</sup> the presence of  $\text{Fe(II)}_{\text{aq}}$  may catalyze changes in the chemistry of Se(VI), forming  
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45 307 ternary surface complex. During the following 5 months of sorption experiments run at pH 5, a  
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47 308 linear co-removal dependency between Se(VI) and  $\text{Fe(II)}_{\text{aq}}$  was detected (Figure 1b). The initial  
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50 309 ratio  $n\text{Fe(II)}_{\text{aq}}/n\text{Se(VI)}_{\text{aq}}$  in the solution was 0.3:1 (*Se(VI)\_pH5*) and the following re-adsorption  
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52 310 ratio was 1:2, so lower than expected for complete Se(VI) reduction by  $\text{Fe(II)}_{\text{aq}}$ , pointing rather to  
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55 311 the secondary mechanism. There was no  $\text{Fe(II)}_{\text{aq}}$  left after 168 days of Se(VI) experiment, but

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4 312 already after 3 months only 0.04 mmol/L of iron was still available in solution (red arrow in Figure  
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6 313 1a and 1b). In fact the Se(VI) concentration in solution was not decreasing anymore, due to Fe(II)<sub>aq</sub>  
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8 314 depletion. Extrapolation of the co-removal results allowed the estimation of an initial aqueous iron  
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10 315 concentration at t<sub>0</sub> equal to 2.4 mmol/L, corresponding to the 5.6 % of maghemite initially present  
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12 316 (before selenate injection). This represents one monolayer of maghemite for the averaged 15 nm  
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14 317 diameter spherical particles, so that electron exchange between the surface and the core of the  
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16 318 magnetite should still be possible.

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22 319 Several studies have shown that reduction of environmental contaminants is effectively catalyzed  
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24 320 by Fe(II)<sub>aq</sub> adsorbed on magnetite,<sup>34,70</sup> montmorillonite,<sup>20</sup> goethite and lepidocrocite<sup>61</sup> and zero-  
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26 321 valent iron.<sup>69</sup> Examination of the reduction of selenate by ZVI<sup>69</sup> and the removal of arsenic by non-  
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28 322 stoichiometric magnetite<sup>35</sup> demonstrated the importance of the initial Fe(II)<sub>aq</sub> concentration on the  
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30 323 extent of pollutant reduction. Moreover, Fe(II)<sub>aq</sub> alone did not show significant Se(VI) reduction.<sup>69</sup>  
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### 35 324 Eh – redox potential

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38 325 The stability and reproducibility of redox potentials (Eh) measured in the filtered solutions were  
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40 326 difficult to achieve due to low ionic strength of the solution, lack of reaction equilibrium  
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42 327 (especially at the early stages of batch experiments) and possible reactions at the electrode  
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44 328 surface.<sup>71</sup> Only negative values of Eh were measured during the first 3 months of the reactions,  
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46 329 confirming overall reducing environmental conditions. At pH 7, redox potential fluctuated  
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48 330 between -0.15 and 0.25 V (Figure S4) during the three months of the experiment. At pH 5, initial  
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50 331 10 days period with more reducing conditions (Eh between -0.15 and -0.33 V), where the drop in  
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52 332 Se(VI) concentration was the fastest, was followed by milder period between 10 days and 3 months  
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4 333 (Eh between 0 and -0.15). The general trends fit well with different stability domains of the  
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6 334 Pourbaix Eh-pH diagrams (Figure S4). The thermodynamically most stable form at both pH was  
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8 335  $\text{Fe}^{2+}$  for iron, in agreement with dissolution reaction. For selenium at pH 7 conditions were  
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11 336 favorable for Se(0), while at pH 5 for both, Se(0) and Se(-II) in a form of either  $\text{HSe}^-$  or  $\text{H}_2\text{Se}$ .

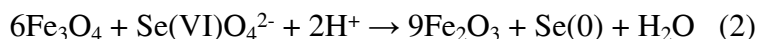
### 14 337 **Mineral transformation – Mössbauer and XRD**

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18 338 Magnetite to maghemite transformation was revealed by both Mössbauer spectrometry and X-ray  
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20 339 diffraction (Figure S5). In the Rietveld refinement process only little freedom was given to the  
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23 340 magnetite and maghemite unit cell parameters ( $a \pm 0.005 \text{ \AA}$ ) to avoid erroneous phase  
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25 341 identification. Analysis of the selected solid samples showed a large correlation between the two  
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28 342 techniques (Table 2 and Figure 2) at pH 5, where a significant degree of transformation occurred,  
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31 343 while at pH 7 XRD tends to underestimate the maghemite percentage in comparison to Mössbauer.  
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33 344 A shift of the XRD peaks related to mineral transformation at pH 5 between 6 h and 168 days is  
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35 345 clearly visible in Figure S5b, especially at the higher angles, while at pH 7 (Figure S5d) the  
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38 346 corresponding higher angle peaks tend to be superimposed. This could indicate that at pH 7 the  
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41 347 low maghemite fraction is not significantly disturbing the magnetite crystal lattice (randomly  
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43 348 distributed  $\text{Fe}^{3+}$  cations), or that the thin oxidized layer at the mineral surface is amorphous, thus  
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45 349 not contributing to the Bragg peaks and only to diffuse scattering.

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49 350 Another important observation is the strong correlation between the degree of magnetite oxidation  
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51 351 and the Se(VI) uptake, as highlighted in Figure 2. At pH 7, 18 % (Mössbauer) of maghemite  
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54 352 formed during the first 6 hours, concomitantly with 1.27 mmol/L of Se(VI) removed from solution,  
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4 353 which corresponds to 1 % of mineral conversion for every 0.07 mmol/L uptake of Se(VI). Between  
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6 354 6 h and 95 days the conversion rate slowed down to 0.035 mmol/L of Se(VI) for each 1 % of  
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8 355 mineral, probably due to partial oxidation of magnetite surface<sup>72</sup> which blocked the electron  
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11 356 transfer.

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14 357 A detailed analysis of the XRD patterns revealed a new peak corresponding to the (100) plane of  
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16 358 trigonal gray Se(0)<sup>73</sup> at  $2.9^\circ$  ( $\lambda = 0.1907 \text{ \AA}$ , Figure S5c), which increased concomitantly with the  
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19 359 Se(VI) uptake and the mineral transformation (1 % of Se(0) after 5 months at pH 7). The redox  
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22 360 process describing the Se(VI) reduction to Se(0) and magnetite oxidation, with an exchange of 6  
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24 361 electrons can be written as:



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31 363 Based on this model equation, with the initial magnetite concentration fixed at 10 g/L, 0.1 g of  
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34 364 maghemite (1 %) should appear after reduction of 0.07 mM of selenate oxyanion by magnetite  
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36 365 (details of calculation in SI). At the same time, consumption of protons should increase the pH of  
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39 366 the solution, as observed in all batch experiments. This ideal stoichiometry was only observed in  
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41 367 the initial phase of the Se(VI) experiment at pH 7. While selenate was still available in the solution  
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44 368 (6.5-7 mmol/L) after few months of the reaction, the limiting factor, which slows down the  
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46 369 adsorption, must have been the access to reducing magnetite sites.

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50 370 Magnetite reacting at pH 5 with Se(VI) for 168 days resulted in about 3.4 % of Se(0) (XRD fitting),  
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52 371 but the main redox reaction describing the process (2) is more complicated, because of the presence  
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55 372 of  $\text{Fe(II)}_{\text{aq}}$  leading to a secondary reaction. In the combined magnetite/ $\text{Fe(II)}_{\text{aq}}$  system the electrons

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4 373 migrate within the bulk and across the solid water interface.<sup>33,73</sup> The partially oxidized, positively  
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6 374 charged magnetite surface can adsorb negatively charged selenate and selenite,<sup>36,64</sup> but the  
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9 375 magnetite surface is also renewed via  $\text{Fe(II)}_{\text{aq}}$ .

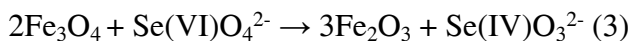
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12 376 The estimated initial maghemite fraction at pH 5, before Se(VI) injection, was equal to 5.6 %, and  
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14 377 increased to 24 % after 6 h. At the same time 1.55 mmol/L of selenate was removed from the  
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17 378 solutions. This corresponds to a selenate concentration drop of 0.084 mmol/L for each 1 % of  
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19 379 oxidized mineral (after subtraction of the maghemite present initially in the solid), thus more than  
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22 380 [Se(VI)] drop estimated from equation (2). In the following 95 days, the selenate removal rate  
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25 381 dropped down to 0.07 mmol/L per 1 % of mineral transformation. If we compare the whole period  
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27 382 of 95 days for the experiments at both pH, without subtraction of the initial maghemite due to  
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29 383 acidic dissolution, the same Se(VI) removal – mineral oxidation ratio is found (0.068 mmol/L for  
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32 384 1 % of mineral oxidation). However the redox reaction at pH 5 is much faster than at pH 7, due to  
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35 385 the additional reducing agent ( $\text{Fe(II)}_{\text{aq}}$ ) and positively charged mineral surface, and continues until  
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37 386  $\text{Fe(II)}_{\text{aq}}$  is depletion of.

#### 387 **Se(VI) reduction – XAS and STEM**

388 The time evolution of selenium speciation on magnetite in *Se(VI)\_pH5* and *Se(VI)\_pH7*  
389 experiments was determined by K-edge XANES spectroscopy, using iterative target  
390 transformation factor analysis (ITFA). All spectra collected for selected solid samples from the  
391 two experimental series were successfully fitted with two components: trigonal Se(0) gray and  
392 outer-sphere aqueous Se(IV) (Table 3, Figures 3). EXAFS data (Figure S6) confirms the presence

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4 393 of the gray elemental form (in contrast to amorphous Se(0) red), and show even more clearly than  
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6 394 XANES the presence of an oxygen shell indicative of Se(IV). While these two oxidation states  
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8 395 were also reported as reduction products of selenate by magnetite and green-rust,<sup>25-26</sup> numerous  
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11 396 literature examples show that selenite can be immobilized by iron containing minerals in form of  
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13 397 stronger inner-sphere (creation of covalent or ionic bonds) or/and weaker outer-sphere  
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15 398 (electrostatic driven sorption) complexes, depending on the experimental conditions.<sup>4,63-64,74-75</sup>  
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18  
19 399 Initial Se(VI) was not detected on the solids, so either all selenate was reduced by electrons from  
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21 400 structural Fe(II) in magnetite (at pH 7), or from both structural and aqueous Fe(II) (at pH 5), or the  
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23 401 weakly adsorbed Se(VI) was removed during filtration.<sup>26</sup>  
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28 402 Selenate at pH 7 was not strongly attracted to the mineral surface, even after hypothetical initial  
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30 403 reduction to Se(IV), due to pH conditions close to mineral isoelectric point (neutral surface).  
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32 404 XANES data fitting showed that in *Se(VI)\_pH7* series the dominating species was gray Se(0)  
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34 405 (Figures 3-4), with a small and constant contributions from Se(IV) (20 %) detected between 3  
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36 406 hours and 62 days, but not at 95 and 293 days. The large share of Se(0) indicates that the main  
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38 407 immobilization mechanism at pH 7 followed the reductive precipitation described by equation (2),  
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40 408 with simultaneous oxidation of magnetite to maghemite, as revealed by Mössbauer data analysis.  
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42 409 The presence of the usually soluble Se(IV) species associated with the solid phase suggests that a  
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44 410 small fraction of selenate was reduced only to selenite at the solid – liquid interface (Se(VI) not  
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46 411 detected in solid, Se(IV) not detected in liquid), due to increasing maghemite layer thickness. ICP-  
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48 412 AES showed no more Se(VI) uptake after 2 weeks of the experiment, so about 30 % of maghemite,  
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50 413 (equivalent to 3 layers), hindered easy electron transfer. The Se(IV) stayed weakly adsorbed on  
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4 414 the oxidized surface during the first 2 months, but desorbed after this period (Figure 4). This  
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6 415 secondary immobilization reaction requires an exchange of only two electrons and no proton  
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9 416 consumption (no  $\text{Fe(II)}_{\text{aq}}$  at pH 7):



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15 418 The *Se(VI)\_pH5* XANES data at 3 h showed only the strong white line of gray Se(0), as a result  
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18 419 of the fast reduction on the magnetite surface (despite the presence of maghemite, due to the acidic  
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20 420 dissolution), which was renewed by  $\text{Fe(II)}_{\text{aq}}$  cations being continuously re-adsorbed. This can be  
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23 421 related to a fast Se(VI) drop in solution measured with ICP-AES during the first two weeks (Figure  
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25 422 1). The selenite fraction appeared at 31 days (18 %) and stayed nearly constant until 293 days (15  
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28 423 %).

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31 424 Based on these data, we can hypothesize that during the initial phase there is a non-perturbed  
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34 425 electron exchange between magnetite and selenate, assisted by  $\text{Fe(II)}_{\text{aq}}$  re-adsorption. As mineral  
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36 426 oxidation is faster than iron re-adsorption, more and more maghemite layers cover the magnetite  
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39 427 core. In this situation, the aqueous iron can only provide a limited number of electrons, which leads  
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41 428 to a partial reduction of selenate to selenite.

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44 429 A monotonic Se(IV) concentration increase reported for solid green rust<sup>25</sup> was attributed to two  
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47 430 parallel reduction processes (selenate to selenite and selenate to elemental selenium). The adsorbed  
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50 431 selenite could not have been reduced to Se(0), due to the depletion of Fe(II) sites in the vicinity of  
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52 432 the adsorption sites. But in our case the aqueous iron renews the mineral redox activity. As the co-  
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55 433 removal ratio shows a linear dependence between 10 minutes and 5 months, we assume that the



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4 434 Fe(II)<sub>aq</sub> adsorption site changes as a function of the available reducing sites on the magnetite  
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6 435 surface. In the initial phase, there are many accessible electrons in the system due to a limited  
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8 436 fraction of maghemite. This favors the fast reduction of selenate to Se(0) on the mineral surface  
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11 437 and proton consumption, which increases the pH (equation (2)). A small increase in pH causes re-  
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13 438 adsorption of the aqueous iron, as in the absence of selenate.<sup>33</sup> So here the aqueous iron only  
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16 439 renews the reducing surface of the mineral, but the re-adsorption is spread over time and takes  
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19 440 several weeks.

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22 441 In the second phase, iron re-adsorbs on a thicker maghemite layer (faster magnetite electron  
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24 442 consumption than electron donation from Fe(II)<sub>aq</sub>), and only partially renews the reducing capacity  
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27 443 of the mineral (an easy electron exchange with the remaining magnetite core is blocked). So the  
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29 444 reducing power allows only for the selenate to selenite reduction, with the partially reduced  
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32 445 oxyanion being adsorbed to maghemite,<sup>64</sup> in the form of thermodynamically favored Fe-Se(IV)O<sub>3</sub>  
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34 446 species.<sup>76</sup> This reaction theoretically consumes two iron cations per selenate anion:



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41 448 but the real redox process is more complicated due to the presence of the underlying mineral.  
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47 450 Selected solids from sorption experiments (*Se(VI)\_pH7*: after 10 minutes and 95 days;  
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49 451 *Se(VI)\_pH5*: after 10 minutes, 6 days, 95 days and 168 days) were examined with TEM, to probe  
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52 452 the shape and size of magnetite particles and the selenium reaction products.  
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4 453 Pure magnetite appeared as a collection of rather spherical 5-50 nm diameter particles, which tend  
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6 454 to aggregate together, even after redistribution in the ultrasonic bath (Figure S2). The pH 5 and 7  
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8 455 Se(VI) samples collected at 10 minutes also showed only magnetite grains in TEM images - their  
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11 456 composition was confirmed by X-ray energy-dispersive spectroscopy (XEDS, data not shown). As  
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13 457 XANES data fitting showed a clear signal from Se(0) at 3 hours (at both pH), the reduction and  
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16 458 crystallization of selenium must have occurred between 10 minutes and 3 hours.

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18 459 Finally, the sample collected after 6 days of reaction in the Se(VI) experiment at pH 5 showed  
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21 460 several Se nanowires as bright elongated areas in the STEM-HAADF image and STEM-XEDS  
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23 461 map (Figure 3 a-b), similar to that observed for goethite/magnetite at pH 8.<sup>25</sup> The largest crystals  
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26 462 reached no more than  $1 \mu\text{m} \times 100\text{-}200 \text{ nm}$ .

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28 463 All the remaining samples showed the development of Se(0) nanowires, which have grown along  
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31 464 the [001] direction, while their thickness remained comparable to the ones observed at 6 days. The  
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33 465 examples in Figure 3 c-d, g-h show magnetite reacted with Se(VI) at pH 5 after 168 days and pH  
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36 466 7 at 95 days. This preferential one-dimensional Se growth direction along the [001] axis is typical  
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38 467 of laboratory Se(0) crystals.<sup>77-78</sup> Two diffraction patterns measured on the particle attached to the  
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41 468 wire and at the wire (Figure 3 e-f) were successfully indexed with Se(0) trigonal phase P3<sub>1</sub>21.<sup>78</sup>  
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44 469 Other forms of Se(IV) were not detected.

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46 470 Although the evidence for the existence of Se(0) nanowires in STEM-HAADF images is clear, it  
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49 471 may seem contradictory to XRD data, where only a small percentage of the gray form was detected.  
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51 472 This can be explained by an uneven distribution of wires in the magnetite matrix. Scanning  
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54 473 different regions of the TEM grids showed plenty of spots where selenium was not detectable at  
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4 474 all on the STEM-XEDS maps, located close to regions with selenium concentrated in the form of  
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6 475 wires. Just like selenium deficient and contaminated areas in the natural environment.  
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11 477 **CONCLUSIONS**  
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14 478 Our studies confirmed the ability of magnetite to remove selenate from water and showed that the  
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17 479 removal mechanism is both pH and  $\text{Fe(II)}_{\text{aq}}$  presence dependent. The highest removal percentage  
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20 480 over the longest time period was observed at pH 5 in presence of  $\text{Fe(II)}_{\text{aq}}$ : 53 % of the initial 8.6  
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22 481 mmol/L selenate was removed from solution after 5 months. The lowest sorption was associated  
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24 482 with pH 7 and the absence of  $\text{Fe(II)}_{\text{aq}}$ : 22 % of the initial 8.6 mmol/L selenate was removed over  
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27 483 the comparable period.  
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30 484 While long trigonal  $\text{Se(0)}$  nanorods were identified in the STEM-HAADF images of samples  
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33 485 collected after  $\geq 6$  days of reaction in both experiments, XANES analysis revealed presence of the  
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36 486 additional selenite species in samples where the maghemite surface layer blocked easy electron  
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38 487 transfer. The proposed mechanism suggests a fast complete reduction of  $\text{Se(VI)}$  to  $\text{Se(0)}$  at the  
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41 488 initial phase of the sorption experiments, related to rapid fall in aqueous selenate. The process  
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43 489 continues at pH 7 until the reducing power of the mineral is spent (10 days – plateau in  $\text{Se(VI)}$   
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46 490 concentration). Meanwhile, at pH 5, the initially dissolved  $\text{Fe(II)}$  partially renews the reducing  
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48 491 capacity of the material, but due to the limited speed of electron delivery, is unable to complete  
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51 492 the selenate reduction, and as a result, the incompletely reduced selenite adsorbs on the maghemite  
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53 493 surface. Selenate uptake continues slowly until the  $\text{Fe(II)}_{\text{aq}}$  is completely removed.  
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4 494 **Environmental relevance**

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6 495 Highly mobile selenate is a concern for the nuclear waste and coal mining industries. Because of  
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9 496 weathering of selenium bearing rocks, such as shales and coal, or of corrosion of steel canisters,  
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11 497 used for spent fuel geological storage, this highly toxic element can escape into the surrounding  
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14 498 environment. However in anoxic environments, pore space and corrosion products often contain  
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16 499 Fe(II), which can actively participate in selenate reductive immobilization. Our study shows that,  
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19 500 in anoxic conditions typical for waste storage, even partially oxidized nanomagnetite particles (6  
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21 501 % of maghemite, 94 % of magnetite) are still capable of reducing the highly mobile selenium  
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24 502 oxyanions to immobile, stable Se(0) form. Moreover, the aqueous Fe(II) leached from the mineral  
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27 503 during stabilization at  $\text{pH} \leq 6$  boosts the reduction process, due to the renewed reducing power of  
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29 504 the mineral surface. This opens a new way for the control of selenium level a variety of critical  
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31 505 effluents.  
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38 507 **AUTHOR CONTRIBUTIONS**

39  
40 508 The manuscript was written through contributions of all authors. All authors have given approval  
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43 509 to the final version of the manuscript.  
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11 517 acknowledged.

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18 519 ABBREVIATIONS

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21 520 ICP-AES - Inductively Coupled Plasma Atomic Emission Spectroscopy

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24 521 IC – Ion Chromatography

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28 522 STEM – Scanning Transmission Electron Microscopy

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31 523 HAADF - High Angular Angle Dark Field

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34 524 RN - radionuclide

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38 525 SAED - Selected Area Electron Diffraction

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41 526 XANES – X-ray Absorption Near-Edge Structure

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44 527 EXAFS – Extended X-ray Absorption Fine Structure

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51 529 FIGURES AND TABLES

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53  
54 530 **Table 1.** Experimental conditions for batch experiments

Batch name	Magnetite concentration [g/L]	pH	Initial total Se(VI) concentration [mM]	Initial Se(VI) concentration [mg/L]
<i>Se(VI)_pH</i> 5	10	5	8.6	679
<i>Se(VI)_pH</i> 7	10	7	8.6	679

531 \* magnetite surface area from BET = 70 g/m<sup>2</sup>

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533 **Table 2.** Degree of magnetite to maghemite conversion from Mössbauer at 77 K and XRD pattern  
534 modeling and versus selenium uptake from ICP-AES.

Se series	Sample collecti on time	% of magnetite to maghemite conversion from XRD data fitting	% of magnetite to maghemite conversion from Mössbauer data		Drop in Se concentrati on with respect to c <sub>0</sub> [mmol/L] from ICP- AES	Solid e <sup>-</sup> release per gram of solid	Se(VI) to Se(0) e <sup>-</sup> consumed per gram of solid	Layers of maghemite on 15 nm spherical nanoparticle (based on 77 K Mossbauer data)
			300 K	77 K				
<i>Se(VI)_pH5</i>	6 h	25(1)	15-20	24	1.55	3.9-6.5E20	5.6E20	2.5
<i>Se(VI)_pH5</i>	6 days	44(1)			3.05	1.4E21	1.1E21	
<i>Se(VI)_pH5</i>	95 days		61-70	64	4.40	1.6-1.8E21	1.6E21	8.1

<i>Se(VI)_pH5</i>	168 days	70(1)			4.58	1.8E21	1.7E21	
<i>Se(VI)_pH7</i>	6 h	9(1)		18	1.27	2.3-4.7E20	4.6E20	1.8
<i>Se(VI)_pH7</i>	6 days	10(1)			1.59	2.6E20	5.7E20	
<i>Se(VI)_pH7</i>	95 days			31	1.71	8.1E20	6.2E20	3.3
<i>Se(VI)_pH7</i>	168 days	10(1)			1.63	2.6E20	5.9E20	

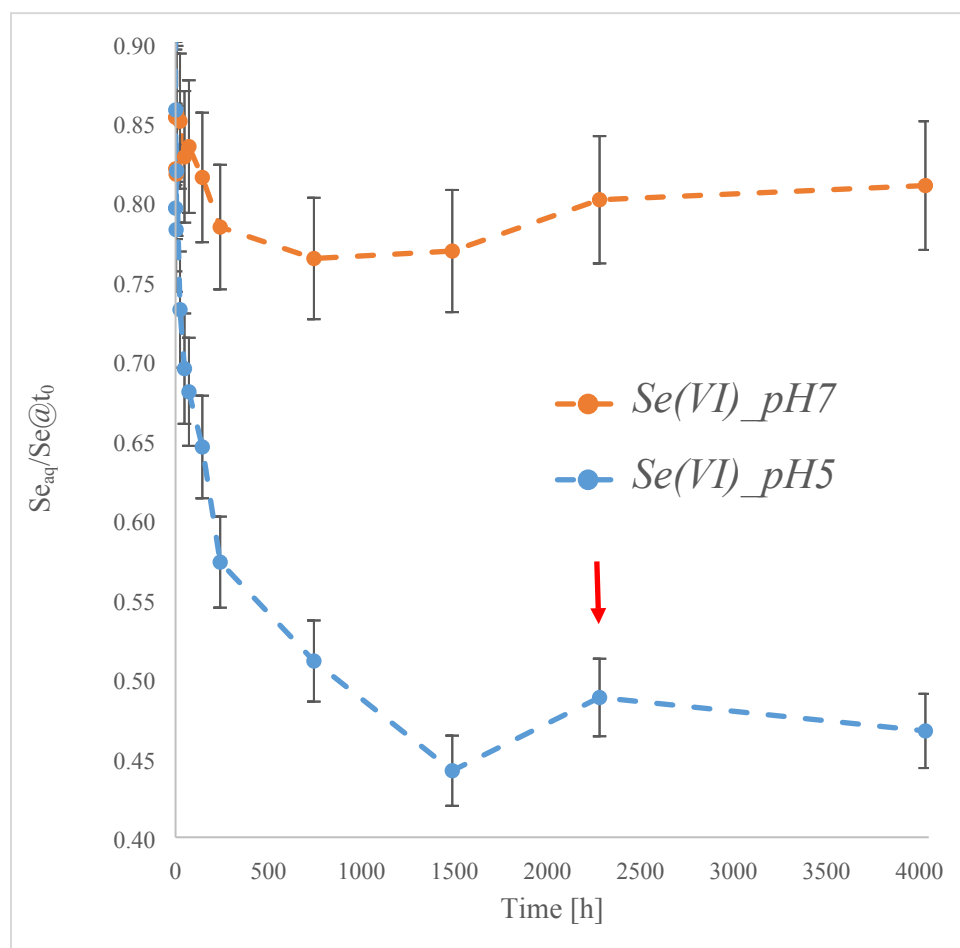
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536 **Table 3.** Se speciation fractions calculated from the iterative target transformation of XANES data.

Se series	Sample collection time	Se (0) gray	Se(IV)	Sum
<i>Se(VI)_pH5</i>	3 h	1.00	0.00	1.00
<i>Se(VI)_pH5</i>	31 d	0.82	0.18	1.00
<i>Se(VI)_pH5</i>	62 d	0.83	0.18	1.01
<i>Se(VI)_pH5</i>	293 d	0.83	0.15	0.99
<i>Se(VI)_pH7</i>	3 h	0.82	0.19	1.01
<i>Se(VI)_pH7</i>	31 d	0.80	0.20	1.00
<i>Se(VI)_pH7</i>	62 d	0.82	0.20	1.01
<i>Se(VI)_pH7</i>	95 d	1.00	0.00	1.00
<i>Se(VI)_pH7</i>	293 d	1.00	0.01	1.00

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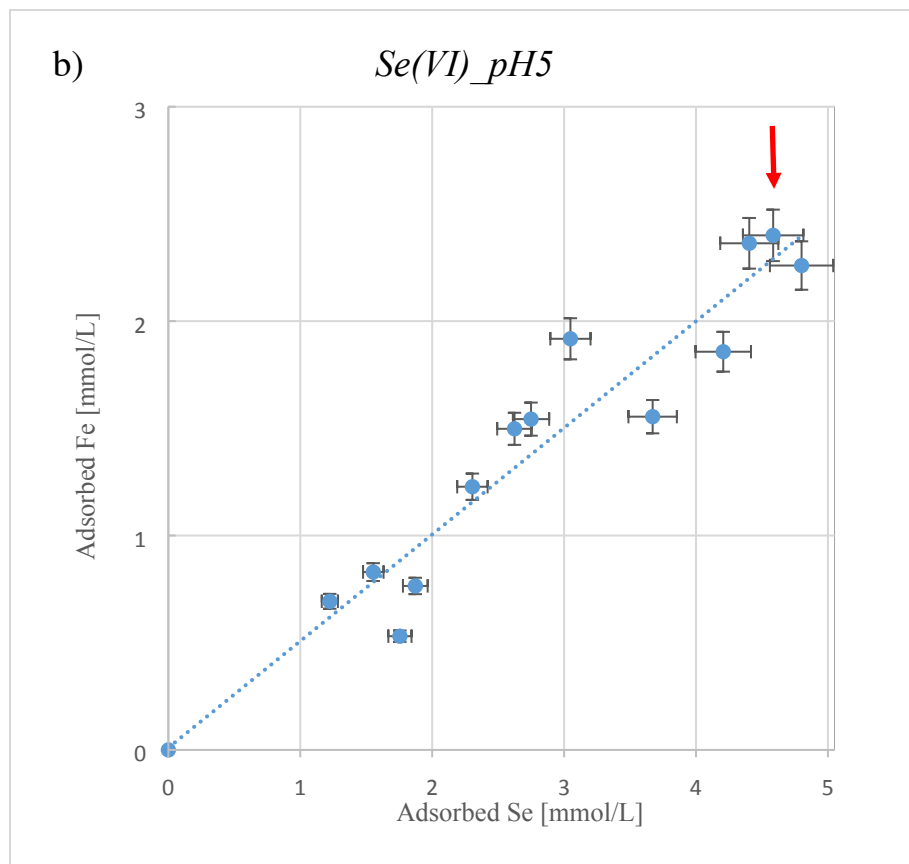
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542 **Figure 1.** Sorption kinetics of RNs observed in the two batch experiments: a) Se(VI) and b) Linear

543 dependence between Se(VI) and Fe(II) sorption found in the experiment at pH 5. As the Fe(II) first

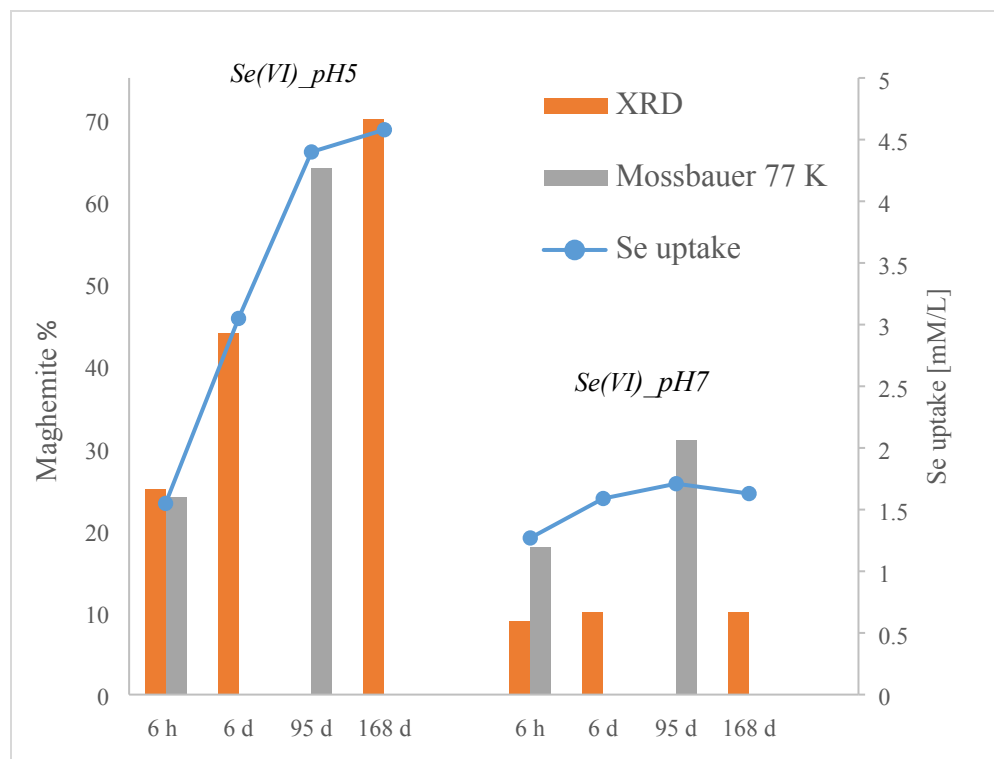
544 measurement was done at 10 min, concentration at time 0 was estimated by interpolation of the

545 linear fitting. Red arrow indicate time of nearly complete adsorption of Fe(II) in *Se(VI)\_pH5*

546 experiment. Error bars represent 5 % error of the ICP-AES measurements.

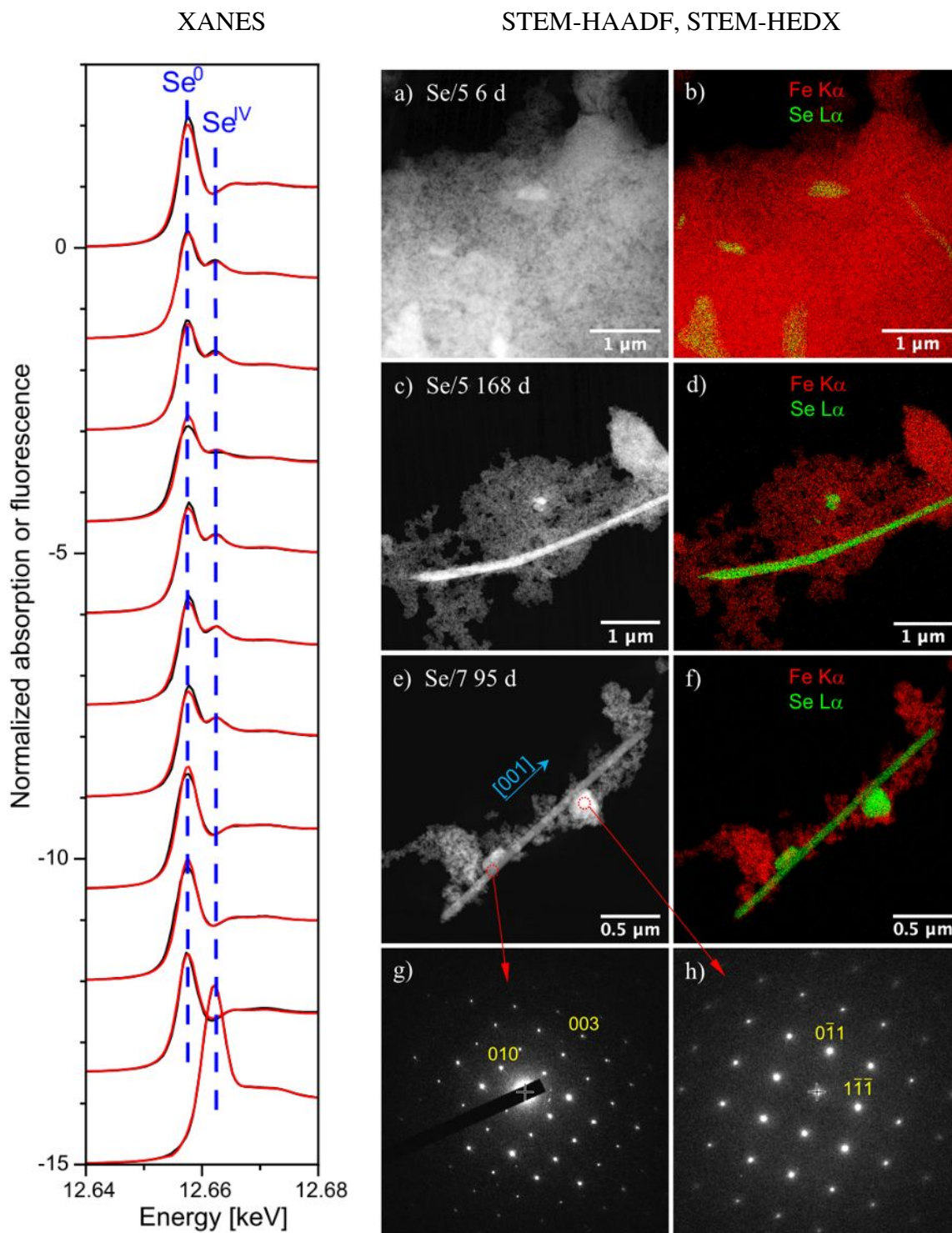
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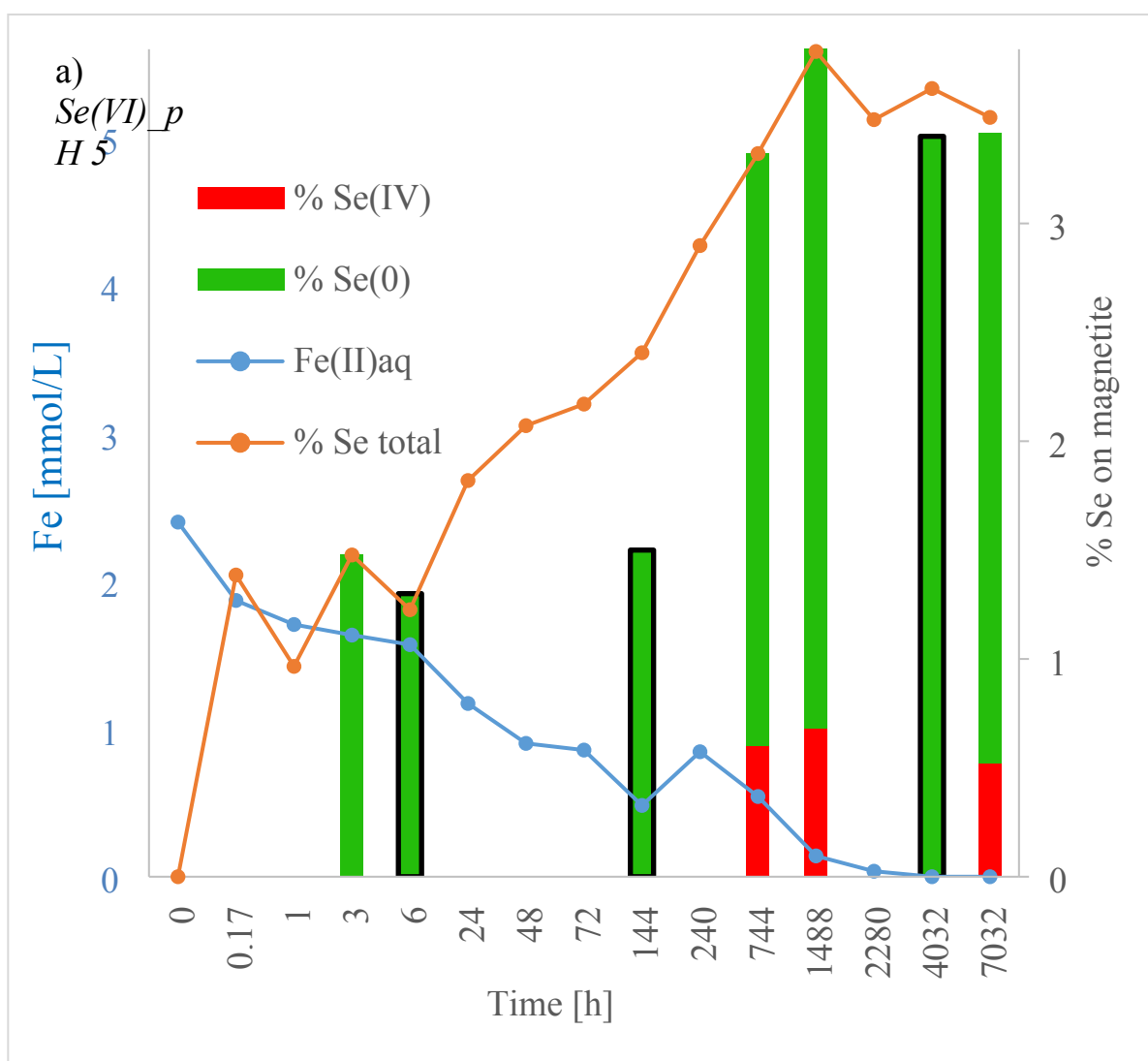
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550 **Figure 2.** Degree of magnetite to maghemite conversion from Mössbauer at 77 K (gray bars) and  
551 XRD pattern modeling (orange bars) vs. selenium uptake from ICP-AES (blue circles).



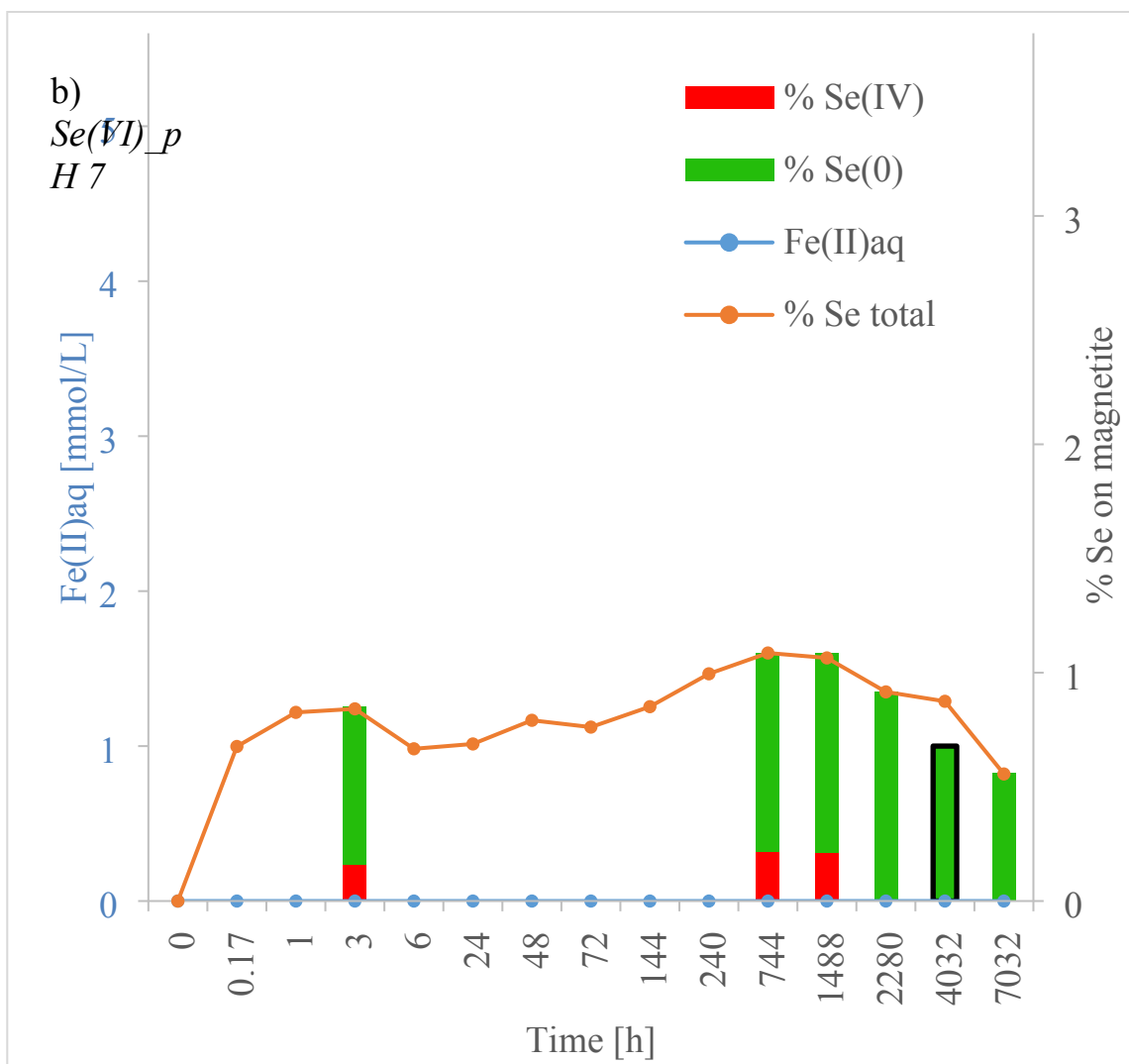
552  
553 **Figure 3.** XANES: Selenium K-edge XAFS spectra of the two time series of Se(VI) experiments  
554 at pH 5 and 7, and the two standard spectra (Se(0) gray and Se(IV) outer sphere). Black lines –

555 experimental data, red lines: reconstruction with two components. STEM-HAADF images (a, c,  
 556 e) and STEM-XEDS maps (b, d, f) of magnetite-Se samples: a-b) *Se(VI)*<sub>pH5</sub>, after 6 days –  
 557 several selenium crystal seeds; c-d) *Se(VI)*<sub>pH5</sub>, after 168 days -with 5 μm long selenium  
 558 nanowire ; e-h) *Se(VI)*<sub>pH7</sub>, after 95 days – 2.5 μm long nanowire with small selenium seeds; g)  
 559 [100] zone axis of P3<sub>1</sub>21 Se(0); h) [211] zone axis of P3<sub>1</sub>21 Se(0).



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564 **Figure 4.** Summary of Fe(II)aq uptake (from ICP-AES: blue dots and line), Se(VI) uptake (from  
 565 ICP-AES: orange dots and line), Se(0) fraction on magnetite (from ICP-AES/XANES – green bars  
 566 – and XRD – green bars with black contours) and Se(IV) fraction (from ICP-AES/XANES: red  
 567 bars) in the four experimental series.

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## SUPPLEMENTARY INFORMATION

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### Nanowire selenium formation upon reaction of 22 selenate with magnetite 23 24 802 25 26 27 803 28 29 30

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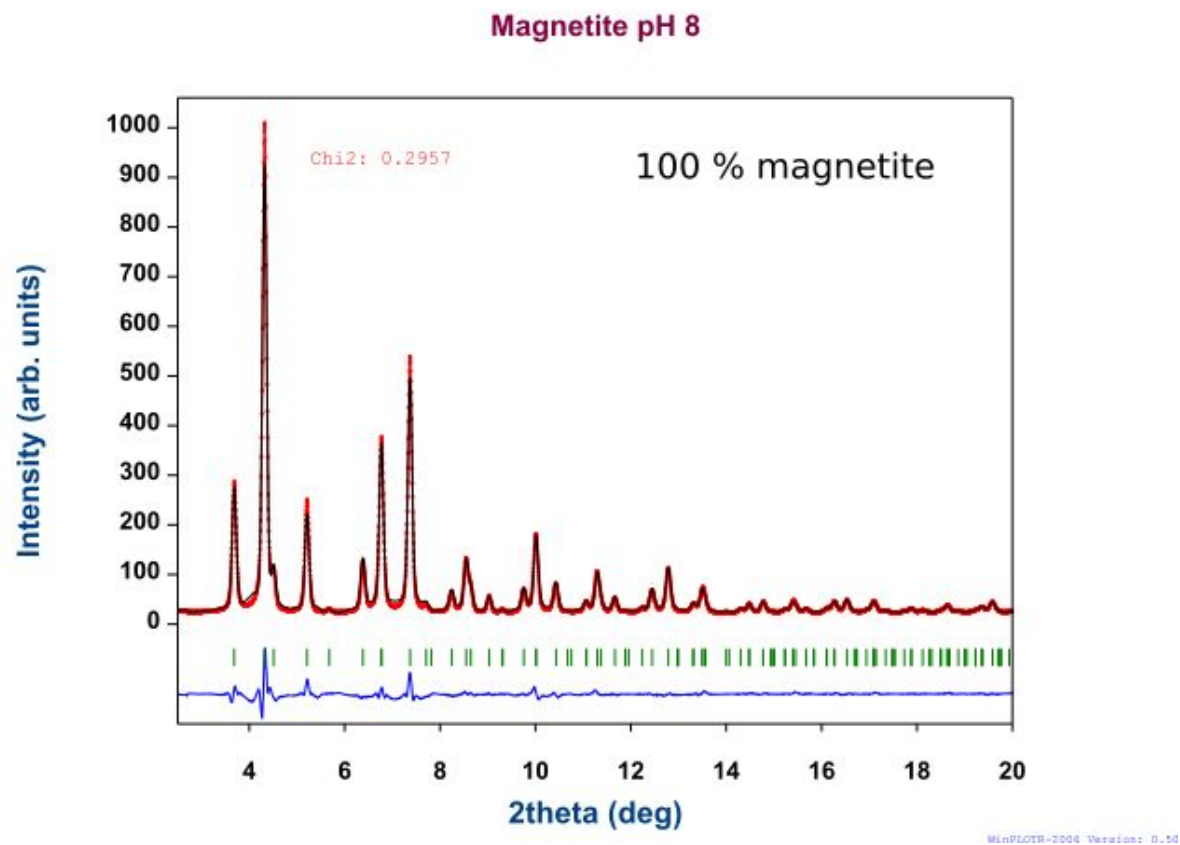
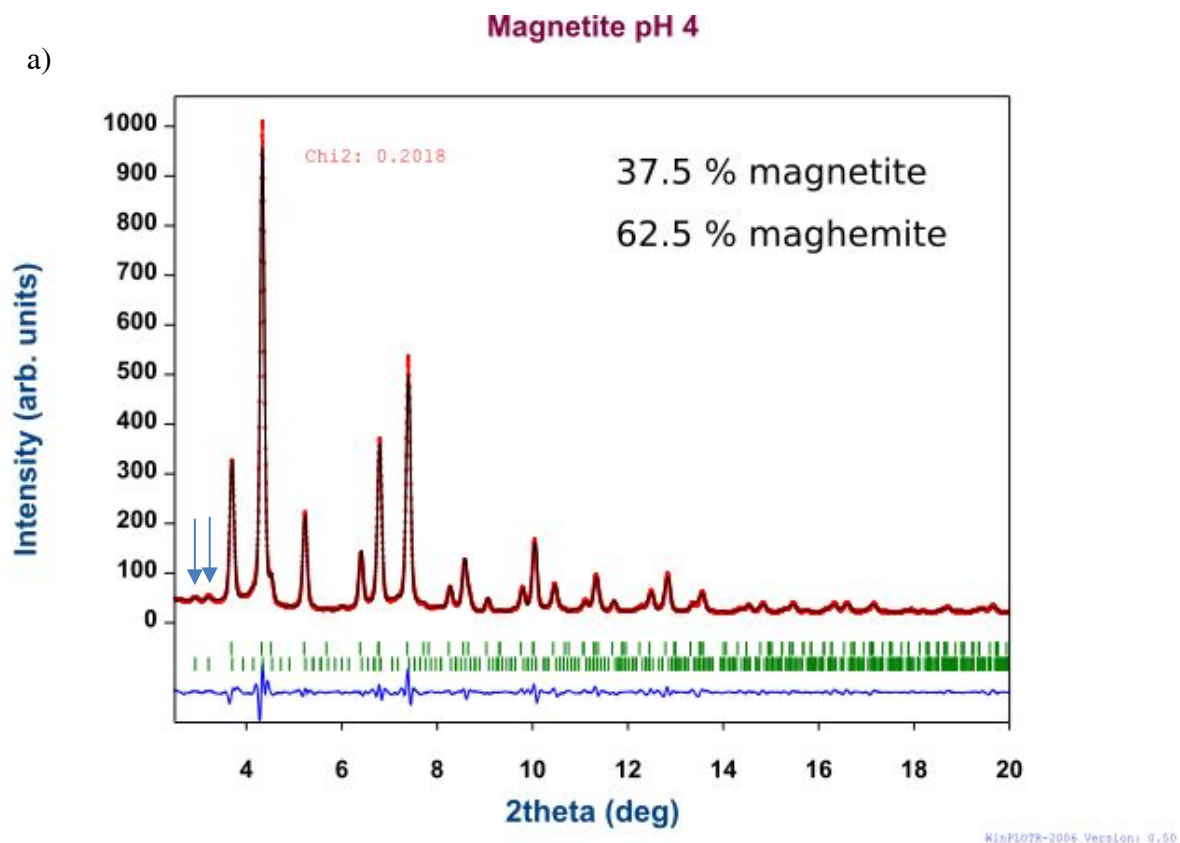
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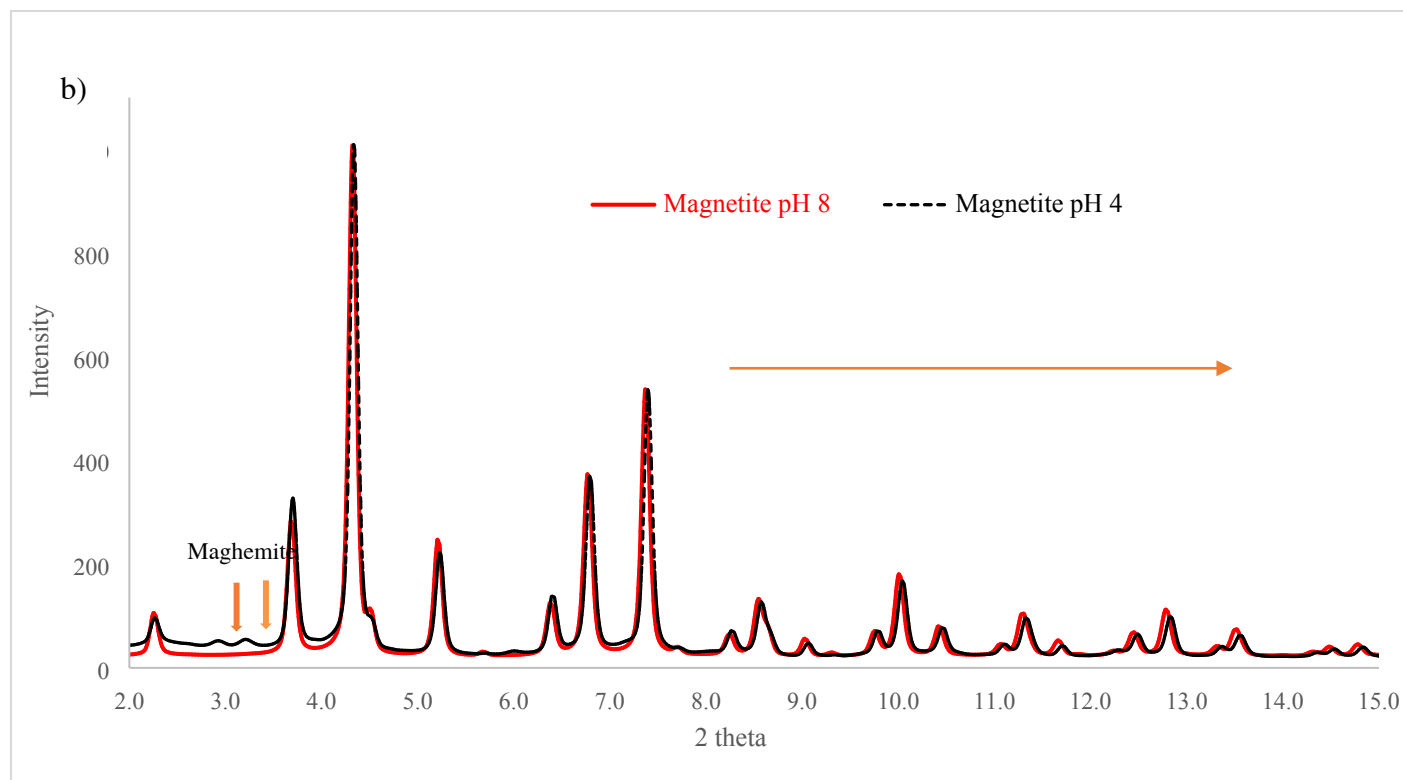
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11 817 <sup>5</sup> ID31 beamline at ESRF, 71 avenue des Martyrs, 38043 Grenoble, France

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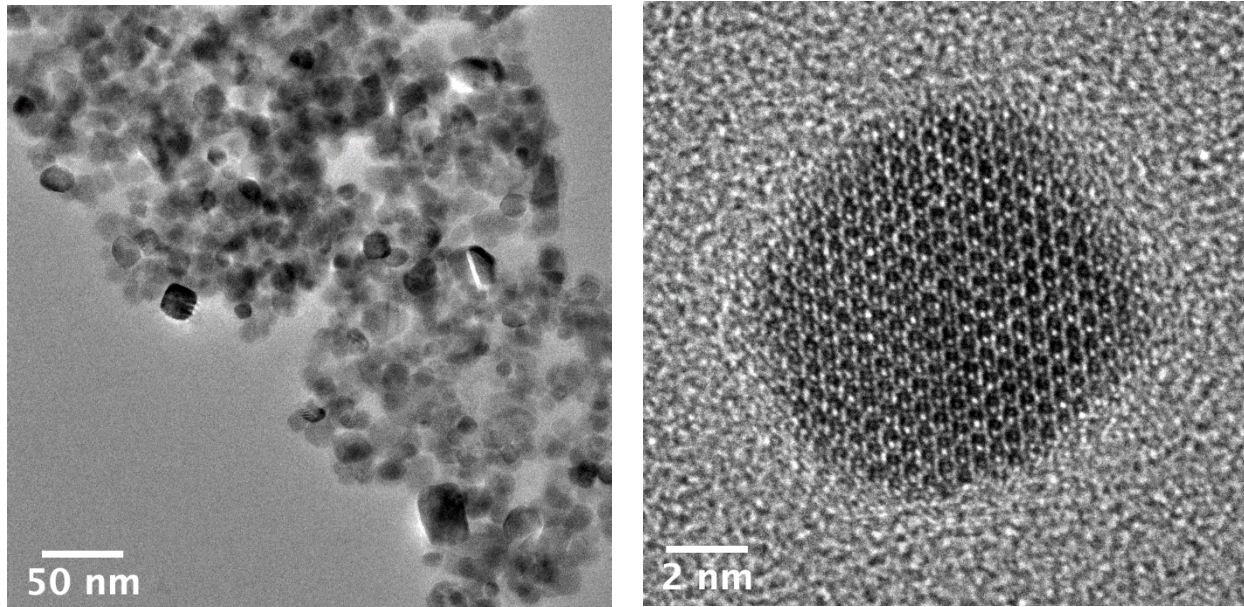


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4 822 **Figure S1.** a) Fitting of XRD patterns of magnetite ( $a = 8.39 \text{ \AA}$ ) stabilized at pH 4 and 8 ( $\lambda = 0.1907$



26 823  $\text{\AA}$ ). Imperfect fitting of the 3 most intense peaks  
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29 824 come from memory effects of the detector. The two blue arrows show peaks of a similar intensity  
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31 825 typical for maghemite ( $a = 3.42 \text{ \AA}$ ). b) Superimposed patterns of Magnetite stabilized at pH 4 and  
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33 826 8 highlighting the peak shift due to magnetite transformation to maghemite and the new peaks at  
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36 827  $2\theta = 2.9$  and  $3.2^\circ$ .  
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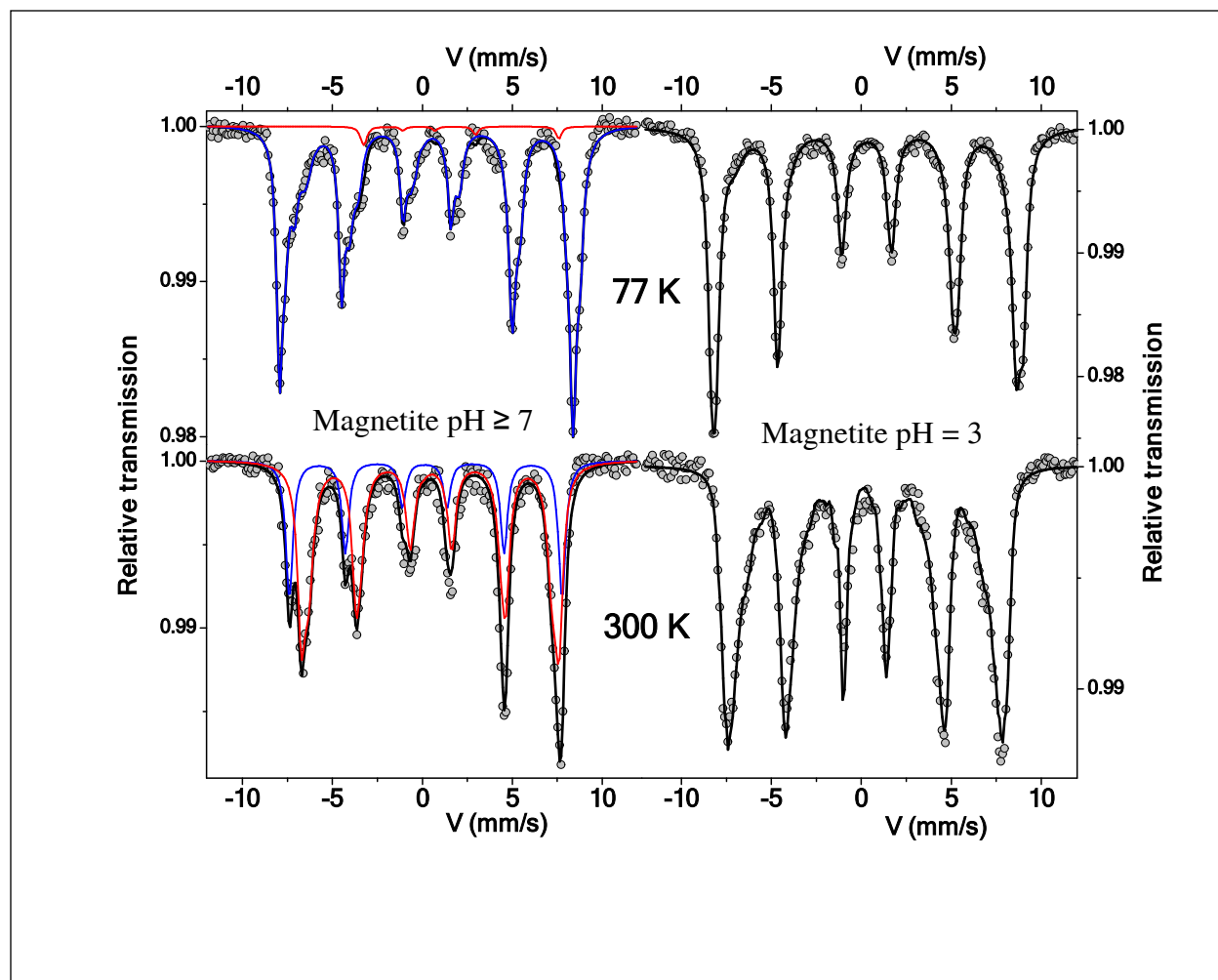
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42 829 **Figure S2.** TEM images of the magnetite stabilized at pH 8: a) TEM – Bright Field, b) High

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44 830 Resolution TEM and corresponding FFT.  
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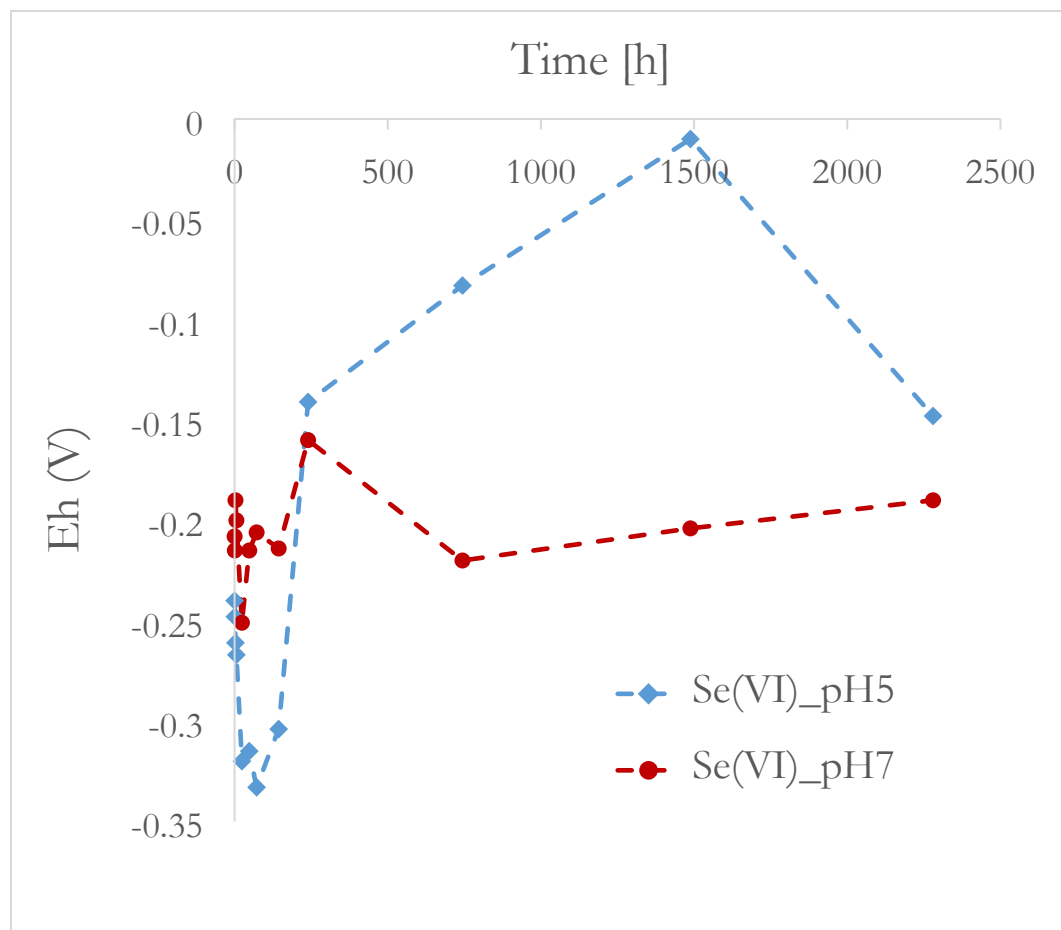
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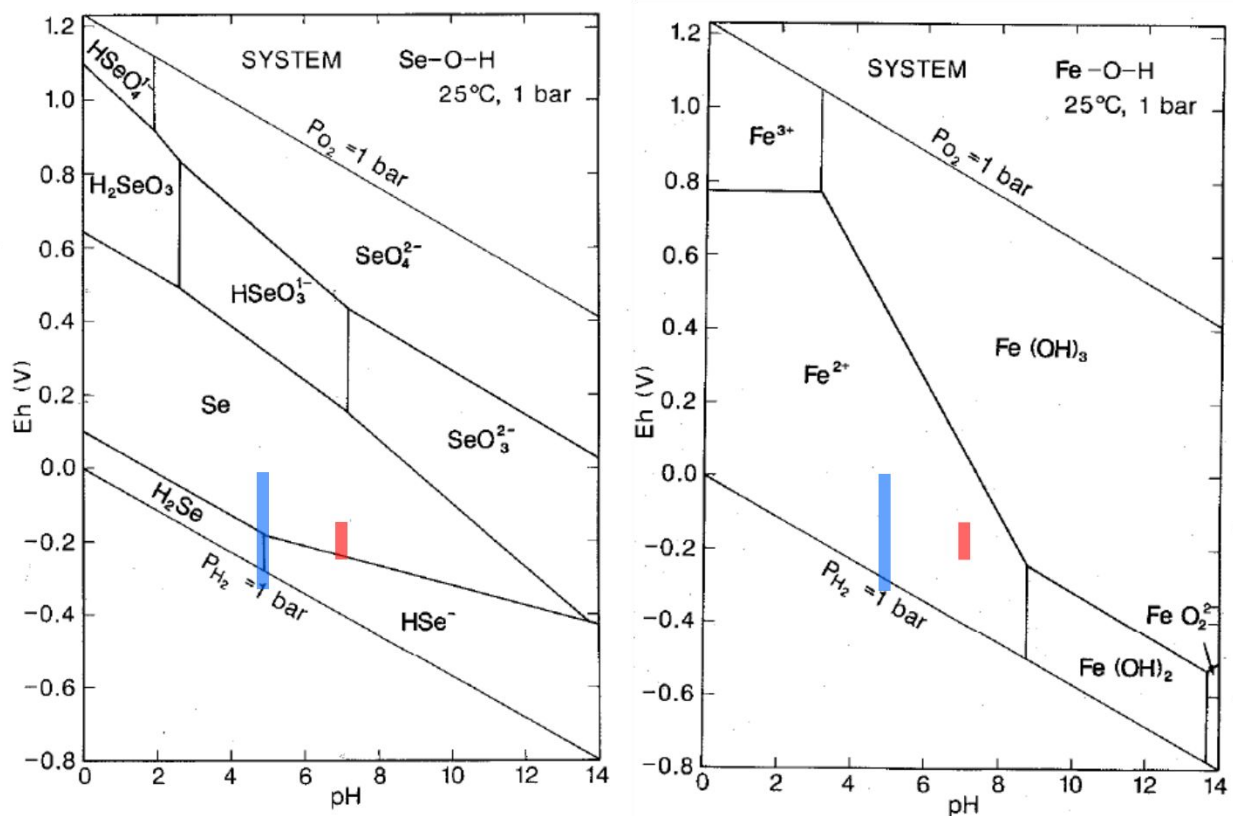
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58 magnetite  $[0\bar{1}11]$  zone axis  
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834 **Figure S3.** Left: Mössbauer spectra of the pure magnetite synthesized in a glovebox, measured at  
835 77 K and 300 K, fitted with three components containing Fe(II) and Fe(III) species; Right:  
836 Mössbauer spectra of the magnetite stabilized at pH 3, containing about 82 % of a maghemite at  
837 77 K and 300 K.





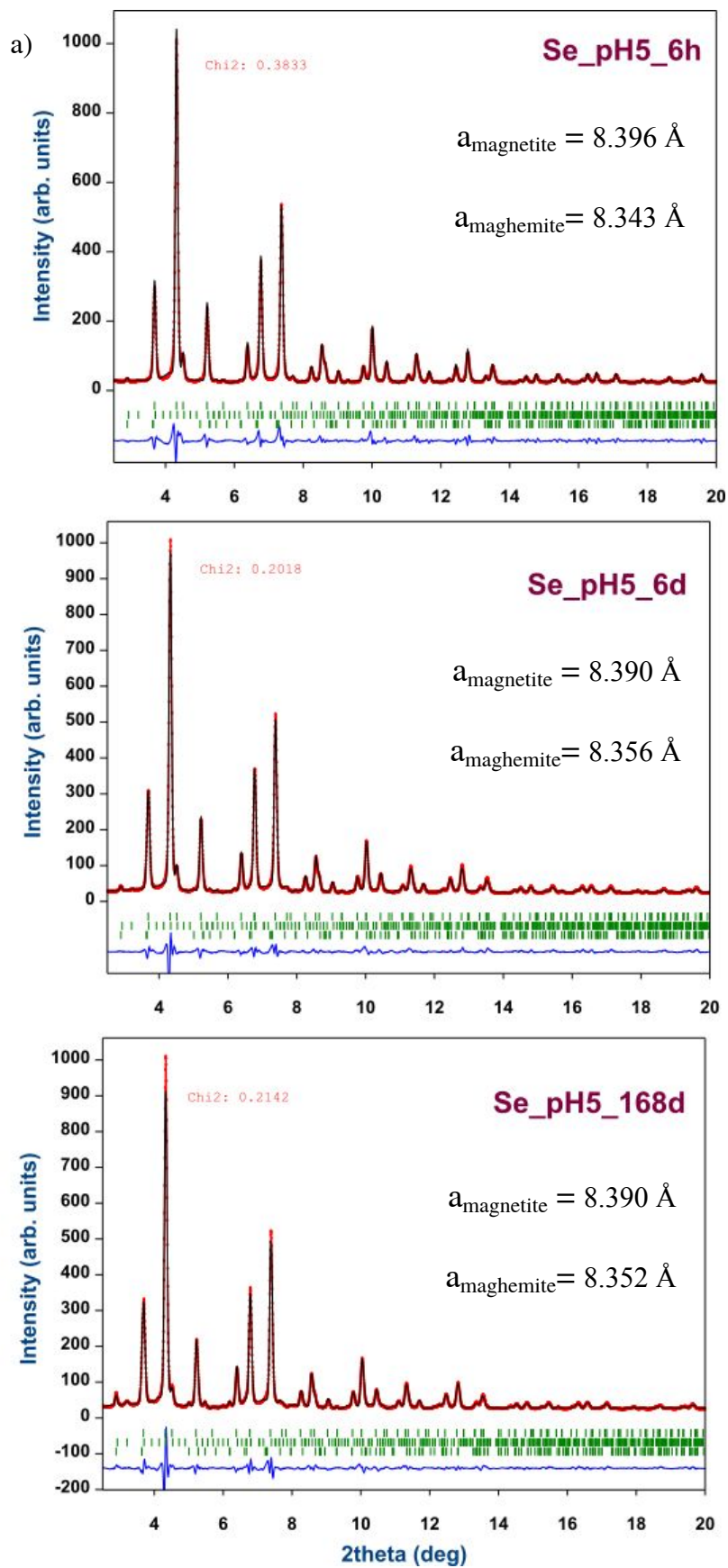
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840 **Figure S4.** Fluctuation of redox potential during 3 months of sorption experiments and Pourbaix  
841 diagrams (Brookins, D.G., (1988), Eh-ph Diagrams for Geochemistry, Springer) for Se and Fe,  
842 showing redox potential – pH dependence of the thermodynamically stable phases. Blue:  
843 Se(VI)\_pH5 and red: Se(VI)\_pH7.

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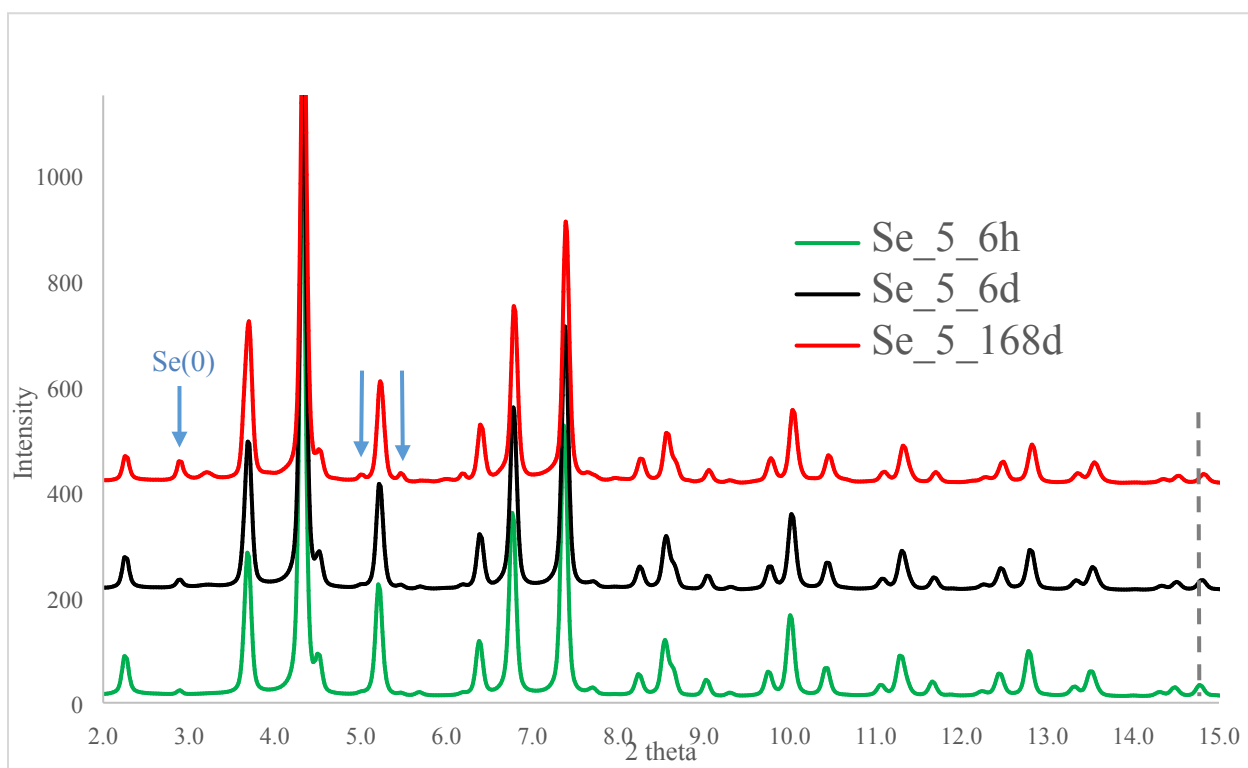




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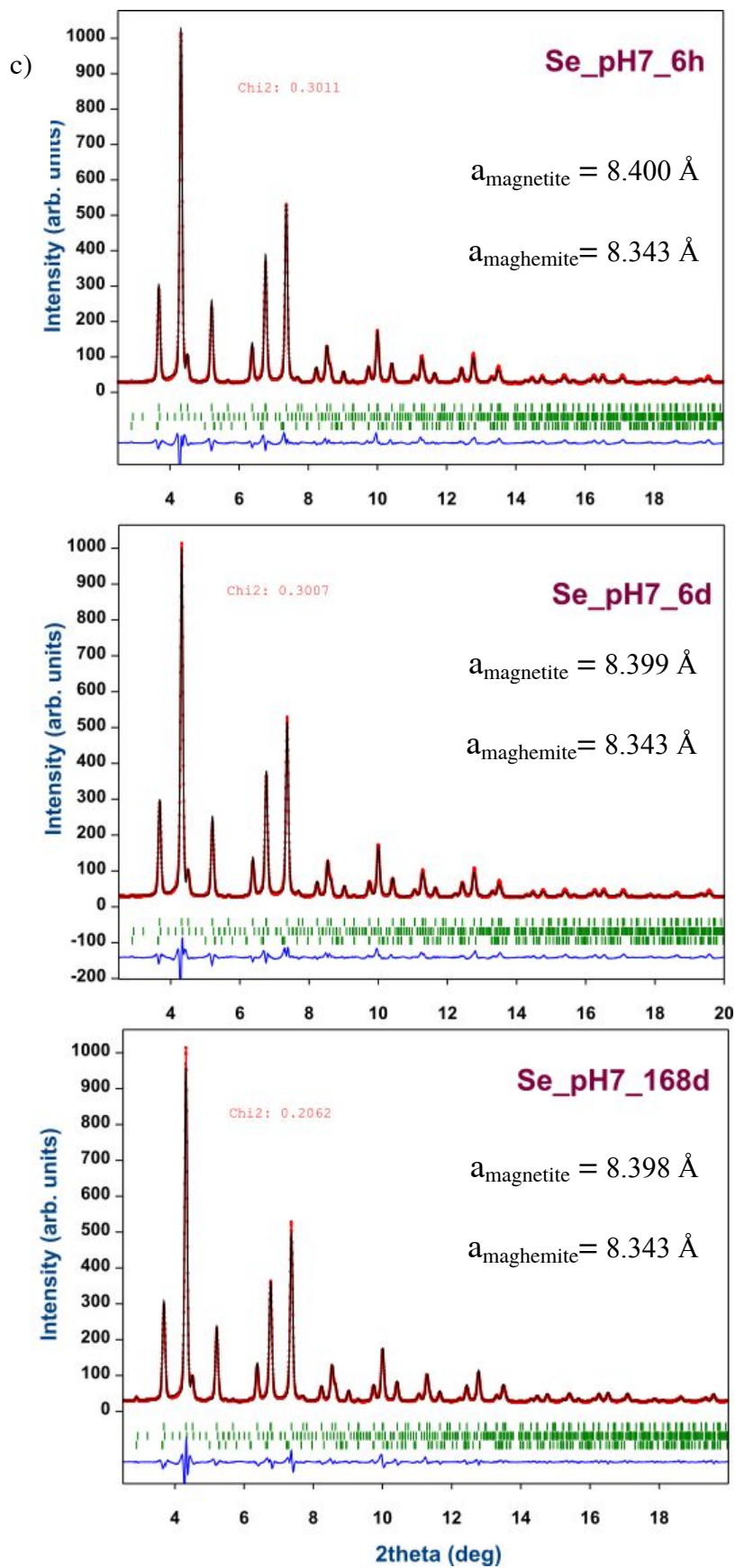
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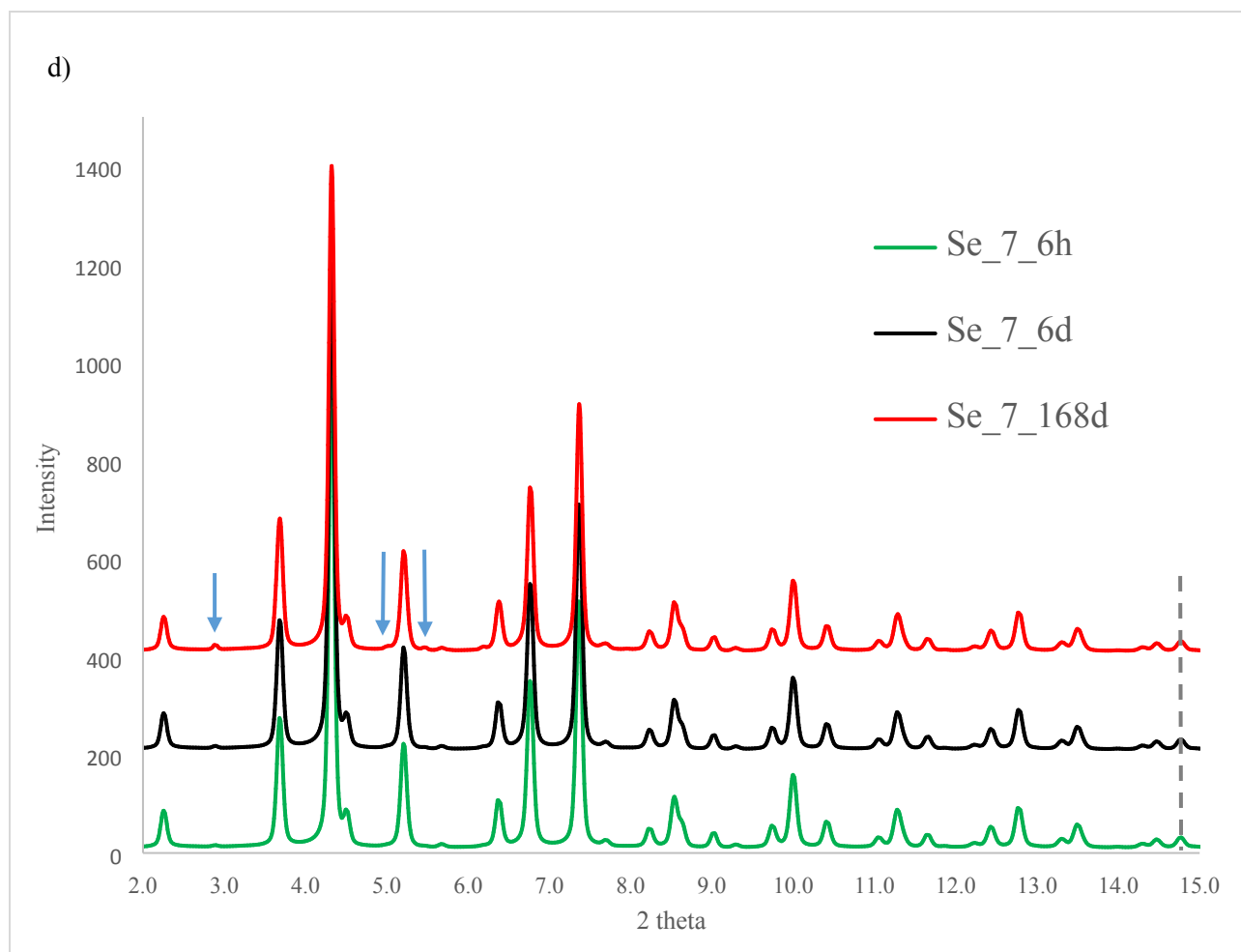


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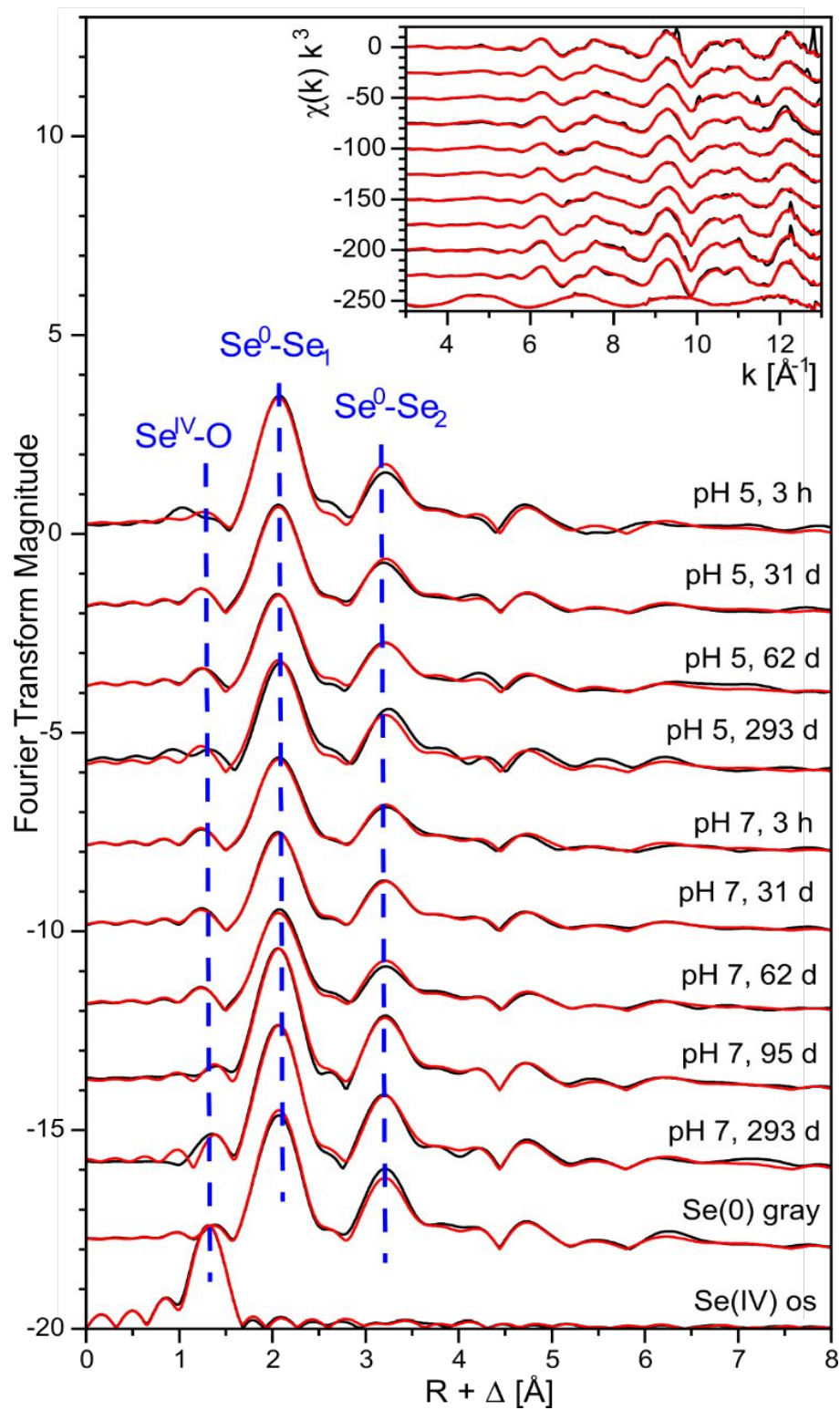
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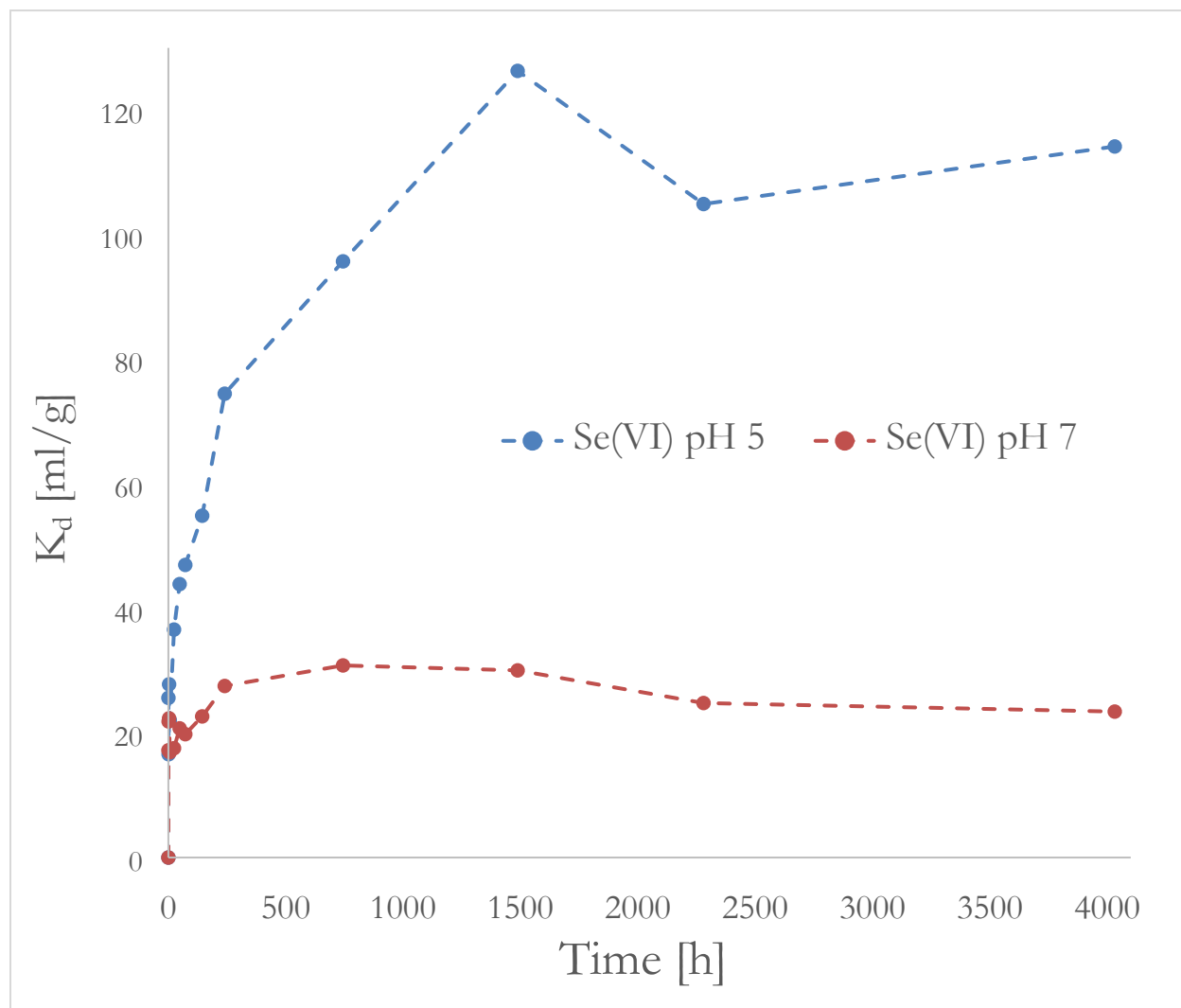
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36 **Figure S5.** a) Results of Se(VI) sorption on magnetite at pH 5 (6 h, 6 days and 168 days) XRD  
37 Rietveld refinement with magnetite, maghemite and Se(0) trigonal; b) superimposed raw data for  
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39 853 Se(VI) sorption on magnetite at pH 5. Blue arrows show peaks from Se(0); c) results of Se(VI)  
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41 854 Se(VI) sorption on magnetite at pH 5. Blue arrows show peaks from Se(0); c) results of Se(VI)  
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43 855 sorption on magnetite at pH 7 (6 h, 6 days and 168 days) XRD Rietveld refinement with  
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45 856 magnetite, maghemite and Se(0) trigonal; d) superimposed raw data for Se(VI) sorption on  
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47 857 magnetite at pH 7. Blue arrows show peaks from Se(0) – lower intensity than in pH 5 series; chi2  
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49 858 reflecting fitting quality is indicated in the figures.  $\lambda = 0.1907 \text{ \AA}$ .

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4 859 Data at pH 5 show the shift of all peaks reflecting transformation to maghemite, while at pH 7  
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6 860 such a shift is not observed.  
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4 862 **Figure S6.** Selenium K-edge EXAFS spectra of selected Se(VI) magnetite samples, along with  
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6 863 gray Se(0) and Se(IV) aquo references. Black lines: experimental data, red lines: reconstruction  
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9 864 with two components.



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47 866 **Figure 7.**  $K_d$  value calculated for Se(VI) series at pH 5 and 7, reflecting Se partitioning between  
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49 867 solid and liquid.

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869 **Table S1.** Results of the kinetics sorption experiments. Magnetite concentration fixed at 10 g/L.

Time [h]	Se(VI) pH 5		Se(VI) pH7	
	Se in solution [ppm/L]	Fe in solution [ppm/L]	Se in solution [ppm/L]	Fe in solution [ppm/L]
0	679	144 (estimated)	679	
0.17	540.5	104.4	579.3	0.2
1	582.4	95.3	557.3	0.1
3	531.2	91.3	555.0	0.3
6	556.4	87.7	580.8	0.3
24	497.1	65.5	577.6	0.0
48	471.9	50.4	562.4	0.1
72	462.0	47.9	566.8	0.1
144	438.4	26.9	553.6	0.0
240	389.2	47.2	532.4	0.1
744	346.9	30.3	518.9	0.0
1488	300.0	7.9	522.1	0.0
2280	331.3	2.1	544.0	0.4
4032	317.0	0.0	550.1	0.4

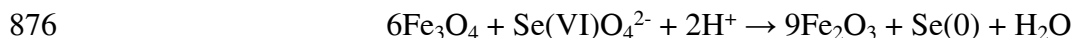
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872 **Calculation based on magnetite to maghemite conversion oxidation and Se(VI) to Se(0)**873 **reduction.**

874 Taking the initial magnetite concentration 10 g/L, one can calculate how much of selenium can

875 be reduced for each 1 % of the mineral, if the redox reaction follows:



877 Molar weights of the two minerals are:

878  $\text{Mw}(\text{magnetite}) = 231.5 \text{ g/mol}$  and  $\text{Mw}(\text{maghemite}) = 159.7 \text{ g/mol}$

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4 879 1 % of the initial mineral (10g/L) gives 0.1 g. Due to difference in mineral mass on the left and  
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6 880 right side (6 \* Mw magnetite = 1389 g and 9 \* Mw maghemite = 1437 g) we can consider 2 cases:  
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8 881 i) how much Se(VI) is reduced for 0.1 g of magnetite, ii) how much Se(VI) is reduced for 0.1 g of  
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11 882 maghemite.

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14 883 From a simple proportion, we can calculate:

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16 884 i) how much Se(VI) reacts with 0.1 g of magnetite, if 1389 g reacts with 1 mol of Se(VI)?

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19 885  $x = 0.1 \text{ g} * 1 \text{ mol} / 1389 \text{ g} = 0.00072 \text{ mol} = 0.072 \text{ mmol}$

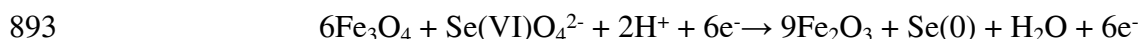
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21 886 ii) how much Se(VI) is needed to produce 0.1 g of maghemite, if 1437 g is produced using 1 mol  
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23 887 of Se(VI)?

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26 888  $x = 0.1 \text{ g} * 1 \text{ mol} / 1437 \text{ g} = 0.0000695 \text{ mol} = 0.0695 \text{ mmol}$

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29 889 Both results are close to **0.07 mmol**.

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34 891 **Calculations of the number of electrons per gram of solid released during magnetite oxidation and**  
35  
36 892 **selenate reduction, if the reaction follows equation 3**



40  
41 894 1) For 100 % mineral transformation in the above reaction 6 moles of magnetite need 6 moles of  
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43 895 electrons. To calculate how many electrons per gram of solid is needed, we need Mw of magnetite  
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45 896 (231.5 g/mol).

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47  
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49 897  $x = 1\text{g} * 6 * 6.02\text{E}23 \text{ electrons} / (6 * 231.5 \text{ g}) = \mathbf{2.6\text{E}21 \text{ electrons}}$

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51 898 Values in table 2 (before last column) are obtained by multiplying this result by percent of the  
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53 899 transformed material.

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4 900

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6 901 2) To calculate the Se(VI) to Se(0) reduction we use the same equation, however it is true only for

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9 902 pH 7 series. At pH 5 we have a second reduction process.

10  
11 903 Example:

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14 904 Se(VI) , pH 7, where 1.27 mmol/L is sorbed on the mineral.

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16 905 For 1 mol of Se(VI) we need 6 mole of electrons. How many electrons are needed for 1.27 mmol

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19 906 of Se(VI)?

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21 907  $x = 1.27 \text{ mmol} * 6 * 6.02E23 \text{ electrons} / 1000\text{mmol} = 4.59E21 \text{ electrons}$

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23  
24 908 This is a value for L which contains 10 g of magnetite. To obtain the value per 1 g we need to

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26 909 divide it by 10.

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